Characterization of rice husks as a biofuel feedstock towards sustainable rural rice processing in Sub-Saharan Africa

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ABSTRACT

Sustainability of rice processing in sub-Saharan Africa is one of the most important aspects in ensuring food security and self-sufficiency of the region, wherein social, economic, and environmental criteria of the processes need to be considered. Rice processing is energy intensive and produces large amounts of by-products, including rice husk that accounts for more than 20% of the paddy by weight, and is currently an underutilized waste that is discarded, endangering the ecosystems and the health of the rural communities. Engelberg and Milltop mill processed rice husks are the most abundant and most unused by-products of rice processing in sub-Saharan Africa.

The sustainability of utilization of rice husk as a biofuel feedstock will greatly increase the overall sustainability of rice processing. Raw rice husk has low energy density and is difficult to handle, thus, in order to increase its viability and adoption by the communities as an alternative source of fuel, it needs to be densified using simple low energy techniques suitable for the local communities to adopt. However, the characteristics of the produced rice husk differ, and they especially depend on the milling methods used. Characterization is an important step towards sustainable utilization of this biomass as a biofuel feedstock.

Densification is of primary importance in considering biomass as an effective biofuel feedstock, because it increases its portability, as well as, energy density. Sustainability and the viability of the densification process determine the commercial utilization of the biomass as a biofuel feedstock. For this reason, the primary chapter of this thesis has focused on increasing the sustainability of rice processing by improving current conventional methods, and the utilization of the rice husk by-products as an energy source. This was followed by a chapter that focused on the effects of process parameters on the densification of raw rice husk without pre-treatment, using locally available binders at medium applied pressures. These primary chapters led to the characterization of the two most abundant rice husks in sub-Saharan Africa; they are products from the single stage Engelberg and the Multi-stage Milltop milling machines. The characterization chapters that followed studied the physical, chemical and

thermochemical characteristics of the Engelberg and the Milltop rice husks, respectively.

More specifically, this work initially studied the existing practices to improve the sustainability of rice processing in sub-Saharan Africa which included: utilization of waste heat from the diesel engines that drive the mills for improved drying and temperature increase of pre-soaking through utilization of solar energy, and also to use the heat content of rice husk as an alternative energy source to firewood. This leads to the optimization and redesign of the existing parboiling stoves to minimize the heat loss to the environment. The results showed that the utilization of rice husk as an alternative fuel and the redesign of the stoves and parboiling vessels will increase the sustainability of rice processing and can be easily adopted by the community. However, it was found that solar energy was not sufficient while the utilization of waste heat from the diesel engines for drying and pre-soaking would be difficult to implement at the rural scale but highly viable at the medium scale, because of the proximity of the parboiling operations located nearby the milling stalls. The study also found that research, development of appropriate technology, and education (RATE) of the rural community is an important way of increasing sustainability through awareness building.

The effect of process parameters on densification of rice husk using locally available binders and a manual hydraulic press at medium applied pressure showed that at the optimum densification moisture content of 15.1%, die pressure, binder type, and binder ratio have significant effects on both the water permeability and densities of the briquettes produced. Densified rice husk bound with paraffin wax, whole *Afzelia africana* aril, and gum Arabic (*Acacia senegal*) were found to be more hydrophobic than the ones with de-oiled *Afzelia africana* aril and groundnut shell. However, de-oiled *Afzelia africana* aril produced briquettes with higher densities than the high lipid whole *Afzelia africana* aril, showing that the fat content affects both permeability and density of the produced rice husk briquettes.

Physical analysis of the rice husk showed that the Engelberg rice husk is significantly different from the multistage Milltop rice husk ($P<0.05$). Particle size analysis of the Engelberg and Milltop produced rice husks showed that the Milltop husks have significantly higher geometric diameter with 95% of the samples by weight, retained by Standard sieve #20 (0.850 mm). The Engelberg rice husks were much smaller with 95% of the particles retained by sieve #100 (0.150 mm). The Engelberg rice husks were much finer with higher bulk and particle densities than the Milltop rice husk samples. Particle size analysis, microstructural analysis using SEM, and statistical analysis showed that the most important components of the Engelberg rice husk samples were immature paddies and broken kernels, while the most important components of the Milltop were unbroken Lemma and Palea with small broken kernels and bran present within the samples. The Engelberg and the Milltop rice husks form two significant groups of rice husks that will require two completely different design parameters to be utilized as biofuel, and it was found that even within the two groups there can be differences that are significant between the samples that could be due to rice ecology, variety, harvesting and other postharvest handling processes other than milling. However, this should not hinder the design of a versatile biofuel production system that will utilize the two as specific groups of rice husks based on their physical characterization.

Chemical analysis of the Engelberg and Milltop rice husks showed that the Milltop samples have lower amounts of proximate starch, protein, and fat compared with the Engelberg samples. The FT-IR results also showed that the Engelberg and Milltop rice husks spectra have unique characteristics that define them as separate groups; with key differences being the quantity of the proximate components that confirmed what was observed during the starch, protein, and fat analyses of the samples. The FT-IR analysis also distinguished the samples with higher immature grains from the rest of the rice husk samples.

Thermochemical characteristics of the Engelberg and the Milltop milled rice husks including proximate composition and higher heating value (HHV) were studied. An effective method for determination of the HHV of rice husk using oxygen bomb calorimeter coupled with comparative analysis of bomb calorimeter residuals, proximate ash, and densified pellet impact resistance was developed. HHV prediction models for the rice husks of the two milling machines were developed. Higher HHV values of the

Engelberg milled rice husk samples compared to the Milltop samples were found to be consistent with their respective higher volatile proximate components. FT-IR and SEM analyses showed that there were no significant differences between the physico-chemical composition of the Engelberg and Milltop rice husk ash samples.

Résumé

La pérennité de la transformation du riz en Afrique sub-Saharienne est l'un des aspects les plus importants pour assurer la sécurité alimentaire et l'autosuffisance dans cette région, tout en prenant en considération les critères sociaux, économiques, et environnementaux des processus. La transformation du riz est très énergivore et produit une grande quantité de sous-produits y compris les écorces de riz qui représentent plus de 20% du poids de la production, et est actuellement un sous-produit gaspillé pouvant mettre en danger les écosystèmes et de la santé des communautés rurales dans cette région. Les écorces de l'Engelberg et de la Milltop sont les plus abondantes en terme de sous-produits les plus sous-utilisés de la transformation du riz en Afrique sub-Saharienne.

L'utilité de l'utilisation des écorces de riz comme matière première de biocarburants permettra d'accroitre considérablement la pérennité de la transformation du riz. L'écorce de riz a une densité d'énergie largement moindre par rapport aux carburants classiques, et pourrait être difficile à gérer. Afin d'accroitre sa viabilité et l'adoption par les communautés locales comme carburant alternatif, il doit être densifié en utilisant des techniques simples à faible énergie que la communauté locale peut adopter. Cependant, les caractéristiques des écorces de riz sont différentes et dépendent notamment du procédé de transformation utilisé. La caractérisation est une étape importante vers l'utilisation durable de cette biomasse comme matière première et biocarburant.

La densification est de première importance dans l'examen de la biomasse comme matière première de biocarburants, car elle augmente sa portabilité, ainsi que, sa densité d'énergie. La durabilité et la viabilité du processus de densification déterminent la probabilité de l'utilisation commerciale de la biomasse comme biocarburant. Pour cette raison, le chapitre principal de cette thèse a porté sur la durabilité de la transformation du riz en améliorant les méthodes actuelles classiques, et l'utilisation de ses sous-produits, en particulier des écorces de riz comme source d'énergie. Ce chapitre a été suivi par une étude de l'effet des paramètres du procédé sur la densification des écorces de riz en utilisant des liants disponibles localement à des

pressions moyennes. Ces chapitres ont conduit à la caractérisation des deux types d'écorces de riz les plus abondants en l'Afrique subsaharienne : produits des moulins à étape unique Engelberg et multi-étape Milltop. Les chapitres de caractérisation qui suivent ont étudié la physique, la chimie, et les caractéristiques thermochimiques des deux différentes écorces de riz.

La première étude a visé la façon d'améliorer la durabilité de la transformation du riz en Afrique sub-saharienne comprenant : L'utilisation de la chaleur perdue par les moteurs diesel qui dirigent les moulins de transformation afin d'améliorer le séchage et le l'efficacité du pré-trempage ; l'utilisation de l'énergie solaire pour le pré-trempage; l'utilisation des écorces de riz comme combustible comme une alternative au bois de chauffage; et l'optimisation et la modification des poêles d'étuvage afin de minimiser la perte de chaleur dans l'environnement. Les résultats ont montré que l'utilisation de l'écorce de riz comme une alternative au bois de chauffage et la modification des poêles va augmenter la pérennité de la transformation de riz et peut être facilement adopté par la communauté locale. Cependant, l'utilisation de l'énergie solaire pour le pré trempage du riz a été jugé non rentable en raison des coûts et de la disponibilité des matériaux. L'utilisation de la chaleur résiduelle du moteur diesel est viable au niveau de la moyenne échelle en raison de la proximité des échoppes de transformation du riz. L'étude a également constaté que le thème proposé (recherche, technologie appropriée, et de l'éducation (RTAE)), est un outil efficace pour augmenter la pérennité de la transformation de riz dans les régions rurales de l'Afrique sub-saharienne.

L'étude des paramètres de la densification des écorces de riz en utilisant des liants disponibles localement et une presse hydraulique manuelle, a des pressions moyennes, a montré que pour une densification optimale le taux d'humidité, le type et la quantité de liant, ont des effets significatifs sur la perméabilité de l'eau et la densité des briquettes produites.

L'analyse physique des écorces de riz a montré une différence significative entre les deux moulins Engelberg et Milltop ($P<0.05$). L'analyse granulométrique a montré que le diamètre géométrique de la Milltop est significativement plus élevé avec 95% des échantillons en poids étant retenu par le tamis Standard #20 (0,850 mm). Les écorces

Engelberg étaient beaucoup plus petites avec 95% des particules en poids retenu par un tamis Standard #100 (0,150 mm). Les écorces de riz Engelberg étaient plus fines et avaient une densité apparente plus élevée en comparaison avec l'écorce de riz Milltop. Les analyses statistiques de la granulométrie et de la microstructure ont montré que le principal composant de l'Engelberg contenait à la fois les composants internes et externes des grains de riz. Tandis que, les écorces de riz Milltop sont composées principalement de la coque extérieure.

L'analyse chimique des écorces de riz Engelberg et Milltop ont montré que les échantillons Milltop avaient une plus petite quantité d'amidon, de protéines et de matières grasses en comparaison avec les échantillons Engelberg. Les résultats de l'analyse FTIR ont également montré que les deux écorces de riz ont des caractéristiques uniques qui les définissent comme groupes; avec les principales différences étant la quantité des composants chimiques qui ont confirmé ce que l'on a observé au cours des analyses de l'amidon, des protéines et des graisses.

L'analyse thermochimique des écorces de riz Engelberg et Milltop impliquant les analyses immédiates et la détermination du pouvoir calorifique supérieur (HHV) a dévelopé une méthode utilisant une bombe calorimétrique. Des modèles prédictifs pour la détermination du HHV des échantillons des écorces de riz ont été développés. Les analyses FTIR et de microscopie SEM ont montrés qu'il n'y avait pas de différences significatives physico-chimiques entre les cendres Engelberg et Milltop.

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PREFACE AND CONTRIBUTION OF AUTHORS

The contribution and role made by authors are as follows: Mr. Mohammed I. Y. Bakari the Ph. D. candidate is the principal author, who designed and carried out all the field research, experiments, data analysis, and wrote the thesis and the manuscripts intended for scientific publications. Dr. Valérie Orsat is the thesis supervisor, who guided the candidate during the entire thesis; she corrected, edited, and reviewed all the chapters of the thesis, as well as, the manuscripts intended for publication. Dr. G.S.V. Raghavan, assisted in editing and reviewing all the chapters of the thesis after it was completed.

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NOMENCLATURE

ρ_b	Bulk density of a biomass (kg/m^3)
ρ_p	Specific density of individual particles (kg/m^3)
φ	Particle shape
c	Material composition
l	Particle length (m)
d	Particle width (m)
p	Applied axial pressure on particle (N/m^2)
mc	Moisture content
PSD	Particle size distribution
P_1	Initial pressure of sample chamber (psi)
P_2	Final pressure of sample chamber (psi)
V_{Cell}	Volume of the chamber containing the sample (m^3)
V_{exp}	Volume of the expansion chamber -the reference chamber (m^3)
V_{samp}	Volume of the sample (m^3)
m_{samp}	Mass of the sample (kg)
CLSM	Confocal scanning laser microscope
DOM	Degree of milling
FT-IR	Fourier transform infra-red spectroscopy

FTIR-ATR	Fourier transform infra-red spectrometer equipped with attenuated total reflection equipment
HHV	High heating value (MJ/kg)
LTO	Low temperature oxidation
MTO	Medium temperature oxidation
HTO	High temperature oxidation
EGA	Evolved gas analysis
TGA	Thermogravimetric analysis
SEM	Scanning electron microscopy
SEM-EDS	Scanning electron microscopy and energy dispersive X-ray spectroscopy
RATE	Research appropriate technology and education
MDGs	Millennium Development Goals
SDGs	Sustainable Development Goals
CAADP	Comprehensive African Agricultural Development Programme
NEPAD	New Partnership for Africa’s Development
TOD	Time of the day

I. GENERAL INTRODUCTION

1.1 BACKGROUND

Alternative and renewable energy from lignocellulosic biomass has recently become a high priority and will play an important role in the long term sustainability of agricultural production. Rice husk is an abundant lignocellulosic biomass waste from rice postharvest processing. In sub-Saharan Africa, the increase in demand for rice as a staple food due to the continuing population growth in the regions where rice is grown and consumed have made rice husk waste an environmental issue. Although rice husks have high calorific value, there are two issues that are preventing their utilization on a large scale as an alternative fuel feedstock. These key issues are due to the variability of the characteristic properties of rice husk obtained from different regions, and portability issues due to their low bulk density. Bakari et al., (2012) in their assessment of the local situation concluded that utilization of rice husk as an alternative to firewood and fossil fuel will increase the sustainability of the post-harvest processing of rice. Goyal et al., (2012) carried a study on the energy utilization pattern of the rice milling industry, and concluded that utilization of rice husk as an alternative to fossil fuel and electricity will increase energy conservation and efficiency.

Rice husk also called rice hull, is the protective shell that protects the grain. It is made up of two leaves called the lemma and palea that are interlocked enclosing the grain. To understand the characteristics of the milling waste referred to as rice husk that is discarded, all the other components of the rice paddy that are removed and discarded as rice husk during the milling process need to be considered. The anatomy of a rice paddy consists of a husk that encloses a brown rice kernel. The brown rice kernel has protective translucent pericarp layers (epicarp, mesocarp & cross layer) followed by the bran layers (aleurone & subaleurone), protecting the embryo and the starchy endosperm (Champagne, 2004). Figure 1.1 shows the longitudinal cross-section of a rice paddy, showing the layers of components that are usually removed to obtain the polished rice grain. During the milling process the lemma-palea interlock is broken by force of rollers or pounding, separating the endosperm from the other components of the paddy. Depending on the milling method, some of the endosperm breaks and is also entrained in the risk husk waste. As well, immature grains may stay intact, without the lemma-palea interlock breaking and are collected as part of the waste.

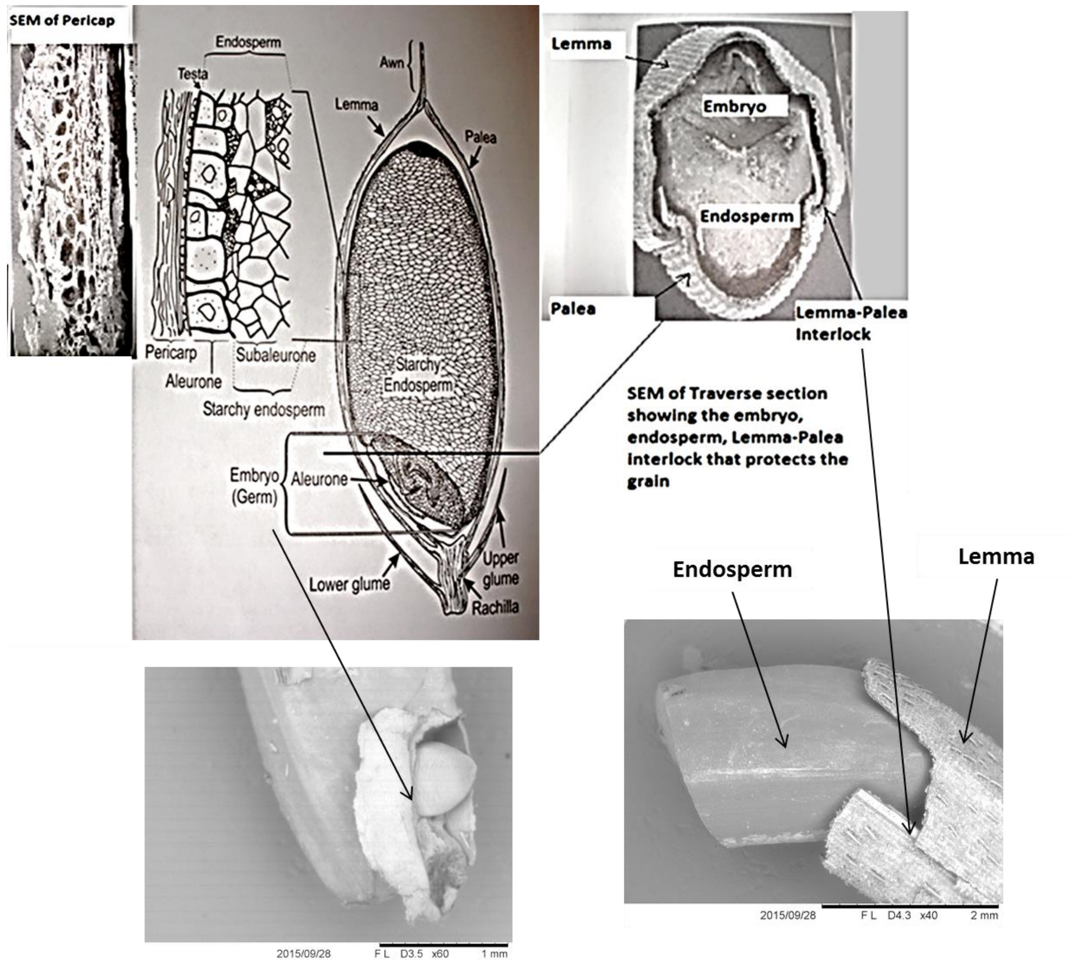


Figure 1.1. Longitudinal cross-section of rice paddy (Champagne, 2004; SEM pictures, 2015)

Hence, in sub-Saharan Africa, the small and medium scale milling waste, referred to as rice husk is a combination of the upper layers of the rice paddy, broken rice, embryo, and immature grains. Different techniques are needed to determine the percentages of these components that make up the rice husk waste. It is thus necessary to determine the characteristics of rice husks in order to adequately use it as a biofuel feedstock.

Rice paddy is one of the most processed crops in the world. Postharvest processing of rice involves drying, parboiling, and milling. Postharvest processing affects the yield of the rice and the amount of the component of the paddy that ends up at the rice husk dump. Optimum harvest and postharvest processing could result in higher yield rice and lower milling waste. Towards this end, the method of milling plays a large role on the overall characterization of rice husk. Chen et al., (1998), carried out a research on two milling systems – single and triple break milling systems and they found that both the surface lipid content of the milled rice and the protein content are influenced by the degree of milling (DOM). In sub-Saharan Africa, the two major milling machines used are the multi-stage Milltop and the single-stage Engelberg machines (JAICAF, 2010). In Uganda, of the total of more than 600 rice mills (small and large scales) the majority are either the single-stage or multistage milling Milltop machines (JAICAF, 2010). The Engelberg mills are most common in the eastern part, while the Milltop dominates in the western region of the country due to historical backgrounds (JAICAF, 2010). Sakurai et al., (2006) carried out a research on miller clusters in Ghana and reported that the majority of the millers use either Engelberg or Milltop (or similar) machines. Bakari et al. (2012) found that the majority of the machines used by the medium and small scale rice processors in the Upper Benue river basin in North Eastern Nigeria were the Engelberg type machines (Figure 1.2). Appiah et al., (2011) carried out a study on determining the postharvest losses of rice in the Ashanti region of Ghana, and reported that the milling machines used in that region are both the single-stage Engelberg type and the multistage (Milltop SB10, and SB30) milling machines (Figure 1.3). Milltop milling machines were found to be more efficient producing 67.3 % head rice yield as compared to the Engelberg milling machines that have a head rice yield of 47.3 % (Appiah et al., 2011).

Figure 1.2. Diesel/electric belt–driven Engelberg machine

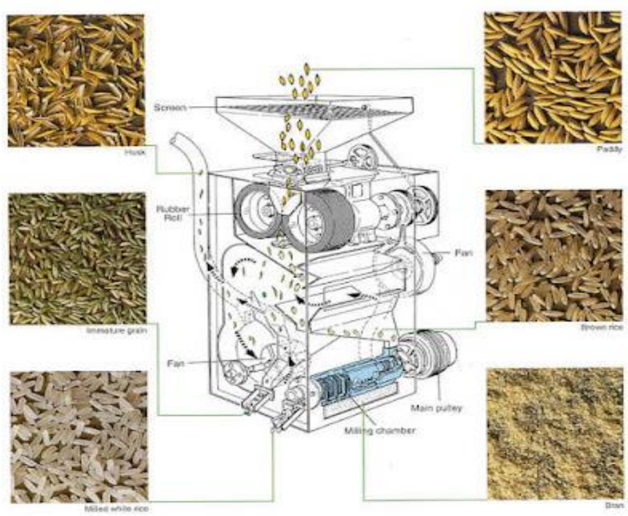


Figure 1.3. Satake Milltop SB30 and SB10 configuration (www.satake.com)

Physical, chemical, thermal and thermochemical properties of rice husk are important in assessing the potential of rice husk as a biofuel feedstock. The physical analysis provides information such as bulk density, particle density, particle size distribution, moisture content and microstructural properties. The chemical analysis provides information on the chemical components including the starch, fat, protein and fibre contents which are important to consider in the densification, biochemical and thermochemical conversion processes. The FT-IR analysis could provide information on the chemical groups that influence densification and thermochemical processes, including silica contents and other mineral contents of the rice husk, and its ash and its fixed carbon components. It can also be used as a tool to determine the quantity of lignocellulosic components (cellulose, hemicelluloses and lignin) of the rice husk (Adapa et al., 2009). The thermochemical analysis could lead to key information such as: the fixed carbon content, ash content, volatile matter content, energy content, thermal, and thermochemical characteristics of the rice husk samples. Physical and chemical characterization of the fixed carbon and ash are very important in the characterization of rice husk. It is well established that char properties greatly affect heterogeneous reactions between char and various gases present in combustion atmospheres such as O_2 and NO (Guerrero et al., 2008). Fewer studies are found in the literature concerning the characterization of chars from the biomass (Guerrero et al., 2008).

The low bulk density makes biomass such as rice husk difficult to handle using standard handling and storage equipment. The initial process of utilization of rice husk as a biofuel feedstock is to increase its density through a process of compaction or densification. Densification can increase the density of biomass from an initial bulk density of 40-200 kg/m^3 to a final compact density of 600-1200 kg/m^3 (Holley, 1983; Adapa et al., 2009). With densified biomass, its ease of handling and storage make it attractive as a fuel feedstock for both thermochemical (combustion furnace, gasifiers, pyrolysis reactor, etc.) and biochemical (fermentation bioreactors for producing fuel such as ethanol, syngas, hydrogen, etc.) energy conversion processes. Effective densification of rice husk, like other biomass, depends on the physical, chemical, thermal and microstructural properties. These properties are based on the variety of rice paddy, regions and conditions where the paddy is grown, and to a greater extent the postharvest processing methods, especially the milling or dehusking methods of the paddy.

1.2 CONTEXT AND HYPOTHESIS OF THE RESEARCH

This research will study the sustainability of rural rice processing in sub-Saharan Africa, and investigate the effect of process parameters on the densification of rice husk in order to characterize the most abundant rice husk locally produced by using either the Engelberg mill or the Milltop mill. The hypothesis of this research is that the milling method used affects the physical, chemical, thermochemical properties of rice husk which in turn affect its densification and energy conversion characteristics.

1.3 SCOPE

The scope of this research is to study the sustainability of rice processing in rural sub-Saharan Africa in order to effectively utilize rice husk as a feedstock for biofuel production. The generic outcome of the study is applicable to the West African rice processing system.

1.4 OBJECTIVES

The overall objective of this research is to study how appropriate processing of rice husks will increase the sustainability of rural rice processing in sub-Saharan Africa; with its application in biofuel production for local use.

The following are the specific objectives of this research.

1. To investigate the varying practices for increasing the probability of achieving sustainability of rice processing in rural sub-Saharan Africa.
2. To study the effects of process parameters including binder type, binder ratio, and die pressure on permeability and density after densification of rice husk without pre-treatment or modification of the raw rice husk.
3. To study the physical characteristics of Engelberg (single-step) and Milltop (multi-step) rice husk samples from sub-Saharan Africa in order to develop physical process parameters for the rice husks to be used as biofuel feedstock.
4. To study the chemical characteristics of the Engelberg (single step) and Milltop (multi-step) rice husks samples from sub-Saharan Africa and develop chemical process parameter ranges, for utilizing the rice husks as biofuel feedstock.
5. To study the thermochemical characteristics of rice husk samples from sub-Saharan Africa and develop an optimum method for obtaining high heating value from rice husks of differing sources using high pressure oxygen bomb calorimetry.

II. GENERAL LITERATURE REVIEW

2.1 Characterization of rice husk – a lignocellulosic biomass

Rice husk is a lignocellulosic biomass resulting from the postharvest processing of paddy rice. It is the protective shell that protects the rice kernel. The husk accounts for 22% of the weight of the paddy. The outer surface of rice husk is relatively rougher than the inner surface that houses the grain (Ndazi et al. 2007). It contains significant amounts of silica (20% w/w) (Ndazi et al., 2007). The silica exists on the outer surface in the form of silicon-cellulose membrane that forms a natural protective layer against termites and micro-organisms attacks on the paddy (Ndazi et al., 2007). The inner surface of the rice husk is smooth and may contain wax and natural fats that provide good shelter for the grain (Ndazi et al., 2007). The method used in postharvest processing practices of paddy rice will help determine the percentage of the outer and inner components of the rice which end up in the rice husk that is discarded as waste. In all rice milling steps, high degree of milling could result in breakage of the kernels which are then entrained into the waste stream and are collected within the waste component of rice husk. The breakages are not only caused by the choice of milling process but also dependent of the rice variety, cultivation conditions, harvest maturity, parboiling methods and drying methods which all affect the strength of the kernel and its resistance to abrasion during milling (Champagne, 2004).

2.2 Physical characterization of rice husk

Proper understanding of the physical properties of biomass is necessary for utilizing these materials as fuel feedstock for thermochemical and biochemical processes. The physical characteristics of rice husk include particle size distribution, bulk density, particle density, and moisture content. These analyses provide the mechanical and inter-particle relationship of the rice husk samples. The importance of moisture content on the physical properties of biomass makes it necessary to determine the moisture content as part of the physical characterization (Zhang et al. 2012). Moisture content also affects the thermochemical properties of biomass. High moisture content decreases the heating value of fuel, which in turn reduces conversion efficiency as a large amount of energy would be used for the initial drying step during the conversion processes (Mansaray and Ghaly, 1997; Zhang et al., 2012).

2.2.1 Physical component analysis

Physical component analysis of the rice husk includes the differentiation of matured paddy that was not dehusked and the presence of immature grains. The physical quality is important because it can be an indicator of the harvest and postharvest processing efficiencies. A novel method for determining the components of the rice husk physically is the utilization of scanning electron microscopy (SEM). SEM provides information on the physical components that make-up the rice husk. Immature grains, broken rice components, impurities, germ, bran, and surface characteristics of the husks can be studied following the milling process. It is an important characterization that has not been carried out to date to compare Engelberg (single-step) and Milltop (multi-step) rice husks. This will be an important contribution for the utilization of the byproducts from single and multistage milling machines as biofuel and industrial feedstocks.

2.2.2 Particle size distribution

Particle size distribution (PSD) of biomass greatly influences the economics and technical aspects of utilizing it as a biofuel feedstock. The influence of PSD on bulk density, flowability, heating rate, diffusion rate, and rate of reaction and densification characteristics of biomass makes it as an important parameter (Mani et al., 2006a & 2006b). Abdullah and Geldart (1999) found that maximization of packing density is possible when there is a small amount of fine particles in a biomass mixture. Decreasing particle size of corn stover grinds resulted in an increase in density and durability of densified pellets and briquettes, due to the fact that smaller particles have more bonding area than larger particles (Mani et al., 2006b; Kaliyan and Morey 2009).

PSD analysis of rice husk samples from the two major milling machines, the Engelberg and the Milltop is very important. The nature of rice husk is highly dependent on the postharvest processing methods, especially the milling process parameters. The two major milling machines studied in this project produce rice husks with different particle size distributions. This study will provide the necessary information on PSD characteristics of rice husks produced from the two milling machines. The standard method for measuring PSD is the ASAE Standard 319.3 (2006b). This method requires the use of stacked standard sieves (ones with largest opening on top) on a mechanical shaker with motor rotating at specific speed for specific time usually 10 minutes (Mani et al., 2006a ; Zhang et al., 2012).

2.2.3 Bulk density

Bulk density (ρ_b) of a biomass is a physical property that depends on material composition (c), particle shape (φ), particle size (l, d), particle orientation (s), specific density of individual particles (ρ_p), particle size distribution (PSD), moisture content (mc), and applied axial pressure (p) (Lam et al., 2007). These relations can be described as:

$$\rho_b = f(c, \rho_p, l, d, \varphi, s, PSD, mc, P) \qquad (2.1)$$

The size parameters, l and d are usually considered in relation to each other using the concept of aspect ratio (l/d) to define whether biomass particles will be considered as cylindrical (l/d>1) or disk (l/d<1). In the case of rice husk, the mill type and degree of milling is an important factor that affects the parameters that define the bulk density of the biomass (Lam et al., 2007). Single-stage Engelberg milled rice husk will be largely considered as disk, while the multistage Milltop rice husk will be largely cylindrical from the preliminary assessment of the physical analysis.

The bulk density affects the economics of collection, transportation, storage, as well as, feeding the material into thermochemical and biochemical conversion systems (Lam et al., 2007; Zhang et al. 2012). It also affects the thermochemical and biochemical processes characteristics of the biomass (Lam et al., 2007). During combustion, the ignition front speed of biomass is inversely proportional to bulk density, while the burning rate tends to decrease linearly (Lam et al., 2007).

Bulk density of rice husk is an important factor in characterizing rice husk. In this research, the bulk density of rice husk from the Engelberg and the Milltop rice husks from different regions will be analyzed. Nowhere in literature has this been done. The contribution of this research will facilitate the design of thermochemical or biochemical conversion systems that can utilize rice husk from these two milling machines as fuel feedstock.

2.2.4 Particle density using helium pycnometry

Biomass particle density affects the interstitial airflow velocity and the heat and mass transfer conditions and ultimately influences reaction parameters such as heat conductivity, burning rate, conversion efficiency and emissions (Igathinathane et al., 2010). Pycnometry has been used in the past to determine the density and porosity of food material biomass using nitrogen and helium as displacement fluids (Moreau and Rosenberg, 1998). The gas penetration rate through the porous media and its variation is an attribute of the porosity of the biomass. Helium gas pycnometry uses the ideal gas law to determine the true volume of the biomass material. The volume of the sample V_{samp} is determined using the following relations (Lam et al., 2008):

$$Vsamp = V_{Cell} - Vexp(\frac{P_1}{P_2} - 1) \quad (2.2)$$

Where:

V_{Cell} = the volume of the chamber containing the sample

V_{exp} = the volume of the expansion chamber -the reference chamber

V_{samp} = the volume of the sample

P_1 = initial pressure of sample chamber when expansion chamber is closed

P_2 = final pressure of sample chamber with the expansion chamber open

The density of the biomass is calculated as:

$$\rho = \frac{m_{Samp}}{V_{Samp}} \quad (2.3)$$

Where:

m_{samp} is mass of the sample

The specific volume of the sample, U_{sample} is calculated as the inverse of the particle density:

$$U_{Samp} = \frac{V_{Samp}}{m_{Samp}} \quad (2.4)$$

2.3 Chemical characterization of rice husk

Chemical characterization of lignocellulosic biomass is necessary in order to utilize it optimally as a feedstock for biofuel and production of other bio-products; because it would exhibit very different properties with respect to traditional fossil fuels and fossil fuel derivatives (Naik et al., 2010). Although there have been several chemical analyses of rice husks in the literature, no study has been carried out to analyze and compare the properties of the Engelberg and Milltop produced rice husks. In sub-Saharan Africa, these two types of rice husks are potentially the most important source of biofuel from agricultural waste in the region. This research will provide the necessary information on how to utilize this abundant biomass, reducing the health and environmental issues it represents, hence increasing the sustainability of rice production, as it depends on appropriate postharvest processing methods adopted in the sub-Saharan Africa region.

2.3.1 Starch analysis

Starch is an important component of agricultural biomass. Its binding characteristics contribute to effective densification of biomass without the need of additional binders. Lignocellulosic biomass with high starch content can be attractive for bioethanol production using biochemical processes. Starch determination methods can be broadly grouped into acid hydrolysis or enzymatic procedures. Acid hydrolysis can only be applied to pure starch samples and thus has limited applications in this study. Reliable quantification of the amount of starch in biomass can be done using the AOAC Standard 2002.02 (2002) and AACC Internationally Approved Method 32-40.01 (2001). The starch content in rice husk is very small. Champagne (2004) reported rice husk starch contents of 1.5%. However, milling methods, especially the degree of milling (DOM), can increase the starch content in rice husk significantly due to the presence of a higher amount of broken rice kernels.

2.3.2 Protein analysis

Protein is another component of biomass that acts as a natural binding agent within the biomass. It facilitates densification of biomass at room temperature without the addition of binding agents. However, the nature of the protein determines the adhesive strength of the protein. Since protein in biomass naturally exists as complex long-chain molecules, its effectiveness as a binder can be improved by treatment using heat or chemicals to break up the long chains into smaller ones. Treated or modified proteins from biomass have been used as adhesives in the production of particle board from rice husks (Ciannamea et al., 2012).

Proteins in rice are found in different parts of the paddy including the endosperm cells (where large molecules of glutelin molecules bind strongly to the starch granules with strong disulphide and/or hydrophobic bonds), the kernel, the husk and the bran (Agboola et al., 2005). Rice protein can be classified into four groups: alkali-soluble glutelins, water-soluble albumins, salt-soluble globulins and alcohol-soluble prolamins (Landers et al., 1994). The protein content in rice husk comes from the inner layer of the rice husk and the broken rice kernels entrained in the rice husk during milling. The analysis of the protein content in the Engelberg and Milltop rice husks will be important in determining the optimal method to best densify these two rice husks. The normal procedure of determining protein content is by measuring the amount of nitrogen in the biomass and then multiplying that nitrogen content by a determined factor (6.25 for most biomass).

The nitrogen content in biomass can be determined chemically or thermochemically. Bledzki et al., (2012), determined the protein content of rice and wheat husk chemically, by dissolving the samples in sulphuric acid in the presence of potassium sulphate; and then titrating the product with hydrochloric acid and calculating the protein content based on the concentration of ammonium hydroxide. Thermochemical protein analysis involves controlled combustion of the biomass and extraction of its nitrogen component. The protein content is then calculated by multiplying the nitrogen content with a factor of 6.25.

2.3.3 Fat analysis

Fat content is another important component of agricultural biomass. Fat can have either a positive or negative effect on the viability of agricultural biomass as an energy or biomaterial feedstock. The higher the fat content, the higher the volatile components of the biomass that can affect the overall heating value of the biomass. The amounts of fat in the biomass affect its compaction characteristics because fat plays several important roles. In the initiation of the compaction process, the fats act as lubricant reducing friction between particles, as they re-align due to the compaction pressure. With the increase in the compaction, the particle to particle interaction increases, initiating the process of bonding due to water soluble proteins and starch. At this stage, depending on the quantity of fat, and because of its hydrophobic nature, the fats negatively affect the bonding process. The fat does so, by inhibiting the protein and starch from forming liquid bridges that will ultimately solidify to form solid-bridge bonding, which are necessary for strong densified biomass pellets and briquettes (Sokhansanj et al., 2005; Mani et al., 2006; Kaliyan and Morey, 2009). Kaliyan and Morey (2009), reported that fat greater than 6.57% reduces durability of biomass, by reducing the densified biomass ability to resist breakage due to externally applied forces. Fat also has a positive influence on densified biomass since a higher fat content increases the hydrophobic properties of densified biomass, helping to prevent moisture uptake.

Fat in rice paddy can be classified as either starch or non-starch lipid. Starch lipids are found in the germ associated with protein and starch granules. Non-starch lipids are found in the aleurone, subaleurone, germ and the hull (to a smaller extent) of the rice paddy (Champagne, 2004). Depending on the degree of milling, most of the non-starch lipids are removed during the milling process and become part of the milled by-products. Based on this fact, it has been suggested that the degree of milling could be determined based on the grain surface lipid quantification (Champagne, 2004).

2.3.4 Fourier Transform Infra-Red (FT-IR) spectroscopy

Fourier Transform Infra-Red (FT-IR) spectroscopy can be used to survey the chemical functional groups that are important in the characterization of biomass. Naik et al., (2010) used FT-IR to characterize Canadian sourced biomass and identified the hemicellulose, cellulose and lignin contents of the wheat straw, barley straw, flax straw, timothy grass, and pinewood samples. Adapa et al., (2011) quantitatively predicted the lignocellulosic components of non-treated and steam exploded barley, canola, oat and wheat using FTIR.

The chemical components of both the outer and the inner surfaces of rice husk were found to be the cause of the weak adhesion between rice husk and binders. The inner surface of rice husks are smooth and contain natural fats that affect adhesion properties of rice husk and binders both physically and chemically (Ndazi et al., 2007). These fats are either in the form of starch or non-starch lipids that are found in different layers of the rice paddy (Champagne, 2004). The outer surface of rice husk is relatively rougher and contains high amount of silicone-cellulose membrane responsible for the insufficient bonding on rice husks surfaces and various binders (Ndazi et al., 2007). Ndazi et al., (2007) studied the inner and outer surface of rice husk, before and after treatment of rice husk with NaOH using FT-IR and were able to identify changes by frequency shifts and peak disappearance at certain frequencies following treatments. In the current study, FT-IR analysis of the sub-Saharan rice husk samples will provide important information on the chemical components present in the rice husks. High absorbance for specific components will provide the relative quantification of the amount of the components among different samples.

Certain types of compounds give strong, broad absorptions, which are very prominent in the IR spectrum. The hydrogen-bonded OH stretching bands of alcohol, phenols, and carboxylic acids are easily recognized at high frequency range (3700-3100 cm^{-1}). The NH_3^+ group in amino acids gives a very broad and unsymmetrical band that extends several hundred wavenumbers. Broad bands associated with bending of NH_2 or NH groups of primary or secondary amines are found at the low-frequency end of the spectrum.

Hydrocarbon can be identified by absorption in the region between 3100 and 2800 cm^{-1}. Aromatic or unsaturated aliphatic =CH groups are identified by absorptions between 3000 and 3100 cm^{-1}. If the absorption is entirely above 3000 cm^{-1}, the compound is probably aromatic or contains only =CH or $=CH_2$ groups. Absorptions above and below 3000 cm^{-1} indicate the presence of both saturated and unsaturated or cyclic hydrocarbon moieties, with strong bands between 1000 and 650 cm^{-1} as confirmation of identifying alkenes or aromatic structures. Sharp bands near 725 cm^{-1} or 1440 cm^{-1} are indications of linear chains containing 4 or more CH_2 groups (Lambert et al. 2011).

Oxygen-containing compounds are important components of lignocellulosic biomass. A strong, broad band between 3500 – 3200 cm^{-1} is usually due to water and the hydrogen-bonded OH stretching mode of an alcohol or a phenol. In the absence of hydrogen-bonding, the OH stretching bands is sharp and appears at higher frequencies (3650-3600 cm^{-1}). Carboxylic acids give very broad OH stretching bands between 3200 and 2700 cm^{-1}, with likely sharp peaks near 3300 cm^{-1} due to CH stretching vibrations.

FTIR characterization of lignin can be based on the peaks within the lignin finger print region: 1800 cm^{-1} to 800 cm^{-1} of the IR spectrum. The most important peaks that characterize lignin in this region are 1593 and 1506 cm^{-1} indicative of aromatic skeletal vibrations, where 1458 and 1420 cm^{-1} are CH deformations, 1328 cm^{-1} represents syringyl ring plus guaiacyl ring, 1234 cm^{-1} is indicative of syringyl ring and C=O stretching, and 1120 cm^{-1} is indicative of the presence of aromatic skeletal vibrations (Zhou et al., 2011). The strong peak at around 1025 cm^{-1} indicates the strong presence of alcohols, carboxylic acids, ethers and esters. Esters have bands from both C=O and C-O-C groups, but none from the OH group. Alcohols have bands from both OH and C-O groups, but no C=O stretching band. Carboxylic acids contain bands in all three regions (Lambert et al., 2011). Also the secondary peak around 1100-1217 cm^{-1} indicates silica presence in the form of cellulose-silicates (Ndazi et al., 2007).

Bands between the regions of 3500-3300 cm^{-1} may indicate the presence of primary and secondary amides which contain nitrogen, but that should be confirmed by a strong doublet in the IR spectrum centered near 1640 cm^{-1} or a sharp band near 2200 cm^{-1} which is a characteristic of a nitrile in the IR spectrum. The C=O (carbonyl) stretching region is one of the most important regions of the spectrum for structural analysis (Lambert et al., 2011). Most organic compounds that contain C=O groups show very strong absorption in the range of 1850 to 1650 cm^{-1}. The actual position of the peaks within this range is characteristic of the compounds.

2.4 Thermal characterization of rice husk

2.4.1 Proximate analysis

Proximate analysis is an important analysis for determining the amount of volatiles, ash and fixed carbon in the biomass. The standard method used for this analysis is the American standard for testing of materials (ASTM 3173-03; ASTM 3174-04; ASTM 3175-02) for solid fuels. The standard practice for proximate analysis of coal and coke is used for proximate analysis of biomass fuel including rice husk. The proportion of the volatiles is an important parameter in the determination of the ignition and thermochemical reactions of the biomass. The proportion of volatiles, fixed carbon and ash contents are important parameters in the design of thermochemical reactors.

2.4.2 Heating value analysis – Bomb calorimetry

Gross calorific value or the gross heating value is an important thermal characteristic of biomass. It provides the high heating value of the material which is the amount of heat produced by the complete combustion of a unit quantity of the material. There are several standards available for measuring the heating value and the most important is likely ASTM D1826 from the American standard for testing materials (ASTM). A bomb calorimeter is the equipment that is used to determine this property. Biomass heating value is an important parameter that determines its viability as a bioenergy feedstock. Heating value of any fuel can be determined either by measurement or prediction (Shen et al., 2012). Experimental bomb calorimetry based on ASTM and other standards is an effective method that is used for heating value determination of biomass. Biomass is usually composed of particulates in the loose form. In order to effectively test it in a bomb calorimeter, the biomass needs to be densified into pellets. However, biomass such as rice husk is difficult to densify without the use of binders or pre-treatment. Several researchers have used binders and other additives as adjuvant to ensure effective densification and complete combustion in the oxygen bomb calorimeter (Sheng et al., 2005; Yin et al., 2011; Shen et al., 2012; Nhuchenhen et al., 2012).

2.5 Densification characterization of rice husk

Portability is an important issue that needs to be addressed before any lignocellulosic biomass can be considered as a biofuel feedstock. Compaction of low bulk density agricultural biomass is a critical and desirable process for sustainable and economic viability of feedstock handling/processing for the biofuel industry. Biomass densification for the production of solid fuel minimizes the volume and maximizes the energy density. Pelleting and briquetting are the two major methods of densifying biomass. The latter is for the production of larger size fuel that can be used in place of firewood, and the former is for the production of fuel for thermo-chemical reactors such as gasifiers, pyrolysis reactors, and other direct combustors. Densification of rice husk is an important step for making rice husk a viable fuel alternative to fossil fuel and firewood. Densified rice husk will be in a more consistent form, and will be easier to characterize. This ease of characterization will enable effective adjustment of transportation and energy conversion systems that will use rice husks from different regions as fuel feedstock.

There are several factors that may affect the physical and thermal properties of densified biomass such as rice husk. These include the pelleting machine variables, pelleting process parameters, binder properties and binder ratio. Panwar et al. (2011) reported that moisture content, compaction pressure, and compaction speed affect the durability and density of briquettes made from mango leaves, eucalyptus leaves, wheat straw, and saw dust. Kaliyan (2009) and Kaliyan & Morey (2006b) suggested that the pelleting machine variables that affect the strength and durability of the pellets include the length to diameter ratio (L/D) of the die, speed of the ring die, gaps between the rolls and the ring die, specific energy input to the pellet mill, and steam conditioning or the high shearing process before pelleting such as feed conditioning in an expander. Kaliyan and Morey (2006a) also found that the bulk density and the durability of the pellets measured after curing at room temperature is slightly higher than those before curing.

Back (1987) reviewed the binding mechanisms in wood and wood products and reported that in order to produce sufficient bonding area, especially in the absence of a binder, the plasticization of the wood polymers above their glass transition temperatures is necessary (Back, 1987; Kaliyan and Morey 2010). Hydrogen bonding is considered as the main type of bonding at lignin and cellulose surface areas and it is important in the press-drying operation of wood (Back, 1987; Kaliyan and Morey 2010). The binding mechanisms in rice husk are not fully understood due to the effect of the high silica content and the inter-molecular bonding between the silica and the carbon atoms. The understanding of the binding mechanism of rice husk using microstructural analysis will provide additional information needed in the development of high energy rice husk pellet using locally available materials as both binders and as energy densifiers. The predictability of the quantity and type of binder that will be required for specific fuel operating parameters will make the development of energy pellets from rice husk and locally available binders easier.

In order to determine the amount of binder needed, the thermal and physical properties of the binders, binding mechanism between rice husk and the binders, and densification process parameters need to be explored. The binding mechanisms between rice husk and the binders will also provide the information on energy requirement during the densification process. The binding mechanism between the biomass and the binder plays an important role on the physical and thermal properties of the densified biomass, and they have to be investigated both at the microscopic and macroscopic levels. At the microscopic level, Chung (1991) suggested that the two criteria for strong adhesion between molecules are the necessary conditions to have a closer than 9Å intimate molecular contact and a sufficient condition of maximum attractive force with minimum energy. Electronic interactions between molecules are the driving force for adhesion. When the maximum attractive force is near the minimum energy, chemical bonds are established. Methods to increase molecular adhesion include applying higher pressure, heating the biomass above the glass transition temperature, and using a solvent such as water (Chung, 1991; Kaliyan and Morey, 2010).

Macroscopically, binding forces between the particles can act through two binding mechanisms, namely: bridgeless-bonding with the help of attraction between particles such as molecular [valence forces (i.e. free chemical bonds), hydrogen bridges, and van der Waals' forces] electrostatic and magnetic forces; and bridge-bonding with a solid bridge between particles due to the crystallization of some ingredients, chemical reaction, hardening of binders, and solidification of melted components. Bridge-bonding or solid bridging is mainly formed during cooling or drying of densified products (Kaliyan and Morey 2010). Tar, molasses and other highly viscous binders exhibit binding behaviour similar to solid bridges and usually form solid bridges after cooling. Cohesion forces within the viscous binder and the adhesion forces at the interface between the binder and the solid particles determine the strength of the bonded material. The strength of the binder is the weaker of the two forces. Rice husks solid components with thin absorption layers can form strong bonds with adjacent particles either by smoothing out surface roughness and increasing the inter-particle contact area or by decreasing the inter-particle distance and allowing the intermolecular (microscopic) attractive forces to participate in the bonding mechanism. The presence of moisture and water soluble natural binders within the rice husk will enable the formation of liquid bridges between the particles that will hold them together by capillary and viscous forces. Subsequent drying will cause the liquid to evaporate leaving bridges or necks between the particles and the formation of solid bridges due the recrystallization of the solid binders. Solid bridges will increase the mechanical strength of the densified products (Bika et al., 2005; Kaliyan and Morey, 2010).

Microstructural studies on grinds of corn stover and switch grass, confirmed that high quality briquettes and pellets can be produced without adding chemical binders (i.e. additives) by thermally activating (softening) the natural binders such as carbohydrates, lignin, protein, starch and fat at their glass transition temperatures and optimum moisture content (Kaliyan and Morey, 2009). Microstructural analysis and the effects of natural binders on densification of rice husk have not been studied in detail, and one of the objectives of this research is to contribute towards the topic.

Rice husk physical and chemical characteristics are important factors that influence the densification characteristics of rice husk. These properties have been found, during preliminary investigation, to be dependent on the milling processes to a great extent. The Engelberg and the Milltop milling machines produced rice husks that have distinct physical and chemical characteristics. The amount of starch, protein, fat, and lignin determines whether the rice husk will need additional binders for densification at a specific pressure, temperature, and other densification operating parameters. In this study, the physical, chemical, and densification characterization will provide the necessary information on the optimum densification parameters for the Engelberg and Milltop rice husks.

2.6 Characterization of rice husk using scanning electron microscopy

Scanning electron microscopy (SEM) is an important tool for physical characterization and correlations with chemical and thermochemical properties of biomass. Physical surface characteristics of biomass determine how the component of the biomass can interact during processes such as densification. Surface characteristics using SEM can also be used to identify key components of the biomass that have special chemical characteristics, such as high silicon content structures.

SEM is also an important tool in the determination of the structure of the biomass as it undergoes thermochemical conversion. During thermochemical conversion, the biomass undergoes physical, chemical, and thermochemical transformation, which greatly influence the surface morphology and characteristics of the by-products of the conversion, such as ash. SEM coupled with other tools such as Fourier transform infrared spectrometry (FT-IR) can effectively be used to analyze the thermochemical conversion process of biomass. Thermochemical characteristics of densified biomass are very important in the design of a carbonaceous thermo-chemical reactor whether it is a combustor, a pyrolysis reactor or a gasifier. The characteristics of both the thermo-conversion process and the thermal characteristics of the by-products of the process are critical. Formation of slag can be a significant issue when utilizing high silicon content biomass such as rice husk. Lindstrom et al. (2010) investigated the slagging characteristics during the combustion of woody biomass pellets made from a range of forest products and concluded that certain concentrations of silicon are prerequisites for the initiation of and the process of slag formation during the combustion process. Characteristics of char produced after the release of volatiles during initial steps of thermochemical processes are affected significantly by operational conditions during these steps. Thermochemical and physical characteristics such as reaction rate and morphology are greatly influenced by the char production processes (Wannapeera et al., 2008).

The silica content in biomass greatly affects the energy content and the design of the ash handling system of thermochemical converters. Low silica containing fuels have higher energy content, and are less abrasive to the structural components of the reactors and the conveyor systems. Soluble levels of silica in the soil, which are present as monosilicic acid or $Si(OH)_4$, highly influence translocation and deposition of silica in plants. During combustion of biomass fuels, atmospheric emissions and solid waste containing heavy metals and other elements are produced from the original feedstock. Some of these elements volatize, calcinate, oxidize and sulphatize based on the combustion temperature and other reactor operating conditions (Bakisgan et al., 2009). Trace elements including heavy metals are considered to be one of the main sources of environmental pollution affecting the ecosystem.

Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) have been used for microstructural and composition analysis of biomass and biomass by-products of combustion. Bakisgan et al. (2009) carried out study of ash contents of hazelnut shells, olive bagasse and wheat straw using SEM-EDS analyses. Tiainen et al. (2002) used SEM-EDS to study the role of ash composition on the problems of bed agglomeration in fluidized bed boilers and found that bed particles were coated in iron rich material during gasification of peat biomass. Van Zwieten (2010) characterized biochars from slow pyrolysis of papermill waste using SEM-EDS, and found that papermill biochars have large degree of macro-porosity. They also found that wood particles can be distinguished from paper sludge particles using EDS due to calcium deposit associated with carbon from the wood. Bharadwaj (2002) carried out a single particle experiments in a Confocal Scanning Laser Microscope (CLSM) coupled with Scanning Electron Microscope (SEM) analysis of partially and fully combusted rice husk particles and concluded that thermally resistant intermolecular bonds between the silica fibres and the carbon may prevent full conversion. Wannapeera et al., (2008) studied the morphology and reactivity of rice husk, rice straw, and corncob chars using SEM and thermogravimetric analysis (TGA); and concluded that chemical components of the original samples influenced pyrolysis rate; hence the reactivity and morphology of the char produced.

Several researchers have studied the pyrolysis and thermochemical conversion processes of rice husk and other biomass at various conditions (Mansaray and Ghaly, 1997, Wannapeera et al., 2008; Bahari, 2012). However, there has not been any study carried out to characterize and compare the combustion by-products of rice husk from the two major milling machines (Engelberg and the Milltop) used in the sub-Saharan Africa region.

Connecting text to Chapter III:

Sustainability of rice processing in sub-Saharan Africa is one of the most important aspects of ensuring food security and self-sufficiency in that region. In chapter 3, a field study was carried out to examine the existing methods to improve the energy and environmental sustainability of rice processing in rural sub-Saharan Africa. The areas studied included an assessment of the methods to improve energy efficiency by: utilization of waste heat from diesel engines for improved drying and heat addition to pre-soaked rice; utilization of solar energy for heating; optimization and redesign of stoves and parboiling vessels; and utilization of rice-husk-derived fuel as an alternative to firewood.

Chapter III: Increasing sustainability of rice processing in rural Sub-Saharan Africa

3.1 Abstract

Energy and environmental sustainability are important considerations for increased rice production. This study examined the energy utilization and sustainability of rice processing in sub-Saharan Africa. The rural small scale rice processors community of Gadan Loko village, in the Song local government, and the sub-urban medium scale rice processors in the Yola local governments of Adamawa state, Nigeria, were selected as the focus of the study. Rice parboiling, the most energy intensive process in rice processing is carried out usually by women who process the rice in small quantities of about 13.2 kg using traditional pots on tripod stoves at the small scale level, and at the medium scale level up to 132 kg batch of rice paddy are parboiled in large drums on tripods using mostly old automotive engine blocks as tripods. The parboiled rice is then sun dried on mats before it is taken to the milling stalls where it is milled using milling machines driven by single cylinder diesel engines. There were large variations in the quality of milled rice due to lack of consistency in processing parameters. Accumulation of rice husk in the community created important environmental and health issues. In this study, methods of improving the sustainability of rice processing were investigated. The areas studied included the utilization of waste heat from the diesel engines for improved drying and efficient pre-soaking; utilization of solar energy for pre-soaking; utilization of rice-husk-derived fuel as an alternative to firewood; and the optimization and redesign of the stoves and parboiling vessels to minimize heat loss to the environment. The results showed that the utilization of rice husk as an alternative fuel and the redesign of the stoves and parboiling vessels will increase the sustainability of rice processing and can be easily adopted by the community. However, it was found that solar energy was not economical and the utilization of waste heat from the diesel engines for drying and pre-soaking would be difficult to implement at the rural scale, because most of the parboiling is done far away from the milling stalls; but the method was feasible for medium suburban outfits where the parboiling and drying are done behind the milling stalls. The study also found that research and development of

appropriate technology and education (RATE) of the rural community is an important way of increasing sustainability.

3.2 Introduction

Sustainable development is recognized as the development that meets the need of the present generations without compromising future generations' ability to meet their own needs staying within system capacity limits. The sustainability concept refers to the integration of environmental, economic, and social dimensions of development (Lacquaniti and Sala, 2009). Sustainability can be considered as a triad of these three factors and the evolving inter-relationship among them (Figure 3.1). The inter-relationship between the triads of sustainability governs the success of efforts to improve the sustainability of a process, thus it is important that any work carried out be based on both the regional and global evolving sustainability criteria (IATA, 2009).

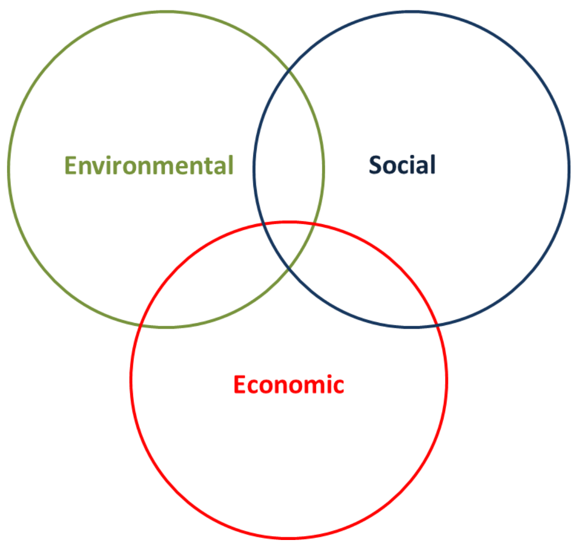


Figure 3.1 Triads of sustainability

Rice is a staple food in sub-Saharan Africa and many other regions of the world. Currently there is an annual increase in demand for rice in the region. The current production, processing and marketing of rice in sub-Saharan Africa in general, is mostly a subsistent one. Even at this subsistence farming level, a large quantity of rice by-product, in the form of husk, is produced and improperly disposed of around the processing plants, creating an environmental issue as shown in Fig. 3.2 and can represent health issues when the fine particles are inhaled. In addition, a huge amount of firewood is utilized during rice parboiling, thereby greatly increasing the destruction of trees (Figures 3.3, 3.4). Rice parboiling is a significant step in rice processing. This process involves the thermal and hydration conditioning of the paddy before removing the hulls and polishing the final product through dehusking and milling. This is an energy intensive process that requires labour and thermal energy. The thermal energy for this process comes exclusively from firewood, and one of the most preferred firewood comes from “Kiriya” (*Prosopis africana*). Kiriya as it is called in the local Hausa language is very important for farming and pastoralist communities of the West African region. The tree’s physical and chemical properties make it attractive for local applications that include medicine, construction, energy, and manufacturing of handles for local tools. Its seeds are also used as food, while its succulent leaves and branches provide food to cattle and goats during the dry season. In addition, the trees fix atmospheric nitrogen that improves the soil fertility in traditional parks and agro-forestry systems (Akaaimo et al., 2006; Weber et al., 2008).

Figure 3.2 Rice husk dumps are environmental hazards to the rice processing communities

Figure 3.3 Truckloads of firewood are consumed daily by rice parboilers

Figure 3.4 Deforestation as a result of complete reliance on firewood

In sub-Saharan Africa, some of the regional governments are putting a lot of resources towards training their rural farming communities and providing fertilizers in order to increase their productivity by 200%-500% increase in tonnage. This means that there will be a sharp increase in rice production, with a concomitant increase in rice processing, with their related expected problem of increased husk production and continued destruction of trees used as firewood for the parboiling of rice. To increase local awareness, educate and empower the local community, the concept of Research Appropriate Technology and Education (RATE), which is discussed in detail later, was motivated by the need for the sub-Saharan African region to achieve the millennium development objective goals (MDG's), specifically numbers one and seven to "eradicate extreme poverty and hunger" and "ensure environmental sustainability", by using innovation and appropriate technology to increase energy and environmental sustainability, as well as, agricultural output. The comprehensive African Agricultural Development Programme (CAADP) was adopted by African leaders under New Partnership for Africa (NEPAD), to eradicate poverty, after they realized the importance of agriculture as key for the economic transformation of African economies. They developed regional economic transformation agendas and food security programs that focused on poverty eradication, skills development, sustainable agricultural output improvement, and sustainable market development. The objective focusses of these programs were to build scientific capacity using essential enabling conditions by adopting appropriate technologies derived from research and development supported by effective themes (FAO, 2002). Most projects have proposed to increase agricultural productivity in the sub-Saharan region, often only by focusing on the sole utilization of advance technology, which may not match the sustainability requirement of the regional agricultural production system (Schumaker, 1973; Carr 1985; Black 2007; Smith 2009; Zelenika, 2011). Appropriate technologies are defined as those technologies that utilize readily available resources of the local communities and comply with environmental, cultural, economic, and resource constraints (Schumacher, 1973; Pearce et al., 2008; Buitenhuis et al., 2010; Zelenika 2011; Pearce 2012).

3.3 Proposal of Research, Appropriate Technology, and Education (RATE) theme as a tool for increased sustainability

The RATE theme proposed in this research is a defining tool on how to investigate the possibility of increasing the sustainability of rice processing in sub-Saharan Africa using appropriate technology. Appropriate technologies are defined as those technologies that utilize readily available resources of the local communities (Schumacher, 1973; Pearce et al., 2008; Buitenhuis et al., 2010; Zelenika 2011; Pearce 2012). Appropriate technology focuses on small scale, locally relevant technologies to improve the lives of underprivileged populations in order to improve grassroots technology development (Butenhuiset et al., 2010). Research, appropriate technology and education (RATE) theme is a proposed method for carrying out research to develop adaptable appropriate technology that will be fabricated locally using locally available skills, and materials (especially industrial by-products that would otherwise end up in waste dumps). The appropriate technology focus of RATE is based on engaging local tradesmen and rice processors on increasing productivity, and improving energy and environmental sustainability of rice processing. The technology developed will address poverty and economic issues by providing employment to the local craftsmen and increasing the quality of products and reduce the production costs for food processors. It will also address the environmental issues that are caused by food processing, by utilizing renewable energy, scrap materials, as well as by-products of rice processing for energy conversion. The RATE theme proposed involved the following:

1) Carrying out research to determine how to increase sustainability of specific processes involved in rice production.
2) Researching and adopting appropriate technologies that can be used to increase the sustainability of the process, by engaging the processors and local craftsmen during the development of appropriate technology, identifying issues relating to:
    a) Cost and availability of materials with the objective focus of utilizing materials that are by-products of other domestic and industrial processes.
    b) Available and appropriate skills necessary for successful development of the technology.
    c) Adapting to issues that could arise based on end-users input.
3) Training both the craftsmen and the processors (end-users) on the importance of the technology including its social, economic, and environmental benefits.
4) Training and guiding the craftsmen during the production process.
5) Guiding and training of the processors (end-users) on how to use the technology.

3.4 Literature review

The parboiling methodology, the type of energy or fuel used, and the ability of the rice processors to utilize rice by-product as energy source all determine the sustainability of the parboiling process. Utilization of the by-products of rice production such as rice husk as fuel instead of firewood will reduce the over use of forest products and its related danger of desertification, will lower carbon and other greenhouse emissions, as well as, reduce the negative environmental effects of unused postharvest wastes.

Soaking or pre-soaking is the first step in the parboiling process that involves hydrating the paddy sufficiently (up to ~30% wet basis (wb)) to enable it to be completely gelatinized in the subsequent heating stage. Pre-soaking temperature and time duration are important parameters for effective pre-soaking. Bhattacharya and Rao (1966a) reported two distinct patterns of hydration, one below gelatinization temperature (GT) and the other above GT. They observed that at low temperatures <75°C, the rice paddy absorbs water slowly and comes to equilibrium at about 30% (wb) of moisture after about 3 to 6 hours of soaking. However, they observed that at a high temperature >75°C, the rate of hydration increased exponentially due gelatinization of starch to unabated hydration level causing the husk enclosure of the paddy to split due to enlargement of the endosperm at a moisture content of 30-35% (wb). The desired temperature for soaking is usually close to, but below, the gelatinization temperature of the rice which varies from 55 to 79°C depending on the variety of the paddy (Juliano et al., 1981). Bhattacharya (1985) proposed that the soaking shall be carried out between 70 °C to 75 °C for 3 to 6 hours, followed by allowing the rice paddy to cool to ambient temperature. Roy et al. (2005) reported that in modern parboiling processes the soaking temperature range is 55 to 70°C for 3 to 6 hours. After soaking, the rice is steamed for a certain period of time to gelatinize the starch completely. After the steaming process, the rice is dried, dehusked and milled. During parboiling, various physicochemical changes occur due to the gelatinization of the starch granules of the rice. These changes play an important role in the next processing operations. Parboiling requires a specific amount of energy for the starch granules in the rice to be gelatinized, any excess energy supplied during this process is released to the surroundings (Islam et al., 2004; Bakari et al., 2010). The knowledge of how much energy is required in rice parboiling is important for optimization of the process, especially in rural sub-Saharan Africa where currently the process is based on traditional methods without any consideration given to the exact temperature required for gelatinization, heat loss to the atmosphere and the available energy in the fuel used for this thermal process (Bhattacharya, 1985; Bhattacharya, 2004). Bakari et al., (2010) reported that in the region of the upper Benue river basin, which is part of the community of Gadan loko, the thermal energy efficiency of the rice parboiling process is between 21.94%-44.83% for the small scale rural rice parboilers and 21.09%-27.89% for the medium scale suburban parboilers. This shows that between 55.17%-78.06% and 72.11-78.91% of the thermal energy that comes from firewood is wasted by heating the atmosphere in the small and the medium scale parboiling processes respectively. This is alarming, when one considers that more than 50% of the trees that are being cut for rice processing are wasted by heating the atmosphere and increasing the carbon loading of the atmosphere.

The milling machines, especially the Engelberg, are usually driven by a Listeroid engine that is water-cooled by two water barrels – a cold and a hot barrel. The dual barrel cooling system enables atmospheric cooling of the combustion cylinders of the engine, by natural convection. The water is supplied to the engine from the cold barrel, and as it cools the barrel it is heated and discharged to the hot barrel which is not only cooled by the atmosphere, but also by some of the hot water being transferred to the cold barrel by one inter-connecting pipe. The temperature of the hot barrel temperature reaches beyond the pre-soaking temperature suggested by Bhattacharya and Rao (1966a), Juliano et al., (1981), Bhattacharya (1985), and Roy et al., (2006). Also the cold barrel temperature is ideal for pre-drying paddies before milling. Sun drying of rice paddy which is commonly used by rice processors, takes about 1-2 days or more, and is dependent on the weather and subject to pollution by dust, insects, and other environmental factors. The longer the time required for drying the higher the chances of negative effects of the environmental factors on the paddy and the rice yield (Roy et al., 2006). Utilization of the cold barrel as a means of drying will significantly reduce the time required for drying the rice paddy, and will increase the yield and quality of the milled rice (Roy et al., 2006). The rice paddies could be dried better in a controlled clean environment rather than on plastic mats where the changing weather determines the drying conditions.

There is abundance of solar energy in the sub-Saharan region; however there is a lack of appropriate technology to harness it, for both thermal and electrical usage. For rural small and medium processing, potential utilization of solar thermal energy for enhanced pre-soaking with appropriate technology is possible. The key is the utilization of local available resources, which include local skills and materials. Thermosyphon solar water system is one of the most appropriate equipment for harnessing solar thermal energy in the sub-Saharan African region. The system is named as such because of the convection-induced water circulation due to thermal gradient and gravity with respect to the vertical distance of the water within the system. It does not require mechanical energy to drive pumps for water circulation. Agbo (2011) studied the performance profile of a themosyphon solar water heater in Southern Nigeria and reported a mean temperature of 81°C and average efficiency of 54% with negligible variations during all the seasons. The efficiency of a solar thermosyphon system depends on various parameters that include the collector performance, which itself is dependent on the materials and design of the collector; the panel reservoir arrangements; operating conditions; and meteorological conditions (Bello et al., 1990; USA DOE, 2000; Agbo, 2011). The amount of solar insolation that the collector can absorb and transform into thermal energy by heating the medium (usually water) within the collector tubes is an important characteristic of the solar thermal system. In the literature (Bello et al., 1990; USA DOE, 2000; Agbo, 2011), most tests previously performed with thermosyphon systems have studied the overall performance, incorporating variations of the collector design as parameters of optimization of the system. In the unique case of using locally available skills, tools and materials, and the utilization of the RATE theme; a method of studying the viability of a low-cost locally fabricated collector using appropriate technology was developed by carrying out an air test without water in the collector tube to assess the viability of using it for heating water. The air test was also used for demonstration purposes as an educational tool; for educating both the local fabricators and the local parboilers on the adoption of appropriate technology. The objective of the approach is to develop the most appropriate solar thermosyphon system that can heat water effectively for improving the paddy pre-soaking temperatures using locally available skills, and materials (most especially, the by-products of other industrial processes that usually end up as waste, impacting the environment negatively); thus, increasing the sustainability of the rice processing process at the social, economic and environmental levels.

The utilization of biomass by-products from agricultural processing has been extensively studied, and one of the most abundant sources is rice husk. The potential for the utilization of agricultural residue biomass as an alternative to conventional fuel is very interesting. However, the development and implementation of an energy conversion system that can be easily adopted and that is competitive with conventional fossil fuel and firewood energy alternatives, is still required (Shafizadeh et al., 1985; Ghaly and Al-Taweel, 1990; Bharadwaj, 2002; Roy et al., 2006; Adapa et al., 2005; Satyanarayan, 2010; Bahari 2012).

The key issues of the utilization of biomass, such as rice husk, is the lower energy density, bulk density and also the determination of effective thermochemical conversion system that will efficiently convert the biomass components into thermal energy. In the sub-Saharan region, the development of an energy conversion system, using appropriate technology to utilize by-products of other industrial processes using the RATE theme, may increase the sustainability of rice processing in that region. However, development of this energy conversion system, in this case to replace the conventional wood stove, will require the adoption of modifications by both the local stove fabricators as well as, as the rice parboilers. Also ideally, the rice husk used as fuel will have to provide thermal performance comparable to firewood. The thermochemical conversion process that occurs in a stove is mostly composed of the combustion at the surface of the fuel in the region of higher temperature where there is abundance of oxygen. Within the fuel itself, multiple simultaneous thermochemical reactions occur reducing the biomass components comprising of hemicellulose, cellulose, and lignin into volatile components that escape to the surface where they are combusted by direct reaction with the oxygen in the atmosphere; the fixed carbon component which is solid is the last to combust and its combustion is highly dependent on oxygen availability, and in most cases for a large part, it may be un-combusted, and will be left within the ash as char. The thermochemical conversion is temperature and oxygen-availability dependent. Therefore, in the development of a rice husk stove, temperature and oxygen availability within the stove are important parameters to be considered. In the case of selecting an appropriate stove design, based on the RATE approach, the capability of local craftsmen to manufacture and acceptance by the local users are also controlling criteria to be considered for the stove development. Adoption and redesign of a biomass stove that the locals are familiar with, increases the chances of the acceptance of the rice husk stove, especially if it shows comparable performance with other biomass stoves.

This study investigated the options to improve the sustainability of rice processing in the sub-Saharan African region. The options looked at: utilizing waste heat from the diesel engines that drive the milling machines for thermal recovery to improve drying and efficient pre-soaking; the utilization of solar energy for pre-soaking; the utilization of rice husks as alternative fuel to firewood; and the optimization and redesign of the stoves and parboiling vessels to minimize heat losses to the environment.

3.5 Objectives

3.5.1 Overall objectives

The overall objective of this research was to identify the most effective methods of improving the triads of sustainability including economic, social, and environment; by engaging both the local craftsmen and rice processors using RATE (Research Appropriate Technology and Education) theme, towards improving the energy and environmental sustainability of the current conventional methods of rice processing for rural small and medium enterprises.

3.5.2 Specific objectives

The specific objectives of the research were:

1. To study the potential of utilization of waste heat from the diesel engines driving the rice mills for improved drying and more efficient pre-soaking.
2. To study the potential of utilization of solar energy for enhanced pre-soaking of rice paddy during the parboiling process.
3. To study the effects of simple modifications of existing stoves for improved energy efficiency by minimizing convective and radiative heat losses to the atmosphere.
4. To study the potential of utilization of rice husk as an alternative to firewood in rice processing.

3.6 Materials and Methods

3.6.1 Materials and Equipment

3.6.1.1 Development of the Research, Appropriate Technology and Education (RATE) tool to increase sustainability.

The equipment and human resources used for this research included the skilled local craftsmen, their workshops and the tools they used in the production of local metal stoves, pots, and other domestic and commercial equipment; and the rice parboiling and rice milling outfits and their operators. Most of the materials used during this study were scrapped commercial and domestic waste including: aluminium and steel sheet metal from the construction industry, discarded metal cans, and materials from discarded electric deep freezers and refrigerators. Most of which were readily available, which ensured that the developed products were from recycled materials that would otherwise end-up at the waste dump, therefore increasing the environmental sustainability of the whole process.

3.6.1.2 Utilization of waste heat from the diesel engines that drive the rice mills for pre-soaking and drying

The materials and equipment used included a Listeroid engine with dual-barrel water cooling system (Figure 3.5), infrared thermometer (Mastercraft model 57-4554-4 with operating range of -20 to 315 °C), digital thermometer (Model 2414-V0270), mercury thermometer (for calibration and verification of electronic thermometers) a fully functional weather station (Bios, Model 313BC), Vernier calipers, 25 litre containers, measuring tape, and a timer.

3.6.1.3 Utilization of solar energy for pre-soaking of rice paddy

Materials and equipment used for the solar experiments included: Infrared thermometer, digital thermometers, mercury bulb thermometer, measuring tape, timer, copper tube (1/2 inch nominal), scrap aluminium sheets (from roofing industry), 4-liters can (reservoir), rubber hoses, fibre glass insulation (from scrapped deep freezers), plywood, low iron 0.006m tempered glass, non- glossy black paint, rubber stoppers, aluminium rivets, hammer, straightening railings, and metal working tool kits used by the local sheet metal workers.

3.6.1.4 Redesign and optimization of conventional stoves to minimize heat loss

Materials and equipment used for the redesign and optimization of conventional block engine tripod stoves included: Scrap sheet metal, digital thermometers, infrared thermometers, mercury bulb thermometer, measuring tape, timer, and local sheet metal workers tool kits.

3.6.1.5 Utilization of rice husk as alternative to firewood

Materials and equipment used for the construction of a stove that was used for the combustion of rice husk as an alternative to firewood included: scrap sheet metal, steel screen mesh, steel wire, measuring tape, local sheet metal workers tool kits and a 4-liters pot. Rice husk from the local mills was used as fuel during the experiments.

Infrared thermometer, digital thermometer (PC Model 2414-V0270), mercury thermometer, weighing scale, and timer were used to study the performance of the stove.

3.6.2 Methods

3.6.2.1 Development of the Research, Appropriate Technology and Education (RATE) tool to increase sustainability.

Local rice processing methods were studied to identify how the local conventional methods could be potentially improved using locally available skills, tools, and scrap raw materials that would otherwise end up as waste; as well as engaging the rice processors in the development of prototypes and research to increase the likelihood of adaptability of the appropriate technology developed during this research. All this was done based on economic, environmental, and social criteria for the purpose of increasing the sustainability of the process by empowering both the skilled craftsmen and the rice processor to participate.

3.6.2.2 Utilization of waste heat from the diesel engines that drives the rice mills for pre-soaking and drying

The utilization of waste heat from the single cylinder diesel engines that drive the milling machines is very attractive (Basunia et al., 1996; Basunia et al., 2008). The temperature of the hot-side barrel could reach temperatures above the gelatinization temperature of the rice. The engine can run efficiently with a hot-side temperature of up to 95 °C. This energy can be easily harnessed by using a heat exchanger that is fabricated locally from copper tubes of 0.0127 m in diameter which matches the size of the engine exhaust pipe; to provide water for pre-soaking at the required temperature of between 70 °C to 75 °C. The cold-side barrel is at the temperature of 35 °C to 45 °C which can be used for effective drying of the paddy, because a more reliable temperature range can be established rather than using the weather-dependent mat sun drying (Basunia and Abe, 1996; Basunia and Abe, 2008). Although this option is viable, it is not practical at the rural scale rice parboiling level because the parboiling is done far away from the milling stalls. However, for the medium scale parboilers this is highly possible, because the parboiling and drying are done behind the milling stalls beside the coolant drums, in the sub-urban medium scale rice processing communities (Figure 3.5).

Basunia and Abe (1996) studied the drying of rough rice using waste heat from an engine. In their study, waste heat from the cooling fins of an air-cooled four-stroke engine was used to dry the paddy with the help of a fan that is coupled to the engine. In their experiments they compared the engine fin temperature, drying air temperature and ambient temperature, and concluded that drying air temperatures of 30 to 37°C was attainable. In the current research, temperatures of the hot and cold barrels of a thermo-syphon cooled Listeroid diesel engine (Figure 3.5) used to drive a milling machine were measured with respect to runtime and ambient temperature. The objective of this research was to determine if the hot and cold barrels could reach the temperatures for pre-soaking and drying of rice paddies respectively; and if so, how long it would take for the two barrels to reach the application temperatures. The factors considered were the running time and ambient temperature; and the responses were the temperatures of both the hot and cold barrels. Two thermometers were inserted into the centers of the hot and cold barrels cooling system. The temperatures of the barrels and the ambient temperature (using a weather station) were recorded every five minutes for a total of 100 minutes. Five sets of experiments were carried out at five different times of the day. The barrels were emptied after every experiment and water at ambient temperature was used to start the next experiment.

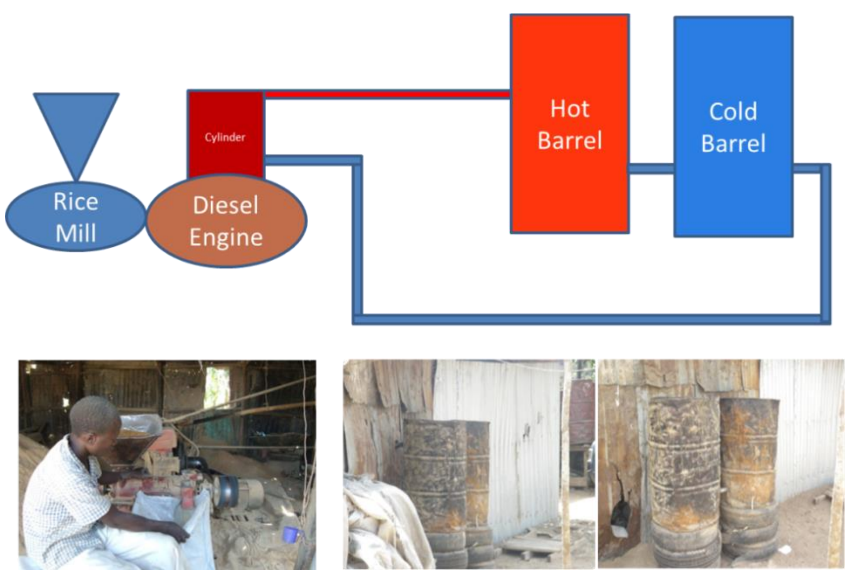


Figure 3.5. Listeroid single cylinder diesel engine thermo-syphon cooling system

3.6.2.3 Utilization of solar energy for pre-soaking of rice paddy

The materials used included scrap aluminum sheets from the roofing industry, copper pipe, fibre glass insulation from scrapped deep freezers, aluminum rivets, black paint, steel clamps, rubber hoses, plywood and low iron tempered glass. The manpower for the construction of the solar thermal system was selected from the local sheet metal workers that usually manufacture local metal stoves and other household metal utensils using locally available scrap metals. The tradesmen were briefly trained on the concept of solar thermal system, and the essential characteristics that determine the system's effectiveness. Following training, the sheet metal workers were given the design and were guided through the construction of the solar panel components (Figure 3.6a).

The solar panel collector was made up of a 0.8 m x 0.4 m aluminium sheet with a 0.0127m diameter copper pipe manually crimped and riveted between the sheet, ensuring full contact between the pipe and the sheet making a solar thermal fin (figure 3.6b). The configuration was adopted based on the input of the local craftsmen based on their skills, their tools, and the availability of scrap materials that were used for the construction of the solar system. The effective collector surface, after the pipe was placed on the aluminium sheet, was 0.8 m x 0.360 m in area. The top of the fin was painted with a locally available non-glossy black paint manufactured by Supernice Incorporated to maximize solar insolation absorbance. The fin was enclosed in an aluminium box with plywood casing at the bottom, and fibreglass insulation between the plywood and the aluminium casing. The top painted part of the collector was covered with 0.0016m glass sheet. The glass enabled the heating of the panel by the greenhouse effect, as well as, it insulated the panel from heat loss to the ambient environment. Most of the solar insolation that penetrated the glass was absorbed by the dark-bodied panel. Also as the panel environment heated up, the glass prevented most of the absorbed heat energy escaping from the panel through convection. Hence, the energy was effectively transferred from the fins of the panel to the cold water pipe through conduction.

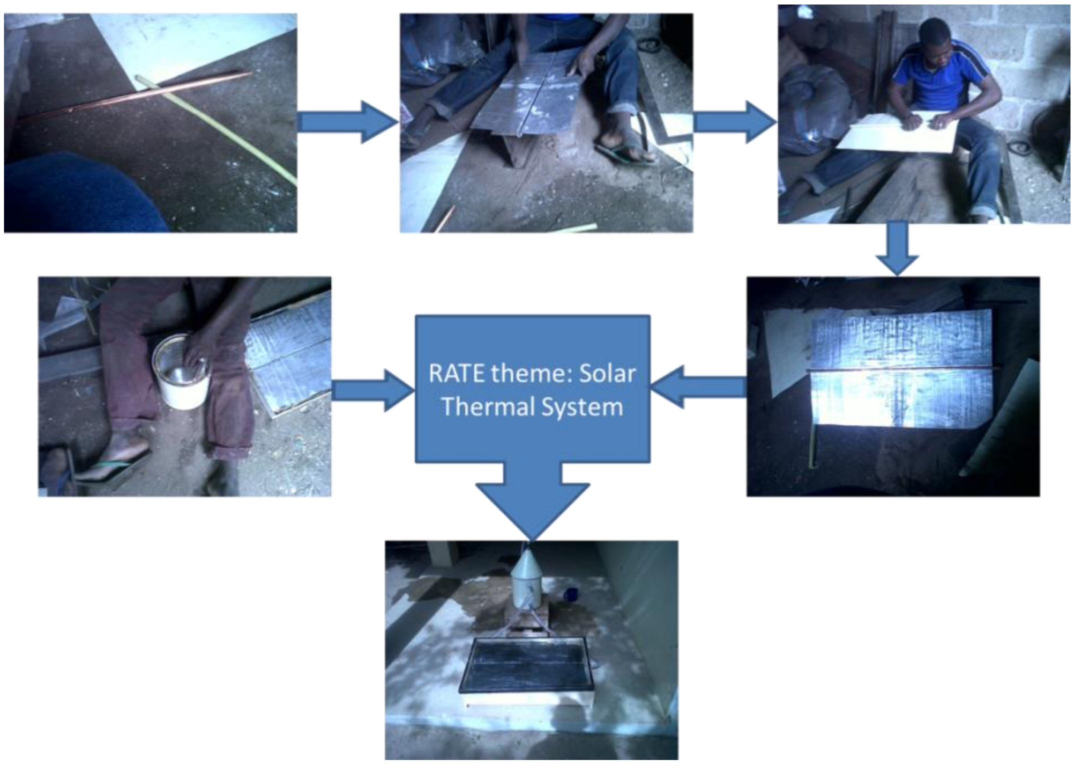


Figure 3.6a. Development of solar thermal system using RATE

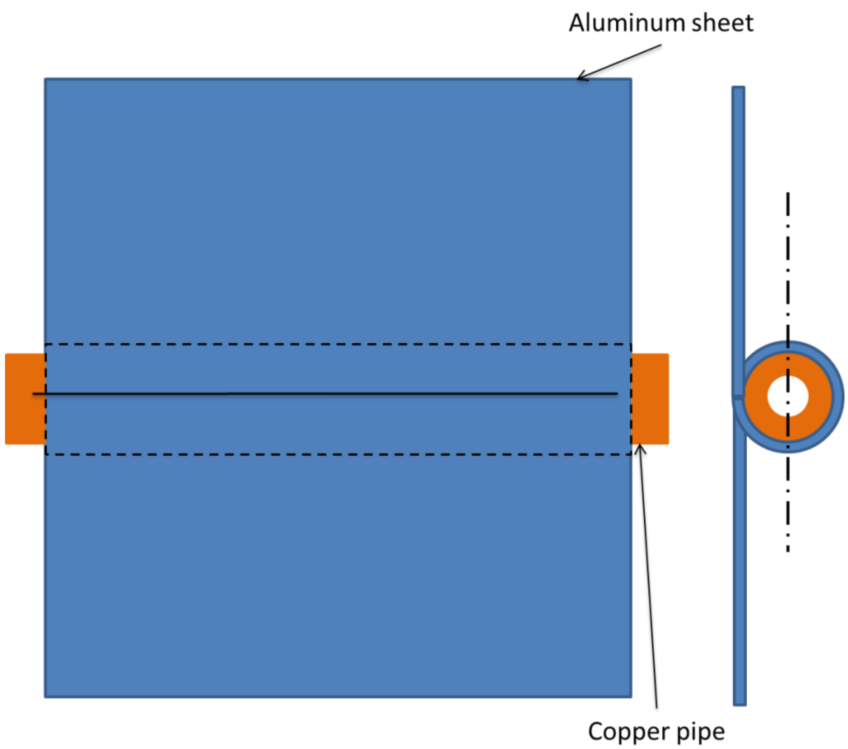


Figure 3.6b. Copper pipe manually crimped and riveted between aluminum sheet

3.6.2.3.1 Solar collector air test

An air test was carried out on the solar fin collector to determine the collector's maximum performance without water, based on factors that included ambient temperature, time of day and heat pipe temperature. One end of the collector was blocked with a solid rubber stopper, and the other end was blocked with a rubber stopper with a concentric hole that held a thermometer. The panel was placed flat in the sun and the intensity of solar insolation was assessed by determining the temperature of the inner tube with respect to time of day, and ambient temperature. The ambient temperature and tube temperature were recorded at 10 minutes intervals for three days from 08:00 to 17:00. Statistical analysis of the experimental results was used to predict the time required to heat up the pipe to a temperature that could be used for pre-soaking of rice paddy during the parboiling process. Response surface methodology was used to determine the effect of the three factors on the tube temperature.

3.6.2.3.2 Solar thermosyphon system performance test

Based on the solar collection air test, a four-liter thermosyphon system (Figure 3.7) was built and tested to determine the time it takes for the temperature to reach the desirable paddy pre-soaking temperatures. The tank was made of a 4-liter stainless steel container that was placed in a fabricated aluminium container with 0.02 m fibre glass insulation. The water tank was connected with the solar panel collector and tested to determine the water temperature with respect to the time of day and ambient temperature, as well as to determine the average time taken for the temperature of the reservoir to reach the paddy pre-soaking temperature. The ambient and reservoir temperatures were recorded at 10 minutes intervals for three days from 8:00 to 17:00.

3.6.2.4 Redesign and optimization of conventional stoves to minimize heat loss

Modification of existing stoves was undertaken to improve efficiency studied based on the RATE (Research Appropriate Technology and Education) theme (Figure 3.7a). Local metal stove fabricators were invited to work with the medium scale parboilers to fabricate a cover to minimize the open space between the tripods and firewood that increased energy loss to the atmosphere. This was done in partnership and consultation between the local craftsmen and the rice parboilers to ensure that it would meet the requirements of the parboilers and improve efficiency. The stove with the sheet metal skirt is described as the "covered stove" while the conventional engine block tripod without skirt is described as the "uncovered stove" in this research (Figure 3.7b). A sheet metal cover was designed by the tradesmen and was tested and its performance was compared to that of the stove without cover. Two stoves were used with and without cover using the same firewood in an alternate fashion recording the ambient temperature, time, and barrel temperature, while the postharvest processors were parboiling rice. During these experiments the parameters measured included: the ambient temperature, time of heating, and temperature of the parboiling barrels. Two tripod parboiling stoves made up of three old automotive engine blocks heating up 40 gallons parboiling barrels were used. The experimental procedure involved the operation of both stoves, each with measured amount of *Prosopis africana* logs. During each test, one of the stoves was covered and the other was left uncovered (the conventional method used by the parboilers), this was alternated to obtain triplicate data from each stove with both covered and uncovered experimental results.

Figure 3.7a. Modification of parboiling stove to improve efficiency using RATE

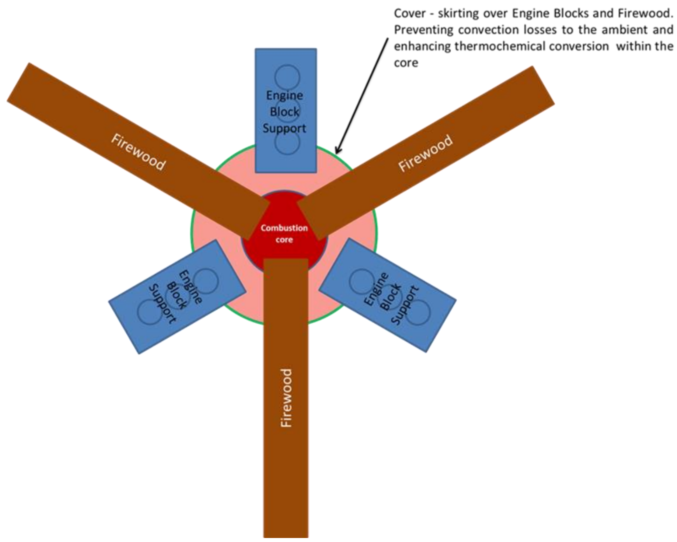


Figure 3.7b. Schematic of the cover to increase efficiency of the conventional stove

3.6.2.5 Utilization of rice husk as an alternative to firewood

Rice husk is an abundant biomass waste from rice postharvest processing. Rice husk from the sub-urban and rural rice mills from the upper Benue river basins was collected and sun dried on mats and used as direct fuel for a modified local sawdust stove. Weighed rice husk was inserted into the stove from the top, and after ignition a two-liter pot was heated to boiling. The time it took for the water to boil, temperature of the water with respect to time, and the ambient temperature during the heating process were recorded using a timer, a thermometer, and a weather station, respectively.

For conventional combustion of sawdust, the locals use a glass pop bottle at the centre air core with packed sawdust biomass around it before covering and igniting. The air core enabled air flow sustains the thermochemical conversion of the biomass. The high silica ash characteristics of rice husk required modification of the stove to ensure continuous effective combustion, because more air was required to initialize full combustion. Therefore, a perfected venturi cone based on RATE theme, i.e. the local craftsmen skills, tools, and availability of local material, was made with a steel screen mesh and a steel wire skeleton was developed and inserted into the conventional saw dust stove to ensure complete combustion and effective removal of rice husk ash and char (Figures 3.8 a & b). The cone made it easier to remove the ash and char by simply lifting the cone out of the stove, emptying it, re-inserting the cone back in place and loading it with additional dried rice husk fuel.

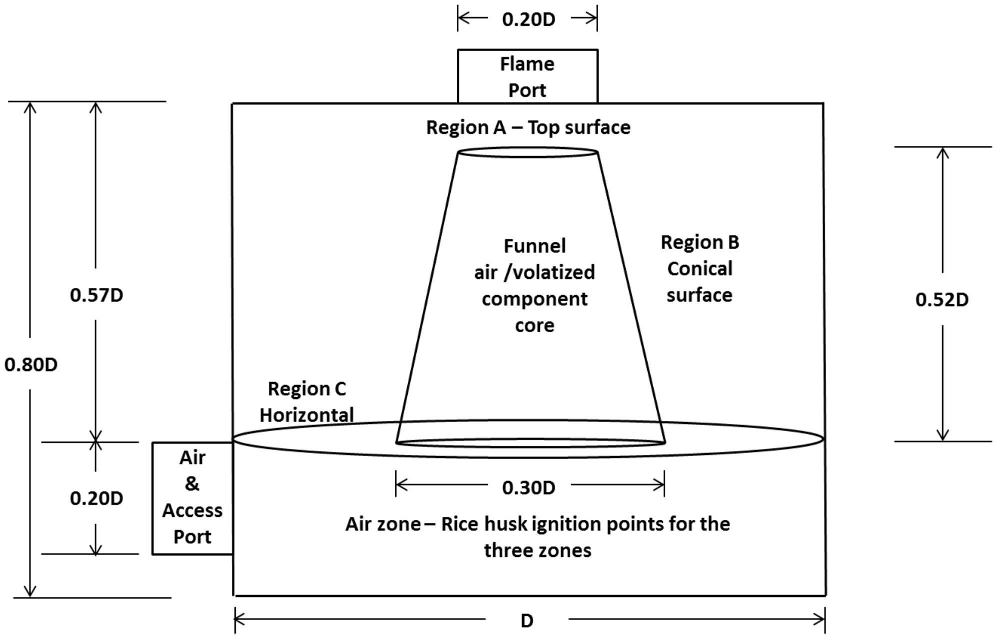


Figure 3.8a. Rice husk stove configuration showing thermochemical processes zones

Figure 3.8b. Rice husk stove picture showing the air access port, access port cover, and the flame port

The objective of the cone configuration is to develop an effective combustion system that can be fabricated by the local tradespersons which will ensure complete rice husk combustion. Three regions of combustion were identified: the top of the cone (region

A), the conical surface (region B) and the horizontal surface (region C). The temperature of the region determines the type of thermochemical conversion that will occur, since the decomposition of the lignocellulosic components is temperature dependent (Ghaly and Al-Taweel, 1990; Bharadwaj, 2002; Bahari, 2012). The objective of this inverted cone configuration is to ensure that full combustion occurs at the flat top of the cone; while due to the rise in temperature of the fuel bulk, pyrolysis and gasification thermochemical conversion processes occur progressively towards the inner section of the rice husk bulk in regions B and C (the conical and the horizontal regions respectively). The volatiles produced during the latter processes are then drawn upwards into the central cone due to venturi and convective draft effects, and are combusted at the top. Ignition of rice husk was done below the cone, and once the rice husk was ignited at all the three regions, there was a continuous flame above the top surface of the cone (region A), at which point the boiling water test experiments were started (Figure 3.9).

(a) Ignition stage (b) Full combustion stage

Figure 3.9 Combustion above the top of the flat cone (Region A)

3.7 Results and Discussion

3.7.1 Utilization of waste heat from the diesel engines that drive the rice mills for pre-soaking and drying

Analysis of the experimentally collected data showed that both running time and ambient temperature have significant effects on both the hot barrel and cold barrel temperatures within the test period of 100 minutes (Figure 3.10). Fitted response of the hot and cold barrel temperatures were obtained at R-square values of 0.95 and 0.99 respectively, both at $p<0.0001$.

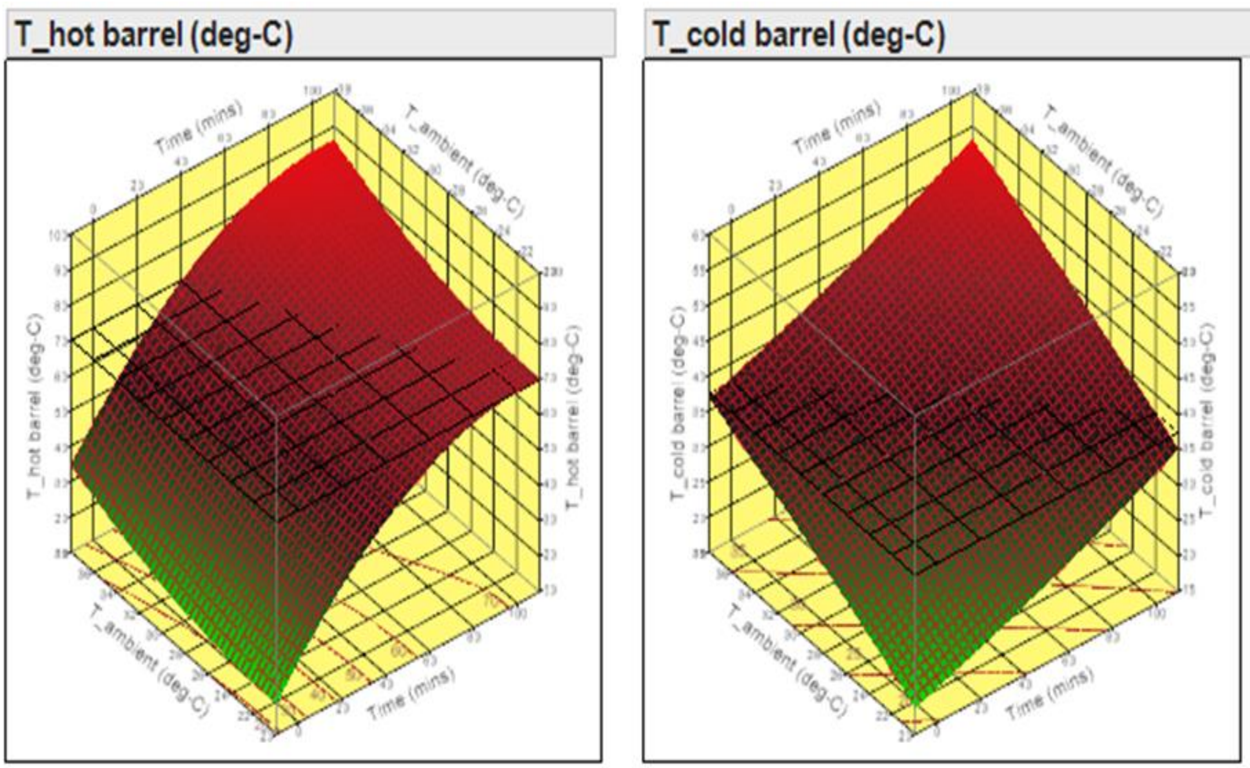


Figure 3.10 Effects of running time and ambient temperature on hot and cold barrels temperatures

The F-Ratio effect test of the results showed both running time ($p<0.0001$ at both linear and quadratic levels) and ambient temperature ($p<0.0001$ at linear level and $p<0.0133$ at quadratic level) were significant on the hot barrel temperature. The model obtained showed that the hot barrel temperature will reach the desired pre-soaking temperature of 70.2°C at a running time of 62 minutes at an average ambient temperature of 32.2°C (Figure 3.11).

Running time was found to be significant on cold barrel temperature at both linear (p<0.0001) and quadratic levels (p<0.0109); and the ambient temperature was significant at linear level (p<0.0001) but was not significant at the quadratic level (p<0.1102). The predicted cold barrel temperature at a running time of 62 minutes was 40.6°C (Figure 3.11). This result showed that both the hot barrel and the cold barrel will reach the temperatures for pre-soaking and drying applications respectively, after 62 minutes of running time at an average ambient temperature of 32.2°C.

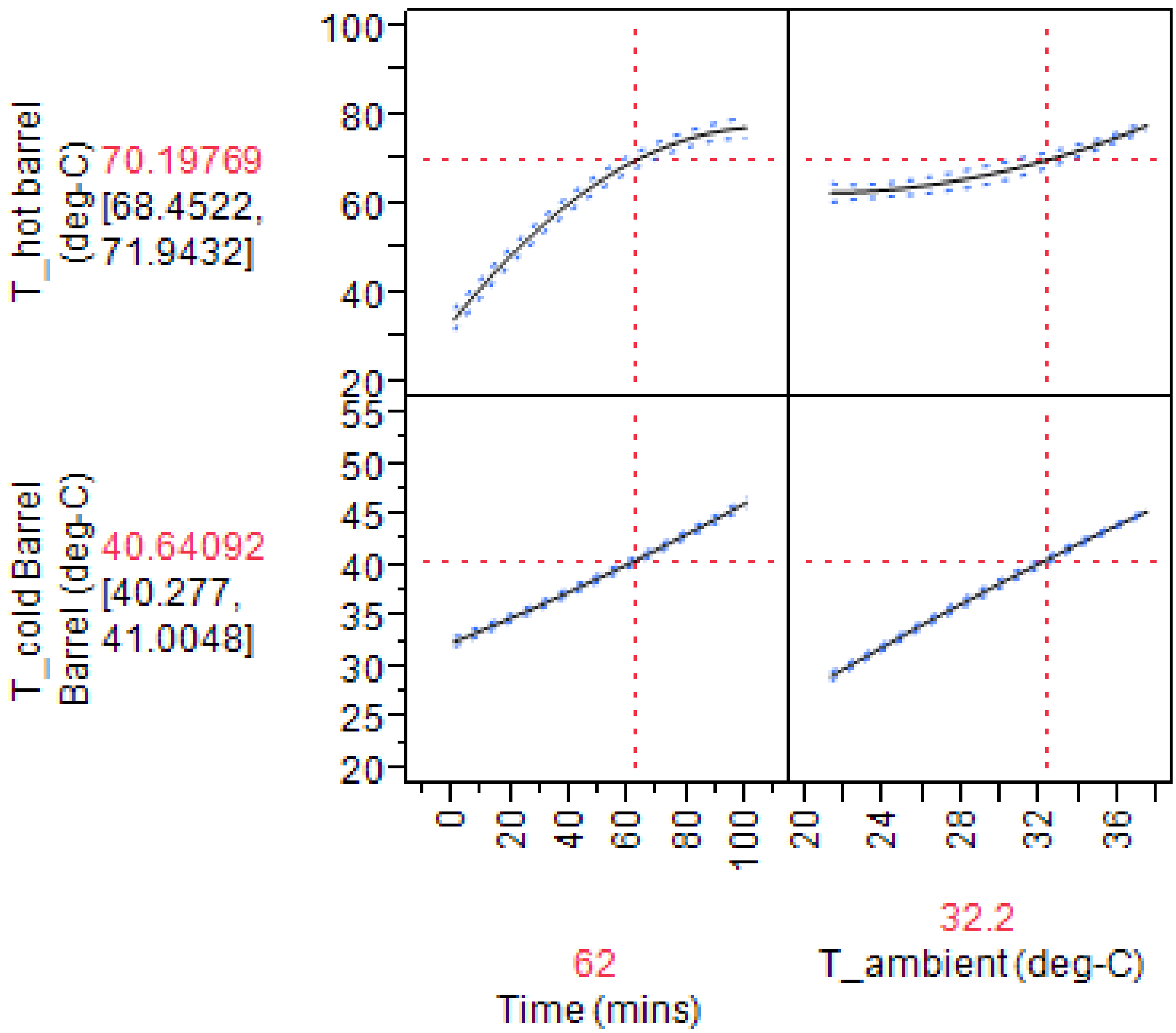


Figure 3.11 Running time and ambient temperature for effective utilization of waste heat from the hot and cold barrels

3.7.2 Results of the utilization of solar energy for pre-soaking of rice paddy

3.7.2.1 Solar collector air test

The average ambient temperature was 33.36 °C (Std. Dev=6.23) for the collector tube air test. It was also observed that the ambient temperature during the three days of the tests had the minimum value of 22.4°C to a maximum value of 43.7°C. The days were sunny, but dry during the time of experiments, with very few clouds.

The minimum tube temperature was found to be 22.5°C and the maximum temperature was 114.7°C. The mean temperature was found to be 78.1°C (Upper Confidence Interval (UCI) = 82.6; Lower Confidence Interval (LCI) =73.6; at α=0.95) with standard deviation of 28.7°C (UCI=32.2; LCI=25.9; at α=0.95). At average ambient temperature of 33.36 °C (Std Dev=6.23), it took a predicted time of 179.5 minutes for the tube to be heated to the pre-soaking temperature range as shown in Figure 3.12.

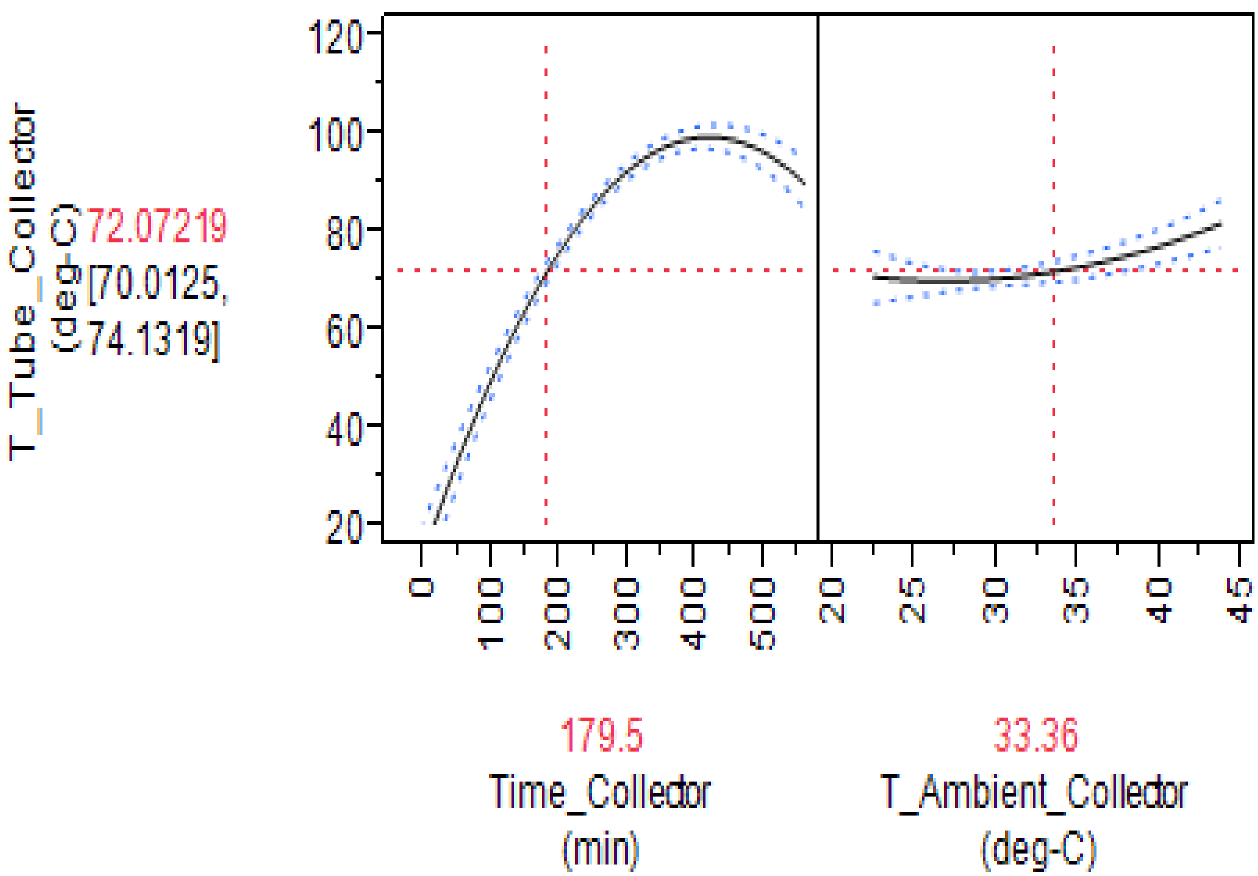


Figure 3.12 Tube temperature with respect to time and ambient temperature

The relationship between time of day (TOD) and tube temperature (Figure 3.13) showed that the tube temperature did not reach rice parboiling temperature until 11:20 am; beyond which the temperature continued to rise to peak at 114.9°C in mid-afternoon. These showed that the earliest time of the day that could be used for pre-soaking will be beyond that time of the day (11:20am).

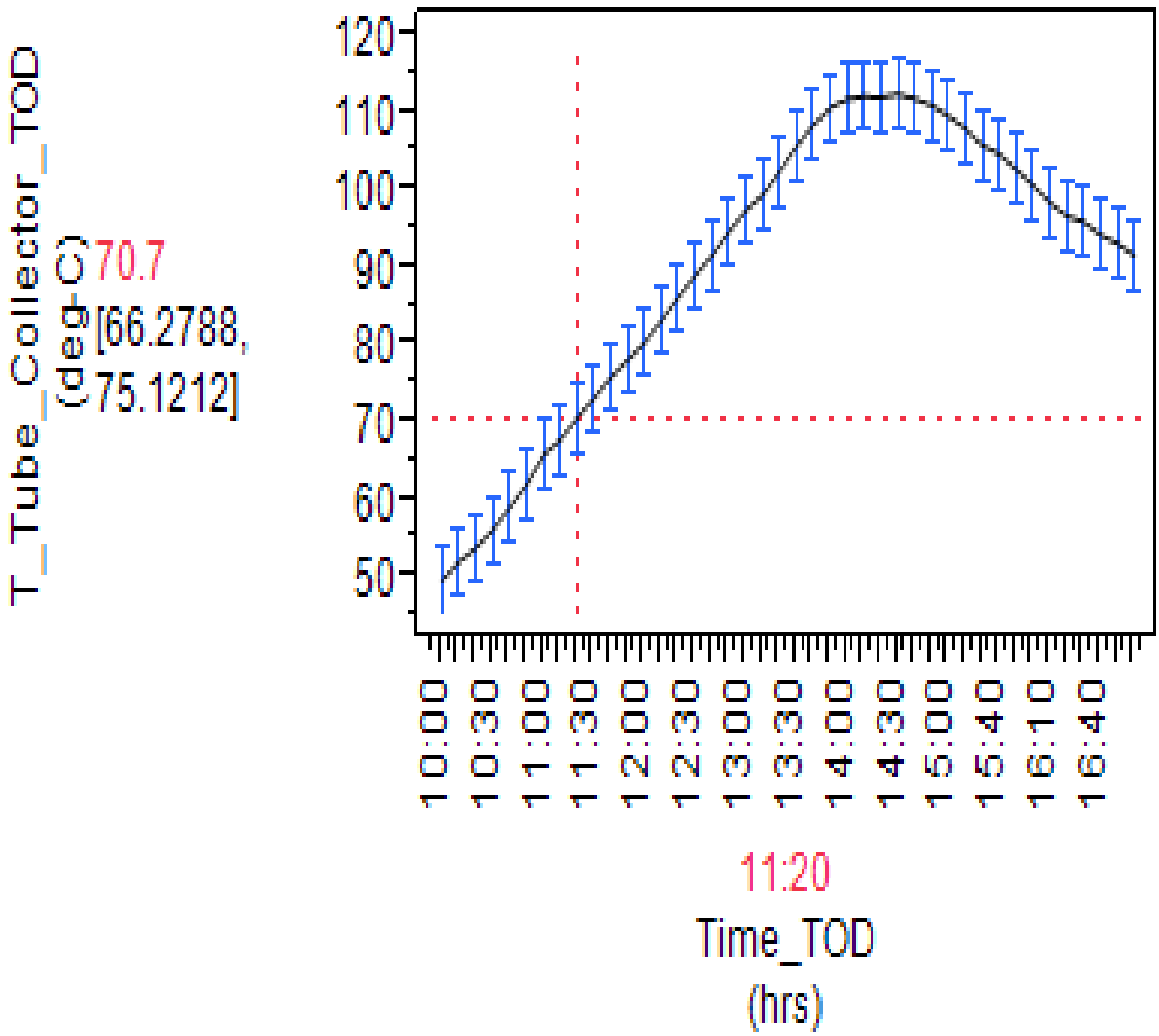


Figure 3.13 Time of day and collector tube temperature relationship

Analysis of results showed that both time of day, ambient temperature, and heating time have significant effects on the tube temperature (Figures 3.13 and 3.14). The test showed that significance of ambient temperature is linear, while heating time is significant at the quadratic level with R-Square value of 0.97 (at $p<0.0001$).

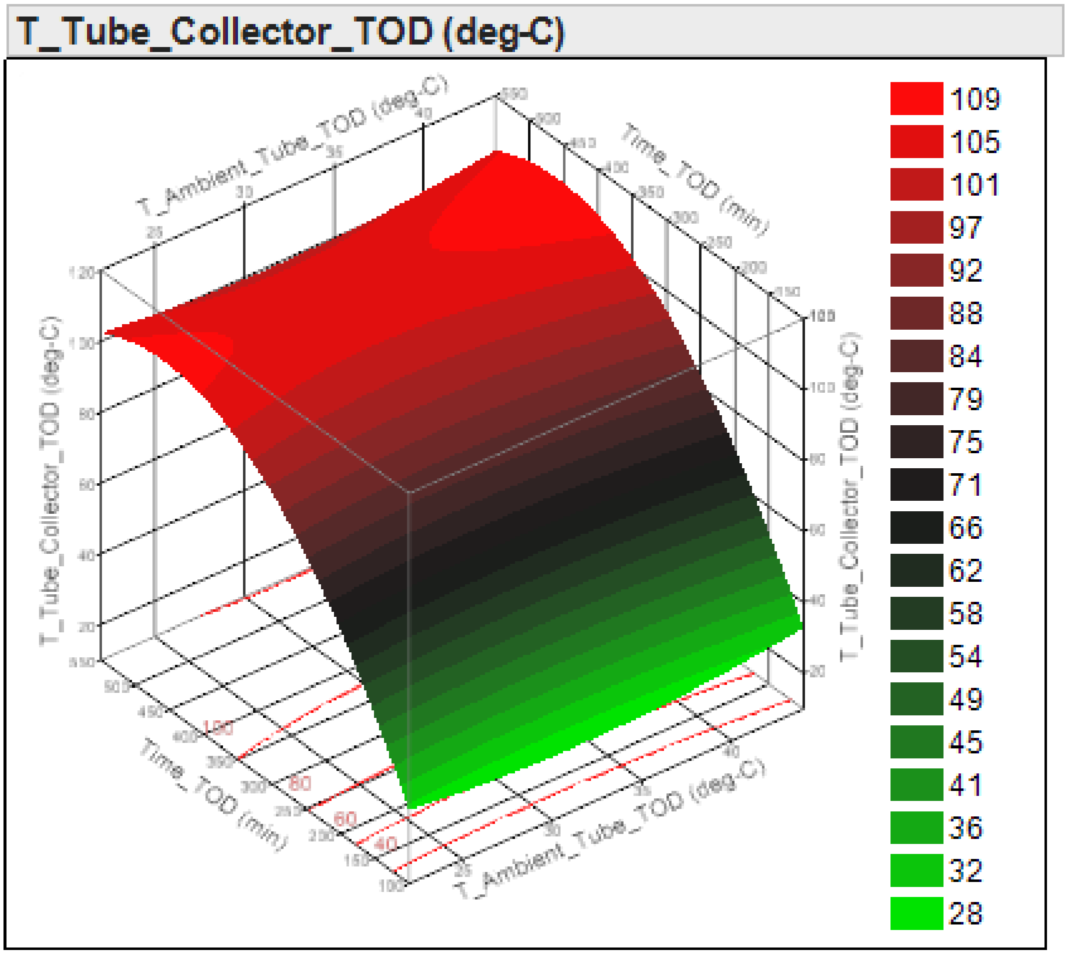


Figure 3.14 Effects of running time and ambient temperature on the collector tube temperature

3.7.2.2 Solar thermosyphon system performance test

The average ambient temperature was 32.97°C (Std. Dev=5.7) during the three days of the solar thermosyphon performance test. The ambient temperature range was between 23.1 to 45.2°C. The days were sunny but dry with very few clouds during the three days of the thermosyphon system performance tests.

The minimum tank temperature was 23.1°C and the maximum temperature was 83.6°C. The mean temperature was found to be 57.8°C (UCI=60.9°C; LCI=54.7°C; at α=0.95), and the standard deviation of 20.1°C (UCI=22.6°C; LCI=18.1°C; at α=0.95). At an average ambient temperature of 32.97°C (with R-Square=0.96) it took 444 minutes for the thermosyphon tank temperature to reach the pre-soaking temperature range as shown in Figure 3.15.

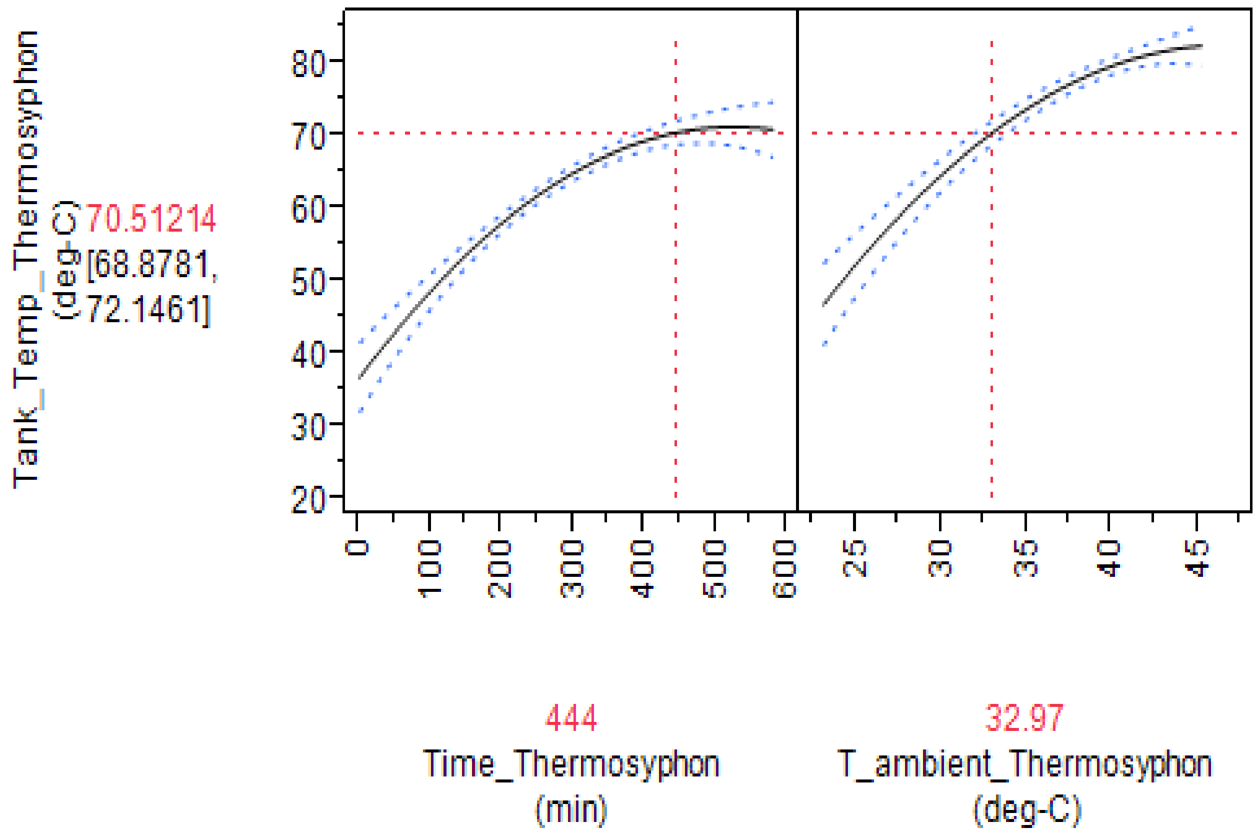


Figure 3.15 Thermosyphon temperature with respect to time and ambient temperature

The relationship between TOD and the tank temperature showed that the temperature of the thermosyphon tank reached the pre-soaking temperature range in the afternoon at around 13:00 as shown in Figure 3.16. This analysis indicated that the thermosyphon system can only be used for pre-soaking beyond that time in the afternoon; which will mean four hours or less of utilization as a thermal energy source for pre-soaking. However, the length of time that this system could be used as a thermal source for pre-soaking could even be lower because no hot water was utilized or taken out of the system during the experiments. Nevertheless, multiple tube solar panels of the same design, could make this thermal system viable at a substantially higher financial cost.

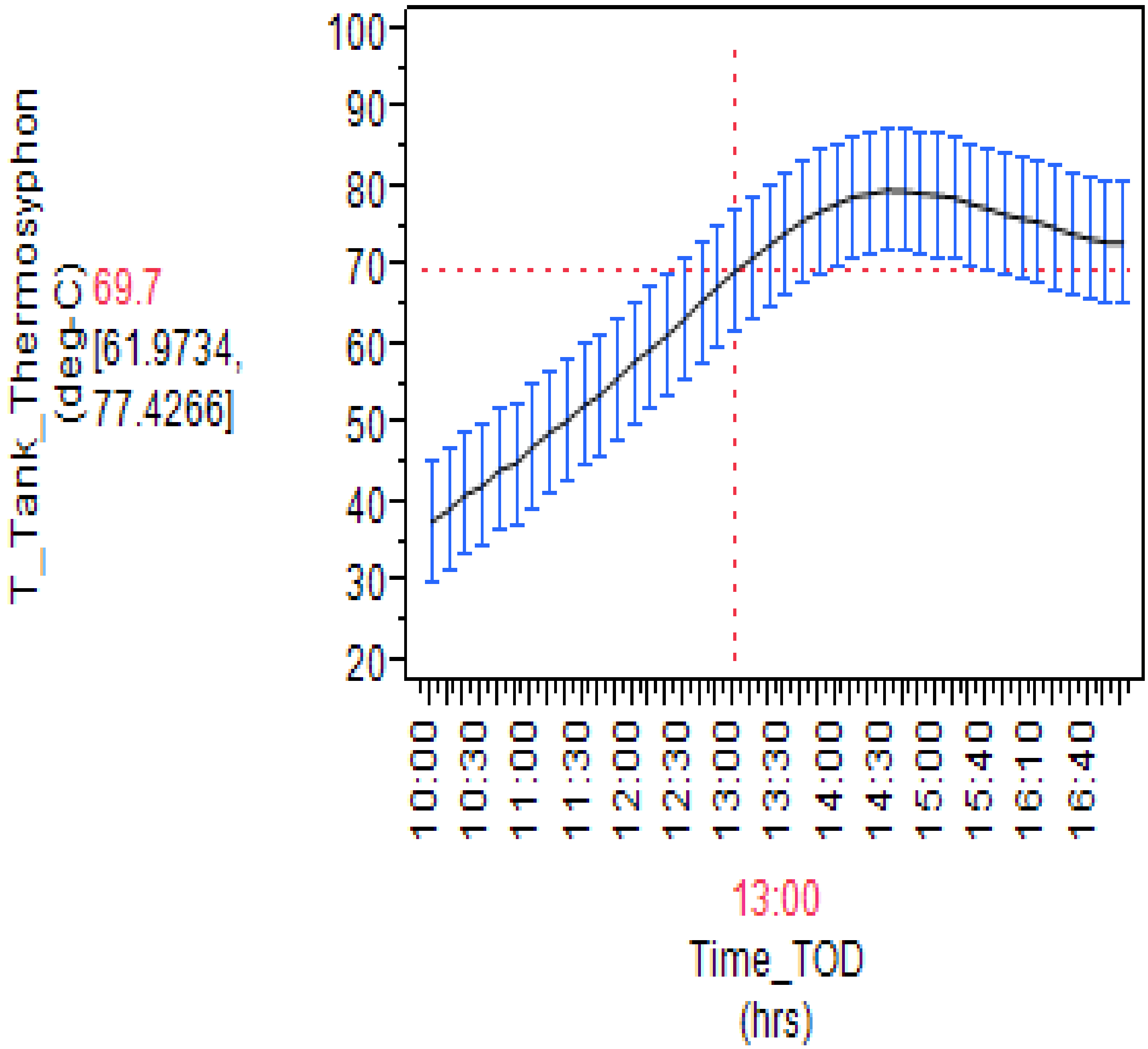


Figure 3.16 Time of day and thermosyphon tank temperature relationship

The test result showed that all factors including time of the day, ambient temperature and time of heating to have significant effect on the thermosyphon tank temperature, and consequently on the performance of the thermosyphon system. As shown in Figure 3.17, the tank temperature reached the desired pre-soaking temperature late in the afternoon and the significance of both time and ambient temperature was at a quadratic level (with R-Square value of 0.95; at $p<0.0001$).

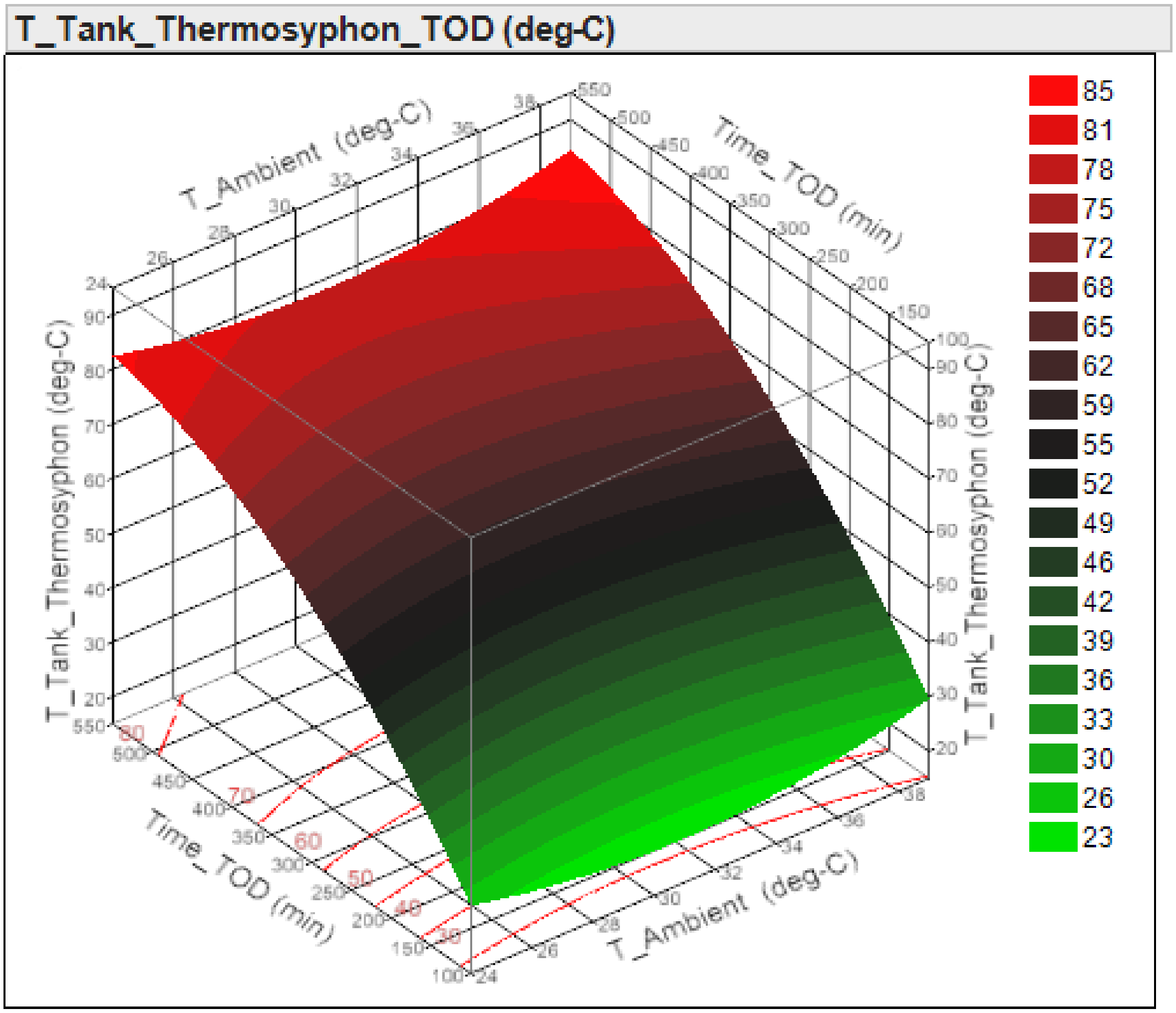


Figure 3.17 Effects of running time and ambient temperature on collector tube temperature

3.7.3 Results on the redesign and optimization of conventional stoves to minimize heat loss

The optimization of the current process involved the enclosing of the stove. This can effectively minimize the convective and radiative energy losses to the atmosphere. This simple improvement will greatly improve parboiling efficiency. Another suggestion involves insulating the vessel and also keeping it covered. This will reduce the thermal losses to the atmosphere through evaporation and convection.

The analysis of temperature data obtained is shown for the actual and predicted plots for both the open stove and the modified covered stove in Figures 3.18 and 3.19 respectively.

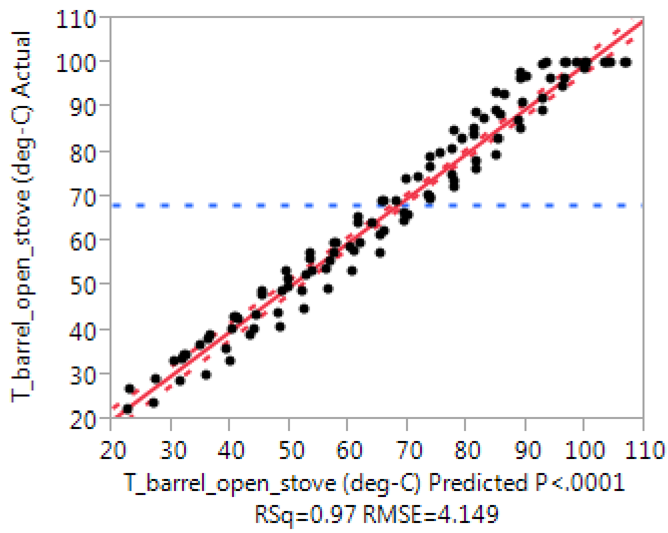


Figure 3.18 Actual vs predicted plot analysis of barrel temperature with respect to ambient temperature and heating time for the open stove

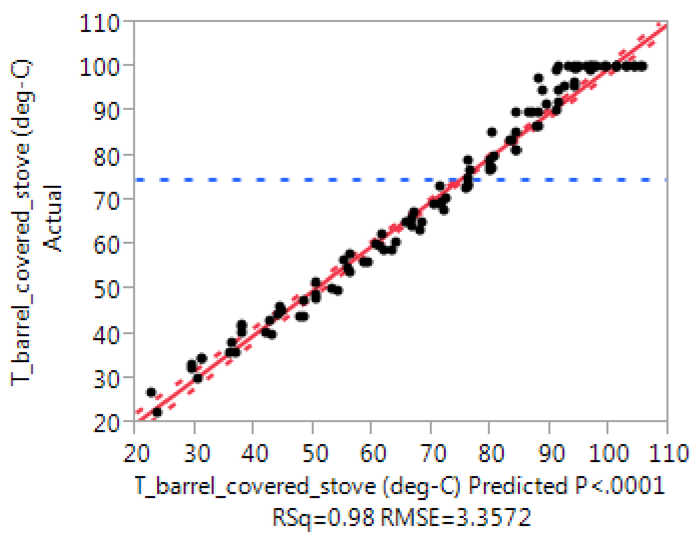


Figure 3.19 Actual vs predicted plot analysis of barrel temperature with respect to ambient temperature and heating time for the covered stove

The model plots obtained based on the data have R-square values of 0.97 and 0.98 for the open and the covered stoves respectively, with ambient temperatures, and time of heating as factors presented in Figures 3.20, 3.21, 3.22, & 3.23.

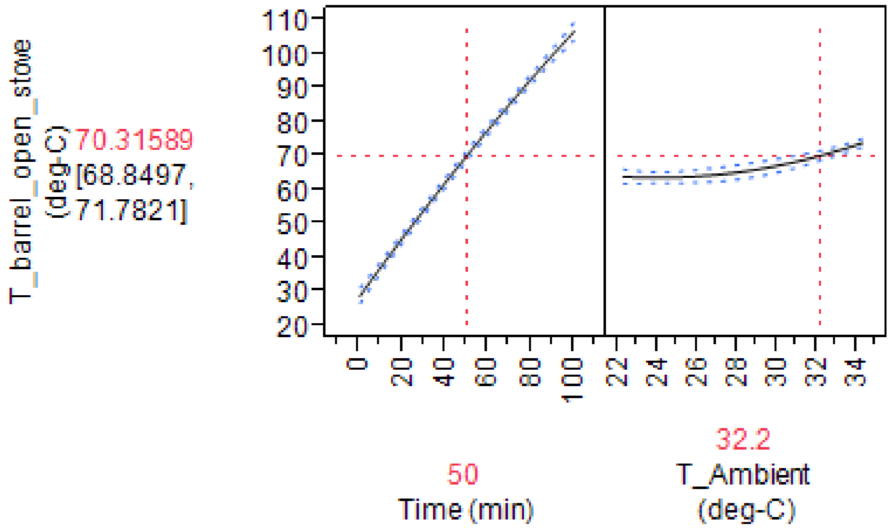


Figure 3.20 Model prediction profile plot of barrel temperature with respect to ambient temperature and heating time for the open stove

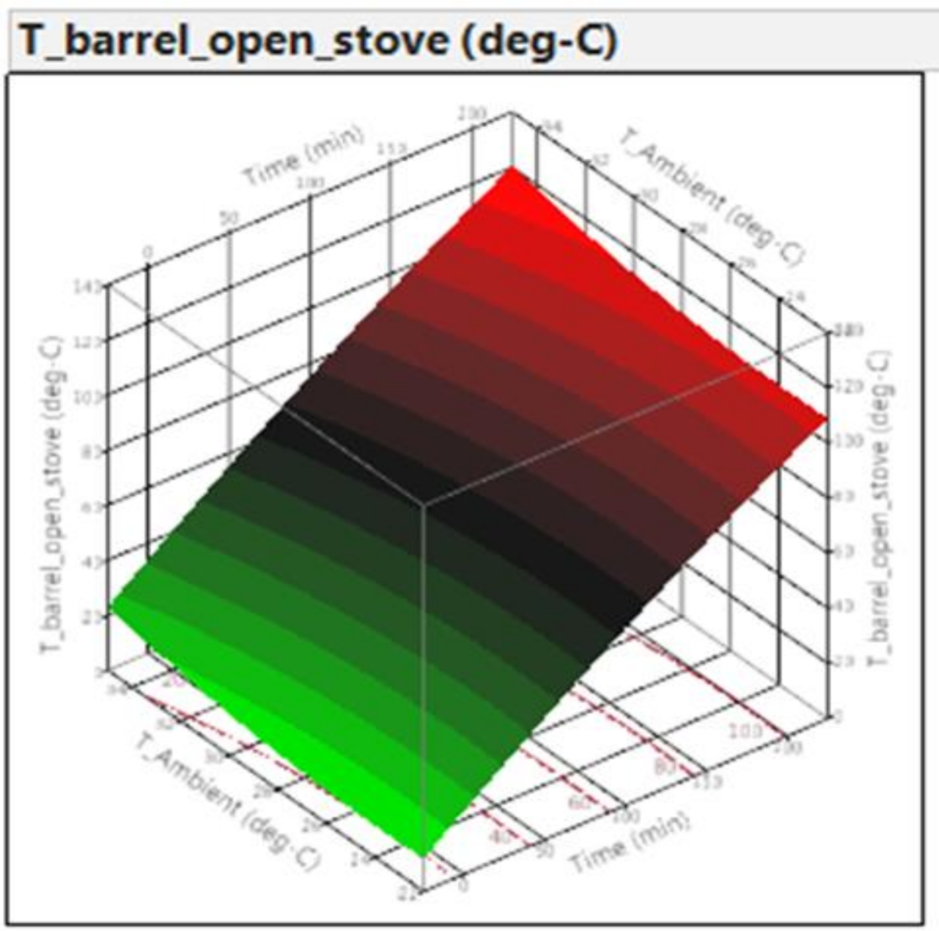


Figure 3.21 Model plot of barrel temperature with respect to ambient temperature and heating time for the open covered stove

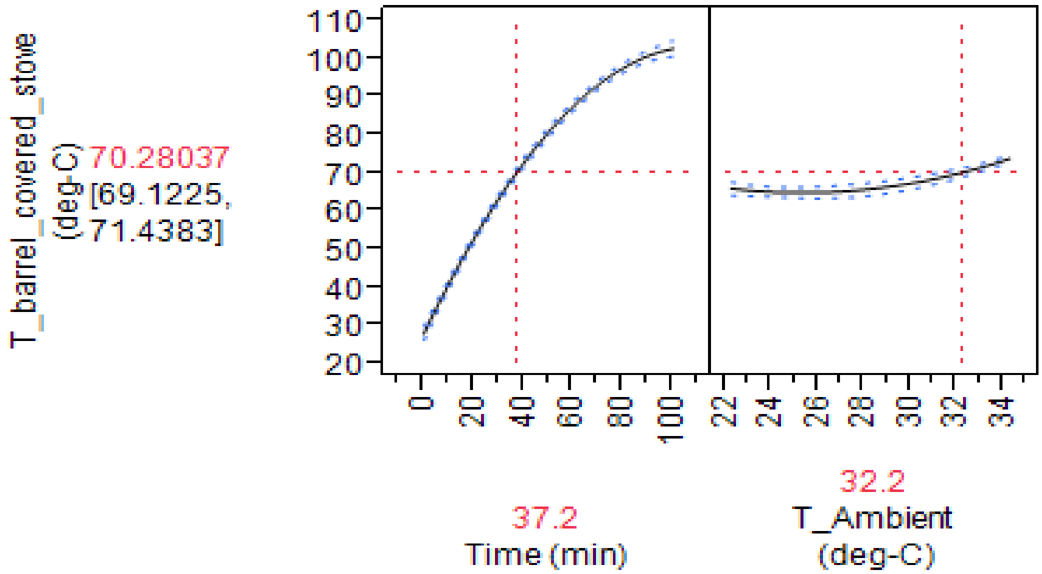


Figure 3.22 Model prediction profile plot of barrel temperature with respect to ambient temperature and heating time for the covered stove

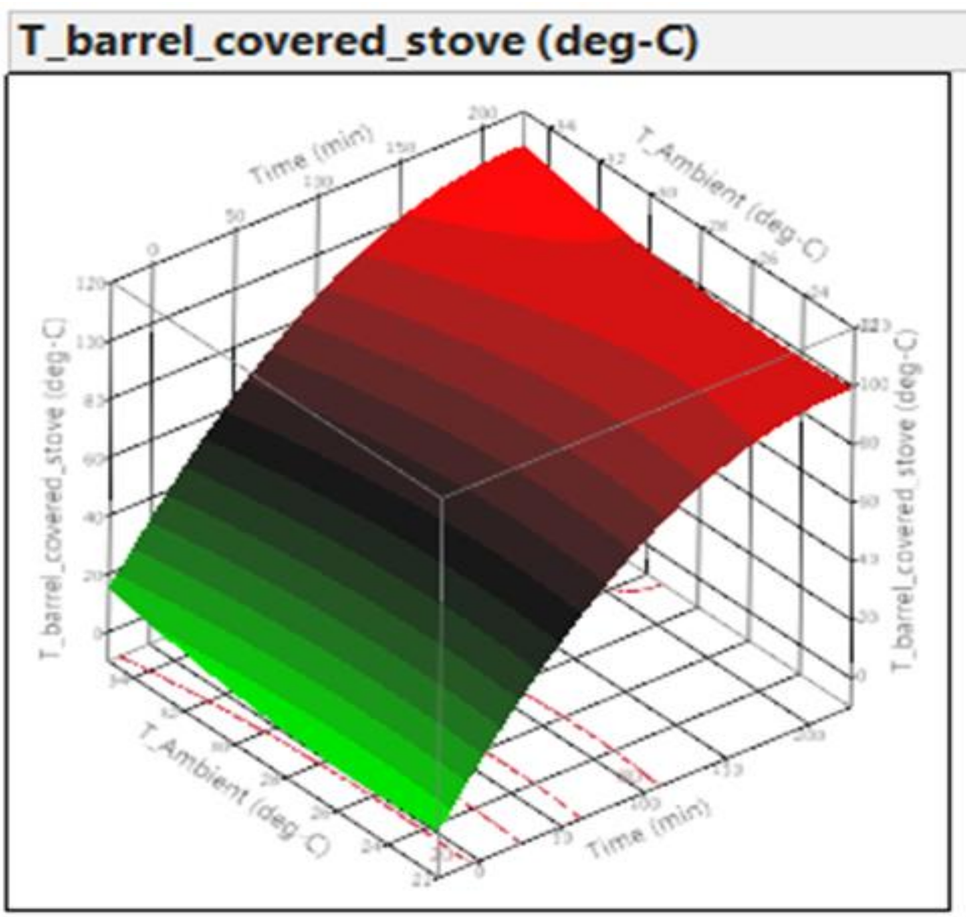


Figure 3.23 Model plot of barrel temperature with respect to ambient temperature and heating time for covered stove

From the results obtained and the prediction analysis, the energy and time savings by covering the stove are significant. The predicted time for heating the water barrel to 70°C with the open conventional stove, at an average ambient temperature, was about 50 minutes; while the time for heating the same amount of water to the same temperature under the same ambient temperature condition for the covered stove was about 37.2 minutes. The results also showed that for the medium scale rice parboiling using the barrels, both the time of heating and the ambient temperature are significant factors on the barrel temperature. An interesting result observed, showed that for the uncovered stove, the relationship factor between the barrel temperature and the time of heating was linear, while the relationship between the barrel temperature and the ambient temperature was found to be quadratic. However, for the covered stove it was found that both the time and ambient factors relationships with the barrel temperature were quadratic. This could have been caused by the rate of convective losses, and also possibly, by the difference in the types of thermochemical conversion processes that occur in the open and covered stove configurations. The possibility of increased gasification/reduction due to lower amount of direct oxidation of the firewood for the covered stove could have raised the temperature of the stove, which could at the same time increase the temperature differential between the ambient and the stove. However, further research beyond the scope of this research will be required to confirm these results.

3.7.4 Results on utilization of rice husk as an alternative to firewood

Utilization of rice husk was found to be the best alternative, of all the ones considered, for increasing sustainability of rice processing, because of the abundance of rice husk. Rice husk is abundant and free; and if it can be used directly as a fuel or fuel feedstock to produce fuel that will replace firewood, the community was willing to adopt it, just as they have adopted the stove using sawdust as fuel. During the experiments, once the combustion began at the flat top of the cone, the temperature of the stove began to rise. The surface temperature above the inverted cone rose significantly which resulted to the carbonation of the steel at the region above the cone, as shown in Figure 3.24 below.

Figure 3.24 Carbonation of the sheet metal above the cone as a result of higher temperature

The predicted versus the actual test results produced by monitoring the boiling water were found to be quadratic with R-square value of 0.98 (at $p<0.0001$) as shown in Figure 3.25. The analysis showed that of the two factors considered, namely the ambient temperature and heating time; heating time is the only significant factor at both quadratic and linear levels with ($p<0.0001$) as shown in Table 3.1 and Figure 3.26.

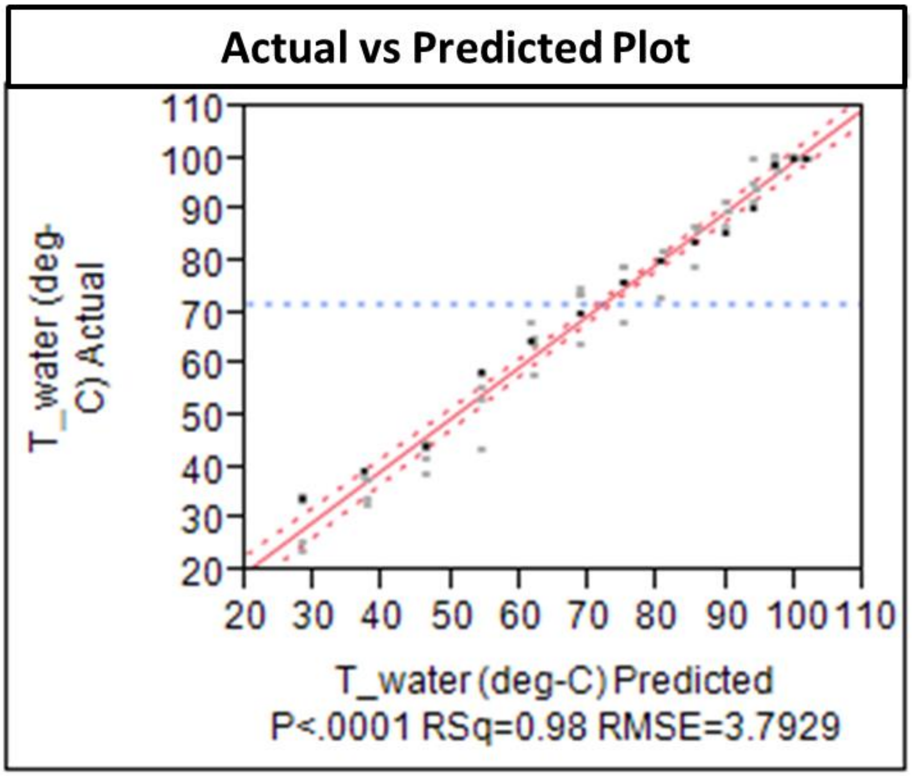


Figure 3.25 Actual vs predicted water temperature during the boiling water test

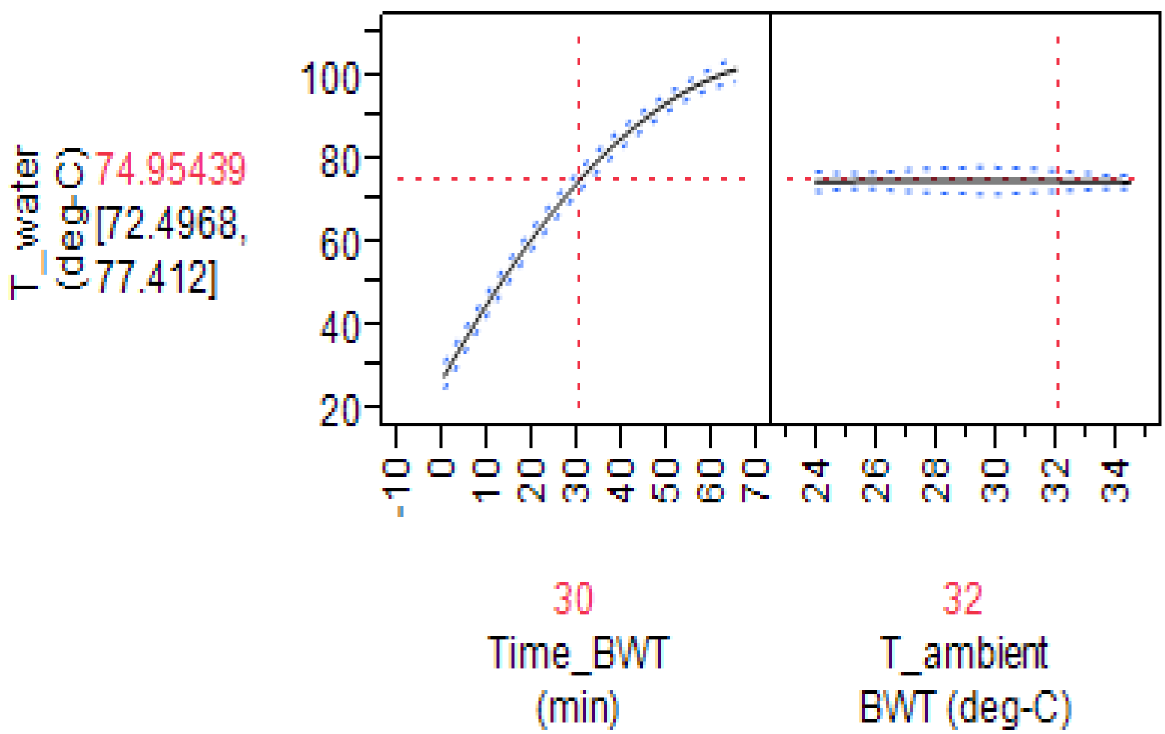


Figure 3.26 Predicted water temperature with respect to heating time and ambient temperature

Table 3.1 – Analysis of variance of boiling water

Effect Tests

Source	Nparm	DF	Sum of Squares	F Ratio	Prob > F
Time_BWT (min)	1	1	32557.427	2263.084	<.0001*
Time_BWT (min)*Time_BWT (min)	1	1	1191.320	82.8093	<.0001*
T_ambient BWT (deg-C)	1	1	0.824	0.0573	0.8116
T_ambient BWT (deg-C)*T_ambient BWT (deg-C)	1	1	0.354	0.0246	0.8758

The results verify that within the experimental setup, the temperature range, and time range of the experiments, ambient temperature was not a significant factor; likely because the rate of heat loss to the atmosphere may not be as significant, compared to heat gain during the heating process. Since the analysis of the results obtained showed that the time is the only significant factor both at linear and quadratic levels, a polynomial model was established using this factor. The polynomial model obtained with heating time as the key factor is presented in Table 3.2, and Figure 3.27. The model also has a R-square value of 0.98 ($p<0.0001$) proving the insignificance of the ambient temperature as a factor on the water temperature during the boiling water test.

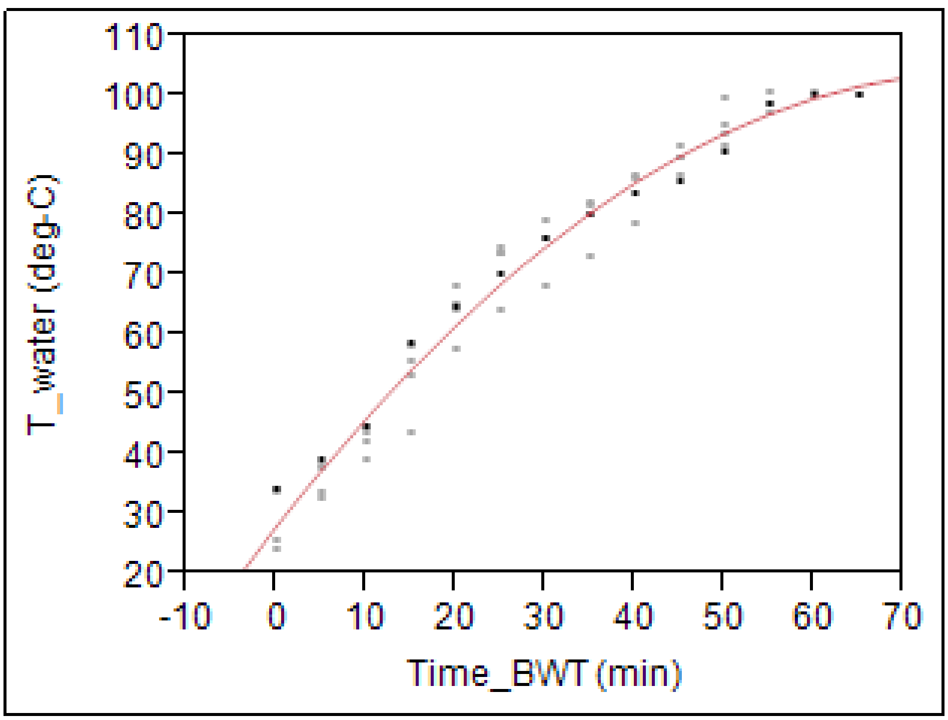


Figure 3.27 Water temperature model with respect to heating time model

Table 3.2 Water temperature with respect to heating time

Polynomial Fit Degree=2

T_water (deg-C) = 40.199781 + 1.1552906*Time_BWT (min) - 0.0121686*(Time_BWT (min)-31.5441)^2

Summary of Fit

RSquare	0.975466
RSquare Adj	0.974711
Root Mean Square Error	3.736026
Mean of Response	71.94265
Observations (or Sum Wgts)	68

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	2	36072.404	18036.2	1292.187
Error	65	907.263	14.0	Prob > F
C. Total	67	36979.666		<.0001*

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	40.199781	0.989319	40.63	<.0001*
Time_BWT (min)	1.1552906	0.023056	50.11	<.0001*
(Time_BWT (min)-31.5441)^2	-0.012169	0.001308	-9.30	<.0001*

3.8 Conclusions

Rice processing is an energy intensive process. The small and medium scale parboilers in sub-Saharan Africa always overlooked the parboiling efficiency, the sustainability and climate change issues that are caused by the current parboiling methods. Valuable trees such as *Prosopis africana* (kiriya) in the parkland and agro-forest are being depleted due to increase in demand for firewood for agricultural processing such as rice parboiling. This paper showed that with simple adaptable modification of the current process, the efficiency of parboiling can be greatly improved. Results showed that the modified stoves reached the desired temperature much faster than the unmodified stove. The utilization of waste biomass such as rice husks as an alternative fuel can greatly improve the sustainability of the parboiling process. The modified stove that uses rice husk as the key fuel developed in this study is a proof that sustainability of rice parboiling can be greatly improved in the sub-Saharan African region using appropriate technology. Another observation during this research was that skills training of the rice processors and the local craftsmen they used to build their processing equipment will be an important step towards increasing sustainability. In summary, the adoption of the concept of RATE (Research Appropriate Technology and Education) will enable the sub-Saharan rural farming communities to increase their productivity in a sustainable way.

Analysis of the result of utilization of waste heat from the hot and cold barrels of the Listeroid engine cooling system, showed that engine running time and ambient temperatures have significant effects on the temperatures of both barrels. It was found that at an average ambient temperature of 32.20℃ the hot and cold barrel temperatures reached an average temperature of 70.20℃ and 40.64℃, respectively. These results showed that the hot and cold barrels can be effectively used for presoaking and drying of the rice paddy, respectively.

The results obtained from the air test of the prototype solar panel and the thermosyphon solar water systems were promising. The panel temperature peaked at 114.9℃ in the mid-afternoon. The results showed that the panel itself will reach paddy presoaking temperature by 11:20 am, making it highly attractive. The thermosiphon system tank temperature peaked at 83.6℃ at an average ambient temperature of 32.97℃. Predicted model (R-square=0.96) developed showed that the thermosiphon system will reach presoaking temperature at around 13:00, meaning that it will not be viable for presoaking during the earlier part of the day. However, multiple tube solar panels of the same design and improved active water circulation could make this thermal system viable, albeit at a higher financial cost.

Simple modification of the conventional tripod stove by developing a cover using the RATE theme, which engaged both the craftsmen and the rice parboilers in the development, significantly reduced the time required to heat the soak paddy to presoaking temperature of 70℃. It took 37.2 minutes for the modified covered stove to reach the presoaking temperature, while it took 50 minutes for the uncovered conventional stove to reach the parboiling temperature. These findings were gladly welcomed by the rice parboilers.

The rice husk stove developed was found to combust rice husk effectively. The boiling water test results was used to develop a polynomial predicted model (R-square =0.98) that showed that at an average ambient temperature of 32℃, the stove can heat water to 74.95℃ in 30 minutes.

3.9 Recommendations

Improvement of the conventional methods and development of new methods using the RATE theme proposed in this research will increase the sustainability of rural rice processing. The adaptation of the RATE by NEPAD and the leaders of sub-Saharan African region; and its implementation in their agricultural development program will increase sustainability of agricultural production. Development of skill acquisition centres that train farmers, postharvest processors, and the local tradesmen that fabricate agricultural equipment; and collaboration with research institutions including the local Universities to develop and design the equipment for the farmers and processors, (which defines RATE) is very important for increasing sustainable agricultural production at the small (rural) and medium scale levels. Since this sector is a potential employer for the local youth and rural community, it will not only help in providing food security, but will also help in reducing poverty, and minimizing social insecurity, that most regions of sub-Saharan Africa are experiencing.

3.9 Contribution of this research

The most important contribution that this research made was the development of the Research Appropriate Technology and Education (RATE) theme, which will enable the sub-Saharan African region to increase sustainability of rice and other agricultural production. This research further studied simple methods of improving the conventional methods of parboiling to increase energy efficiency and environmental sustainability. Three non-conventional thermal energy systems including: Utilization of waste heat from diesel engines, a solar thermal thermosyphon system, and a rice husk stove were developed and tested based on the RATE theme to determine their viability and acceptance by the rice post-harvest processors in the region.

3.10 Limitation of study

This study focused on the development of simple methods for increasing sustainability of rice processing through research, development of appropriate technology and the education of the locals to ensure the likely adoption of technology. The approach developed called RATE (Research Appropriate Technology and Education) is a valuable tool for engaging both the craftsmen and end-user postharvest food processors in the development of appropriate technology improvements to the conventional equipment and processes currently used by the locals. RATE can be used by the regional governments and research institutions in the sub-Saharan region, as well as, in all developing nations to increase agricultural production sustainability. However, the availability of resources for the research, type of technology developed, and educational resources available will determine the success of this technology transfer approach. Also the effective engagement of the triads of sustainability will determine how much this approach can increase long term sustainability.

Connecting text to Chapter IV

In chapter 3, the utilization of rice husk, as an alternative to firewood and fossil fuel, was found to be an effective method of increasing sustainability of rice processing in sub-Saharan Africa. Rice husk is currently dumped as waste creating both environmental and health hazard. Its utilization as a fuel feedstock will not only reduce or eliminate the negative ecological impact, but will also create employment for both the tradesmen fabricating rice husk stoves and, makers and marketers of rice husk fuel briquettes and pellets. In order to effectively characterize rice husk and compare the characteristics between the Engelberg and the Milltop produced rice husks, the effects of process parameters including physical, chemical, and die pressure on the characteristics of densified rice husk need to be studied. In chapter 4, the effects of process parameters on the densification of the rice husk were studied. This included the utilization of binders with different chemical composition at different ratios, and die pressures, to determine their effect on the density and the water permeability of the rice husk samples. Another objective was to explore the possibility of densifying rice husk without pre-treatment or size reduction at lower pressures minimizing the amount of the energy required for densification. Chapter 4 includes a method on how to characterize rice husk and the binding effects as a function of chemical composition on densification characteristics of rice husk, and the opening of a new approach on how to densify rice husk with limited modification of the feedstock; to increase sustainability of the process. The research also provided information on what are the important characteristics of the Engelberg and the Milltop rice husks that will determine the densification processing approach of the distinct biomass used as biofuel feedstock.

Chapter IV: Effect of process parameters on densification of rice husk at medium pressure

4.1 Abstract

Rice husk is a potential feedstock for biomass densification for energy usage via combustion. However, its low density and difficulty in handling requires that it be densified into briquettes or pellets. In this study, raw rice husk with geometric mean diameter of 1.669 mm was densified at medium pressures (42.5 – 70.8 MPa), and at established optimum moisture content of 15%, using a manual hydraulic press. Effect of process parameters including binder type, binder ratio, and die pressure; on density and water permeability of the densified rice husk were studied. The water absorption ratio ranged from 1.40-2.27 and the briquettes densities ranged from 390 - 780 kg/m^3 (0.39-0.78 g/cm^3). FTIR-ATR, chemical composition analysis, and proximate analysis based on ASTM standards, were used to investigate the characteristics of both the rice husks and binders. The results showed that die pressure, binder type, and binder ratio have significant effects on both the water absorption and density of briquettes produced. Rice husk briquettes expand mostly longitudinally (ratio = 1.940-3.089) and to a lesser extent radially (ratio = 1.0122-1.022) after insertion into water. Die pressure and binder types were found to be the significant factors that affected expansion ratios. Densified rice husks bound with paraffin wax, whole *Afzelia africana* aril and groundnut shell, and gum arabic (*Acacia senegal*) were found to be more hydrophobic than the ones with de-oiled *Afzelia africana* aril and groundnut shell. However, de-oiled *Afzelia africana* aril produced briquettes with higher densities than the high lipid whole *Afzelia africana* aril, showing that fat content affects both the permeability and density of rice husk briquettes.

4.2 Introduction

Biomass waste from postharvest processing is a potential energy feedstock that can replace or complement firewood and fossil fuels. Although rice husks, like many other waste biomass, have high calorific value, the major issue that limits the utilization of this abundant biomass as a fuel is its low bulk density, low energy density, and difficulty in handling. Densified rice husk in the form of pellets or briquettes using binding agents could make an attractive feedstock for biomass energy. Densification can increase the density of biomass from an initial bulk density of 40-200 kg/m^3 to a final compact density of 600-1200 kg/m^3 (Holley, 1983; Mani et al., 2003; Obernberger & Theck, 2004; McMullen et al., 2005; Adapa et al., 2009). Densified biomass may be easily handled using standard handling and storage equipment, and can be easily adopted as a fuel for thermochemical (combustion furnace, gasifiers, pyrolysis reactors), as well as, biochemical (fermentation processes producing biofuels such as ethanol) energy conversion.

4.3 Literature review

The physicochemical characteristics of both the biomass to be densified and the binders that will be used are important in determining the strength of the bond at both macroscopic and microscopic levels. Upon densification, many agricultural biomass materials result in poorly formed pellets or compacts that are more often dusty, difficult to handle and costly to manufacture, due principally to an incomplete understanding of their binding characteristics (Sokhansanj et al., 2005). Rice husks especially, have poor binding characteristics by nature. Both the outer and inner surfaces of rice husk have characteristics that negatively affect their binding properties (Figures 4.1 and 4.2). The high silica content of the rough outer protective surface of rice husk does not adhere well to binders while the inner smooth surface contains wax and natural fats that affect the binder-rice husk interaction both macroscopically and microscopically. From Figure 4.1, some of the needle-like trichomes can be seen still attached to the outer epidermis; also cracks can be seen splitting the outer lemma due to the force of the milling rollers. The outer epidermis cells run longitudinally and have thick high silica content walls with the trichomes projecting between the longitudinal rows of the epidermis cells (Champagne, 2010). Figure 4.2, shows the inner surface which is smoother with components of bran, broken rice and pieces of the pericarp layer.

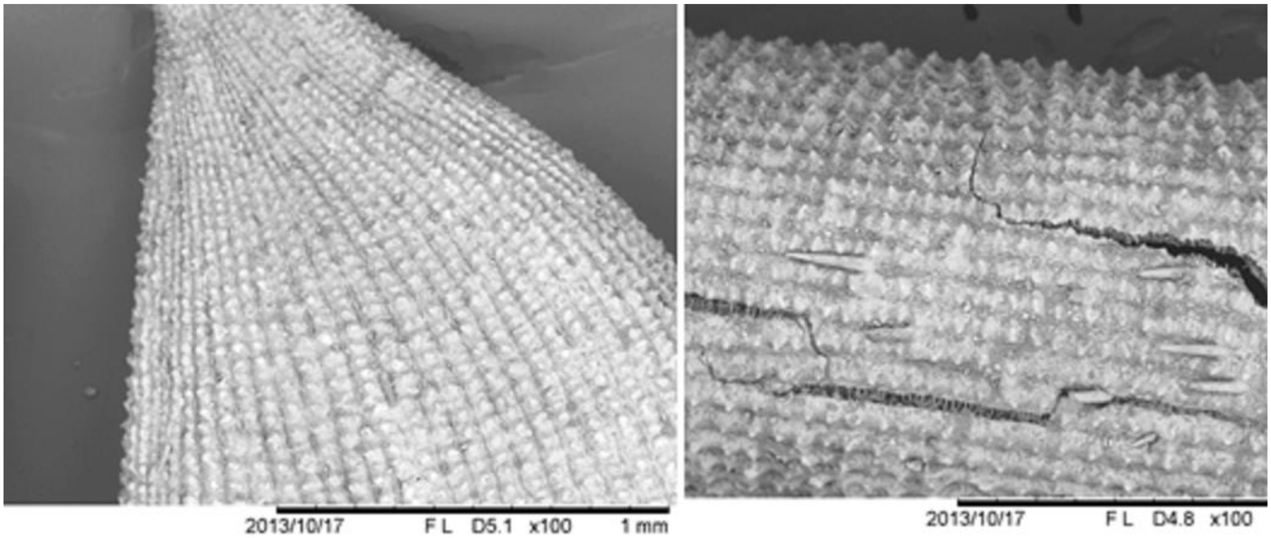


Figure 4.1. SEM of the outer surface of multistage mill rice husk observed using Hitachi TM3000 Tabletop SEM

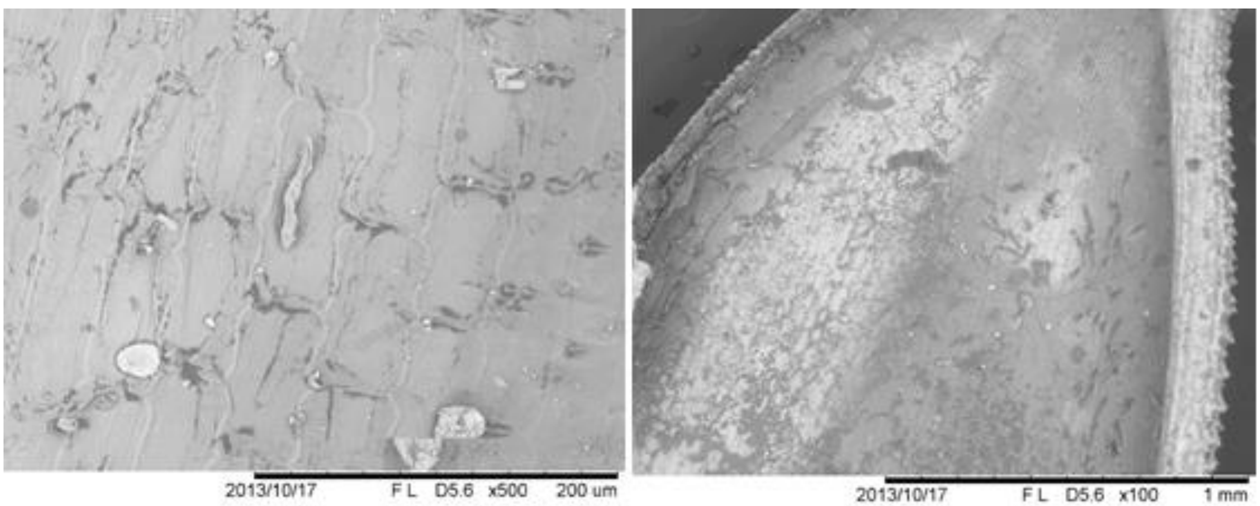


Figure 4.2. SEM of the inner surface of multistage mill rice husk observed using Hitachi T3000 SEM

Pretreatment of biomass such as rice husk has been found to improve its binding characteristics (Adapa et al., 2002; Ndazi et al., 2007; Lam et al., 2009). Ndazi et al. (2007) studied the inner and outer surface of rice husk, before and after its treatment with NaOH and concluded that this pretreatment improved the binding characteristics. This occurred because the treatment removed some of the silica and other surface impurities in both the inner and outer surfaces of the rice husk that includes the wax and fat (Ndazi et al., 2007). Another method of pretreatment is steam explosion which requires considerable energy input. Steam explosion is an energy intensive process that can improve the densification properties of biomass by activating and restructuring the native lignin in the biomass fibre. In this process, biomass is subjected to saturated steam at temperatures of 180-240 °C, and pressures of 1034-3447 kPa, for 5-10 minutes, followed by which the treated biomass is rapidly subjected to atmospheric conditions with drastic effects, that include improved hydrophobic and adhesion properties of the biomass structure (Li et al., 2007; Startsev et al., 2000; Donohoe et al., 2008; Lam et al., 2009).

However, both chemical and steam explosion pretreatments have environmental, energy and financial costs, which may inhibit or reduce the attractiveness of rice husk as an alternative biofuel feedstock, in the developing world, where rice husk is abundant and the need for its use as an alternative energy, at a low cost, is the greatest. Therefore, instead of considering the use of a pretreatment, utilization of locally available binders can be explored to increase effective binding during densification of raw rice husk. Effective binders, at both macroscopic and microscopic levels could help make raw rice husk an effective alternative to firewood and fossil fuel. Chang (1991) suggested that the criteria for effective binding at the microscopic level include intimate molecular contact and a sufficient condition of maximum attractive force with minimum activation energy. At microscopic level, electron attraction between molecules is the driving force for adhesion (Kaliyan and Morey, 2010). At macroscopic level, the modes of bonding are bridgeless bonding due to electrostatic and magnetic forces and bridge-bonding with solid bridge between particles due to crystallization of some ingredients, chemical reactions, hardening of the binder, and solidification of melted components (Bika et al., 2005; Kaliyan and Morey, 2010).

Moisture content during densification is an important parameter because it facilitates macroscopic bonding and the development of solid bridges that bind biomass upon drying. Mani et al. (2006) and Kaliyan and Morey (2009) reported that moisture content of 10 – 15% is optimum for densification of many biomass including switch grass and corn stover. Panwar et al. (2011) reported that an optimum moisture content of 8% at die pressure of 100 MPa and holding time of 10s produced the highest density sawdust briquettes. Panwar et al. (2011) also observed that at moisture content of ≤4%, densified sawdust became fragile within a few days, absorbing moisture from the environment and expanding significantly. Rice husk inner and outer physical properties (Figures 4.1 and 4.2) that are not conducive to binding, make the determination of optimum moisture content especially important for subsequent investigation of the effect of other process parameters. Preliminary experiments for determination of optimum moisture revealed that at a moisture content <10%, the mass losses due to simple handling were significant, with the bonded husk readily peeling off the briquettes. Hence, to determine the optimum moisture content for the rice husk, experiments were designed at moisture contents in the range of 10 – 20% to determine the optimum moisture content for minimum mass loss during handling, at medium densification die pressures using five locally available binders.

The physicochemical characteristics of the biomass to be densified and the binders that will be used are important in determining the strength of the bond at both macroscopic and microscopic levels. Thorough investigation of the characteristics of rice husks and binders on the success of rice husk densification is important in the production of high quality densified rice husk briquettes.

4.4 Objectives

4.4.1 Overall objectives

The overall objectives of this research were to investigate the effects of process parameters on the quality of densified rice husk briquettes produced manually at medium pressures; using five binders (gum arabic, paraffin wax, groundnut shell**,** *Afzelia africana* aril (whole), *Afzelia africana* aril (de-oiled) at three binding ratios (2.5, 5.0, 7.5%); without any other pre-treatment.

4.4.2 Specific objectives

The specific objectives of the research were:

1. To study the effects of moisture content, die pressure, binder types, and binder ratio on the densification characteristics of rice husk, including: water permeability, expansion ratio due to water immersion, and density.

2. To determine the optimum moisture content for densification of rice husk.

3. To study the effects of chemical components of binders on the densification characteristics of rice husk.

4. To determine the optimum process parameters for the densification of rice husk at medium die pressure using the five binders, at optimum moisture content.

4.5 Materials and Methods

4.5.1 Rice husk and binder preparation

Rice husk from Cote D'Ivoire obtained from the Africa Rice Centre in Benin was used for these experiments. The rice husk was obtained from a multi-stage rice milling process. No modification was made to the rice husk, except for the removal of stalks of straws, debris, and other foreign materials. Paraffin wax (Flix-o PARAFFINE brand) was purchased from a distributor in Montreal, Canada. Gum arabic and *Afzelia africana* aril were obtained from Nigeria. Groundnut shell came from the de-shelling of whole groundnuts (Yellow Label brand, product of USA and marketed by Loblaws Canada Inc., a major Canadian grocer) that were purchased from a local grocery store, in Montreal, Canada. The binders were all ground to a fine powder that passes through the standard #100 sieve, for the experiments.

4.5.2 Optimum moisture determination for rice husk densification

At low moisture content, densified rice husk is friable and has a tendency to break upon handling, while an optimum moisture content exists to reduce the friability of the product. To assess that, the tendency of the densified rice husk to break was determined using the ASTM D440-86 (ASTM, 2002) method, which determines the percentage weight loss after 10 repeated drops from a 1.83 meter height onto a concrete surface (Lindsay and Vossoughi, 1989; ASTM, 2006; Techniti et al., 2012). A completely randomized experimental design using the JMP statistical software (SAS Institute Inc.) was utilized to determine the optimum moisture for densification of the rice husk. Factors included binder type (Gum arabic (GA), groundnut shell (GS), paraffin wax (WAX), whole *Afzelia africana* aril (AAW) and deoiled *Afzelia africana* aril (AAP)); die pressure (42.5 MPa, 56.7 MPa, and 70.8 MPa) with holding time of 30s; binder content (2.5%, 5.0%, and 7.5 %); and moisture content (10%, 15%, and 20%). The response was measured as weight loss after ten drops of the densified briquettes on a concrete floor. Response surface methodology was used to determine the optimum moisture content as the one with the minimum weight loss after the drop tests. The impact tests were carried out 24 hours after the briquettes were made.

4.5.3 Physical characterization of rice husk

4.5.3.1 Particle size analysis

Particle size distribution of the rice husk sample was determined using ASABE Standard S319 (ASABE standards, 2006b). For each test, 100g of the sample was placed and shaken for 10 minutes on a stack of sieves arranged on a mechanical shaker with the sieve with the largest openings on top and the one with smallest openings at the bottom. Standard sieves #6, 10, 20, 35, 60, 100, 140, and 200; with sieve opening sizes of 3.360, 2.0, 0.850, 0.500, 0.250, 0.150, 0.106, and 0.075 mm respectively, were used for this experiment. Three replicates of this experiment were carried out and the geometric mean diameter was determined.

4.5.3.2 Bulk density

Materials bulk density of the rice husk was determined according to ASABE Standard S269.4 (ASABE standards, 2007) for cubes, pellets, and crumbles. This was done by carefully filling a standard 500 ml cylindrical container with the sample incrementally. After filling 1/3rd part of the container with the sample, it was tapped on a wooden table ten times to allow the material to settle down, before continuing the rest of the filling. Once the container was full, the excess material was removed by moving a steel blade in a zigzag pattern across the top (Mani et al., 2006). The bulk density of the sample was calculated as mass per unit volume.

4.5.3.3 Microstructural analysis

Microstructural surface analysis of the multistage mill rice husk sample was carried out using the Hitachi TM3000 tabletop scanning electron microscope (SEM). The samples were placed on a carbon pad and placed in the SEM. Both the outer surface and the inner surfaces of the rice husk samples were investigated to study the structural characteristics of the rice husk and to determine if there were entrained kernel sub-particles, such as broken rice and bran within the rice husk.

4.5.4 Proximate analysis of rice husk and binders

The proximate analysis of materials provides information on the percentage of the thermochemical component that the rice husk is made up, which includes: moisture, volatiles, fixed carbon, and ash contents. These are all important thermochemical characteristics of biomass as a fuel. Proximate analysis of the rice husk and binders was conducted using American Standards of Testing Materials (ASTM: 3173; 3174; and 3175) for gaseous fuels, coal and coke. Muffled furnace (SYBRON-Thermolyne), desiccators, crucibles, and a high accuracy digital scale were used for these analyses. Three replicates were carried out for each experimental combination.

4.5.4.1 Moisture content

The moisture content was determined using the American Society of Agricultural and Biological Engineers (ASABE) standard S358.2 (ASABE, 2006a), as the best choice since biomass materials such as the rice husk and the chosen binders are highly volatile. This method is similar to the sparkling fuel procedure, ASTM 3173-03 (ASTM 2003). Triplicate samples of the rice husk samples were oven dried at 103±2°C for 24 hours during which the samples were weighed until a constant weight was obtained.

4.5.4.2 Ash content

Ash content was determined based on the ASTM 3174-04 standard (ASTM, 2004). Three replicates of 1.0 g samples were placed in crucibles at a temperature of 750±10°C for 1 hour. The crucibles were then removed and placed in desiccators to cool, and then weighed to determine the ash content (Panwar et al., 2011).

4.5.4.3 Volatile matter

The ASTM D-3175-02 (ASTM, 2002) procedure was used to determine the volatile matter content. Three replicates weighing 1.0 g of the samples, contained in covered crucibles, were placed in a muffled furnace maintained at a temperature of 950±10°C for 6 minutes. Then the crucibles were removed and placed in desiccators, and were then weighed after cooling. The amount of volatile matter in the sample was determined as the weight loss on a dry matter basis (ASTM, 2006; Panwar et al., 2011).

4.5.4.4 Fixed carbon

The percentage fixed carbon of the samples was calculated as the weight of the solids left in the crucible following the determination of the volatile components (ASTM D-3175-02) minus the ash content obtained from the ASTM 3174-04 experiments (Panwar et al., 2011).

4.5.5 Chemical composition analysis

Chemical proximate composition analyses were carried out to determine the protein, fat, and other organic components of rice husk sample and of the five selected binders.

4.5.5.1 Protein analysis

The protein content of the rice husk and binders was determined using the Leco TruSpec N analyzer, an instrument that determines nitrogen content of a variety of materials including food, feed, oilseeds, fertilizers, meat and oils. Replicate samples weighing 0.120g were placed in aluminum foil cups and weighed on a Sartorius CP1245, 4 decimal digits weighing scale that was networked to the Leco machine. Leco TruSpec is a three stage thermochemical analyzer. The first stage was the purging stage, where the encapsulated capsule was loaded and purged. The second stage involved the combustion of the sample at 950°C in an oxygen furnace and then in an afterburner at 850°C. The combustion gases were filtered, cooled in a thermo-electric cooler, dehydrated, and then stored in a ballast. The final stage began with the injection of oxygen into the ballast and mixing the combustion gases. The homogeneous gases were then purged into a 3cc aliquot loop and then transferred to a helium carrier that was swept through a hot copper electrode to remove oxygen and change NO_x to N_2, and then through “Lecosorb” (a patented chemical of Leco Inc. that absorbs CO_2) and “Anhydrone” (Magnesium perchlorate) to remove CO_2 and H_2 respectively. A thermal conductivity cell was then used to determine the nitrogen content. The nitrogen contents of the samples were multiplied by 6.25 to obtain the protein content.

4.5.5.2 Fat analysis

Fat content of the samples were determined using AOAC standard 945.16 (AOAC, 1990). AFIA (2007) reported that this method has a significantly lower coefficient of variation than any other non-hydrolysis methods. Three replicates of the samples weighing 3 to 5 g were placed in a thimble in a Soxhlet extractor, and petroleum ether was used as the solvent for the extraction. The fat content was determined as the mass ratio of the extracted fat and the original sample on a dry basis.

4.5.5.3 Chemical component analysis using FT-IR

Fourier transform infra-red spectrometer with attenuated transmission response (FTIR-ATR) was used to study the range of chemical functional groups that affect adhesion in both the rice husk and binders. A Thermo Scientific Nicolet iS5 FT-IR equipped with iD5 ATR diamond crystal accessory was used for the analysis. Three replicates of the samples were scanned at IR range of interest between 4000 cm^{-1} to 500 cm^{-1} for 15 seconds with a spectrum reported as an average of 64 scans.

4.5.6 Medium pressure experimental methods

Cylindrical briquettes were made from a piston and die setup (with die dimensions of Length= 50.6mm and diameter=19.0mm) using a Harco manual hydraulic press (Figure 4.3) at die pressures of 42.5, 56.7, and 70.8 MPa; binder concentrations of 2.5, 5.0, 7.5%; at optimum moisture content (determined to be 15% as presented in section 4.6.1). Rice husk weighing 2.00 g was placed into the cylinder and was densified using the press. During densification, a holding time of 30 seconds at the applied pressure was maintained, in order to prevent the spring-back effect of the rice husk particles (Adapa et al., 2006; Mani et al., 2006). A full factorial experimental design with three replicates was used.

Figure 4.3. Harco manual hydraulic press equipped with pressure gauge

4.5.6.1 Density experiments

Density was determined using the water displacement method (Panwar et al., 2011). Briquettes covered with paraffin oil of known density were weighed and then submerged in water to determine the volume after weighing (Panwar et al., 2011). The densities were tested 24 hours after the briquettes were made.

4.5.6.2 Water absorption rate experiments

Water absorption test was carried out by placing the samples in a water bath at room temperature (around 22 °C) for 30 seconds, and then the samples were immediately placed in an aluminum pan that was tared on a weighing scale. The weight of the soaked sample was recorded; and the longitudinal and radial parameters were measured after 30 seconds, and repeated until maximum measures for both parameters were obtained. The water absorption ratio or “permeability” was calculated as:

$$\textit{Water absorption ratio} = \frac{\textit{Weight of soaked briquette}}{\textit{Original weight}} \quad (1)$$

The longitudinal expansion ratio was measured as the ratio of the expanded height of the soaked briquettes to the original height of the briquette:

$$\textit{Longitudinal Expansion Ratio} = \frac{\textit{Height of soaked briquette}}{\textit{Original height}} \quad (2)$$

The radial expansion ratio was measured as the ratio of the diameter of the soaked briquettes to the original diameter of the briquette:

$$\textit{Radial Expansion Ratio} = \frac{\textit{Diameter of soaked briquette}}{\textit{Original diameter}} \quad (3)$$

Statistical analyses including ANOVA, Tukey-Kramer, Student's t, and Response Surface Method (RSM) analysis were carried out using JMP10 statistical software.

4.6 Results and Discussion

4.6.1 Optimum moisture content for the purpose of rice husk densification

Determination of the optimum moisture content based on response surface methodology (RSM) showed a predicted minimum value of weight loss at an optimum moisture content of 15.190%, with fitted R-square value of 0.962 at $p<0.0001$ (Figure 4.4). The minimum weight loss occurred at a die pressure of 58.353 MPa and binder ratio of 5.033%. The F-Ratio effect tests showed that moisture content and binder types were the most significant factors affecting mass loss during the impact test (Figure 4.5); with the significance of the binder type at $p<0.0001$ and the significance of moisture content at $p<0.0003$ at the quadratic level. However, effect tests of die pressure and binder ratio were at $p<0.0776$ and $p<0.2126$; and $p<0.5724$ and $p<0.9033$, at the quadratic and linear levels respectively (Figure 4.4).

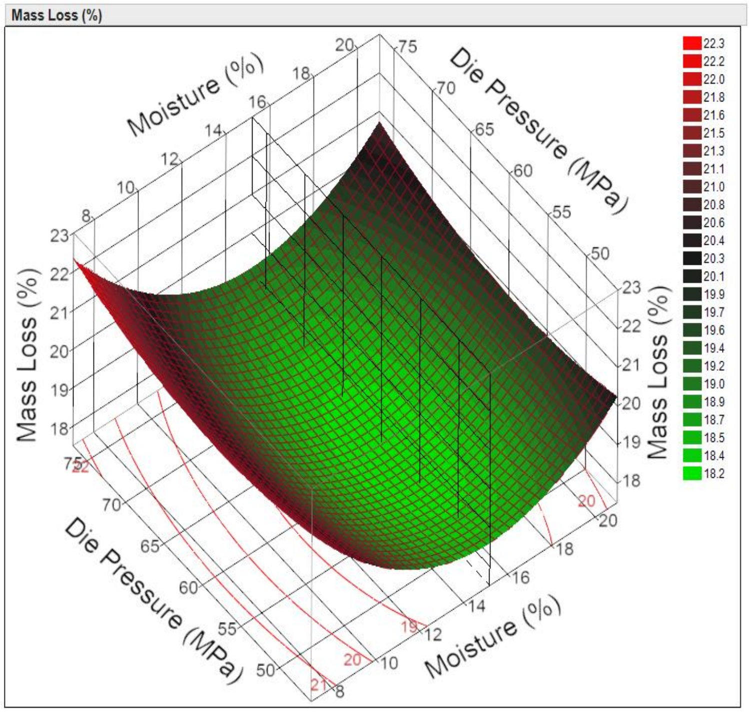


Figure 4.4. Response surface determination of optimum moisture content for a least friable rice husk pellet

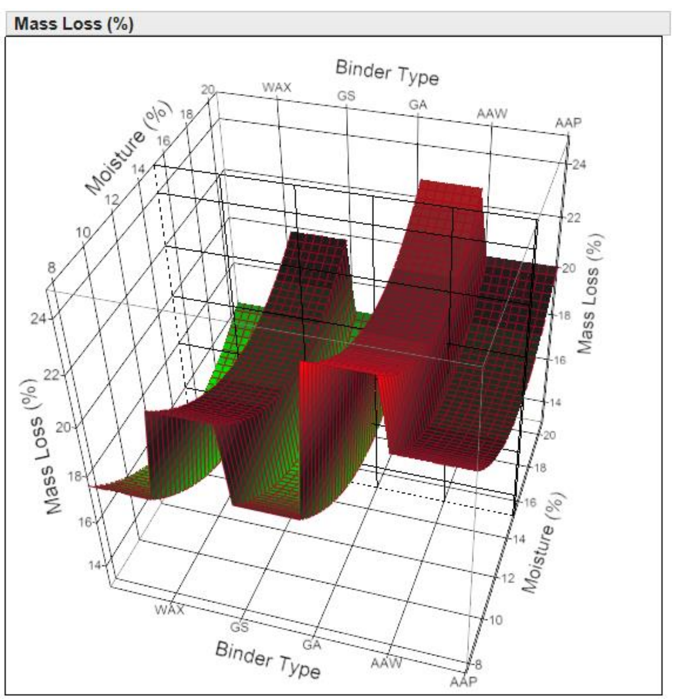


Figure 4.5. Binder type effects on optimum moisture content for a least friable rice husk pellet

The prediction profilers also showed that AAW bonded briquettes have the highest mass loss during impact while the wax bonded briquettes have the lowest mass loss (Figure 4.6).

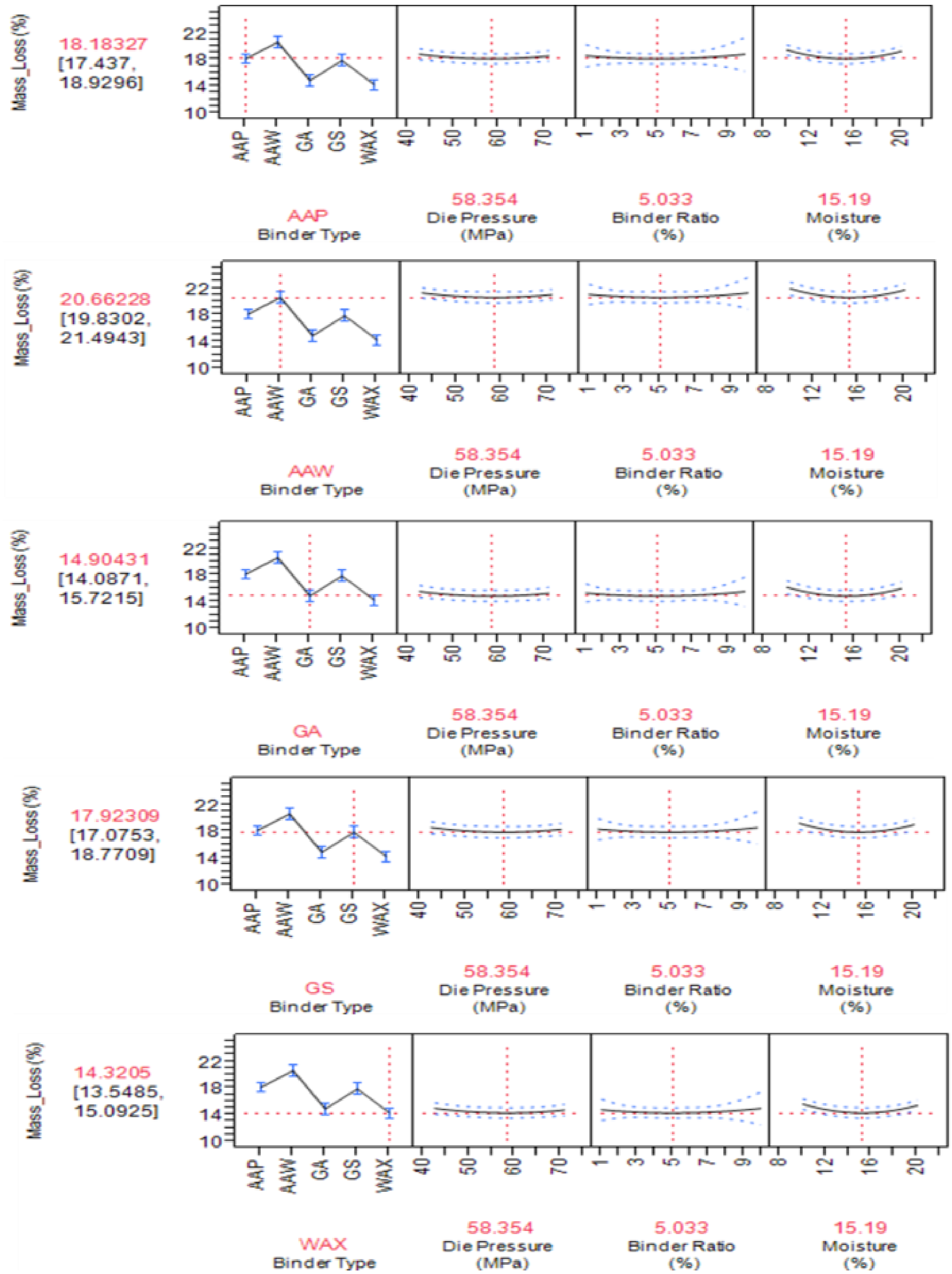


Figure 4.6. Mass loss with respect to binders used at optimum moisture content

Based on this analysis, full factorial experiments to determine the effects of binder types, binder ratio and die pressure on permeability and density of briquettes were carried out at 15% moisture content.

4.6.2 Characterization of the rice husk

Bulk density of the rice husk was 137 kg/m^3 and the particle density was 196 kg/m^3. Geometric mean diameter of the rice husk was 1669 µm. Particle analysis showed that 91.08% of the rice husk particles were retained by standard sieve 20 (850 µm) and larger (Figure 4.7). Proximate analysis results based on ASTM standards (ASTM, 2006) showed that the average moisture content of the rice husk was 7.630%, volatile content was 60.571%, fixed carbon content was 14.414% and ash content was 25.016%. Chemical compositional analysis of the rice husk showed that the protein and fat content of the rice husk were 2.280% and 0.291% respectively.

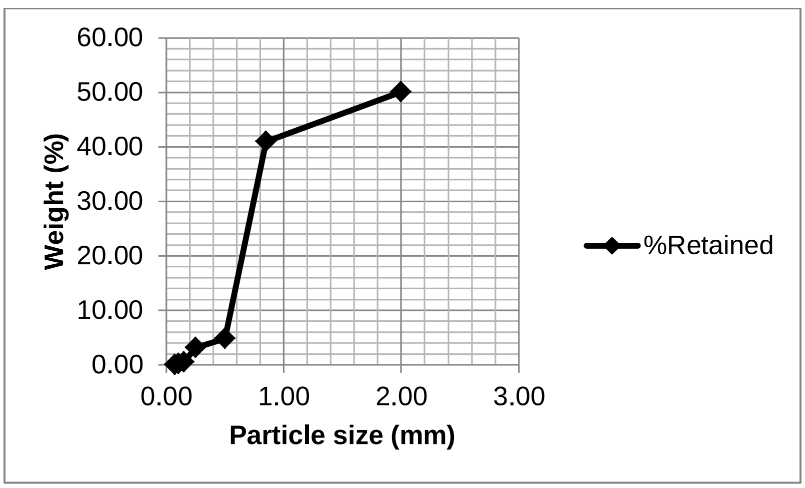


Figure 4.7. Particle size distribution of the rice husk

The FT-IR spectrum of the rice husk (Figure 4.8) has a broad, strong peak near 3300 cm^{-1}, due to CH stretching vibrations. The strong peak around 1650 cm^{-1} indicated the C=O stretching of a carbonyl group in this sub-Saharan rice husks. The strong peak at around 1025 cm^{-1} confirms the strong presence of alcohols, carboxylic acids, ethers and esters (Lambert et al., 2011). Also the secondary peak around 1100-1217 cm^{-1} indicated the presence of silica in the form of cellulose-silicates (Ndazi et al., 2007), which was confirmed from the proximate analysis ash content.

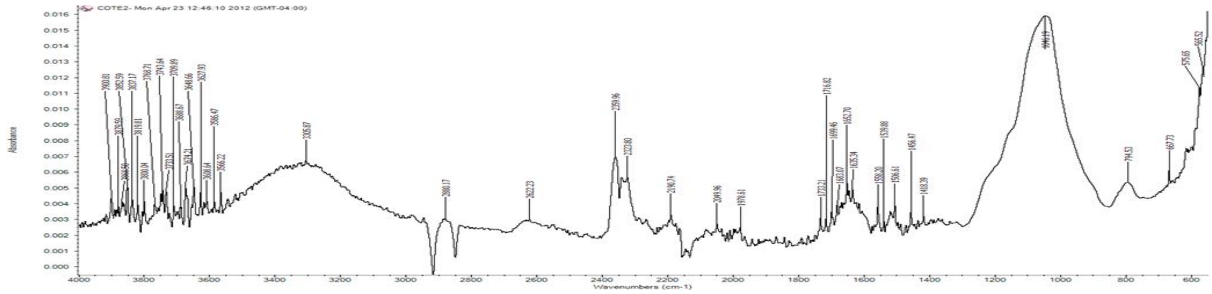


Figure 4.8. FT-IR spectrum of rice husk

4.6.3 Characterization of selected binders

4.6.3.1 Gum arabic (GA)

Gum arabic is principally a carbohydrate with approximately 44% of galactose, 13% of rhamnose, 27% of arabinose, and 16% of glucuronic and 4-O-Methyl glucuronic acid (William et al., 2006; Assaf et al., 2009). Islam (1997) reported that the proteins of gum arabic are arabinogalactan protein (AGP), and glycoprotein (GP). Proteins in gum arabic are covalently linked to carbohydrates and are believed to be mostly responsible for its emulsifying properties. Gum arabic has only trace lipid contents which are attached to AGP. The lipids increase the effectiveness of gum arabic as an emulsifier. The average protein content of the gum arabic that was used in this experiment was 1.713% and the fat content was 0.914%. Proximate analysis of the gum arabic showed that the moisture content was 3.534%, volatiles content was 83.966%, fixed carbon content was 14.094%, and ash content was 1.940%. FT-IR analysis (Figure 4.9) showed a broad peak between 3600 – 3000 cm^{-1} that was due to water and OH stretching bands of alcohols, phenols and carboxylic acids. The peaks at 1600 cm^{-1} and 1418 cm^{-1} were characteristics of amides indicating the presence of glycoprotein (Vigano et al., 2003).

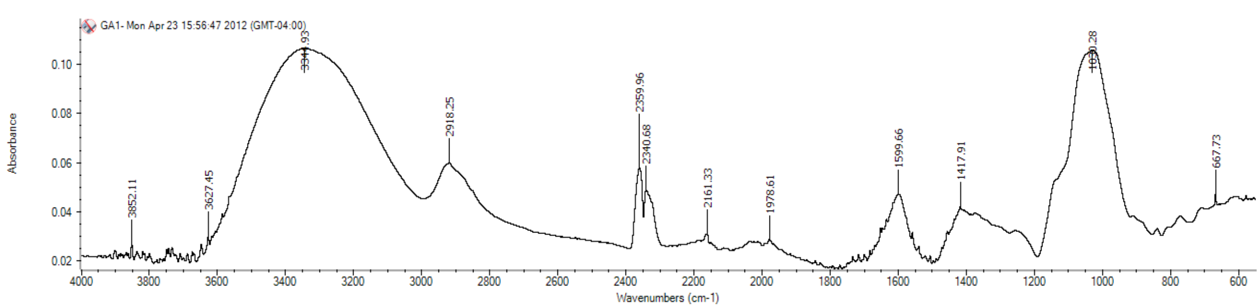


Figure 4.9. FT-IR spectrum of gum arabic

4.6.3.2 Groundnut shell (GS)

The chemical composition of groundnut shell includes carbohydrates, protein and traces of lipids. Groundnuts shell has high content of cellulose, hemicellulose and lignin. The FT-IR spectra of the groundnut shell used as a binder in this experiment showed a broad peak between 3600 – 3000 cm^{-1} that is due to the water and OH stretching bands of alcohols, phenols and carboxylic acids (Figure 4.10). The peak at 2922 cm^{-1} confirms the presence of aromatic and unsaturated aliphatic =CH groups; and the peaks at 1263 cm^{-1}, 1372 cm^{-1}, and 1507 cm^{-1} are characteristics of guaiacyl lignin, syringyl lignin and aromatic skeletal vibrations respectively (Chen, 2005; Wei et al., 2009; Kang et al., 2012). Protein content of the groundnut shell used in this experiment was 5.126% which confirms the broad band observed at 2200 cm^{-1} for the presence of amides. Fat content was 1.251%. Proximate analysis results based on ASTM standards (ASTM, 2006) showed that the moisture, volatile, fixed carbon and ash contents were 3.266%, 79.598%, 18.400% and 2.002%, respectively.

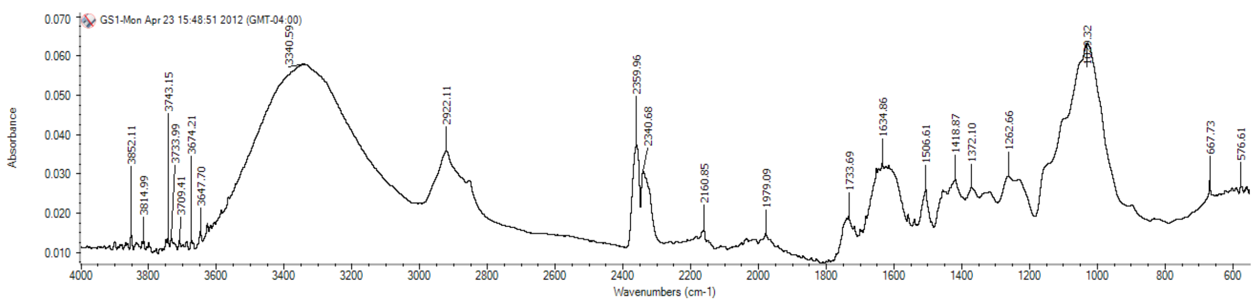


Figure 4.10. FT-IR spectrum of groundnut shell

4.6.3.3 Paraffin wax (wax)

Paraffin wax is made up of methylene groups with peaks around 2919 cm^{-1}, and 2851 cm^{-1} as signatures showing the antisymmetric and symmetric stretching vibrations of CH in methylene. The small absorption band at 2956 cm^{-1} was the symmetric stretching of the CH_3 of silicone (Figure 4.11). The small peaks at 1462 cm^{-1} and 719 cm^{-1} were the weak absorptions of the CH_2 bending mode in Paraffin (Gonzalez-Gaitano and Ferrer, 2013).

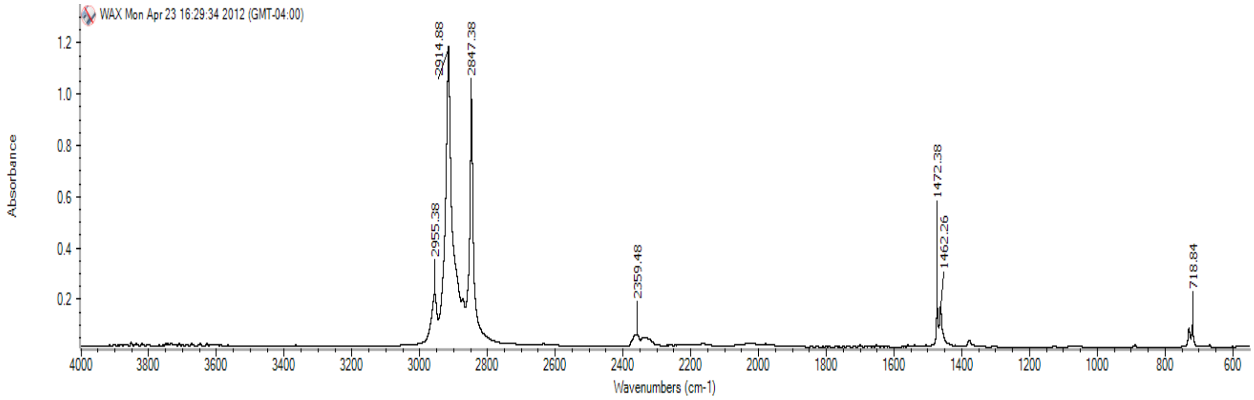


Figure 4.11. FT-IR spectrum of Paraffin wax

4.6.3.4 *Afzelia africana* aril whole (AAW)

Afzelia africana aril contains a high amount of fat. The fat analysis results showed that the oil content of the aril was 49.13±1.36%. Protein content was found to be 3.49%. FT-IR spectrum (Figure 4.12) showed a low broad peak at the region between 3600 cm^{-1} and 3000 cm^{-1} indicating the content of carbohydrates and OH vibration. The most significant peaks were at 2920 cm^{-1} and 2851 cm^{-1} which were signatures of asymmetric and symmetric stretching vibrations of CH in methylene. The peaks at 1462 cm^{-1} and 1464 cm^{-1} were due to CH_2 bending. The broad peak between 1462 cm^{-1} and 400 cm^{-1} that have sharp peaks at 1160 cm^{-1}, 1098 cm^{-1} and 718 cm^{-1} peaks indicated the strong presence of alcohols, carboxylic acids, ethers and esters. The latter having bands from both C=O and C-O-C groups, but none from the OH group. Proximate analysis results showed that the moisture, volatile, fixed carbon and ash contents were 2.768%, 91.069%, 5.373% and 3.558% respectively. Gussoni et al., (1994) carried out NMR analysis of *Afzelia cuanzensis* aril and found similar chemical components. Proximate analysis results based on ASTM (ASTM, 2006) standards showed that the moisture, volatile, fixed carbon, and ash contents were 2.768%, 91.069%, 5.373% and 3.558%, respectively.

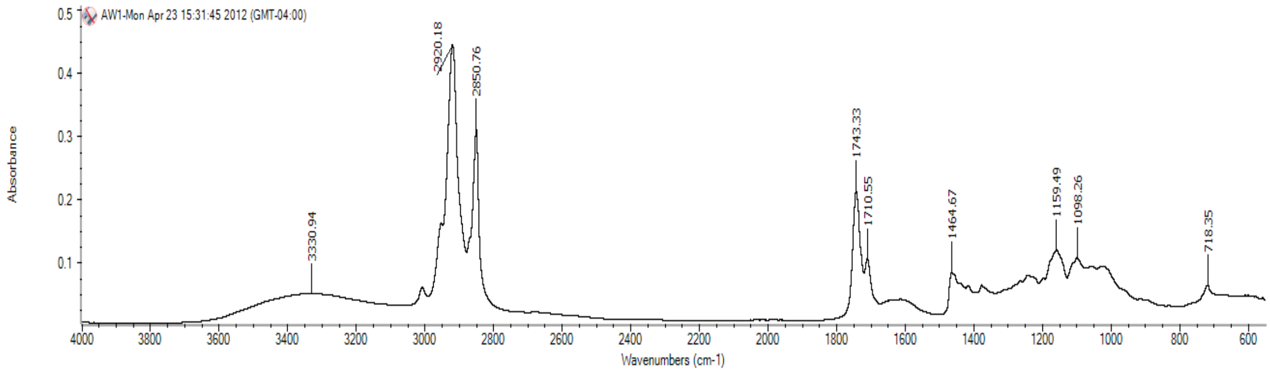


Figure 4.12. FT-IR spectrum of *Afzelia africana* whole

4.6.3.5 *Afzelia africana* aril deoiled (AAP)

The de-oiled aril of *Afzelia africana* contains no fat and has a protein content of 7.42%. It has the highest protein content of the 5 binders used. Proximate analysis results based on ASTM standards (ASTM, 2006) showed that it has a moisture content of 6.765%, volatile content of 81.027%, fixed carbon content of 12.157%, and ash content of 6.816%. The FT-IR spectra (Figure 4.13) of de-oiled *Afzelia africana* showed that it has a significant amount of carbohydrates as well as amide I and II.

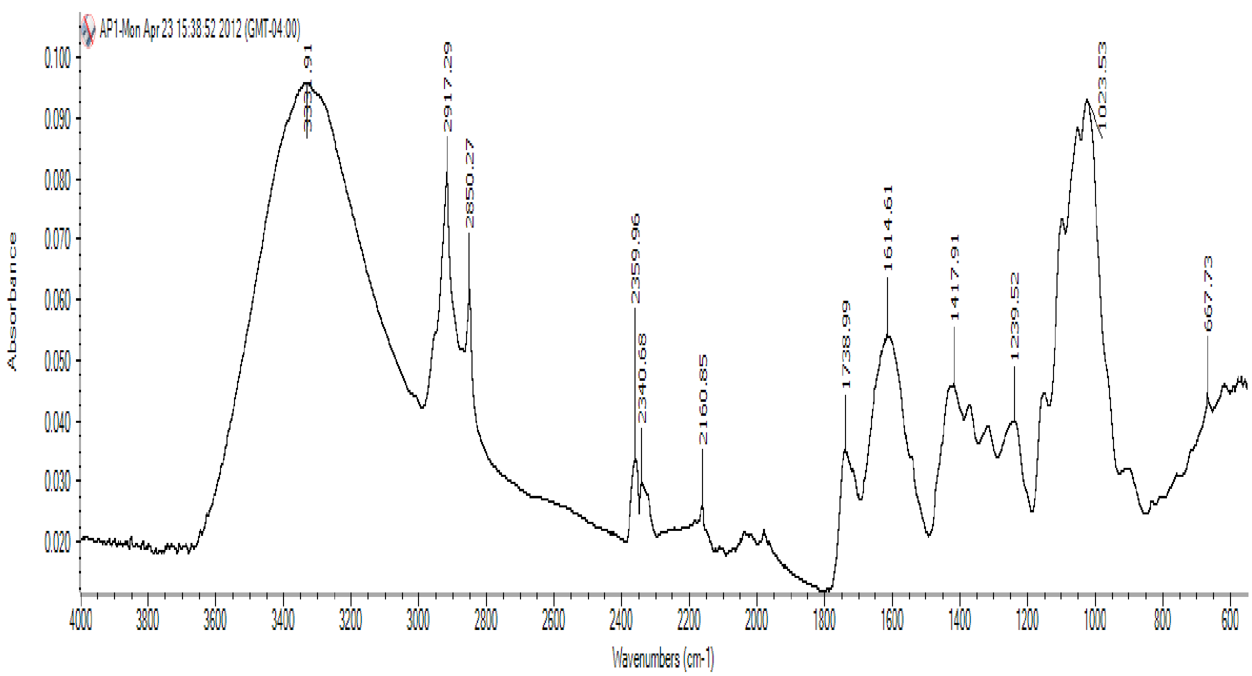


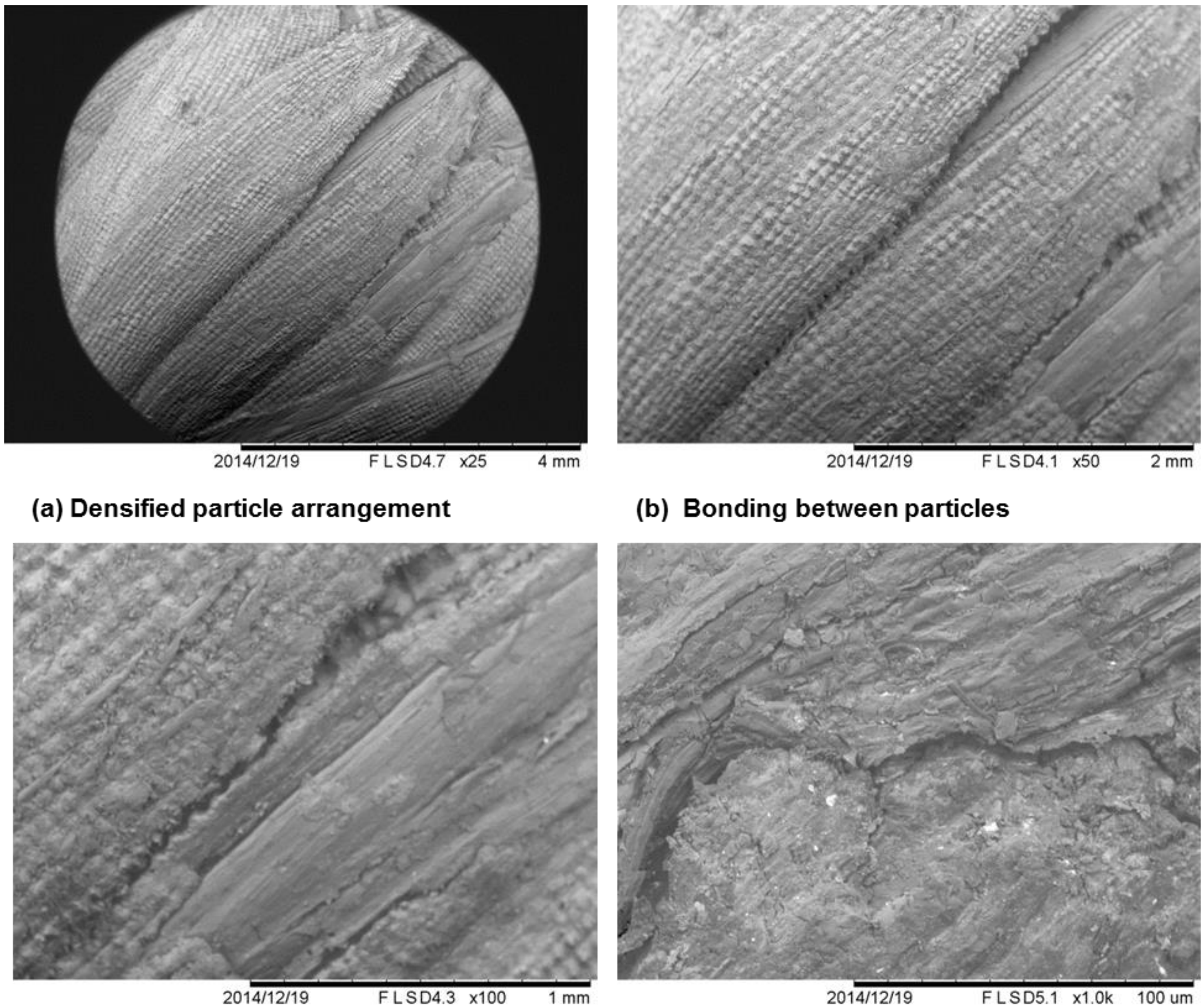
Figure 4.13. FT-IR spectrum of *Afzelia africana* de-oiled

4.6.4 Effects of medium pressures, binder types and binder concentrations on water absorption

Densified briquettes were produced at all die pressures and binder concentrations at the optimized moisture content of 15%. The pellets produced were stable, and were easily handled without significant disintegration (Figure 4.14).

Figure 4.14. Densified rice husk briquettes

SEM of the radial surface of the cylindrical briquettes showed the effect of the densification on the rice husk (Figure 4.15). During the densification process it was obvious that the rice husk particles arranged themselves in the traverse direction with the binding forces including solid bridging keeping the adjacent rice husk tightly bound, forming a solid briquette. The solid binder components can dissolve in the water (moisture content), forming liquid binders that can wet and spread within the interstices between primary particles, forming liquid bridges that hold the rice particles together by capillary and viscous forces, which recrystallize to form solid bridges upon drying of the densified rice husk. The solid bridges hold the particles together and impart mechanical strength to the densified rice husk briquettes (Bika et al., 2005; Kaliyan and Morey, 2010).



(a) Densified particle arrangement **(b) Bonding between particles**

(c) Bonding between outer inner component **(d) Crushing effect at higher die pressure**

Figure 4.15. SEM of densified rice husk briquettes

During the water absorption experiments, it was observed that the briquettes mostly expanded longitudinally (Figure 4.16). Both the density and gain in mass varied with the binder concentration, binder type, and die pressure. The longitudinal expansion could be due to the fact that during the densification process the rice husk particles collapsed in the traverse direction, before bonding at high die pressure due to the formation of solid bridges and other binding forces. In the reverse, during the water absorption tests, these bridges were soaked and weakened allowing the particles to attain their original forms. But at very high die pressures the particles were crushed together minimizing longitudinal expansion during subsequent soaking.

Figure 4.16. Briquettes expanded mostly longitudinally after insertion into water

The experimental results obtained showed that the binder type, binder concentration and die pressure governed the water absorption of the briquettes. The full-factorial randomized experimental results showed that binder concentration, binder type and die pressure have significant effects on the water absorption/permeability ratio of the rice husk briquettes. Response surface method analysis carried out showed fitted results having a R-square value of 0.926 at $p<0.0001$; and within the levels considered for all binders, it was found that higher binder ratios and higher die pressures minimized the water absorption/permeability ratio of the briquettes (Figure 4.17).

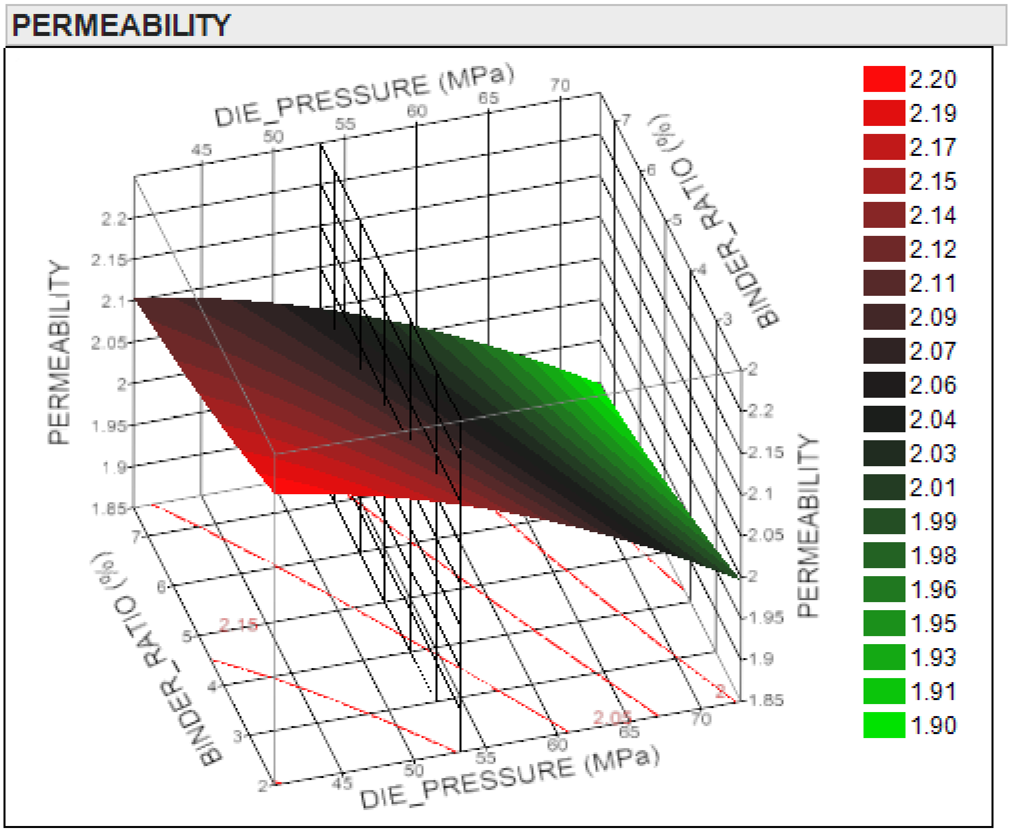


Figure 4.17. Binder concentration ratio and die pressure effects on permeability

The F-Ratio effect test for permeability showed that binder type (with $p<0.0001$) and die pressure (with $p<0.0001$ at linear and $p<0.0258$ at quadratic level) were the most significant factors. The binder concentration ratio was also found to be significant at linear level with $p<0.0001$, but not significant at the quadratic level with $p<0.05505$.

Longitudinal and radial experimental results showed that all the factors have significant effects on permeability of the densified rice husk. However, the analysis of the results showed that die pressure revealed important information on the briquettes' water absorption characteristics. The analysis of the results yielded fitted models of the radial and longitudinal expansion ratios, with R-square values of 0.93 and 0.86 respectively, at $p<0.0001$. The results showed that for all the binders, at lower pressures, up to the saddle point solution at die pressures of 53.267 MPa the longitudinal expansion increased with die pressure (Figure 4.18). The F-Ratio effect test for longitudinal expansion ratio showed that binder type (with $p<0.0001$) and die pressure (with $p<0.0001$ at linear and $p<0.0258$ at quadratic level) were the most significant factors. Binder ratio was also found to be significant at linear level with $p<0.0396$, but not significant at the quadratic level with $p<0.2696$.

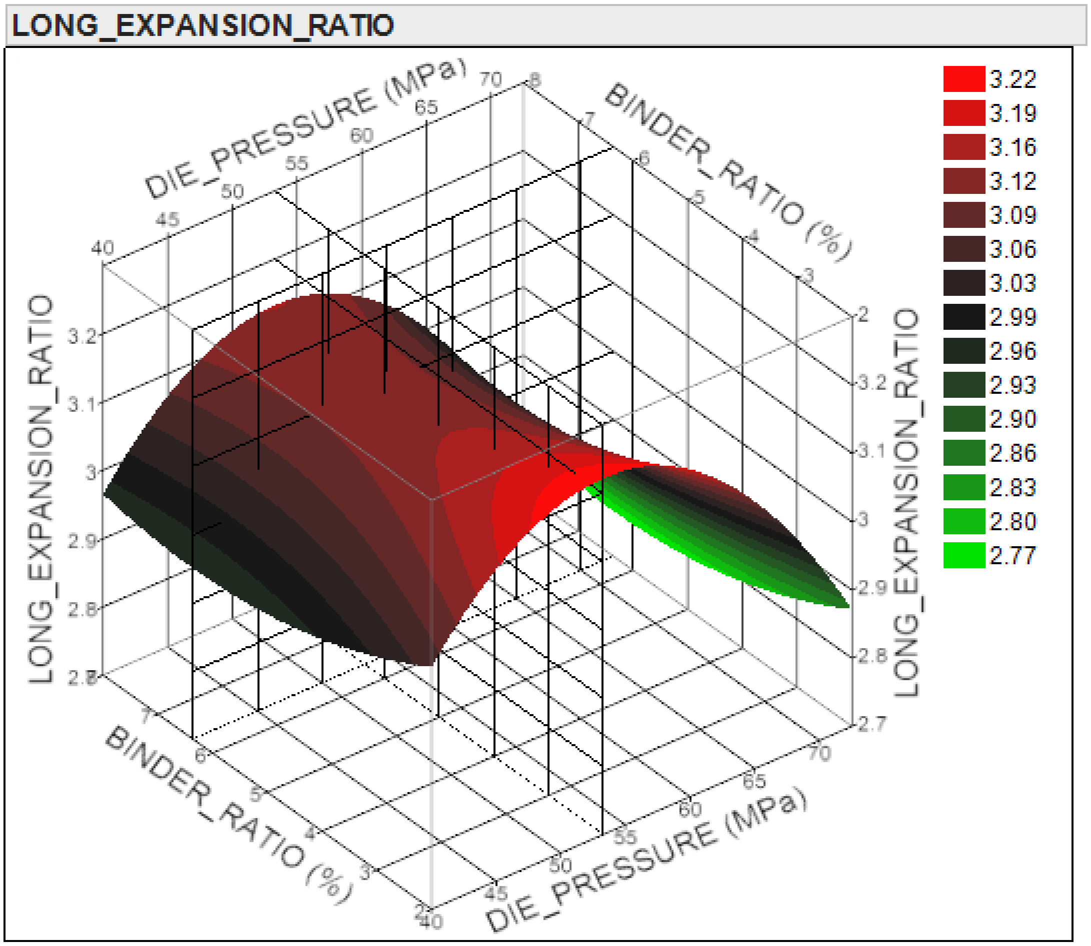


Figure 4.18. Longitudinal expansion ratio of briquettes

However, the radial expansion ratio continuously decreased with the increase of die pressure from the maximum experienced at the lowest pressure (Figure 4.19). The F-Ratio effect test for radial expansion showed that binder type (with $p<0.0001$) and die pressure (with $p<0.0001$ at linear and $p<0.0295$ at quadratic level) were the most significant factors. Binder ratio was also found to be significant at linear level with $p<0.0001$, but not significant at the quadratic level with $p<0.3792$.

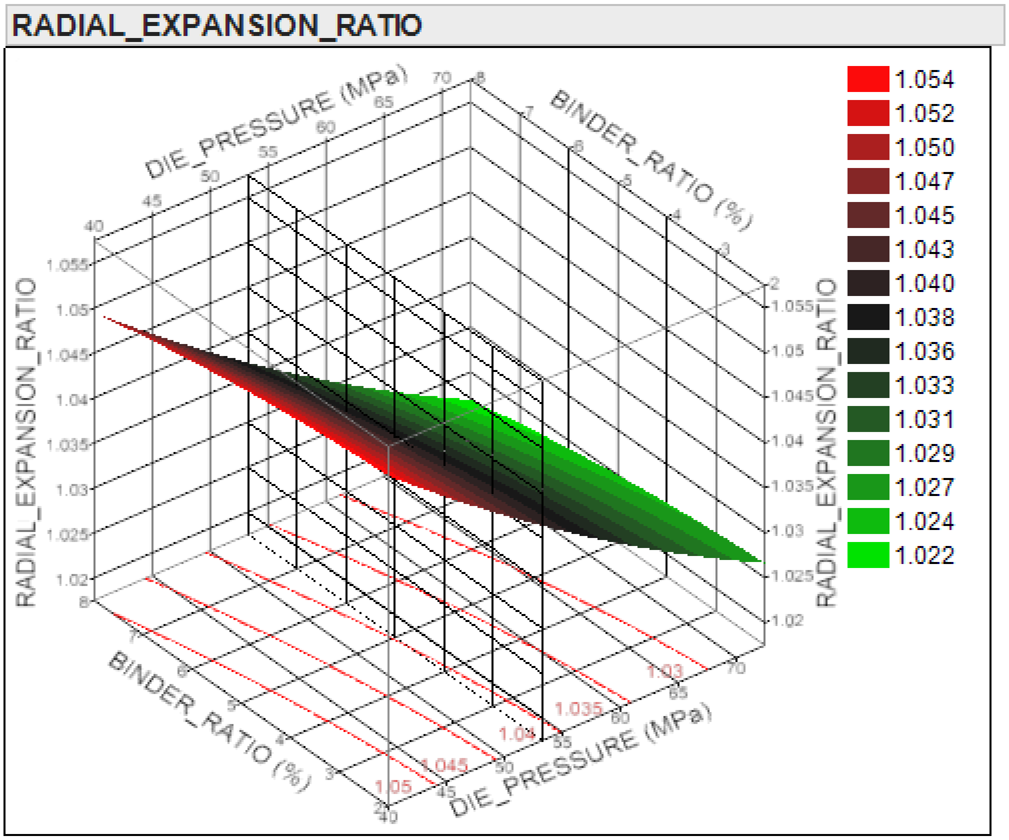


Figure 4.19. Radial expansion ratio of briquettes

At die pressures at the saddle point and beyond, increase in die pressure resulted into a significant decrease on both the longitudinal and radial expansions which translated to a resistance to water absorption. These relationships could also define the effective densification pressures at medium die pressures. From this analysis it is possible to conclude that the rice husk can be effectively densified for optimum water-resistance beyond the critical value of 53.267 MPa, with a binder concentration of 6.354%. Figure 4.20 shows the relationships of the expansion ratios to the permeability at the optimum factor levels.

Comparative analysis of the effect of binder types showed significant variability of permeability based on the binder types (Figure 4.20). The results also showed two distinct classes of binders: the ones with higher permeability (AAP and GS) and the ones with lower permeability (AAW, GA, and Wax). From the chemical analysis and FT-IR, it was found that AAW and Wax have a high esters' content; while gum Arabic, with its high carbohydrates covalently linked with protein in the form of a biopolymer that forms arabinogalactan, might have improved its effectiveness as a binder, thus minimizing water absorption. On the other hand, AAP is lipid free and the content of lipids is also small in GS, and both these binders showed higher water absorbance.

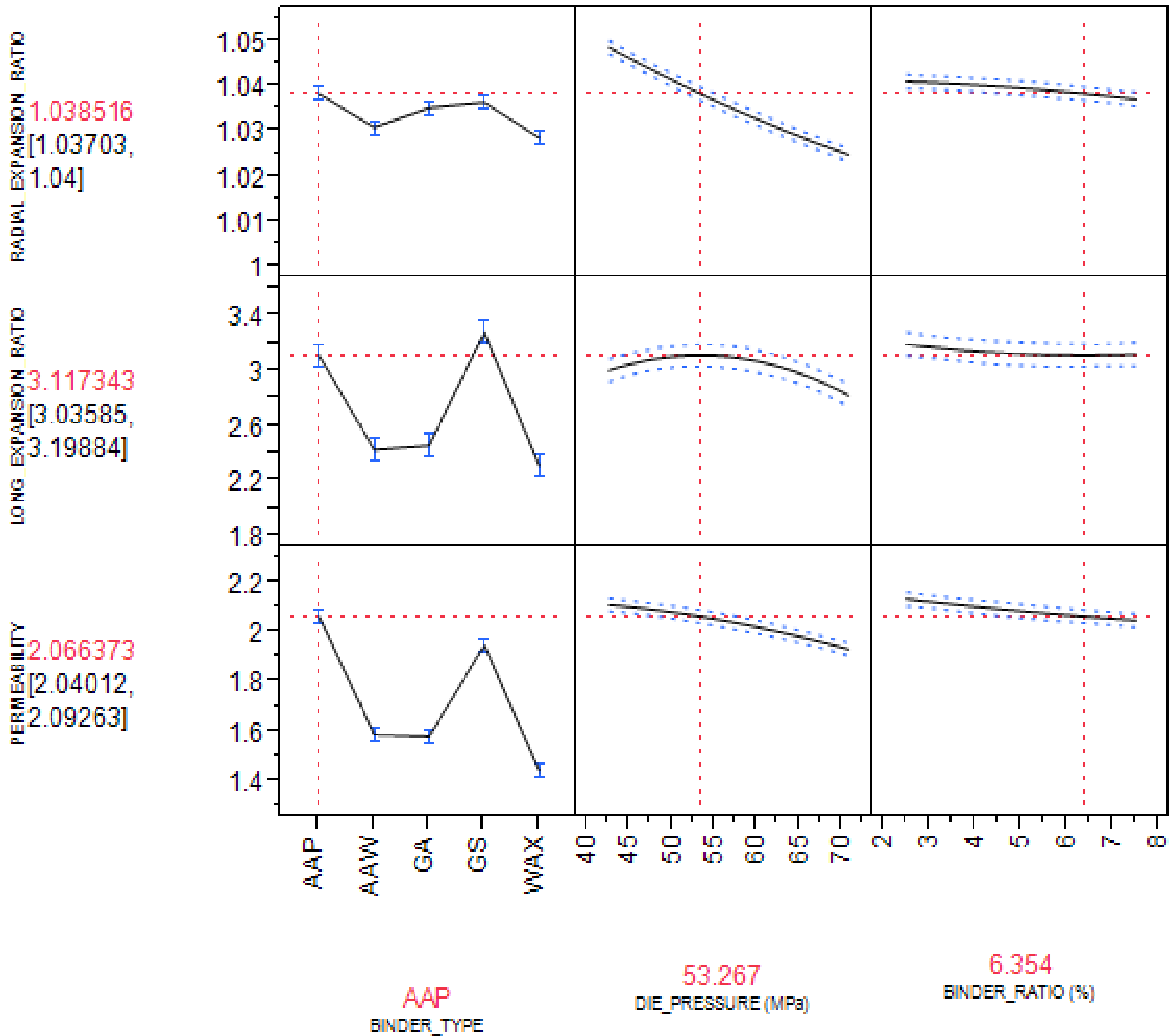


Figure 4.20. Effects of binder type on permeability, radial and longitudinal expansion ratios of briquettes

4.6.5 Effects of medium pressures, binder types and binder ratios on density

The experimental results obtained showed that all the tested process parameters have significant effects on the density of briquettes. The response surface analysis carried out showed a fitted R-square value of 0.889 at p<0.001, illustrating that within the range of the factors considered, all binder types, higher binder ratios and higher die pressure all increased the density of the briquettes (Figure 4.21).

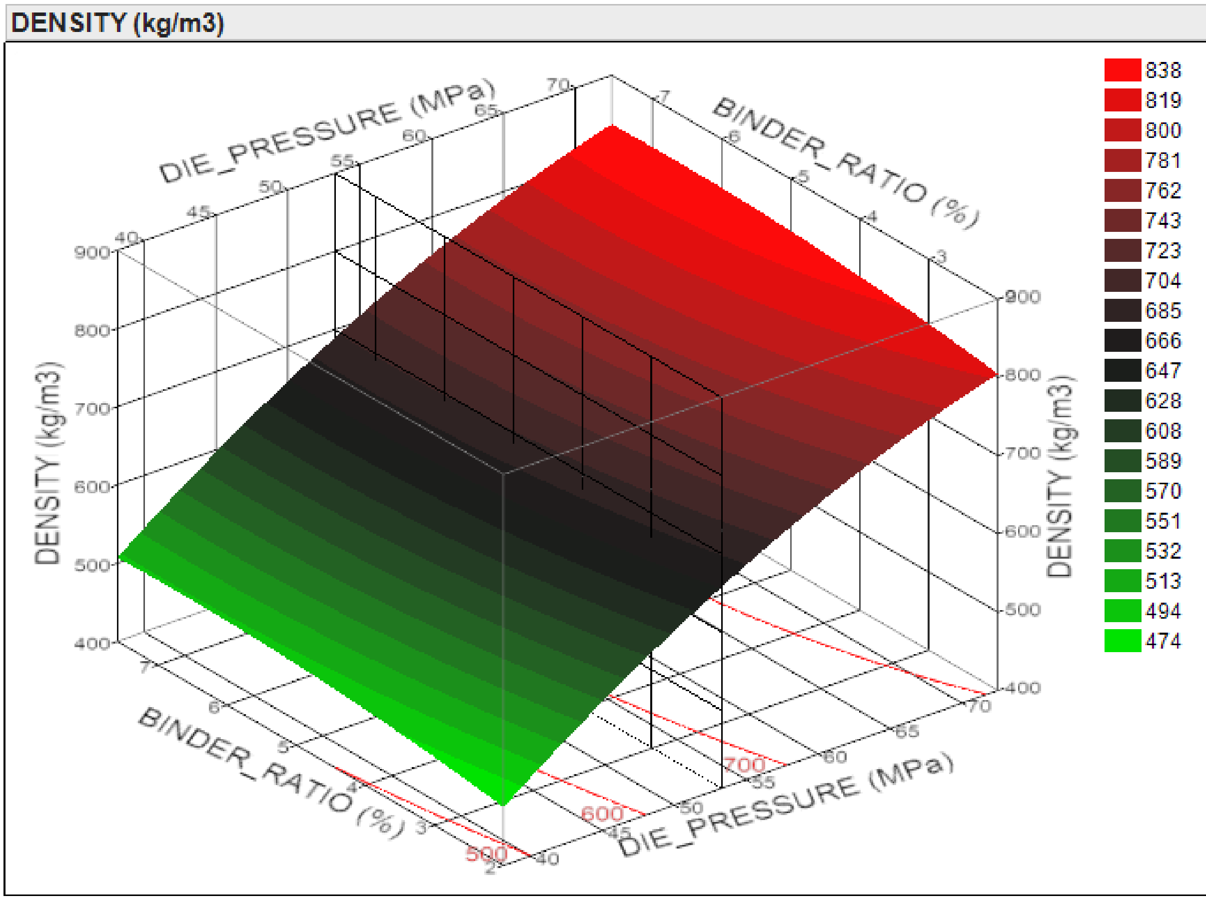


Figure 4.21. Effects of process parameters on density

The F-Ratio effect test showed that binder type (with $p<0.0001$) and die pressure (with $p<0.0001$ at linear and $p<0.0011$ at quadratic level) were the most significant factors. Binder ratio was also found to be significant at linear level with $p<0.0036$, but not significant at the quadratic level with $p<0.2298$.

Comparative analysis of the effect of binder type in Figure 4.22, showed the variability of density based on binder types. Deoiled *Afzelia africana* aril (AAP) bonded briquettes have the highest predicted densities based on the analysis, followed by paraffin wax (WAX), gum arabic (GA), and groundnut shell bonded briquettes. Whole *Afzelia africana* aril (AAW) had the lowest density. One of the interesting things about this result is the comparative analysis of AAP and AAW since the only difference in chemical composition is the lipid content. The result showed that in the case of *Afzelia africana* aril, the fat or lipid content reduced the density of the briquettes. However, in the case of WAX bonded briquettes they showed higher density, although lower than AAP bonded briquettes. FT-IR and chemical analysis showed that WAX is largely composed of methylene groups, while AAW was composed of methylene groups, as well as, carbohydrates and proteins. This indicates that interaction between the lipids, proteins, and carbohydrates within a binder could affect its binding characteristics, especially for the density of the briquettes (Figure 4.22).

Kaliyan and Morey (2009) carried out microstructural studies of densification of grinds of corn stover and switch grass; and confirmed that natural binders such as water soluble carbohydrates, lignin, protein, starch, and lipids produced highly dense, strong, and durable briquettes and pellets. However, lipids at higher concentration can reduce the quality of briquettes by inhibiting the binding properties of water-soluble starch and protein; because of their hydrophobic nature (Briggs et al., 1999; Kaliyan and Morey, 2009).

Lipids have been reported to act as lubricants between the biomass particles, reducing the effects of die pressure during densification (Kaliyan and Morey, 2009). However, the hydrophobic nature of lipids as a binder makes the densified briquettes more hydrophobic at the expense of density and durability (Briggs, 1999; Kaliyan and Morey 2009). The only interesting exception observed in this investigation was the effect of paraffin wax used as a binder, on the density and permeability of rice husk briquettes. Although paraffin wax is composed of methylene group, it not only contributed in making the briquettes hydrophobic, but also resulted in higher density briquettes. This observation could be explained by the thermal properties of paraffin which is solid at room temperature and starts melting at 37 degrees Celsius. During densification, energy is generated as heat, which starts melting the paraffin wax, as the pressure is further applied the melted wax forms liquid bridges, which solidify quickly at room temperature to form solid bridges, resulting into high density and hydrophobic briquettes. This is similar to the findings of Thomas et al. (1998), and Kaliyan and Morey (2009), who reported that natural fat and wax in the cell wall of biomass, may come out of the cell wall and act as a binding component between particles and make solid bridges, which may positively influence pellet density and durability.

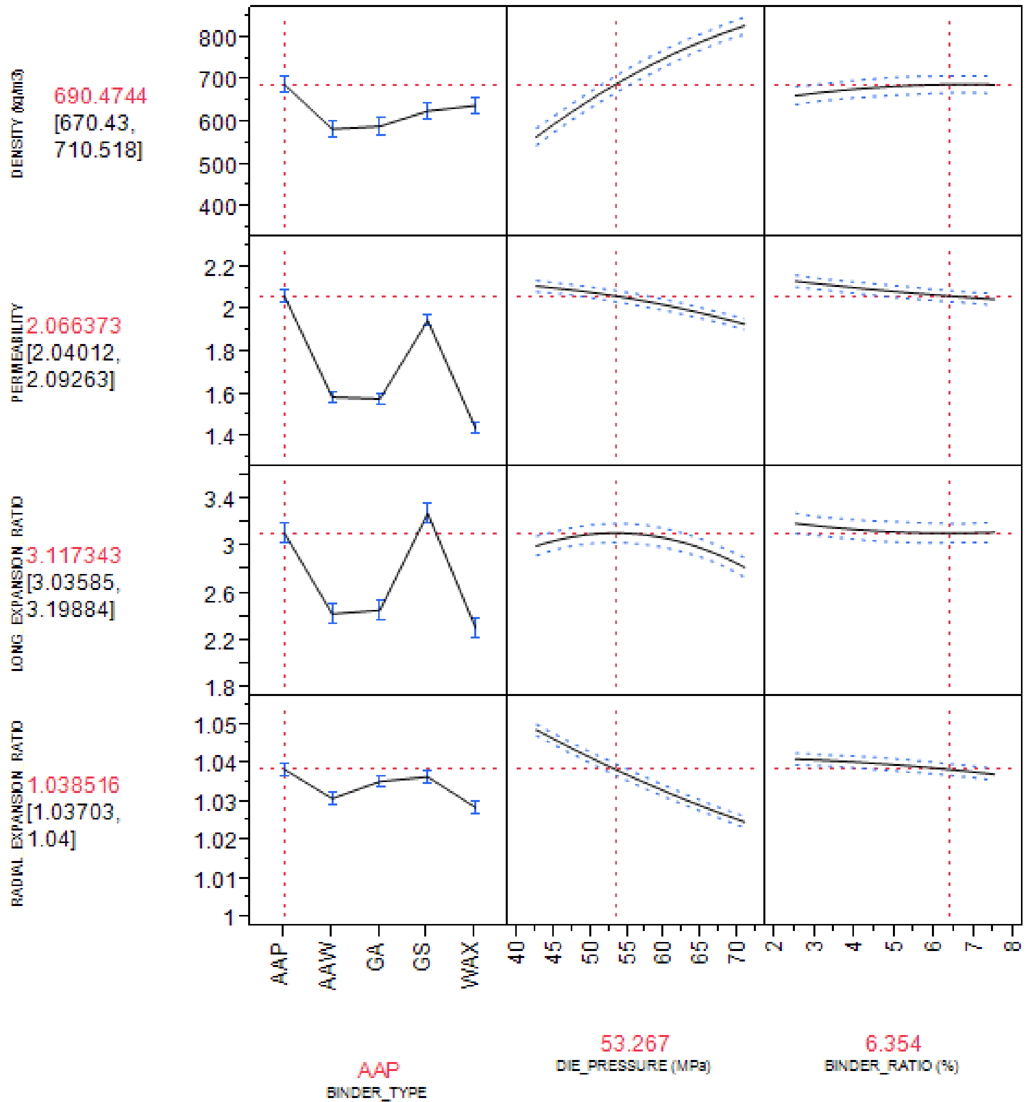


Figure 4.22. Comparative analysis of the effects of process parameters on density and permeability

4.6.6 Effects of lipids on expansion ratio, water absorption and density

One way ANOVA, Student's t test, Tukey-Kramer, and Best Hsu's MCB analyses at $\alpha=0.05$, were used to compare briquettes bonded with AAW and APP. The results showed that high lipid content of binders improved the hydrophobic characteristics of briquettes, but reduced the density of the briquettes (Figures 4.23- 4.26). This important test showed the significance of the lipid content in binders, since the only difference between AAW and the de-oiled AAP was the lipid content.

Figure 4.23 shows the effects of lipid content on the longitudinal expansion ratio. One way ANOVA (α=0.05), showed that there was a significant difference ($p<0.0001$) between the high lipid AAW and the de-oiled AAP's longitudinal expansion ratios. Student's t, Tukey-Kramer, and Hsu's MCB tests confirmed that significance.

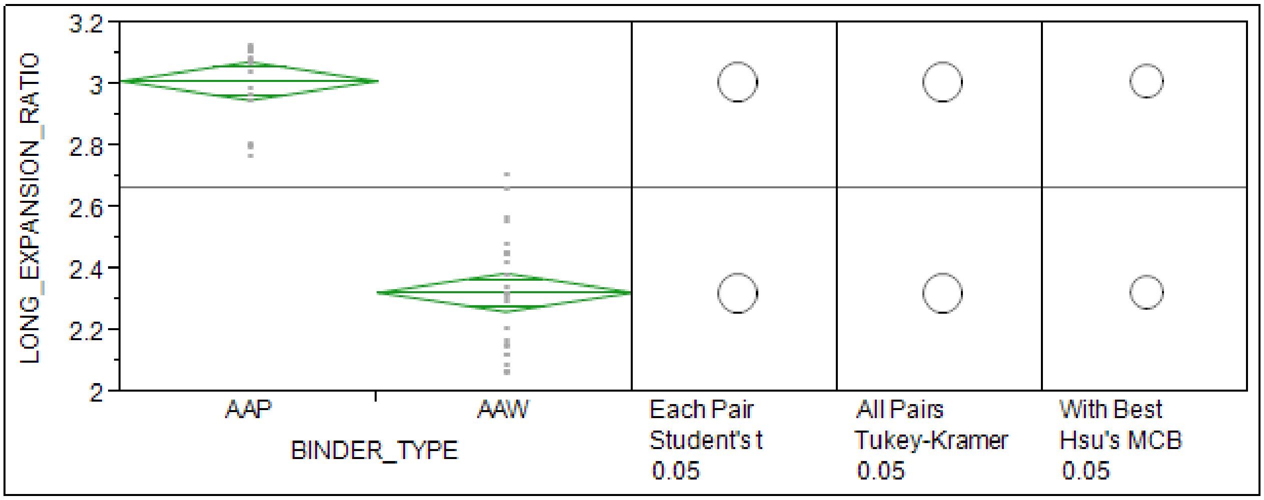


Figure 4.23. Comparative analysis of effects of lipids on longitudinal expansion

Figure 4.24 shows the effects of lipid content on the radial expansion ratio. One way ANOVA (α=0.05), showed that there was a significant difference ($p<0.0078$) between the high lipid AAW and the de-oiled AAP's radial expansion ratios. Student's t, Tukey-Kramer, and Hsu's MCB tests confirmed that significance.

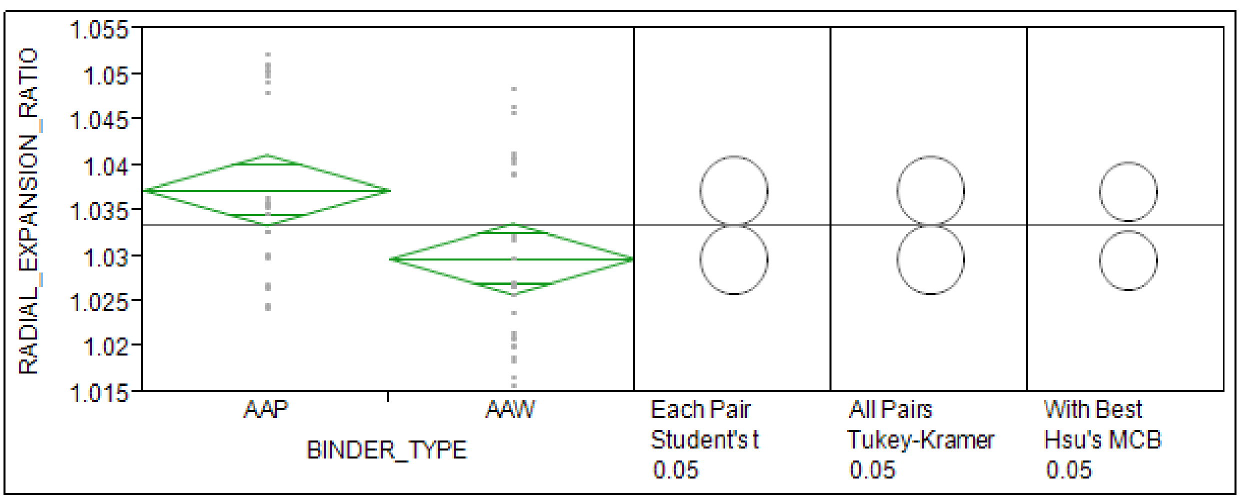


Figure 4.24. Comparative analysis of effects of lipids on radial expansion

Figure 4.25 shows the effects of the lipid content on water absorption/permeability. One way ANOVA (α=0.05), showed that there was a significant difference ($p<0.0001$)

between the high lipid AAW and the de-oiled AAP's permeability. Student's t, Tukey-Kramer, and Hsu's MCB tests confirmed that significance.

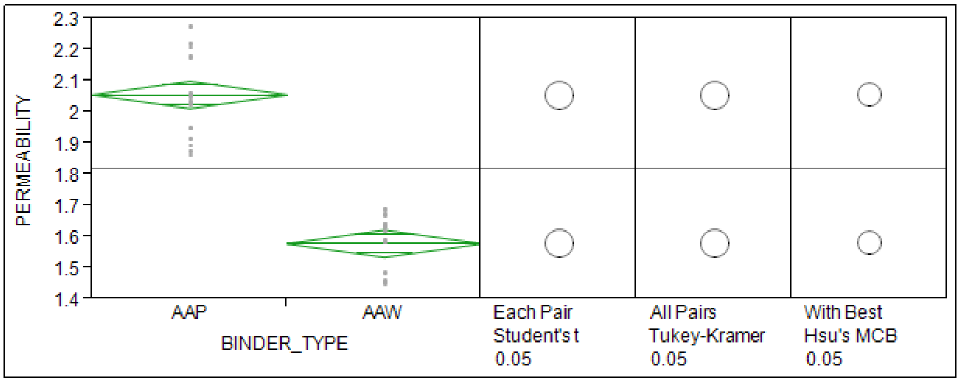


Figure 4.25. Comparative analysis of effects of lipids on water absorption/permeability

Figure 4.26 shows the effects of lipid content on density. One way ANOVA (α=0.05), showed that there was a significant difference ($p<0.0002$) between the high lipid AAW and the de-oiled AAP's density. Student's t, Tukey-Kramer, and Hsu's MCB tests confirmed that significance.

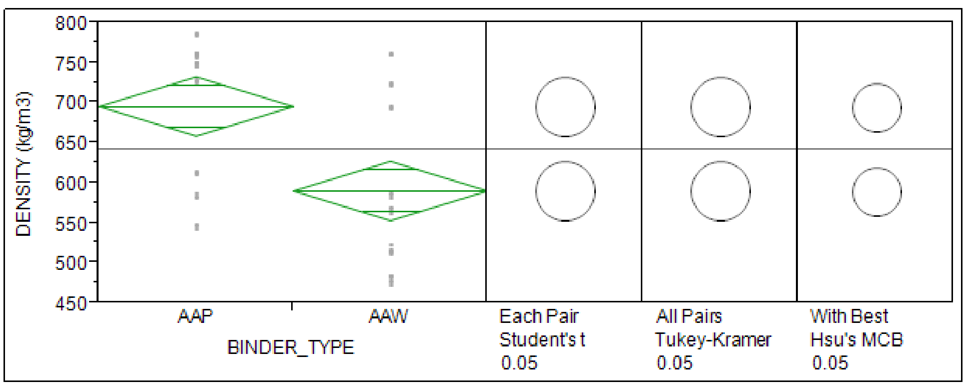


Figure 4.26. Comparative analysis of effects of lipids on density

4.7 Conclusions

The results from these experiments showed that rice husk can be densified effectively without pretreatment or size reduction using locally available binders.   An optimized moisture content of 15% enables the production of less friable densified rice husk briquettes at medium pressures. The results showed that process parameters, including binder type, binder concentration ratio, and die pressure all affect the density and water absorption/permeability of the briquettes. It was found that water absorption was lower at higher pressures and higher binder ratios; and density increased with die pressures for all binders. Paraffin wax (WAX), *Afzelia africana* aril whole (AAW), and gum arabic (GA) have the lowest permeability; and de-oiled *Afzelia africana* aril (AAP) and groundnut shell (GS) have the highest. AAP, WAX, and GS produced briquettes presented the highest densities, while AAW briquettes exhibited the lowest densities. This led to the conclusion that lipid content and interaction between lipid, protein and carbohydrate contents within the binders affect water absorption and densities of densified rice husk briquettes. Also comparative analysis of the high lipid AAW and de-oiled AAP led to the conclusion that the lipid content of binders improved the hydrophobic characteristics of the briquettes, but reduced their density; since the only difference between the two binders was the lipid content. The analysis of all the results showed that a durable rice husk briquette can be produced at minimum medium die pressure of 53.267 MPa, binder ratio of 6.354%, and an optimum moisture content of 15.190%; which was found to be the saddle point where an increase in die pressure and binder ratio would positively affect expansion ratios, water absorption, and densities of the briquettes.

4.8 Recommendations

Densification of rice husk is an important step that will make rice husk a viable alternative to firewood in the sub-Saharan region. The knowledge and understanding of the physical, chemical, and thermochemical characteristics of rice husk are necessary to ensure effective densification and the possibility of utilization of the densified rice husk as a competitive alternative to firewood and fossil fuel.

Higher density rice husk, produced at higher densification pressures, can be utilized as fuel feedstock, while briquettes with the highest water absorption can be an attractive bedding that can be used not only to provide comfort to animals, but also a means of manure absorption mechanism that can later be easily spread in the field mixed with soil.

4.9 Contribution of this research

The determination of the optimum moisture content for the densification of rice husk, and the possibility of using the five binders (gum Arabic, *Afzelia africana* aril (whole), *Afzelia africana* (deoiled), groundnut shell, and paraffin wax), for medium die pressure densification is an important contribution. These findings will encourage low energy densification of rice husk at the rural level in sub-Saharan Africa. The findings will not only make rice husk an alternative to firewood, but they will also provide employment for youths, hence meeting all the criteria of the triads of sustainability. The findings which show that rice husk briquettes can be produced with low energy usage as both an energy alternative to firewood, as well as, manure absorbing bedding for animals, are also very important contributions. One key issue of rice production in the sub-Saharan region is lack of fertilizer; this research opens up a research avenue for lightly densified rice husk as a manure collecting mechanism in the sub-Saharan rice producing regions.

4.10 Limitation of study

This study investigated the effect of process parameters that included binder type, binder ratio, moisture content, and die pressures on the density and water absorption of rice husk briquettes. This research provides a platform for the opportunity for sustainable utilization of rice husk, which is an abundant agricultural by-product in rice processing regions.

Connecting text to Chapter V

Physical characteristics of biomass are a key determinant of its viability as a biofuel feedstock, as well as, to establish what kind of process parameters need consideration during the design of handling and energy conversion systems that will utilize biomass as biofuel feedstock. The effective utilization of Engelberg and Milltop rice husks will increase the sustainability of rice processing in sub-Saharan Africa. Parameters such as particle size distribution, bulk and particle densities, moisture content, and microstructural characteristics are important in processing biomass as biofuel feedstock. Microstructural analysis of the rice husks from the two mills shows the physical presence of broken rice grains, brans, germs, immature grains, as well as full paddy that were not de-husked during the milling processes. To date, no studies have been carried to compare the physical characteristics of the Engelberg and Milltop produced rice husks.

Chapter V: Physical characterization of the Engelberg and Milltop rice husks

5.1 Abstract

Rice husk is a lignocellulosic biomass waste from the postharvest processing of rice and accounts for between 20-22% of the rough paddy (Wei et al., 2009; Yousuf et al., 2008). Rice husk can be used as an alternative fuel to firewood and fossil fuel. Utilization of rice husk can greatly improve the sustainability of post-harvest rice processing. Biomass characterization is the most important step in the development and design of any biofuel process that will utilize biomass as fuel feedstock. The characteristic properties of waste agricultural biomass depend on several factors including the parent plant variety, cultivation region, climatic condition during cultivation and to a greater extent the postharvest processing method used. This investigation involved the physical characterization of ten rice husk samples from three rice varieties (Kaiso, NERICA-1, and Super) from Uganda. The rice husks used in this study were by-products of two milling machines, the Milltop and the Engelberg, which are the most popular machines used in sub-Saharan Africa, by the small and medium scale processors. It was found that the mill type used, and to a lesser extent the variety and the region where the rice husk comes from, affect the physical properties of the rice husks. Rice husk from the Milltop machines were found to be lighter and contain less broken rice and bran than the rice husk obtained from the Engelberg machines. Particle size analysis showed that the Milltop produced husk residues which have larger geometric diameters with 95% of the particles retained by standard sieve #20 (0.850 mm); while the Engelberg rice husk particles were much smaller with standard sieve #100 (0.150mm) retaining 95% of the particles. The bulk density ranged from 120.88 – 155.48 kg/m^3 (Standard deviation=14.95), and 506.95-579.18 kg/m^3 (Standard deviation=30.53) for the Milltop and Engelberg rice husks respectively. The mean particle density for the Milltop rice husk was 192.82 kg/m^3 (Standard deviation=21.88) and ranged from 168.34-221.97 kg/m^3; while the much denser Engelberg particles had a mean particle density of 569.88 kg/m^3 (Standard deviation=34.15) and ranged from 523-616.62 kg/m^3. Microstructural analysis of the Milltop and Engelberg rice husks showed that the Engelberg had more broken rice kernels at larger particle sizes than

the Milltop. Particle size distribution, microstructural and statistical analysis of the rice husks showed that the largest components of the Engelberg were immature rice paddies and broken rice, while the largest components of the Milltop were unbroken lemma and palea with small broken rice kernel and bran in the inner side. Microstructural analysis also showed that the Nerica-1 variety rice husk had less cracks and more full lemma and palea components that resisted damage during milling, than the trichrome bearing tested varieties Super and Kaiso.

5.2 Introduction

Rice husk is a lignocellulosic biomass residue from the postharvest processing of rice that accounts for 20-22% of the total weight of the rice paddy (Wei et al., 2009; Yousuf et al., 2008). The energy content of this abundant biomass makes it one of the most available renewable energy that can be converted into bio-energy. In sub-Saharan Africa, most of the rice husk is dumped or sometimes burnt as a means of disposal instead of being used as an alternative to firewood and fossil fuel in the energy intensive postharvest processing of rice. All this contributes negatively to the environment and reduces the sustainability of rice processing.

Biomass characterization is one of the most important steps in the development and design of any biofuel process that will utilize biomass as fuel feedstock. The characteristic properties of waste agricultural biomass depend on several factors including the parent plant variety, cultivation region, climatic condition during cultivation and to a greater extent the postharvest processing method. In rice producing regions, plant genetic research has developed rice paddy varieties that have high yield and meet the preferential requirement of the consumers. Their focus also includes developing rice varieties that can go through parboiling, drying, and milling processes with minimal breakage and optimum physical and cooking qualities. These, in essence, have some effects on the characteristics of the rice husks produced from the dehusking and polishing of the rough rice paddies.

5.3 Literature review

The physical characterization of rice husk includes particle size distribution, bulk density, particle density, porosity, and moisture content determination. These analyses provide the mechanical and inter-particle relationship of the rice husk samples. The physical properties of a given biomass material greatly influence the design and operation of handling, biochemical, and thermochemical conversion systems that utilize the biomass as an energy feedstock. High moisture content decreases the heating value of the fuel, which in turn reduces the conversion efficiency as a large amount of energy would be used for the initial drying step during the conversion processes (Zhang et al., 2012; Mansaray and Ghaly, 1997; Zhang et al., 2012). High moisture content also influences the handling of biomass. Biomass materials are often handled in baled forms, which involve a lot of handling, transportation and storage costs because of the low bulk density of bales. One of the solutions to reducing handling, transportation and storage costs is the densification of the biomass materials into briquettes, pellets or cubes with bulk densities of 600-1200 kg/m^3 (Holley, 1983; Obernberger and Theck, 2004; McMullen et al., 2005; Adapa et al., 2009; Kaliyan and Morey, 2009; Kaliyan and Morey, 2010). In order to utilize biomass as an energy feedstock it needs to be compacted into pellets or briquettes so as to be handled by available conveyors, feeders, and transportation systems easily and economically.

The particle size distribution affects the flowability, heating diffusion and rate of reaction (Zhang et al., 2012). The particle size also affects the compaction characteristics of the biomass (Mani et al., 2006; Kaliyan and Morey, 2009). The bulk and particle densities affect the economics of collection, transportation as well as feeding of the material into a thermochemical conversion system (Zhang et al., 2012). The particle density and porosity affect the interstitial airflow velocity and the heat and mass transfer conditions and ultimately influence reaction parameters such as heat conductivity, burning rate, conversion efficiency and emissions (Igathinathane et al., 2008; Zhang et al., 2012). Abdullah and Geldart (1999) found that maximization of packing density is possible when there is a small amount of fine particles in a biomass mixture. Decreasing particle size of corn stover grinds resulted in increasing the density and durability of densified pellets and briquettes, due to the fact that smaller particles have more bonding area than larger particles (Mani et al., 2006; Kaliyan and Morey 2009).

Bulk density of a biomass is a physical property that depends on material composition, particle shape, particle size, particle size distribution, moisture content, and applied axial pressure (Lam et al., 2007). In the case of rice husk, the mill type and degree of milling are important factors that affect the parameters that define the bulk density of rice husk (Lam et. al., 2007).

Particle density of a biomass is the true density of the biomass, and can be defined as mass of the biomass that can be contained within a specific volume, without voids. Pycnometry has been used to determine the density of food material and biomass using nitrogen and helium as displacement fluids (Moreau and Rosenberg, 1998). Helium gas pycnometry uses the ideal gas law, and accomplishes that by measurement of skeletal volumes of particles by observing the reduction of gas capacity in the sample chamber caused by the presence of the sample (Micrometrics 1305 Operator manual).

A novel method for determining the components of the rice husk physically is the utilization of scanning electron microscopy (SEM). SEM provides surface information on the components that make the rice husk including: immature grains, broken rice components, impurities, germ, characteristics of the bran, and structure of the husks after undergoing the milling process. It is an important surface characterization technique that has not been used as of yet to compare Engelberg and Milltop rice husks. This will be an important contribution in the characterization of rice by-products produced from single and multistage milling machines to be used as industrial feedstocks for bio-energy sources.

5.4 Objectives

5.4.1 Overall objective

The overall objective of this research is to study the physical characteristics of Engelberg and Milltop rice husks in order to determine the physical process parameters that are important for their use as bio-energy feedstocks.

5.4.2 Specific objectives

The specific objectives of this research were:

1. To study the particle distribution of the Engelberg and Milltop rice husks
2. To study the bulk density of the Engelberg and Milltop rice husks
3. To study the particle density of the Engelberg and Milltop rice husks
4. To utilize SEM to confirm the physical characteristics of the Engelberg and Milltop rice husks

5.5 Materials and Methods

5.5.1 Materials

Rice husk samples obtained from different regions of Uganda were used for this study. The rice husk samples were collected from milling stalls processing rice from established farms where the paddy was grown, with known types of rice variety, and type of milling machine used to de-husk and polish the grain. The samples detailed information is listed in Table 5.1.

Table 5.1 Rice husk samples identification

Sample	Source	Variety	Farm	Mill Type
A	Doho irrigation scheme	Kaiso	Farm 3	Milltop SB30
B	Doho irrigation scheme	Kaiso	Farm 1	Milltop SB30
C	Lira (Abolete)	Super	Abolete	Milltop SB30
D	Doho irrigation scheme	Kaiso	Farm2	Milltop SB30
E	Nuya- Acholi	NERICA-1	Nuya-Acholi	Milltop SB30
F	Lira	Super	Lira	Engelberg
G	Lira	Super	Lira	Engelberg
H	Lira	Super	Lira	Engelberg
I	Lira	Super	Lira	Engelberg
J	Lira	Super	Lira	Engelberg

5.5.2 Methods

5.5.2.1 Moisture content

The moisture content was determined using the American Society of Agricultural and Biological Engineers (ASABE) standard S358.2 (ASABE, 2006a). This method is similar to ASTM 2010 used by Zhang et al. (2012). Triplicate samples of the rice husk were oven dried at 103±2°C for 24 hours and the samples were weighed until a constant weight was obtained.

5.5.2.2 Particle size analysis

Particle distribution of the rice husk sample was determined using ASAE Standard S319 (ASABE, 2006b) method. For each test, 100 g of the sample was placed on the top sieve of a stack of eight US standard sieves, arranged from the largest to the smallest opening. Standard sieves #6, 10, 20, 35, 60, 100, 140, and 200; with sieve opening sizes of 3.360, 2.0, 0.850, 0.500, 0.250, 0.150, 0.106, and 0.075 mm respectively, were used for this experiment (Table 5.2). Three replicates of this experiment were carried out and the geometric mean diameter was determined.

The sieves were mounted on an electric motor-driven mechanical shaker and covered with a sieve lid. The shaker was operated at the speed of 350 rpm for 30 minutes. The particles collected in each sieve were weighed. The data collected was used to determine the particle size distribution of the samples. Triplicate samples of rice husk were analyzed.

Table 5.2 Standard sieve sizes

Standard Sieve #	Size (mm)
6	3.360
10	2.000
20	0.850
35	0.500
60	0.250
100	0.150
140	0.106
200	0.075

5.5.2.3 Bulk density

The bulk density of the rice husk sample was determined by carefully filling a standard 600ml cylindrical container with the sample incrementally. After filling 1/3 portions of the container with the rice husk, the container was tapped on a wooden table 10 times to allow the material to settle down, before continuing (ASAE Standard S269.4 DEC91 (ASABE standards, 2007); Zhang et al. (2012)). Once the container was full, the excess material at the top was removed by moving a steel rod in a zigzag pattern (Mani et al., 2006). The bulk density of the sample was calculated as mass per unit volume. Three replicates of this experiment were carried out.

5.5.2.4 Particle density

A gas pycnometer (Micrometrics 1305) was used to determine the particle densities of the samples by calculating the displaced volume of helium gas by a known mass of material. Three replicates of this experiment were carried out. The pycnometer accomplishes the measurement of skeletal volumes by observing the reduction of gas capacity in the sample chamber caused by the presence of the sample (Micromeritics 1305 operator manual). The gas recommended for these measurements is helium, which has the ability to penetrate even the smallest pores and surface irregularities. The volume obtained permits computation of the optimum theoretical density of the solid comprising the sample with the exception of closed pores, which would be inaccessible. The pycnometer has two chambers of variable sizes; the cell or the sample chamber and the expansion chamber. The sample is placed in the sample chamber and charged to a gas pressure of 20 psig (137.9 kPa). A valve connecting the cell (sample) chamber to the expansion chamber is then opened and the pressures in the expansion chamber before and after the valve is released are recorded as P_1 and d P_2 respectively.

5.5.2.5 Microstructural analysis of rice husk using SEM

The rice husk samples were studied using Hitachi TM3000 tabletop scanning electron microscope (SEM) at different magnification levels with the objective of studying the surface and sub-surface structures, as well as, other entrained components within the rice husk.

5.6 Results and Discussion

5.6.1 Moisture content

The moisture content of rice husk samples ranged from 5.08 to 6.51 %, with a pooled mean moisture content of 5.90% and standard deviation of 0.43% (Figure 5.1 and Table 5.3).

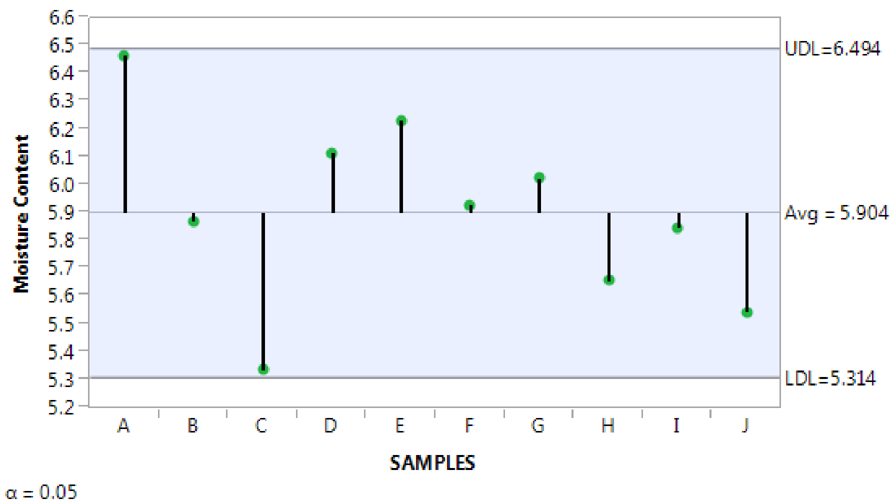


Figure 5.1. Analysis of means of moisture contents of rice husk samples

Table 5.3 ANOVA means of samples moisture contents

Level	Number	Mean	Std Error	Lower 95%	Upper 95%
A	3	6.46867	0.20037	6.0507	6.8866
B	3	5.87100	0.20037	5.4530	6.2890
C	3	5.33767	0.20037	4.9197	5.7556
D	3	6.11633	0.20037	5.6984	6.5343
E	3	6.23500	0.20037	5.8170	6.6530
F	3	5.93000	0.20037	5.5120	6.3480
G	3	6.02800	0.20037	5.6100	6.4460
H	3	5.65800	0.20037	5.2400	6.0760
I	3	5.84967	0.20037	5.4317	6.2676
J	3	5.54433	0.20037	5.1264	5.9623

5.6.2 Particle size distribution analysis

The results obtained showed two trends of particle size distribution that relate to the types of milling machines used - the Milltop and the Engelberg machines. The Milltop rice husks have a higher geometric mean diameter than the Engelberg mill rice husks (Figure 5.2).

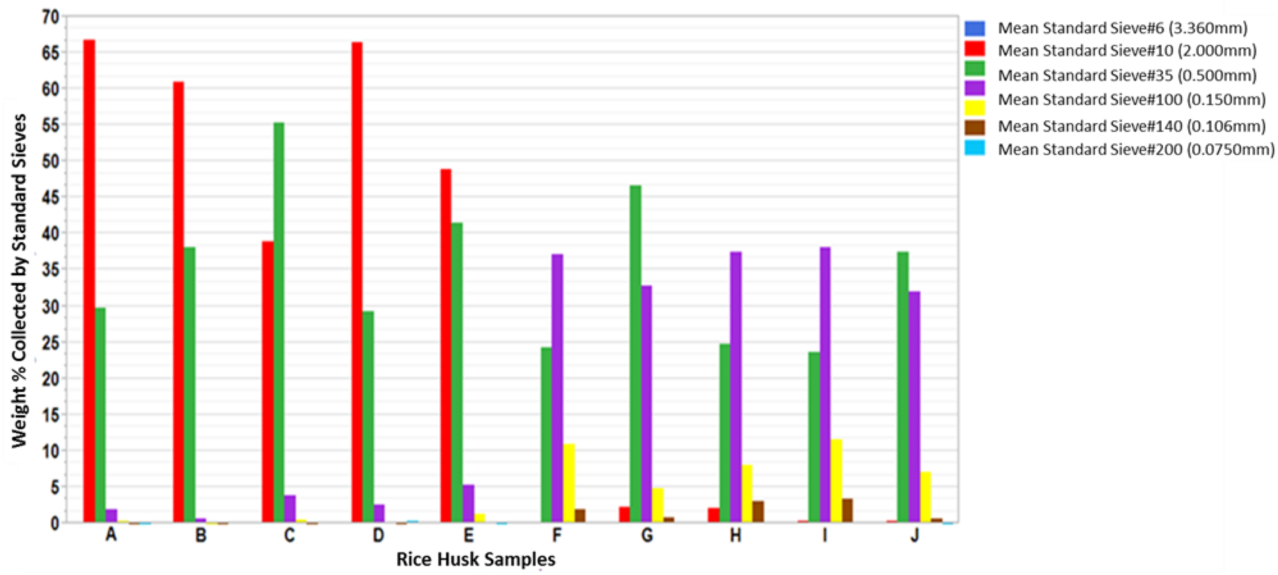


Figure 5.2. Particle size distribution of rice husk samples

5.6.2.1 Particle size distribution analysis of the Milltop rice husk

Particle size analysis results of the Milltop rice husk samples showed that the Kaiso and Super varieties (A, B, & D), with exception of sample C have the highest mean diameters, with a pooled mean of 64.73% collected by the #10 Standard sieve, and cumulative mean of 96.84% retained by #20 Standard sieve. The Nerica-1 (E) was found to have a smaller mean diameter than samples A, B, and D with 48.9% of the sample collected by Standard sieve #10, and cumulative mean of 90.38% retained by Standard sieve #20. However, the results obtained for sample C showed that it has the smallest retention by Standard sieve #10 of 38.98%, but a very high retention by sieve #20 of 55.31%; higher than all the other Milltop samples, which resulted into a cumulative retention of 93.92% by Standard sieve #20. This was likely due to the fact that, sample C had the largest amount of broken pieces of the lemma and palea that occurred during the milling process. Unlike the other Milltop samples, where most of the lemma and palea components were collected by Standard sieve #10; in the case of sample C, the cracked lemma and palea, and the smaller broken-off pieces were mostly collected by Standard sieve #20, and the smaller lower sieves, respectively.

Microstructural analysis of the Milltop rice showed that particles are larger, with a small amount of small particles are shown in Figure 5.3. More than 90% of the particles were larger than Standard sieve #20 (0.850 mm) (Figure 5.4).

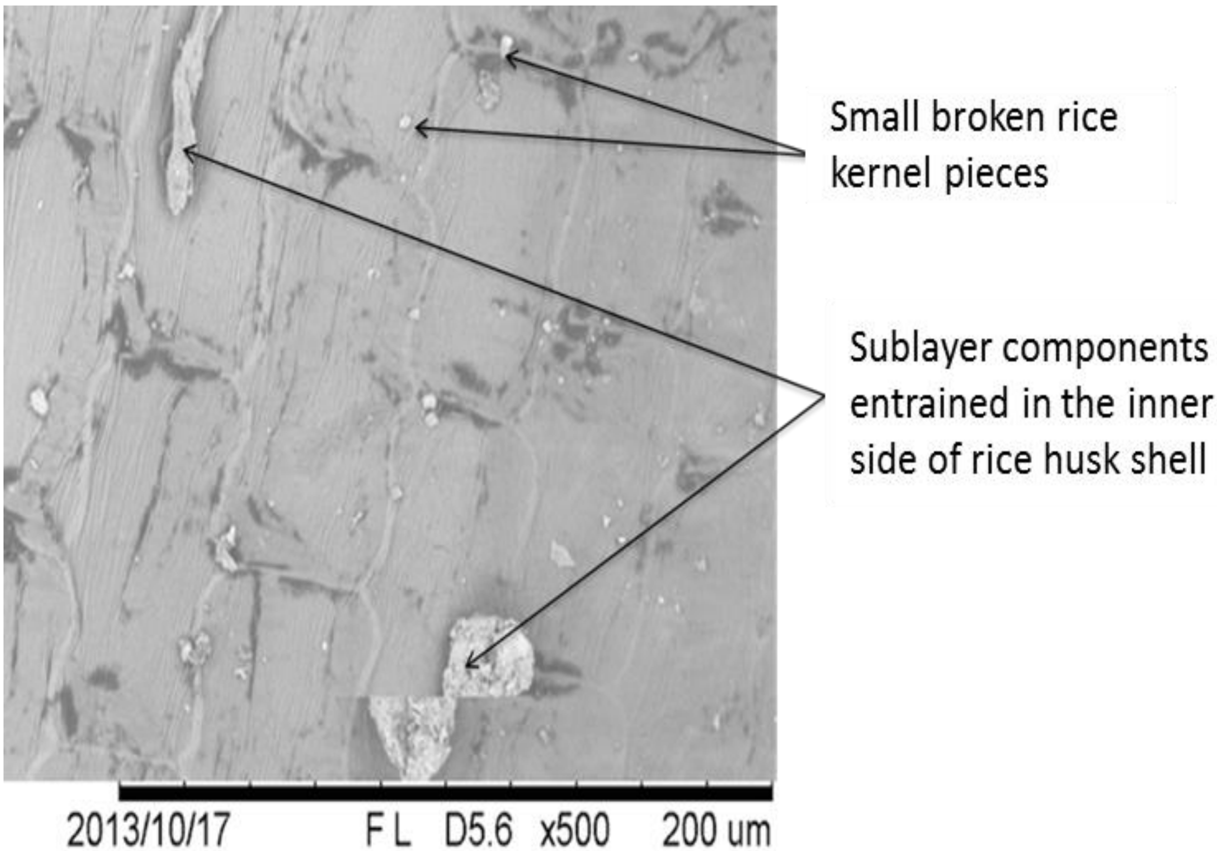


Figure 5.3. SEM shows that Milltop rice husk samples have very small amount of broken kernels and sublayer bran components

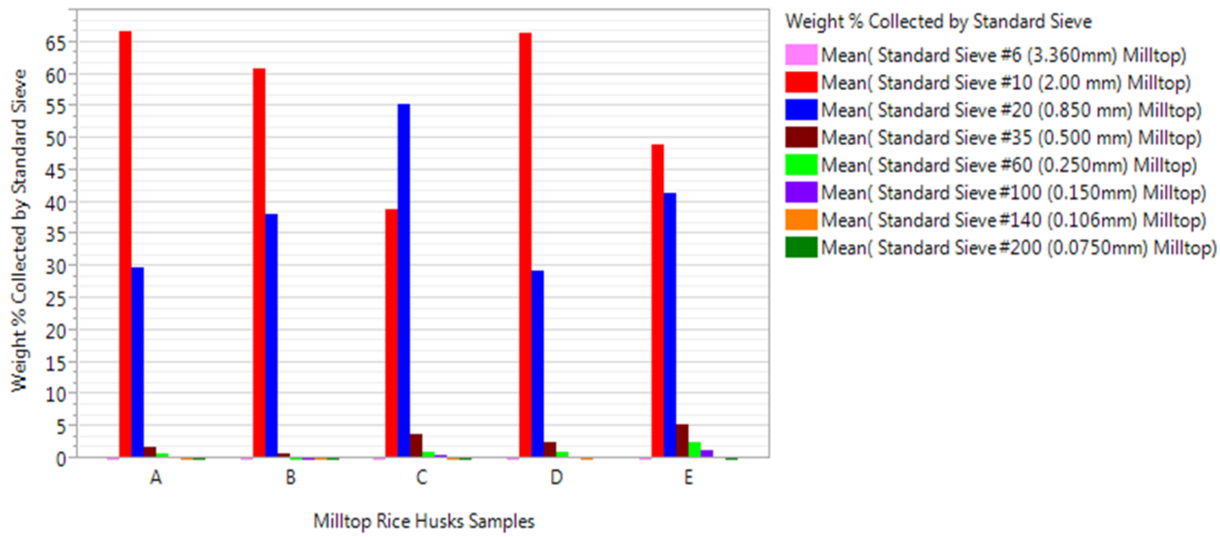


Figure 5.4. Particle size distribution of the Milltop mill rice husk

The prediction model generated based on these results showed a best polynomial fit with R-square value of 0.86 (Figures 5.5 & 5.6)

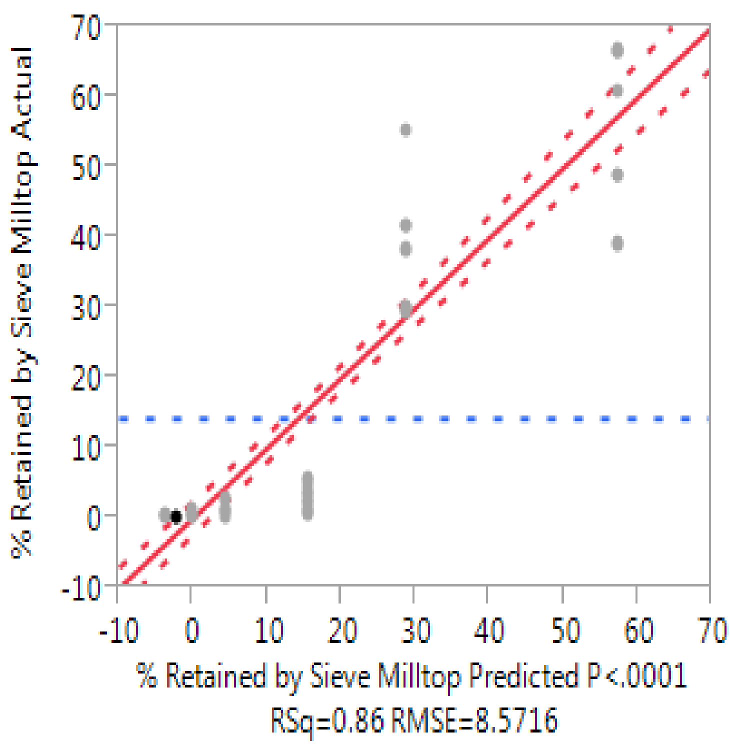


Figure 5.5. Prediction plot of the amount of Milltop particles collected by individual standard sieves

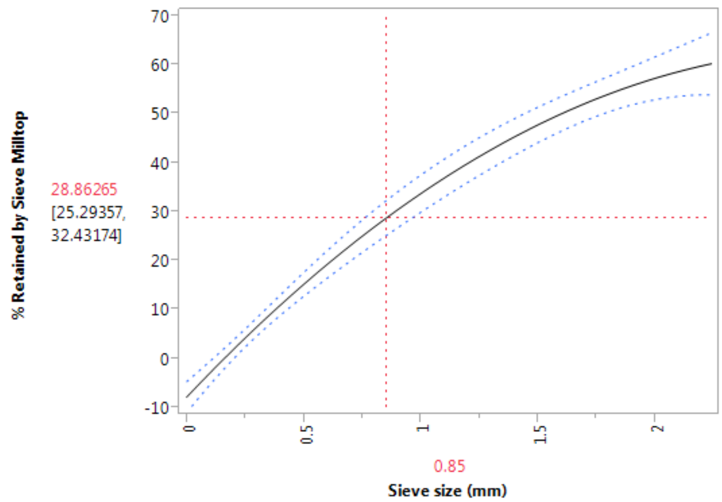


Figure 5.6. Prediction model profile of the amount of Milltop particles collected by individual standard sieves

The predicted model parameters showed that the sieve size is a significant parameter both at the linear and quadratic levels as shown in Table 5.4. The predicted model based on individual sieves provides a tool to estimate the particle size distribution of the Milltop rice husk based on desired standard sieve. This is an important tool that can be used in the design of handling, densification and thermochemical equipment.

Table 5.4 Parameter estimates of predicted model of the amount of Milltop particles collected by individual sieves

Term	**Estimate**	**Std Error**	**t Ratio**	**Prob>|t|**
Intercept	-4.726938	1.146173	-4.12	<.0001*
Sieve size (mm)	40.426052	2.769277	14.60	<.0001*
(Sieve size (mm)-0.55698)*(Sieve size (mm)-0.55698)	-8.997844	2.587033	-3.48	0.0007*

Figures 5.7, 5.8, and Table 5.5, show the prediction plot, prediction model, and the predicted parameters of the cumulative Milltop particles collected by a sieve size, including the amount collected by sieves that have larger openings that are above the standard sieve. A polynomial (quadratic) predicted plot with R-square value=0.92 was obtained. The prediction model showed that sieve #20 (0.850mm) and smaller will retain 95% of all the Milltop rice particles (Figure 5.8).

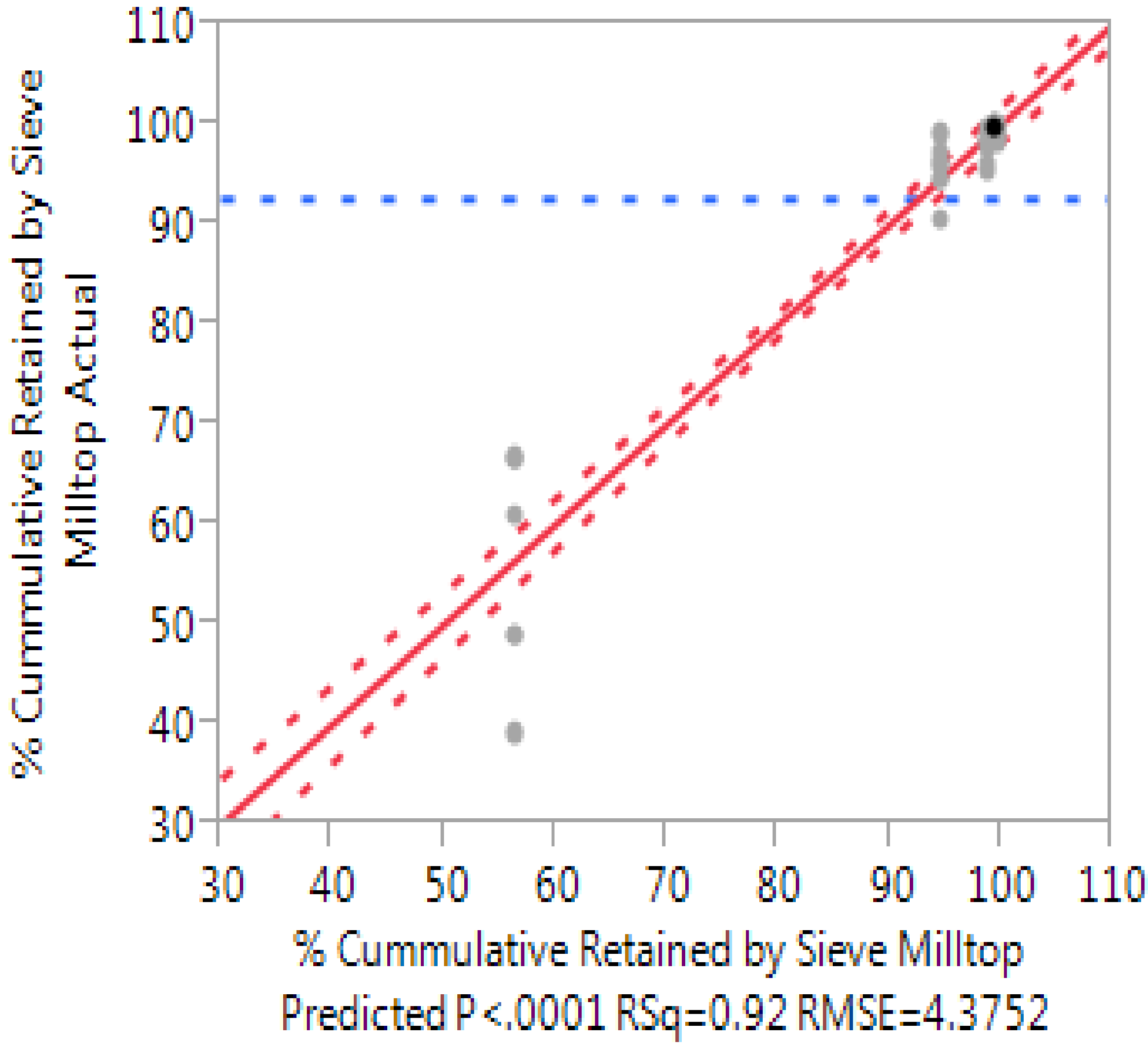


Figure 5.7. Prediction plot of cumulative Milltop particles collected by individual standard sieves

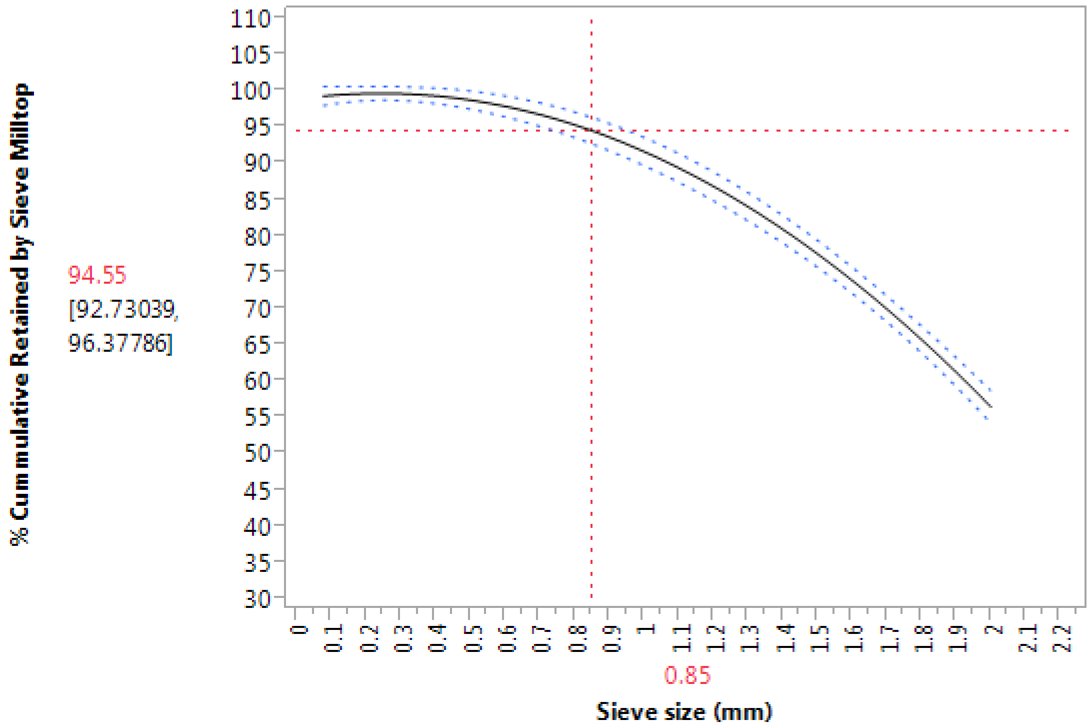


Figure 5.8. Prediction model profile of cumulative Milltop particles collected by individual standard sieves

Table 5.5 Parameter estimates of predicted model of cumulative Milltop particles collected by individual sieves

Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	103.31787	0.589036	175.40	<.0001*
Sieve size (mm)	-8.942938	1.411437	-6.34	<.0001*
(Sieve size (mm)-0.56157)*(Sieve size (mm)-0.56157)	-13.98868	1.325387	-10.55	<.0001*

The one way analysis of variance (ANOVA) (α=0.05) of the amount of rice husk collected by sieve #10 and sieve #20 confirms these findings (Figures 5.9 & 5.10; and Tables 5.6 & 5.7). The ANOVA also shows how individual samples differ with the amount retained by each of the two sieves. Figure 5.9 showed that samples A, B, and D have the highest retention by sieve #10 because they are larger; while, samples C and E have the lowest retention by the #10 sieve.

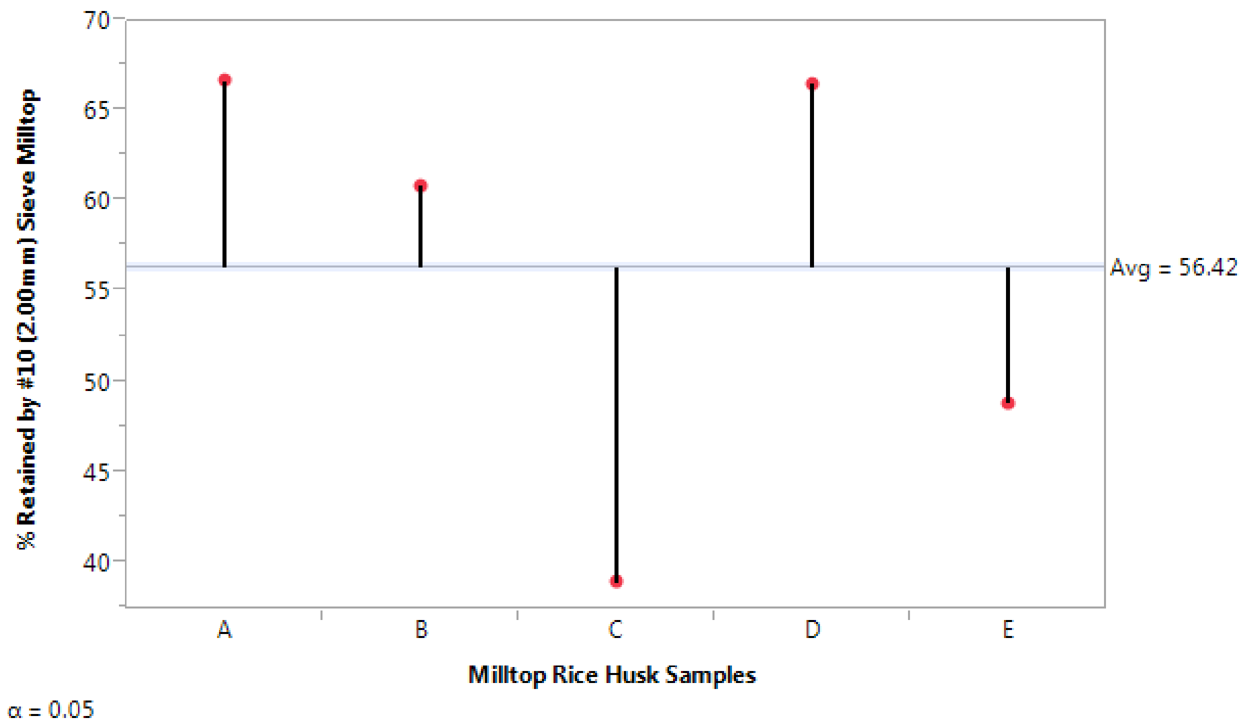


Figure 5.9. Analysis of means of % cumulative Milltop rice husk retained by #10 Standard sieve

Table 5.6 ANOVA means of % cumulative Milltop samples retained by sieve #10

Sample	Number	Mean	Std Error	Lower 95%	Upper 95%
A	3	66.7333	0.09690	66.517	66.949
B	3	60.9333	0.09690	60.717	61.149
C	3	38.9833	0.09690	38.767	39.199
D	3	66.5333	0.09690	66.317	66.749
E	3	48.9000	0.09690	48.684	49.116

ANOVA analysis (α=0.05) of the cumulative percentage of rice husk retained by sieve #20 showed that samples A, B, C, and D have the highest % retained by the sieve as shown in Figure 5.10 and Table 5.7.

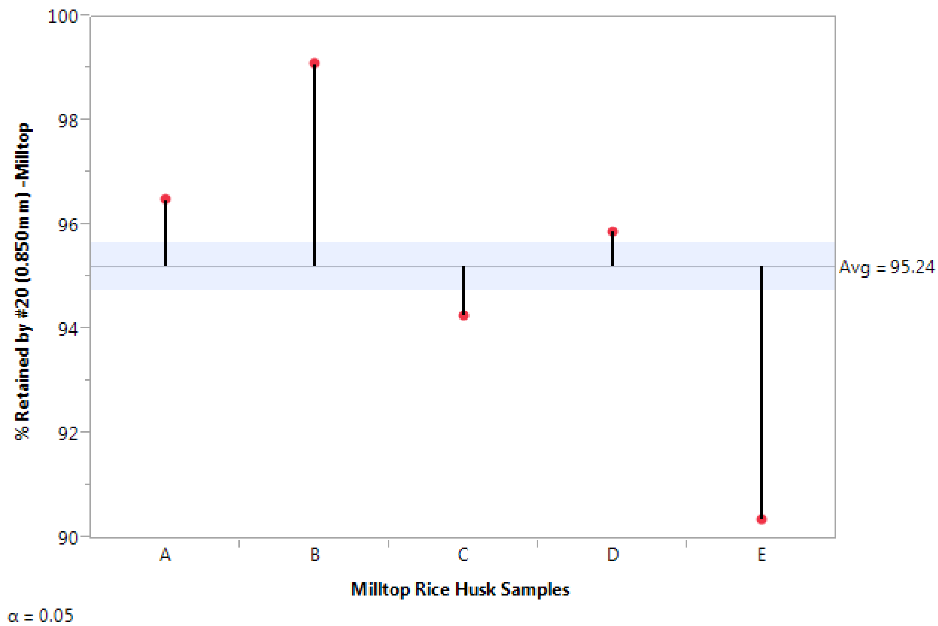


Figure 5.10. Analysis of means of % cumulative Milltop rice husk retained by #20 Standard sieve

Table 5.7 ANOVA means of % cumulative Milltop samples retained by sieve #20

Level	Number	Mean	Std Error	Lower 95%	Upper 95%
A	3	96.5100	0.16728	96.137	96.883
B	3	99.1067	0.16728	98.734	99.479
C	3	94.2933	0.16728	93.921	94.666
D	3	95.8967	0.16728	95.524	96.269
E	3	90.3767	0.16728	90.004	90.749

Microstructural analysis of the rice husk samples showed that samples A, B, C, and D all have trichomes, but sample E does not. Another important difference observed was that lemma and palea of sample C had more cracks compared to samples A, B, and D resulting into smaller particles in sample C. However, all the samples A to D have cracks due to milling. Possible explanation of the observed result could be attributed to both the trichomes (Figures 5.11 & 5.12) and the cracked husks increasing the traverse size of particles and enabling their retention by the large opening sieve #10.

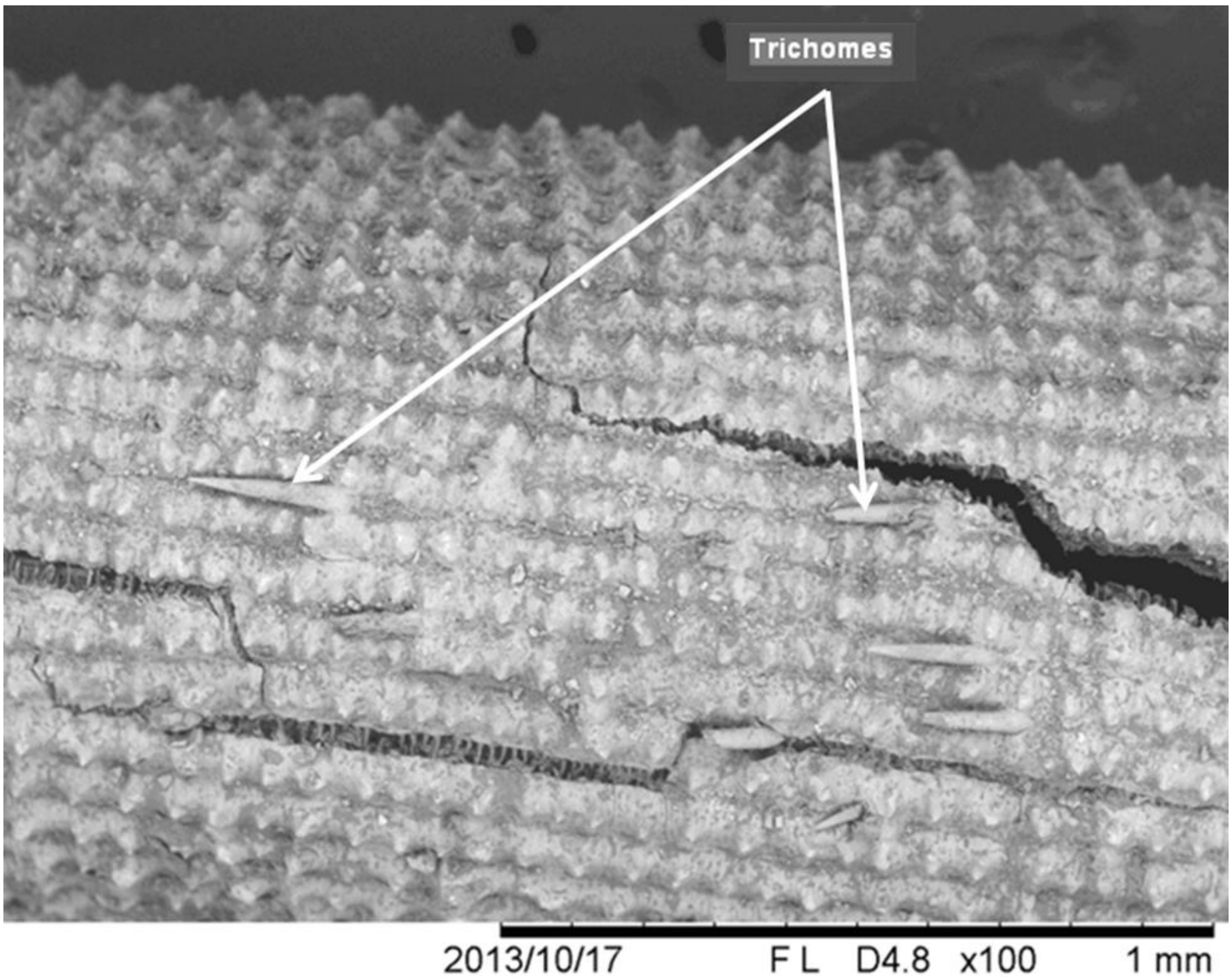
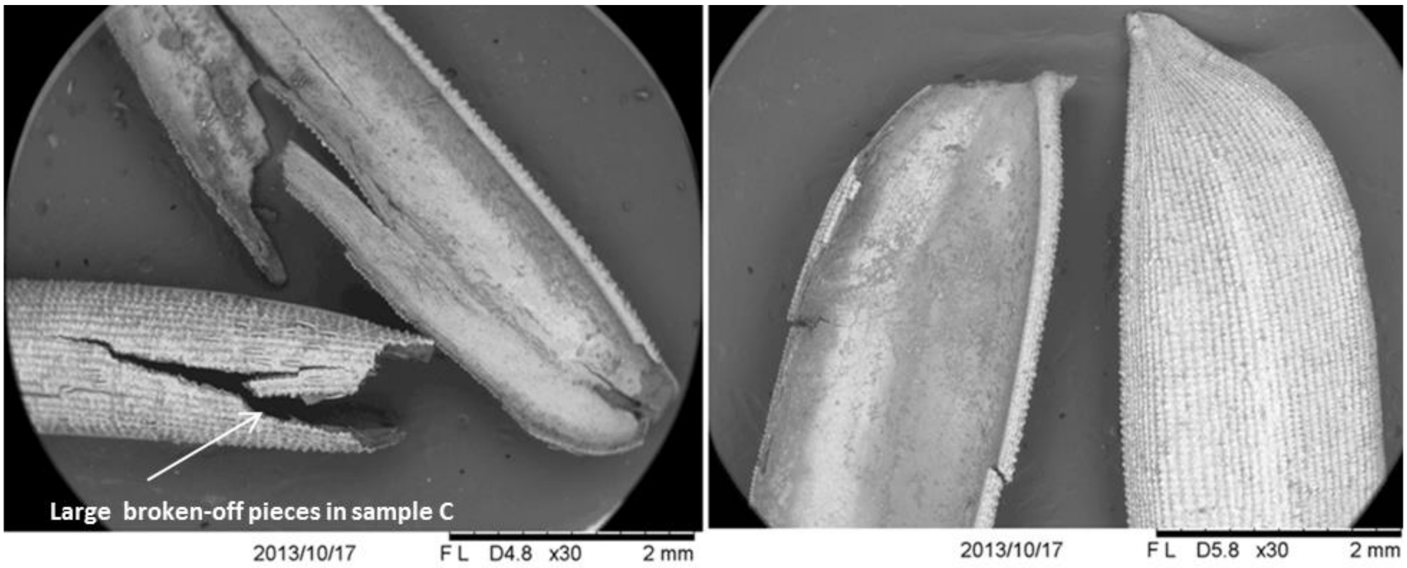


Figure 5.11. SEM showing the trichomes

Sample E, the Nerica-1 variety, had a mean 48.1% retention by Standard sieve #10, and 41.48% retention by sieve #20, this could be due to the fact that most of the lemma were retained by sieve #10 (2.00 mm) and the palea component were retained by sieve #20. Microstructural analysis of sample E (Figure 5.11 (b)) shows that the lemma and palea components withstood the milling process with very small cracks.



(a) Cracks and broken pieces in sample C

(b) Lemma & palea of sample E were solid & no trichomes

Figure 5.12. SEM of samples C and E showing the cracks and broken off pieces

5.6.2.2 Particle analysis of Engelberg rice husk

Engelberg rice husks have much finer components with more entrained components of broken rice, bran, and immature grains (Figure 5.13). The retention of the Engelberg rice husk was observed for all the sieves from #2 to #200, with two distinctive peaks at the #20 (0.850mm) and #35 (0.500mm). This revealed two distinctive groups: one with large particle components that were due to the high amount of immature grains or large broken rice kernels; and the other, with smaller pieces of broken rice kernels and fewer immature grains.

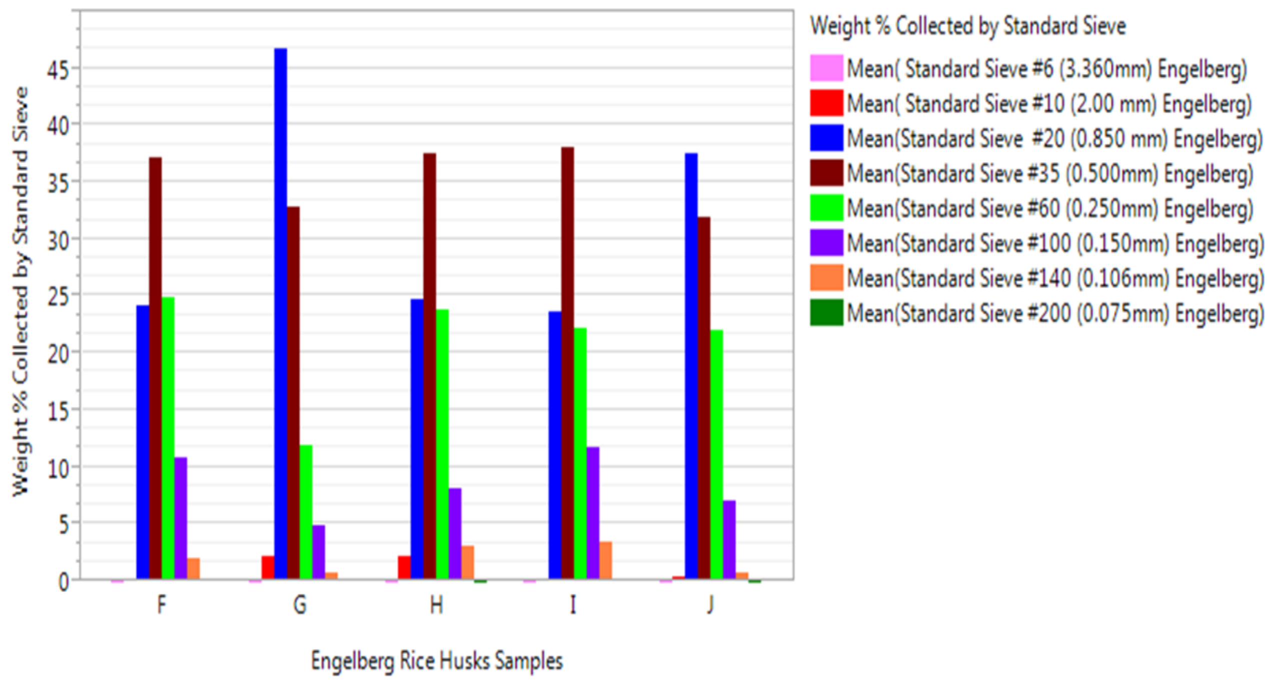
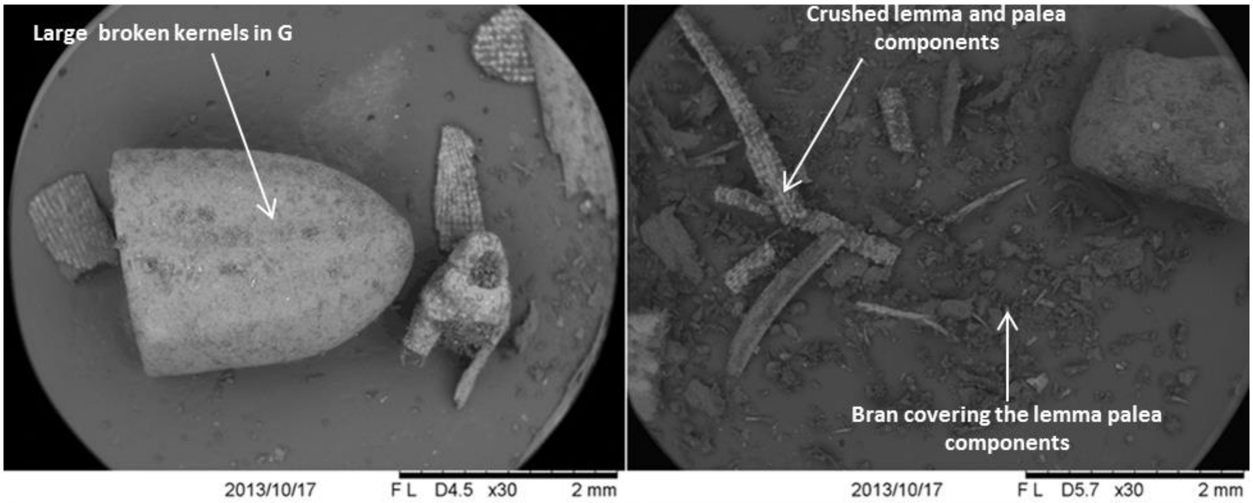


Figure 5.13. Particle size distribution of the Engelberg mill rice husk

Samples G and J fell into the former category, while sample F, H, and I, fell into the latter category. The figure also showed that the amount of rice husk retained by sieve #20 and sieve #35 defined the two groups or categories. Examination of the groups showed that the ones below the overall mean (F, H, & I), had less broken rice and fewer immature grains. However, the groups above the overall average have two distinctive characteristics: Sample G has significantly higher contents of large broken rice kernels entrained, than any of the samples and it also contains immature grains (Figure 5.14). The large amount of broken kernels and the entrained immature grains must have been the cause of high retention of the sample by Standard sieve #20. From the results, it is obvious that the large retention of sample G by sieve #20 is due to poor milling efficiency, possibly compounded by less than ideal harvesting timing, parboiling, and drying methods.



(a) Large broken kernels in Sample G

(b) Fewer broken kernels in sample F, H, & I

Figure 5.14. Particle size distribution of the Engelberg mill rice husk

Sample J on the other hand, did not have a large amount of broken rice kernels, but instead had the largest amount of immature grains, which were retained to the largest extent by sieve #20 (Figure 5.15). From the observed results, the high retention of sample J by sieve #20 can be attributed to the possible poor harvesting timing that led to a high content of immature grains. This might have also been compounded by poor growing season conditions, and other ecological conditions.

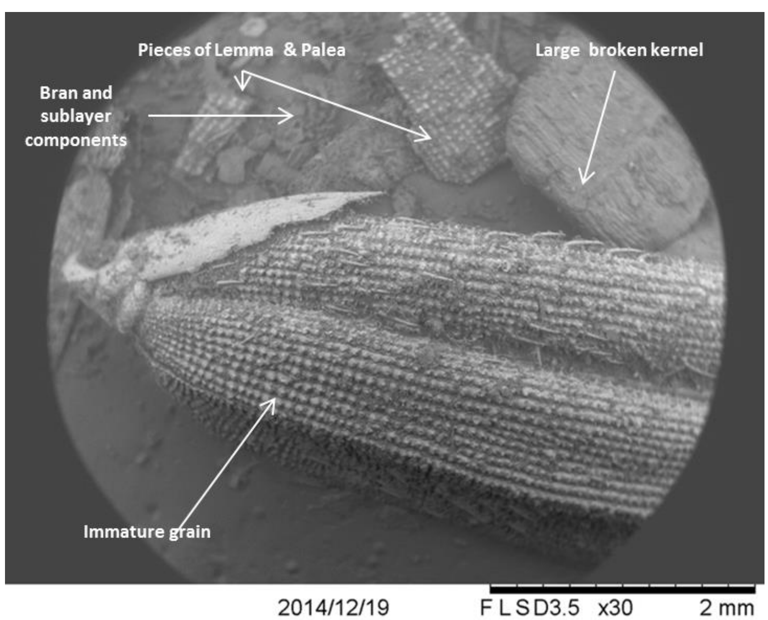


Figure 5.15. Immature grain in sample J

The large broken rice kernel must have resulted in the high percentage of the samples being retained by sieve #20 (0.850 mm). The ANOVA analysis of the amount of Engelberg rice husk retained by sieve #20 is as shown in Figure 5.16 and Table 5.8. The results showed that the mean cumulative retention by sieve #20 (0.850mm) was 32.41 %, with the samples G and J having the retention means of 37.78 and 48.91 % respectively; while samples F, H, and I have retention means of 24.51, 26.97, and 23.91% respectively.

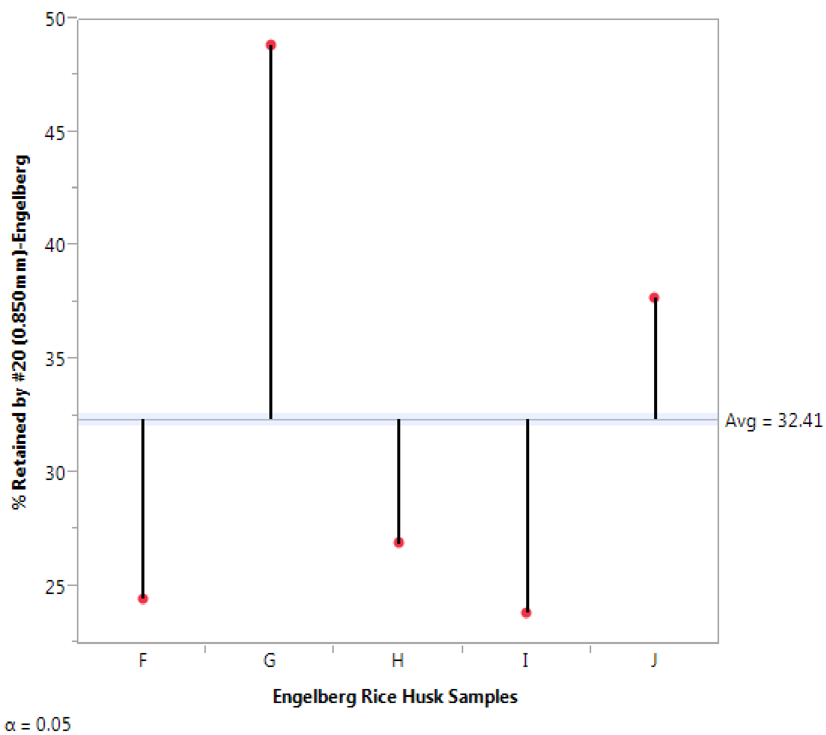


Figure 5.16. Analysis of means of % cumulative Engelberg rice husk retained by sieve #20 (0.850 mm)

Table 5.8. ANOVA means of % cumulative retention by sieve #20 (0.850mm)

Level	Number	Mean	Std Error	Lower 95%	Upper 95%
F	3	24.5100	0.10652	24.273	24.747
G	3	48.9100	0.10652	48.673	49.147
H	3	26.9667	0.10652	26.729	27.204
I	3	23.9067	0.10652	23.669	24.144
J	3	37.7767	0.10652	37.539	38.014

More than 50% of the Engelberg rice particles were collected by Standard sieve #35 (0.500mm) as shown in Figure 5.17. The ANOVA of the samples retained by Standard sieve #35 showed that the mean of % cumulative Engelberg particles retained ranged from 61.67% to 81.77%; with sample G showing the highest retention (Table 5.9).

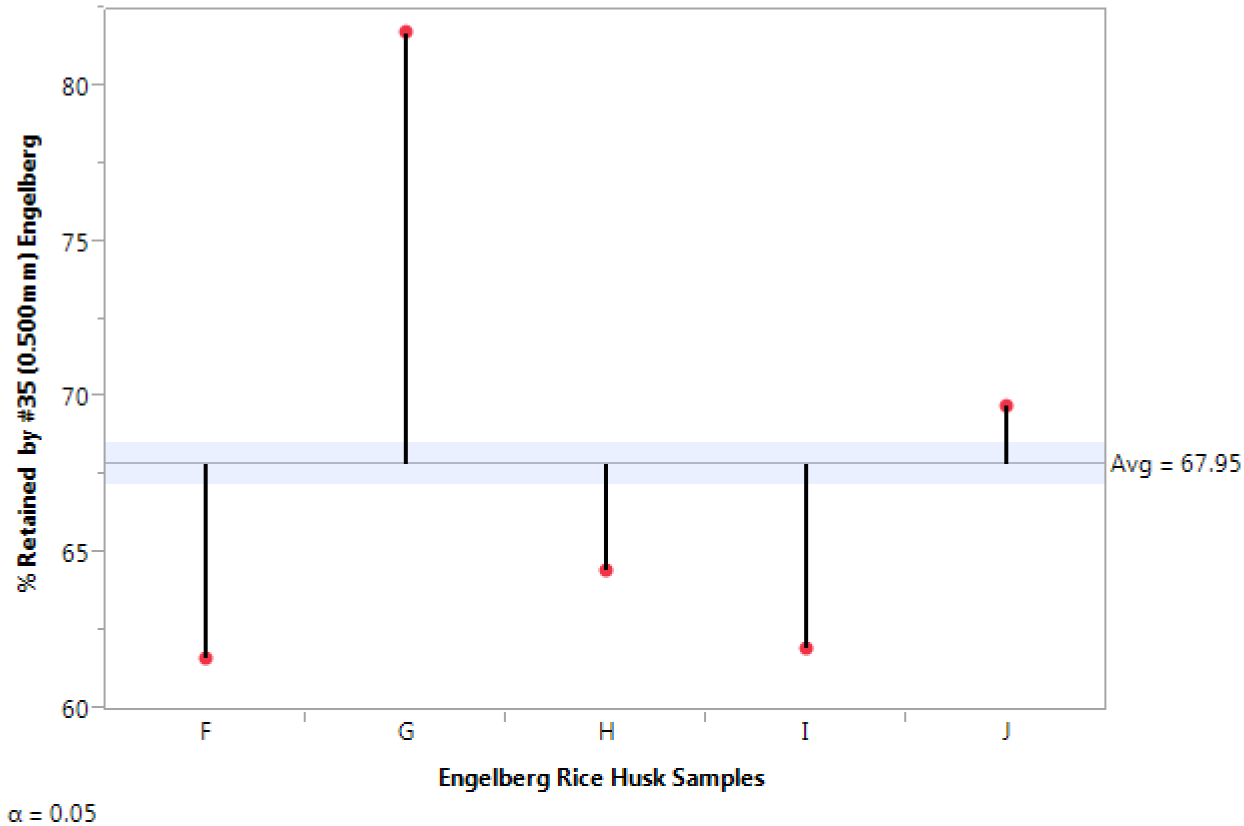


Figure 5.17. Analysis of means of % cumulative Engelberg rice husk retained by Sieve #35 (0.500 mm)

Table 5.9 ANOVA means of % cumulative retention by sieve #35 (0.500mm)

Level	Number	Mean	Std Error	Lower 95%	Upper 95%
F	3	61.6867	0.24180	61.148	62.225
G	3	81.7700	0.24180	81.231	82.309
H	3	64.5100	0.24180	63.971	65.049
I	3	62.0017	0.24180	61.463	62.540
J	3	69.8033	0.24180	69.265	70.342

Sieve # 60 (0.250 mm) retained a % cumulative mean ranging between 84.22 to 93.60 % for the Engelberg rice husk samples (Figure 5.18). ANOVA means of the rice husk samples showed samples G and J have the highest retention with % cumulative retention of 93.60% and 91.77% respectively; confirming the two categories observed from the collection by all the other Standard sieves (Table 5.10).

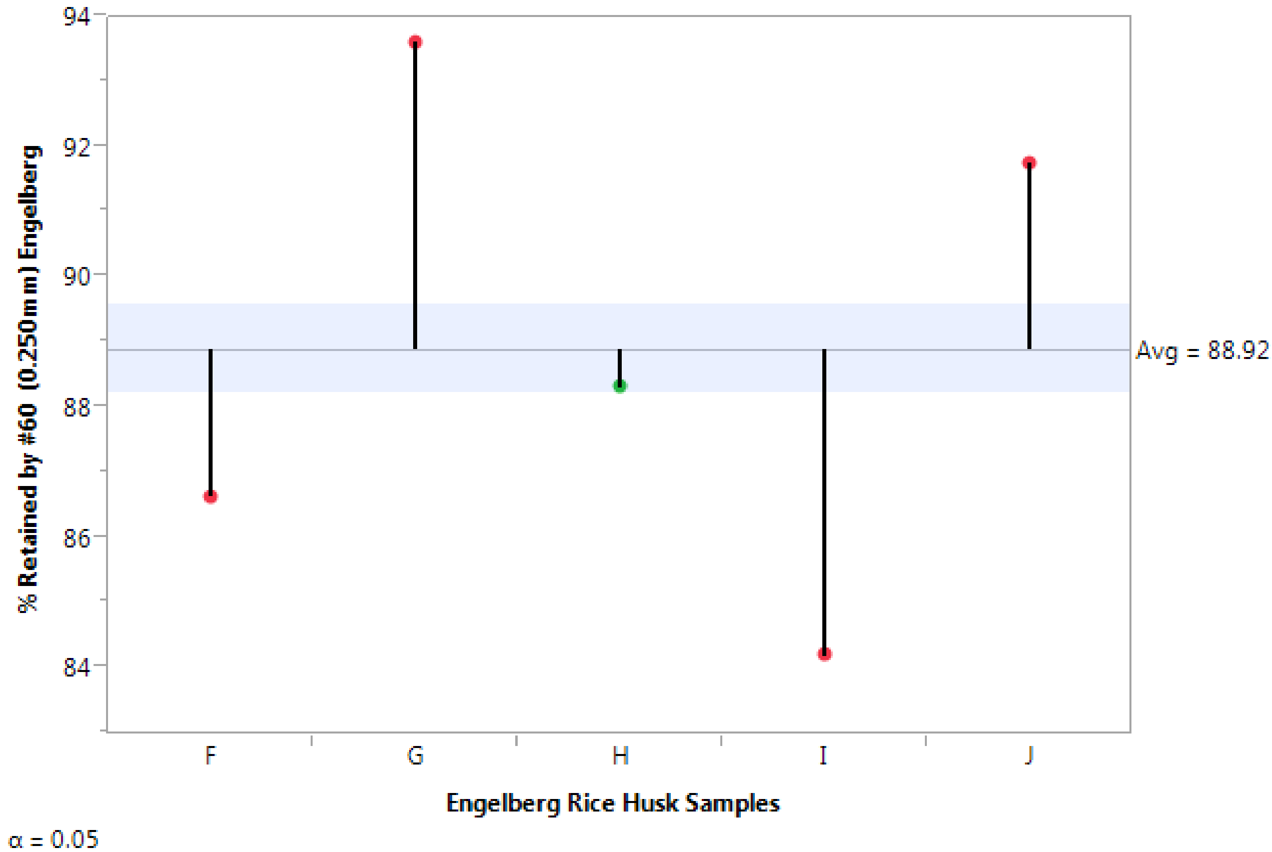


Figure 5.18. Analysis of means of % cumulative Engelberg rice husk retained by sieve #60 (0.250 mm)

Table 5.10 ANOVA means of % cumulative retention by sieve #60 (0.250mm)

Level	Number	Mean	Std Error	Lower 95%	Upper 95%
F	3	86.6600	0.25124	86.100	87.220
G	3	93.6300	0.25124	93.070	94.190
H	3	88.3400	0.25124	87.780	88.900
I	3	84.2150	0.25124	83.655	84.775
J	3	91.7733	0.25124	91.214	92.333

More than 95% of the Engelberg rice husk samples were retained by Standard sieve #100 (0.150 mm) and higher # (Figure 5.19). ANOVA means of the rice husk samples showed that samples G and J have the highest cumulative retention (Table 5.11).

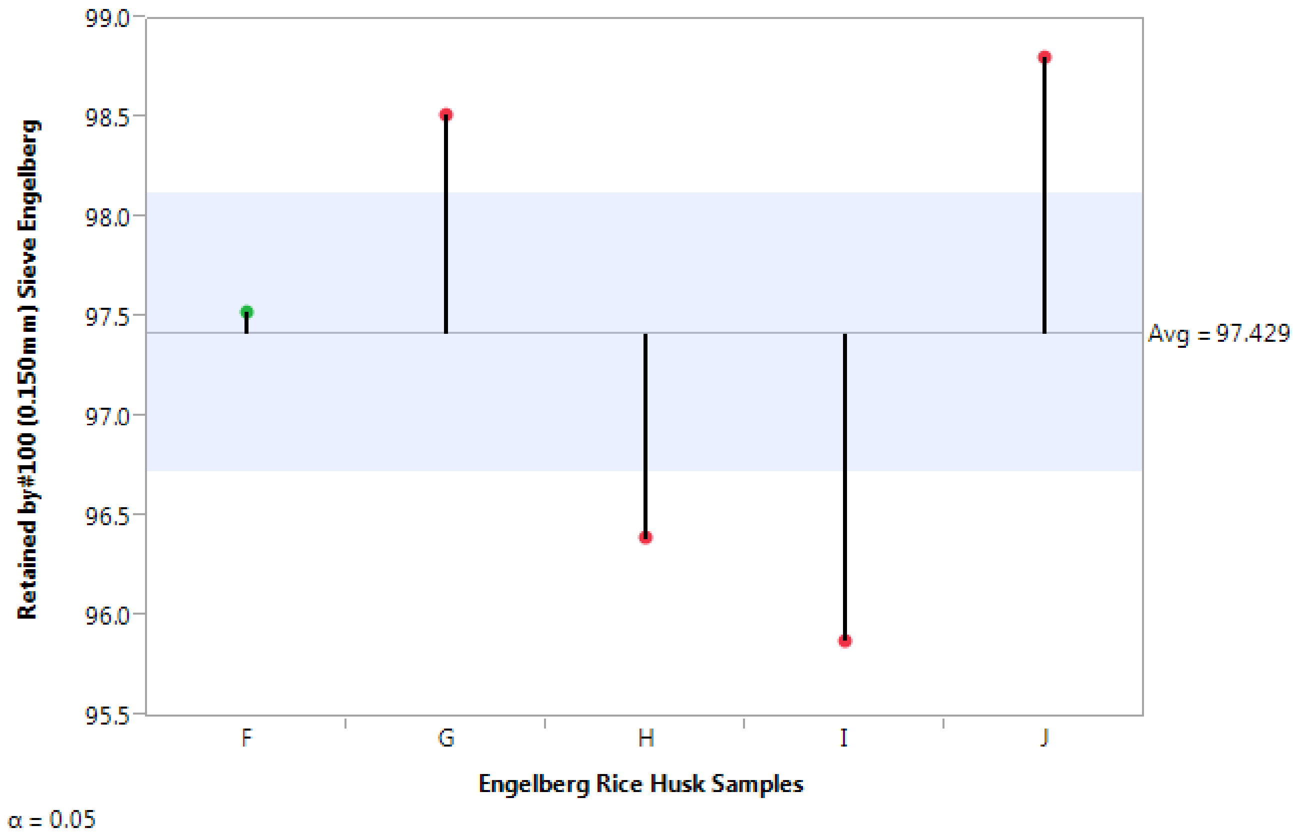


Figure 5.19. Analysis of means of % cumulative Engelberg rice husk retained by Sieve #100 (0.150 mm)

Table 5.11 ANOVA means of % cumulative retention by sieve #100 (0.150mm)

Level	Number	Mean	Std Error	Lower 95%	Upper 95%
F	3	97.5300	0.25588	96.960	98.100
G	3	98.5233	0.25588	97.953	99.093
H	3	96.3967	0.25588	95.827	96.967
I	3	95.8833	0.25588	95.313	96.453
J	3	98.8100	0.25588	98.240	99.380

The prediction model for percentage of Engelberg rice particles retained by a specific sieve was a 2nd order polynomial fit with R-square value of 0.82 (Figures 5.20 & 5.21). The model parameters showed that the sieve size is a significant parameter both at the linear and quadratic levels as shown in Table 5.12. This model provides a tool to estimate particle size distribution of the Engelberg rice husk based on sieve size of interest, making it an important tool for the design of handling and thermochemical equipment.

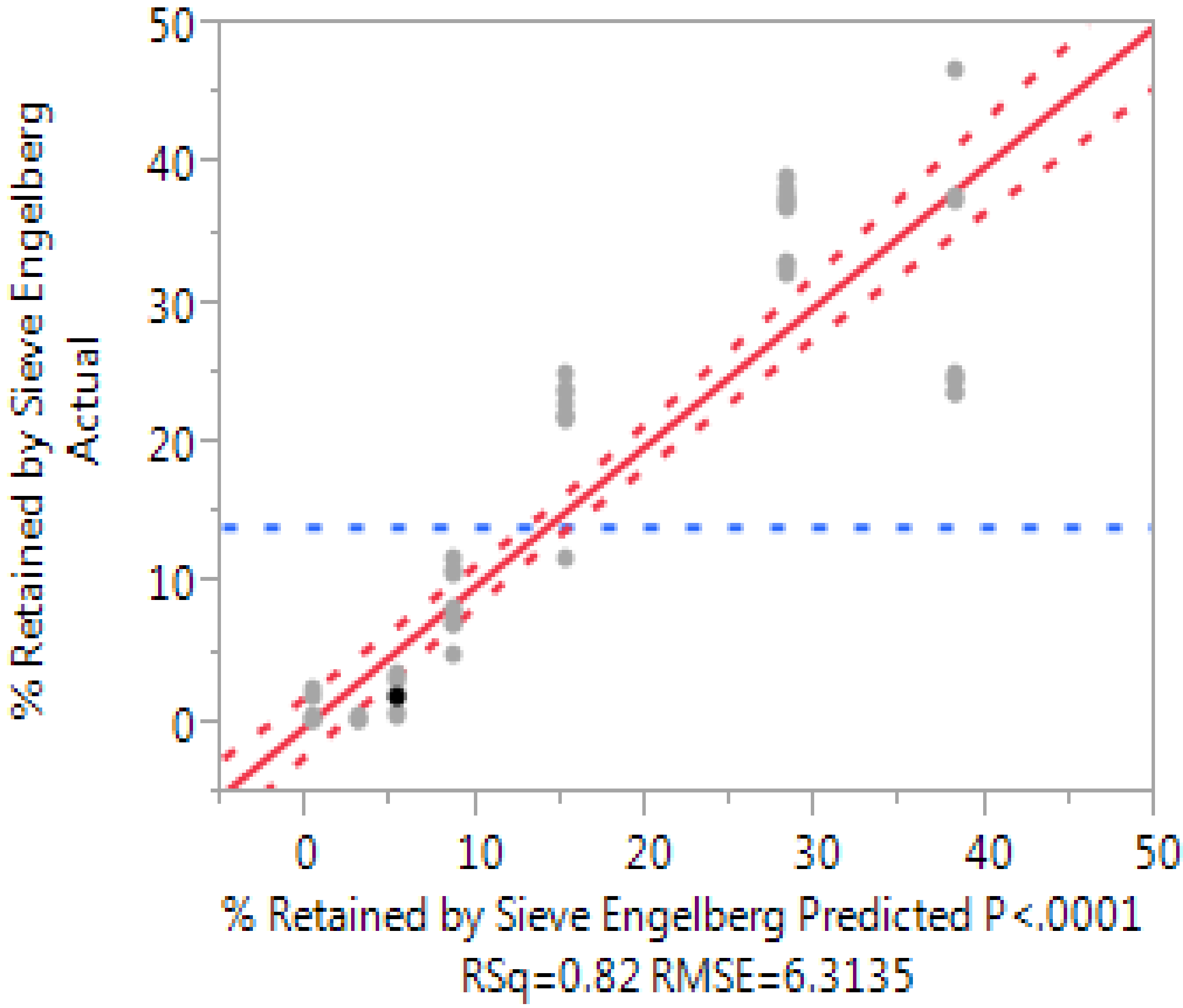


Figure 5.20. Prediction plot of the amount of Engelberg particles collected by individual standard sieves

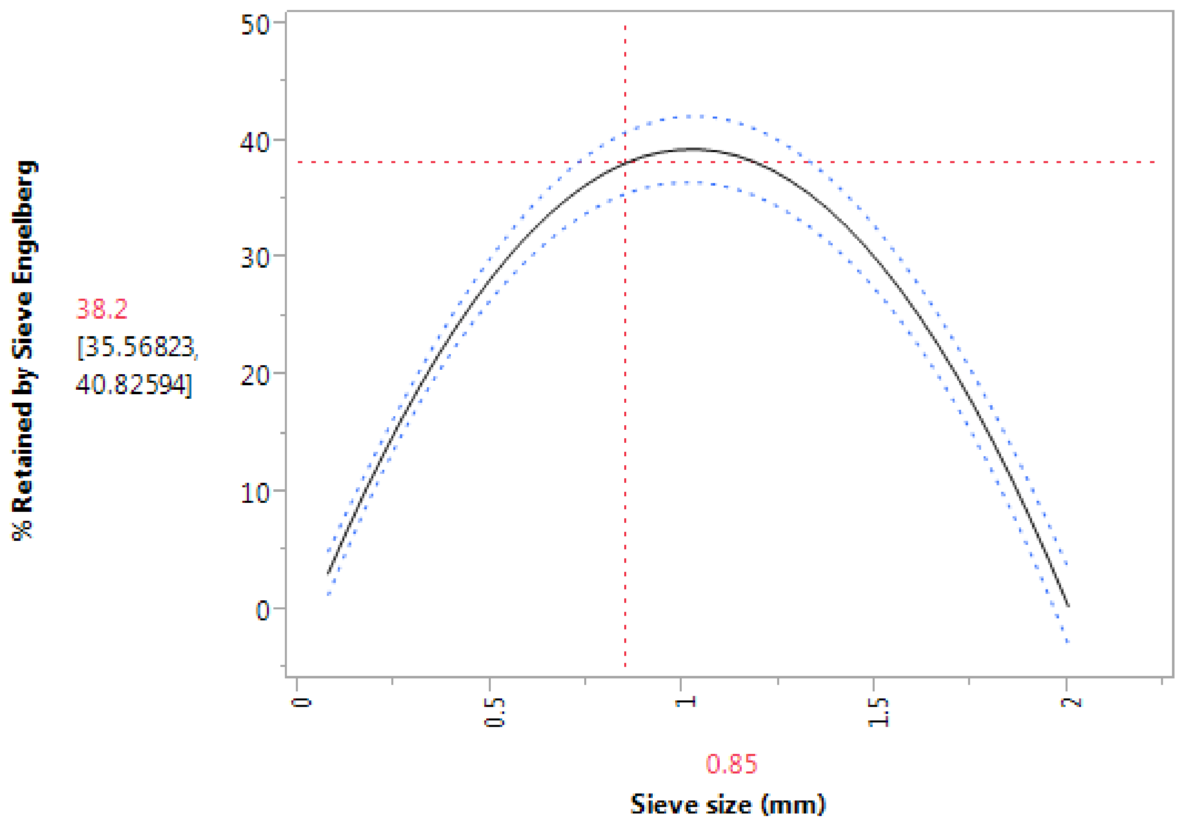


Figure 5.21. Prediction model profile of the amount of Engelberg particles collected by individual standard sieves

Table 5.12 Parameter estimates of predicted model of the amount of Engelberg particles collected by individual sieves

Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	9.7143	0.844	11.51	<.0001*
Sieve size (mm)	37.6137	2.040	18.44	<.0001*
(Sieve size (mm)-0.55698)*(Sieve size (mm)-0.55698)	-40.6350	1.906	-21.32	0.0001*

Figures 5.22 and 5.23 and Table 5.13, showed the prediction plot, prediction model, and prediction parameters of the cumulative Engelberg particles by a standard sieve, which included the amount collected by sieves that have larger openings that are above the standard sieve. A polynomial (quadratic) predicted plot with R-square value of 0.97 was

obtained. The model predicted that 95% of the particles of the Engelberg rice husk samples will be collected by a sieve size=0.158 mm, thus indicating that Standard sieve size #100 (0.150 mm) will collect more than 95% of the rice husk samples by weight (Figure 5.23).

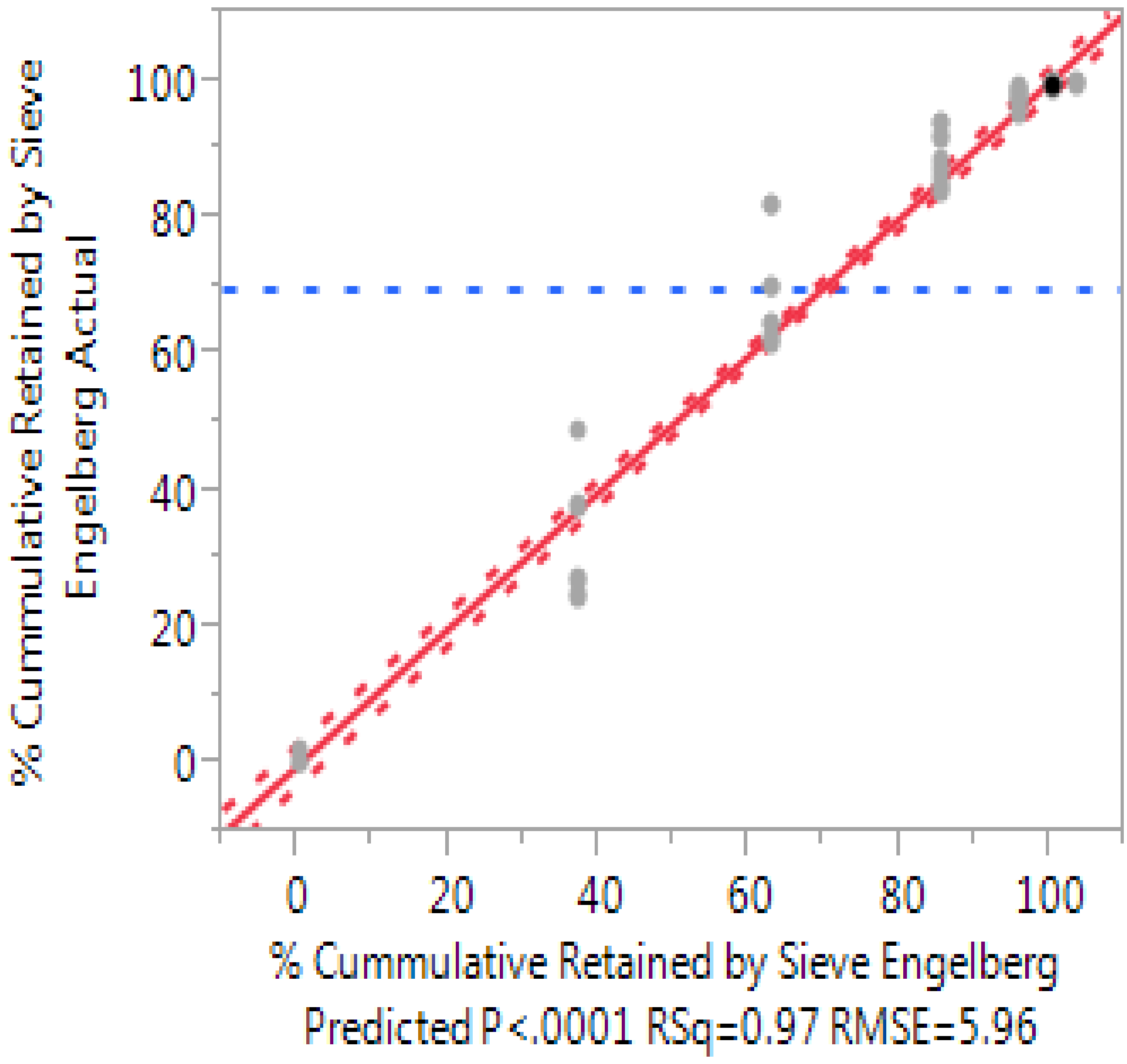


Figure 5.22. Prediction plot of cumulative Milltop particles collected by individual standard sieves husk

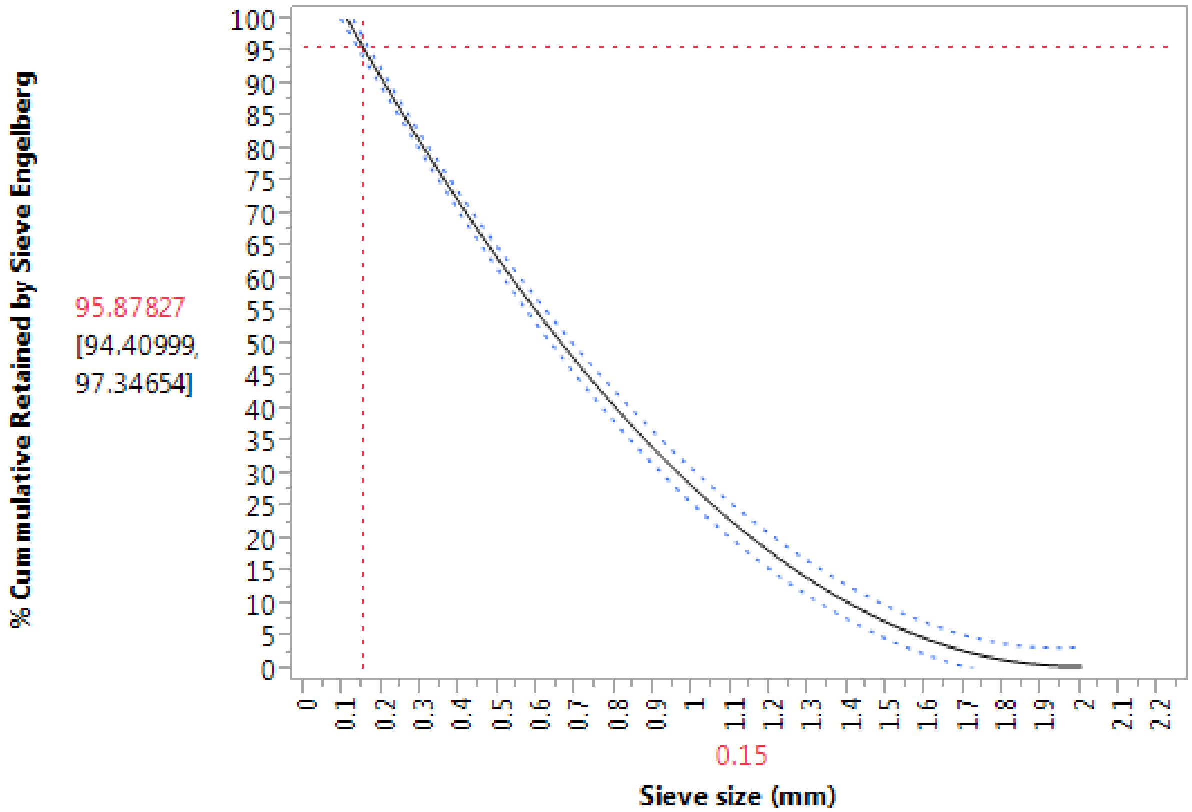


Figure 5.23. Prediction model profile of cumulative Engelberg particles collected by individual standard sieves

Table 5.13 Parameter estimates of predicted model of cumulative Milltop particles collected by individual sieves

Term	**Estimate**	**Std Error**	**t Ratio**	**Prob>|t|**
Intercept	103.220	0.8023	128.65	<.0001*
Sieve size (mm)	-80.491	1.9226	-41.87	<.0001*
(Sieve size (mm)-0.55698)*(Sieve size (mm)-0.55698)	28.176	1.8054	15.61	<.0001*

5.6.3 Bulk density

The bulk densities of the rice husk samples showed that the mill type played a big role on the density of the rice husks. The bulk densities of the Milltop and the Engelberg rice husks samples were 120.88 - 155 kg/m^3 and 506.95 – 579.18 kg/m^3, respectively. Zhang et al. (2012) reported that particle distribution significantly affects bulk densities of plant materials just as observed in this analysis. The bulk densities of the Engelberg rice husks were much higher than that of the Milltop rice husks.

5.6.3.1 Bulk density of Milltop rice husk

The Milltop rice husk mean bulk density was 135.38 kg/m^3 with standard deviation of 14.95 kg/m^3, and ranged from 120.88 to 155.48 kg/m^3. Samples A and E have the lowest bulk densities as shown in Figure 5.24 and Table 5.14.

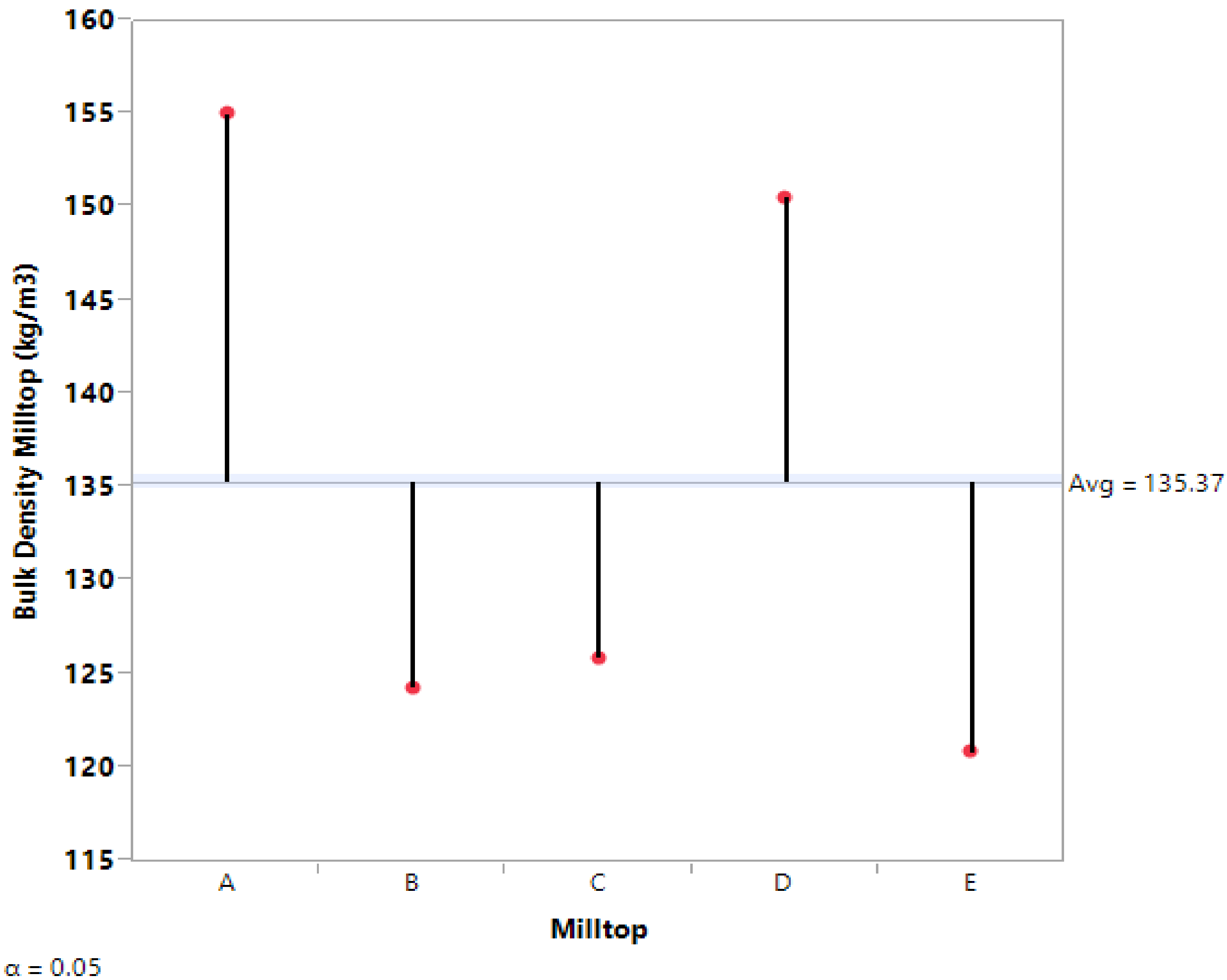


Figure 5.24. Analysis of means of Milltop rice husks bulk density

Table 5.14 ANOVA means of bulk densities of Milltop rice husks

Level	Number	Mean	Std Error	Lower 95%	Upper 95%
A	3	155.128	0.13781	154.82	155.43
B	3	124.319	0.13781	124.01	124.63
C	3	125.956	0.13781	125.65	126.26
D	3	150.589	0.13781	150.28	150.90
E	3	120.883	0.13781	120.58	121.19

5.6.3.2 Bulk density of Engelberg rice husk

The mean bulk density of the Engelberg rice was husk 546.62 kg/m^3 with standard deviation of 30.53 kg/m^3, and ranged from 506.95 to 579.18 kg/m^3. Samples I and J have the lowest bulk densities as shown in Figure 25 and Table 5.15.

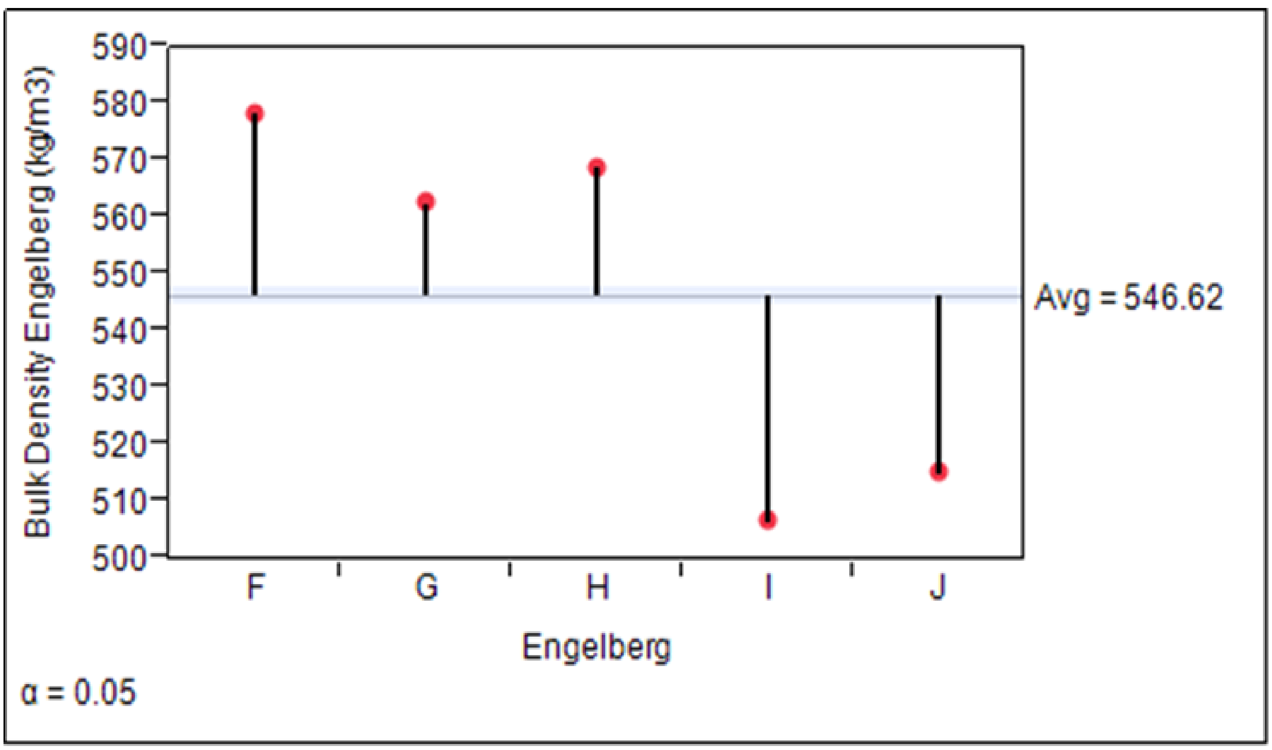


Figure 5.25. Analysis of means of Engelberg rice husks bulk density

Table 5.15 ANOVA means of Engelberg rice husk bulk densities

Level	Number	Mean	Std Error	Lower 95%	Upper 95%
F	3	578.664	0.56058	577.41	579.91
G	3	562.983	0.56058	561.73	564.23
H	3	569.092	0.56058	567.84	570.34
I	3	506.960	0.56058	505.71	508.21
J	3	515.389	0.56058	514.14	516.64

5.6.4 Particle density

The particle densities of the rice husk samples ranged from 168.31 to 221.97 kg/m^3 for the Milltop, and 523.38 to 616.62 kg/m^3 for the Engelberg rice husks. This result further demonstrates that transportation, handling, and densification cost may be more economical for the Engelberg mill rice husks, because it is denser.

5.6.4.1 Particle density of Milltop rice husk

The mean particle density of the Milltop rice was 192.82 kg/m^3 with a standard deviation of 21.88 kg/m^3. Samples C and D have the highest particle densities with mean densities of 220.69 and 212.12 kg/m^3, respectively. The samples with lowest densities were samples A and E with mean densities of 168.70 and 166.49 kg/m^3, respectively. The results showed that sample E, the NERICA variety has the lowest density (Figure 5.26 & Table 5.16). This interesting result, confirmed the nature of sample E, observed during microstructural analysis and particle size distribution. Sample E did not have trichomes; and the lemma and palea were its main components; it also had few cracked kernels, some broken pieces, and small entrained subcomponents including bran and rice embryo.

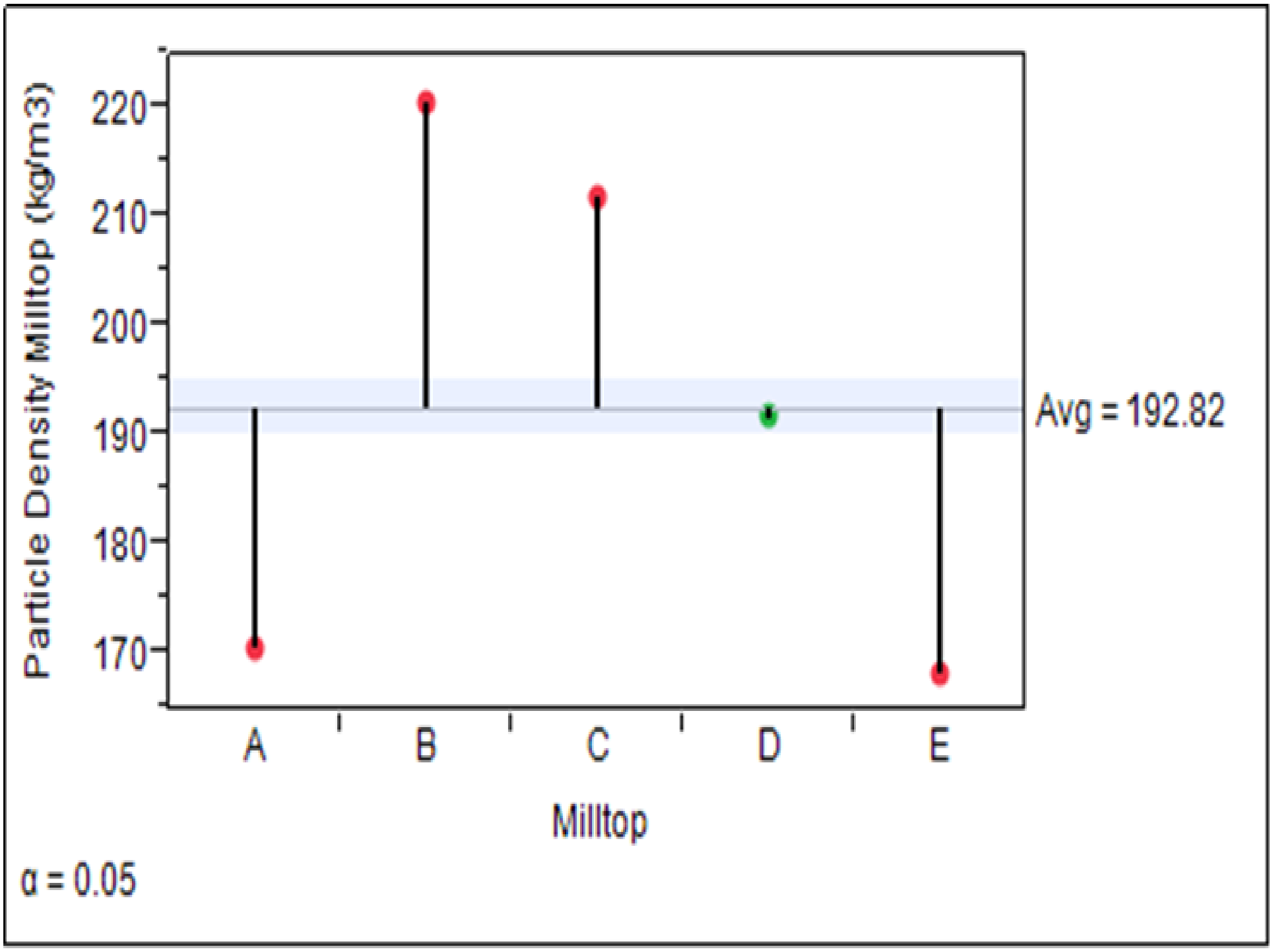


Figure 5.26. Analysis of means of Milltop rice husks particle density

Table 5.16 ANOVA means of Milltop rice husks particle densities

Level	Number	Mean	Std Error	Lower 95%	Upper 95%
A	3	170.827	0.95660	168.70	172.96
B	3	220.690	0.95660	218.56	222.82
C	3	212.121	0.95660	209.99	214.25
D	3	191.975	0.95660	189.84	194.11
E	3	168.491	0.95660	166.36	170.62

5.6.4.2 Particle density of Engelberg rice husk

The mean particle density of the Engelberg rice husk was 569.88 kg/m^3 with a standard deviation of 34.15 kg/m^3. Sample F has the highest particle density, while sample J has the lowest (Figure 5.27 & Table 5.17).

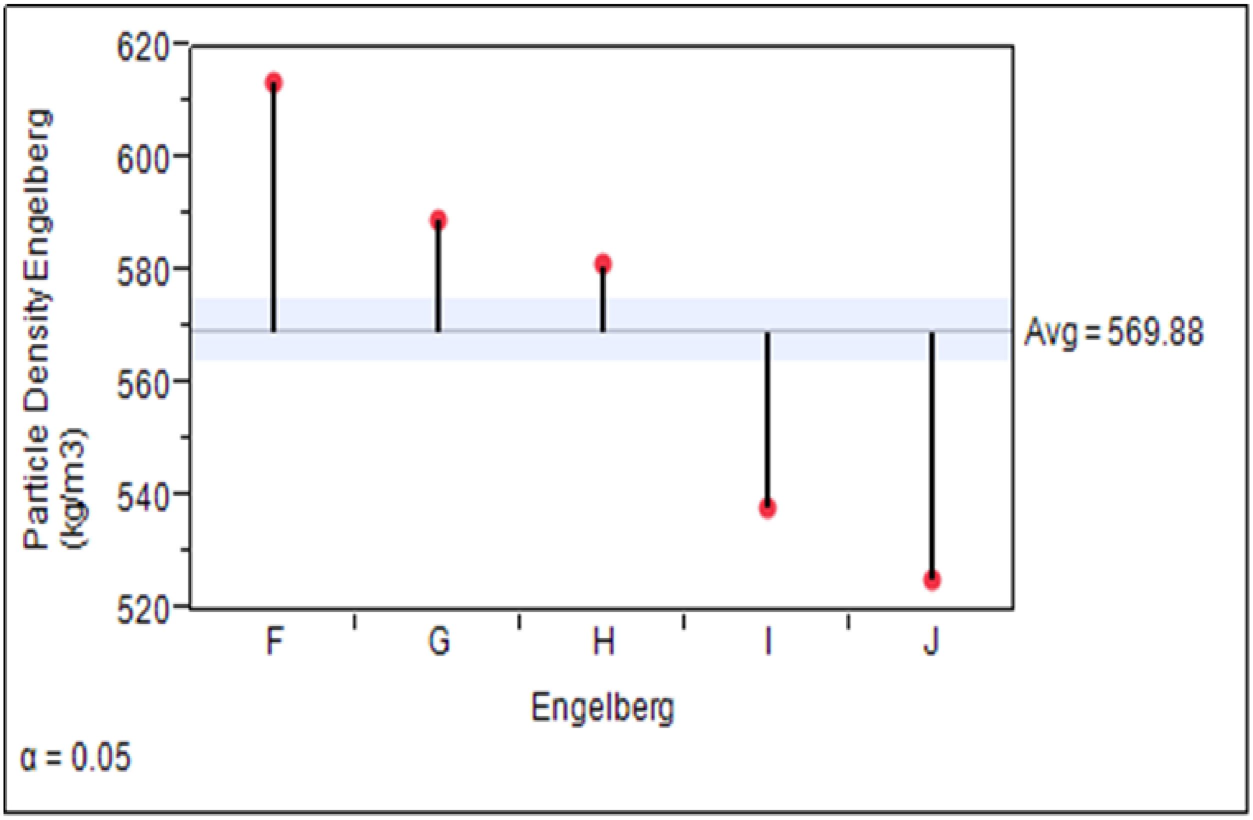


Figure 5.27. Analysis of means of Engelberg rice husk particle density

Table 5.17 ANOVA means of % cumulative retention by sieve #100 (0.150mm)

Level	Number	Mean	Std Error	Lower 95%	Upper 95%
F	3	613.896	2.0022	609.43	618.36
G	3	589.712	2.0022	585.25	594.17
H	3	581.576	2.0022	577.11	586.04
I	3	538.552	2.0022	534.09	543.01
J	3	525.679	2.0022	521.22	530.14

The low density observed for sample J, could be attributed to the high content of immature grains. Microstructural analysis has shown that sample J has large amount of immature grains that might have contributed to its lower density (Figure 5.28).

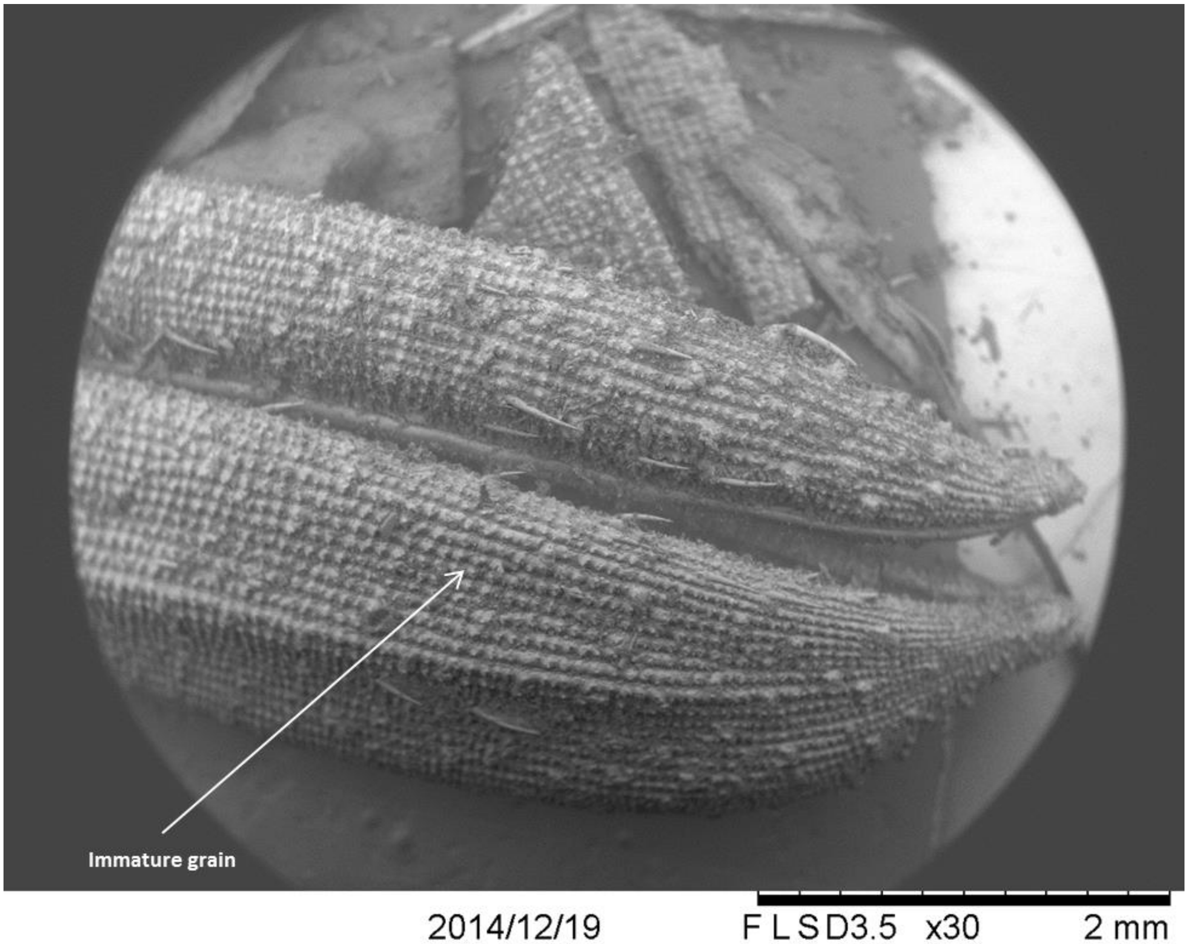


Figure 5.28. Immature grain in sample J

5.7 Conclusions

The particle size distribution results showed that the Milltop rice husks particles were much larger than the Engelberg rice husks with 95% of the particles larger than the #20 (0.850mm) Standard sieve. The particle size distribution of the Milltop rice husk can be estimated by Standard sieves within sizes of #20 and #10 (within 0.850 to 2.00 mm), due to the fact that the major components of these samples were the lemma and palea outer structures of the rice paddy, with very small amount of the inner sublayer and small pieces of broken kernels, that were collected by the smaller opening Standard sieves. However, the result observed also showed that based on variety, broken pieces of the lemma and palea could also contribute to the amount of smaller pieces collected. The prediction model for the Milltop rice husk obtained was a 2nd order polynomial with R-square=0.86, predicting the amount of rice husk particles that will be collected by individual sieves within the range tested. The smaller particles of Engelberg rice husk samples were retained in all the Standard sieve sizes used within sieve size #200 to #10, with 95% of the particles retained by Standard sieve #100 (0.150 mm). The presence of large broken rice kernels and immature grains was found to correlate with the above average retention of samples by #20 and #35 Standard sieves. A 2nd order polynomial prediction model of R-square value=0.82, predicting the amount of Engelberg rice husk particles that will be retained by individual sieves within the range was obtained. The models from these experimental results, including the cumulative models developed, will be important tools for designing rice husk handling, densification, and thermochemical equipment, which require particle distribution as one of the design parameters.

The bulk and particle densities of the Milltop rice husk were found to be much smaller compared to the Engelberg rice husk samples, due to the fact that the Engelberg samples contains more broken kernels and sublayer components, as a result of the single step metal roller milling process. The bulk density of the Milltop rice husk ranged between the means of 120.883 and 155.128 kg/m^3 compared to the Engelberg bulk density within the range of 515.389 and 578.664 kg/m^3. The particle density of the Milltop rice husk ranged between the means of 168.491 and 170.827 kg/m^3 compared to the Engelberg rice particle density with a range of 525.679 and 613.896 kg/m^3. The bulk and particle densities showed that the handling and transportation of the raw Engelberg rice husk will be more economical than the Milltop, because of its higher density. The Milltop may require onsite densification to increase density and reduce handling volume and transportation cost.

5.8 Recommendations

The physical characterizations of the Milltop and Engelberg rice husks have shown that the two rice husks have unique characteristics that define them as a group. The parameters developed in this research will be important tools for designing handling, densification, and thermochemical equipment. Particle analysis of the rice husk samples revealed important pre-harvesting and post-harvest processes issues that ultimately could have affected rice kernel yield. The utilization of this research procedure using Standard sieves #10 and #20 for the Milltop, sieves #20 and # 35 for the Engelberg will be valuable during quality assessment of rice production.

Sieves #10 and #20 can be related to the flowability of the Milltop samples due to the presence of structures such as trichomes, and the existence of breakages of the rice husk outer shells due to milling gap, variety characteristics, or other conditions that could be defined by further investigations. For the Engelberg rice husk, sieves #20 and #35 could be used to investigate whether there were pre-harvesting and post-harvesting processing issues. High retention by sieve #20 for the Engelberg could indicate the existence of larger particles, which can be correlated to high contents of large broken rice kernels or high content of immature grains; which can both be attributed to pre-harvesting and post-harvesting sub-optimal processes.

Bulk and particle densities obtained showed that in the case of the Engelberg, the densities were higher because of the high concentration of smaller and denser particles of the inner sublayer and broken kernels; this could make it economically feasible to package and transport the bulk Engelberg to a central location for preprocessing and densification of the fuel feedstock. However, in the case of the Milltop rice husk, onsite preprocessing and densification at the mill-site will be ideal, in order to reduce the cost of transportation of the light and bulky Milltop rice husk.

5.9 Contribution of this research

The physical parameters and models that define these two groups of rice husks were defined and developed. There has not been any research to date comparing the physical characteristics of these two rice husks. The research will motivate the design of handling and thermochemical equipment that will utilize the two rice husks as fuel feedstock.

5.10 Limitation of study

This study was based on the analysis of ten different samples of Milltop and Engelberg produced rice husks obtained from the sub-Saharan country of Uganda. The results obtained can be effectively used as estimation parameter tools for design of thermochemical and handling equipment for Milltop and Engelberg rice husks. The study also showed that certain physical characteristics could be possibly related to cultivation methods, rice variety, harvest, and post-harvest conditions. However, further research on the direct effects and correlations of the physical characteristics will be necessary, in order to effectively correlate certain conditions to the physical characteristics of the rice husk. This investigation opens up research opportunities for the utilization of physical characterization for the development of many empirical and semi-empirical models, using large quantity of data, for predicting quality of many processing steps in the rice production.

Connecting text to Chapter VI

Chemical characterization of biomass is necessary in order to utilize it appropriately as a biofuel feedstock; as different biomass exhibits varying chemical characteristics. Proximate composition including starch content, protein content, and fat content are important parameters that are required during the design of handling and energy conversion systems that will utilize effectively the biomass as biofuel feedstock. Utilization of the Engelberg and Milltop rice husks as fuel will increase the sustainability of rice processing in rural sub-Saharan Africa, by reducing energy cost, providing employment for the craftsmen and as well as, reduce the over-exploitation of firewood. The chemical characterization including SEM and FT-IR will provide important information about the Engelberg and the Milltop rice husks. No studies have been reported comparing the chemical characteristics of the Engelberg and Milltop rice husks.

Chapter: VI: Chemical characterization of the Engelberg and Milltop processed rice husks

6.1 Abstract

Rice husk is an abundant lignocellulosic biomass waste that can be used as a feedstock for biofuel production. Chemical properties of rice husks from two different milling machines, the Engelberg and the Milltop, from different regions of Uganda were analyzed. The starch contents of the biomass were found to be between 0.89 to 7.97 %, the protein contents were found to range between 2.29 to 6.30%, and the fat contents ranged between 0.29 to 4.16%. Milltop samples A and E have comparatively higher starch contents than the other Milltop samples. However, most of the Milltop samples have smaller amounts of proximate starch, protein, and fat compared to the Engelberg samples. SEM of sample A revealed that there were a lot of broken rice in the inner shell, and also quite a few of the shells had cracks and others completely broke off during the milling process, which might have likely caused the breakage of the milled rice that was entrained in the husk; thereby increasing the starch content. The fat contents of the Milltop rice husk samples were found to be insignificant compared to the Engelberg samples; ranging from 0.29 to 0.81% and 1.65 to 4.16%, respectively. FT-IR measurements of the rice husk samples showed the presence of both saturated and unsaturated hydrocarbon moieties, with a broad, strong peak near 3300 cm^{-1}. This also suggested the presence of alkynes (≡CH). The strong peak around 1650 cm^{-1} indicated the C=O stretching of a carbonyl group in the sub-Saharan rice husks. The strong peak at around 1025 cm^{-1} indicated the strong presence of carboxylic acids, ethers and esters. The FT-IR results obtained also showed that the Engelberg and Milltop rice husks spectra have unique characteristics that defined them as a group; with the key difference being the quantity of the proximate components; confirming what was observed during the starch, protein and fat analyses. Chemical analysis and the FT-IR spectra showed that both milling machines significantly affected the chemical properties of the rice husks. The FT-IR spectra were compared with the spectra obtained by Ndazi et al. (2007) for the inner and outer surfaces of rice husk and it was found that the Engelberg rice husk showed higher peaks for esters and amides, indicating that the Engelberg rice husk has more of the inner and sublayer components than the Milltop

rice husks; this was also confirmed by the chemical composition analysis. FT-IR analysis also distinguished the samples with higher immature grains from the rest of the rice husk samples; clearly indicating possible harvesting timing issues, with respect to the collected samples.

6.2 Introduction

Rice husk consists of the outer protective structure that consists of two shells – the lemma and palea. These shells enclose and protect the inner components including the translucent pericarp, the sublayer soft protective elements of the aleurone and sub-aleurone layers enclosing the rice kernel that is attached to the embryo. The outer protective lemma and palea shells have high silicon contents with protective cones, and in some varieties, especially the *Oriza globemmera* that is native to sub-Saharan Africa, have needle-like structures called the trichomes that protect the shells against pest and other harsh environmental conditions. The inner sublayers including the pericarp, and aleurone and sub aleurone layers are soft protectors of the kernel and embryo/germ, and have higher lipid content.

Chemical characteristics of the rice husk and all the rice paddy components are defined by the functional purpose of their components in propagating the reproduction and life cycle of the rice plant. The hard outer components are made up of cellulose, hemicellulose, and lignin; interlaced in a silicon matrix, protecting the rice paddy (Bhadrawaj, 2002; Bhadrawaj et al., 2004; Ndazi et al., 2007). The translucent pericarp, and the sublayer components, also called bran, consists of cellulose, hemicellulose, and lignin, interlaced with lipids and proteins that are providing a soft protective housing/shell to the high-carbohydrates kernel and the high protein embryo/germ.

During the milling process, the key objective is to obtain the high carbohydrate kernel with minimal breakage or deformation as a staple for human diet. The milling process, hence, involves the splitting of the lemma and palea shells to release the kernel covered by the inner sublayer components, as an initial process. The released covered kernel, also called brown rice, is then polished to remove the sublayer components and also separating the premier product - the kernel from the embryo/germ.

Reviewing the milling process, based on the by-products produced, the de-shelling or de-husking process produces the high silica lemma and palea as key by-products; and the second process produces the sublayer component that is composed of bran. In the Engelberg milling process the two processes are carried out simultaneously in what is termed as a single pass process using rollers that de-husk and polish the kernel in one step. While in the Milltop milling process, the two processes are carried in two stages: de-husking to remove the outer shell and polishing to remove the sublayer bran component.

Chemical characterization of all lignocellulosic biomass is necessary in order to utilize biomass appropriately as a feedstock for biofuel and chemical production, because it exhibits varying properties different from traditional fossil fuels and fossil fuel derivatives (Naik et al., 2010). Although there have been several chemical analyses of rice husks in the literature (Mansaray and Ghaly, 1997; Ndazi et al., 2007), no study has been carried out to analyze and compare the properties of the Engelberg and Milltop produced rice husks. In sub-Saharan Africa, these two rice husks are potentially the most important source of biofuel from agricultural waste in the region. This research will provide the necessary information on how to utilize this abundant biomass, which is a danger to the ecosystem if left unused; hence, increasing the sustainability of rice postharvest processing in sub-Saharan Africa.

6.3 Literature review

6.3.1 Starch analysis

Starch is an important component of agricultural biomass. Its binding characteristics contribute to effective densification of biomass without the need of additional binders. Also lignocellulosic biomass with high starch content is attractive for bioethanol production using biochemical processes. Starch determination methods can be broadly grouped into acid hydrolysis or enzymatic procedure. Acid hydrolysis can only be applied to pure starch samples and thus has limited applications. To reliably quantify the amount of starch in a biomass, the AOAC Official Method AOAC 2002.02 (2002) and AACCI Approved Method AACCI 32-40.01 (2001) can be used. The starch content in rice husk is however very small. Champagne (2004) and Bledzki et al., (2010) reported rice husk starch contents of 1.5% and 3%, respectively. However, milling methods, especially the degree of milling (DOM), can increase the starch content significantly due to the amount of broken rice and bran the biomass may contain.

6.3.2 Protein analysis

Protein is another component of biomass that acts as a natural binding agent within the biomass. It facilitates densification of biomass at room temperature without the addition of binding agents. However, the nature of the protein determines the adhesive strength of the protein. Since protein in biomass naturally exists as complex long-chain molecules, its effectiveness as a binder can be improved by treatment using heat or chemicals to break up the long chains into smaller ones. Treated or modified proteins from biomass such as rice bran and soybean have been used as adhesives in the production of particle board from rice husks (Pan et al., 2006; Ciannamea et al., 2010).

Proteins in rice are found in different parts of the paddy including the endosperm cells (where large molecules of glutelin bind strongly to the starch granules with strong disulphide and/or hydrophobic bonds), the kernel, the husk and the bran (Seung-Taik, et al., 1999; Agboola et al., 2005). Rice protein can be classified into four groups: alkali-soluble glutelins, water-soluble albumins, salt-soluble globulins and alcohol-soluble prolamins (Landers et al., 1994). The protein content in rice husk comes from the inner layer of the rice husk and the broken rice kernels entrained in the rice husk during milling. Chen et al. (1998) found that kernel thickness and degree of milling (DOM) have significant effects on the protein content of the rice kernel, and consequently, of the rice husk which is the by-product of milling.

The analysis of the protein content in the Engelberg and Milltop rice husk will be important in determining the optimal method on how to densify these two rice husks. The normal procedure of determining protein content is by measuring the amount of nitrogen in the biomass and then multiplying that nitrogen content by a determined factor (6.25 for most biomass). The nitrogen content in biomass can be determined chemically or thermochemically. Bledzki et al. (2010) determined the protein content of rice and wheat husk chemically, by dissolving the samples in sulphuric acid in the presence of potassium sulphate; and then titrated the product with hydrochloric acid and calculated the protein content based on the concentration of ammonium hydroxide. In this study, the protein content of the rice husk samples will be determined using the Leco TruSpec N analyzer, an instrument that determines nitrogen content of a variety of materials including foods, feeds, oilseeds, fertilizers, meat and oils. Leco TruSpec is a three stage thermochemical analyzer. The first stage is the purging stage, where the encapsulated capsule is loaded and purged. The second stage involves the combustion of the sample at 950°C in an oxygen furnace and then in an afterburner at 850°C. The combustion gases are then filtered, cooled in a thermo-electric cooler, dehydrated and then stored in ballast. The final stage begins with the injection of oxygen into the ballast and mixing the combustion gases. The homogenous gases are then purged into a 3cc aliquot loop and then transferred to a helium carrier that is swept through a hot copper to remove oxygen and change NO_x to N_2, and then through "Lecosorb" and "Anhydrone" to remove CO_2 and H_2 respectively. A thermal conductivity cell is then used to determine the nitrogen content. The protein content is then calculated by multiplying it with a factor of 6.25.

6.3.3 Fat analysis

Fat content is another important component of agricultural biomass. Fat can have either positive or negative effect on the viability of agricultural biomass as an energy or biomaterial feedstock. The amount of fat in the biomass affects its compaction characteristics. Kaliyan and Morey (2010), reported that fat greater than 6.57% reduces durability of biomass because it acts as a lubricant between the particles, as well as, between the die wall and the particles reducing the effective pressure within the die that results in lower durability. Fat's hydrophobic nature can also reduce the binding capabilities of water soluble binders such as starch, protein, and fibre (Kaliyan and Morey, 2010). Fat also has some positive influence on the densification of biomass since the higher fat content increases the hydrophobic properties of densified biomass.

Fat in rice paddy can be classified as either starch or non-starch lipid. Starch lipids are found in the germ associated with protein and starch granules. Non-starch lipids are found in the aleurone, subaleurone, germ and the hull (to a smaller extent) of the rice paddy (Champagne, 2004). Depending on the degree of milling, most of the non-starch lipids are removed during the milling process and become part of the mill by-products.

Based on these facts, it has been suggested that the degree of milling could be determined based on the grain surface lipid quantification (Champagne, 2004).

6.3.4 Fourier Transform Infra-Red (FT-IR) spectroscopy

Fourier Transform Infra-Red (FT-IR) spectrometry can be used to determine the chemical functional groups that are important in the characterization of biomass. Naik et al., (2010) used FT-IR to characterize Canadian biomass and identified the hemicellulose, cellulose and lignin contents of wheat straw, barley straw, flax straw, timothy grass, and pinewood samples. Adapa (2011) quantitatively predicted lignocellulosic components of non-treated and steam exploded barley, canola, oat and wheat using FTIR.

The chemical components of both the outer and the inner surfaces of rice husk were found to be the cause of the weak adhesion between rice husk and binders. The inner surface of rice husks is smooth and contains natural fats that affect adhesion properties of rice husk and binders both physically and chemically (Ndazi et al., 2007). The outer surface of rice husk is relatively rougher and contains high amounts of the silicone-cellulose membrane responsible for insufficient bonding on rice husks surfaces and various binders (Ndazi et al., 2007). Ndazi et al., (2007) studied the inner and outer surface of rice husk, before and after treatment of rice husk with NaOH using FT-IR and were able to identify changes due to frequency shifts and peak disappearance at certain frequencies after treatments. In this study, FT-IR analysis of the sub-Saharan rice husk samples will provide important information on the chemical components present in the rice husks. High absorbance for specifics components will provide the relative quantification of the amounts of each of the components among different samples.

Certain types of compounds give strong, broad absorptions, which are very prominent in the IR spectrum. The hydrogen-bonded OH stretching bands of alcohol, phenols, and carboxylic acids are easily recognized at high frequency range (3700-3100 cm^{-1}). NH_3^+ group of amino acids gives a very broad and unsymmetrical band that extends several hundred wavenumbers. Broad bands associated with bending of NH_2 or NH groups of primary or secondary amines are found at the low-frequency end of the spectrum.

Hydrocarbons can be identified by absorption in the region between 3100 and 2800 cm^{-1}. Aromatic or unsaturated aliphatic =CH groups are identified by absorptions between

3000 and 3100 cm^{-1}. If the absorption is entirely above 3000cm^{-1}, the compound is probably aromatic or contains only =CH or =CH_2 groups. Absorptions above and below 3000 cm^{-1} indicate the presence of both saturated and unsaturated or cyclic hydrocarbon moieties, with strong bands between 1000 and 650 cm^{-1} as confirmation identifying of alkenes or aromatic structures. Sharp bands near 725 cm^{-1} or 1440 cm^{-1} are indications of linear chains containing 4 or more CH_2 groups (Lambert et al. 2011).

Oxygen-containing compounds are important components of lignocellulosic biomass. A strong, broad band between 3500 – 3200 cm^{-1} is usually due to water and the hydrogen-bonded OH stretching mode of an alcohol or a phenol. In the absence of hydrogen-bonding, the OH stretching bands is sharp and at higher frequencies (3650-3600 cm^{-1}). Carboxylic acids give very broad OH stretching bands between 3200 and 2700 cm^{-1}, with likely, sharp peaks near 3300 cm^{-1} due to CH stretching vibrations.

FTIR characterization of lignin can be based on the peaks within the lignin finger print region: 1800 cm^{-1} to 800 cm^{-1} of the IR spectrum. The most important peaks that characterize lignin in this region are 1593 and 1506 cm^{-1} indicative of aromatic skeletal vibrations, where 1458 and 1420 cm^{-1} are CH deformations, 1328 cm^{-1} represents syringyl ring plus guaiacyl ring, 1234 cm^{-1} is indicative of syringyl ring and C=O stretching, and 1120 cm^{-1} is indicative of the presence of aromatic skeletal vibrations. (Zhou et al., 2011). The strong peak at around 1025 cm^{-1} indicates the strong presence of alcohols, carboxylic acids, ethers and esters. Esters have bands from both C=O and C-O-C groups, but none from the OH group. Alcohols have bands from both OH and C-O groups, but no C=O stretching band. Carboxylic acids contain bands in all three regions (Lambert et al., 2011). Also the secondary peak around 1100-1217 cm^{-1} indicates the presence of silica in the form of cellulose-silicates (Ndazi et al., 2007).

Bands between the regions of 3500-3300 cm^{-1} may indicate the presence of primary and secondary amides which contain nitrogen, but that should be confirmed by a strong doublet in the IR spectrum centered near 1640 cm^{-1} or a sharp band near 2200 cm^{-1} which is a characteristic of a nitrile group. The C=O (carbonyl) stretching region is one of the most important regions of the spectrum for structural analysis (Lambert et al., 2011). Most organic compounds that contain C=O groups show very strong absorption in the range of 1850 to 1650 cm^{-1}. The actual position of the peaks within this range is characteristic of those compounds.

Silica content in biomass greatly affects the energy content and the design of the ash handling system of thermochemical converters. Low silica containing fuels have higher energy content, and are less abrasive to the structural components of the reactors and the conveyor systems. The silica content in the biomass can be determined using FT-IR analysis. The origin or type of soil where the parent plant was grown may also be determined. The FTIR information is important for the utilization of the rice husk as a biofuel feedstock, as well as, for identification of postharvest processing inefficiencies and how they may be identified and be resolved.

6.4 Objectives

6.4.1 Overall Objective

The overall objective of this research was to study the chemical characteristics of the Engelberg and Milltop rice husks, in order to determine the chemical process parameters that are important for their use as bio-energy feedstocks.

6.4.2 Specific objectives

The specific objectives of this research were:

1. To study the proximate starch composition of the Engelberg and Milltop rice husks
2. To study the proximate protein composition of the Engelberg and Milltop rice husks
3. To study the proximate fat composition of the Engelberg and Milltop rice husks
4. To utilize FTIR-ATR to identify the chemical characteristics of the key chemical groups that constitute the Engelberg and Milltop rice husks

6.5 Materials and Methods

6.5.1 Equipment

The equipment used for this research included: Hitachi T3000 scanning electron microscope, Leco Truspec thermochemical nitrogen analyzer, Soxhlet extractor, and FTIR-ATR (Thermo-Scientific Nicolet-is5).

6.5.2 Materials

Rice husks obtained from different regions of Uganda were used for this study. The rice husk samples were collected from milling stalls that process rice from established farms where paddy is grown, with known type of rice variety, and known type of milling machine used to de-husk and polish the grain. The identification of the husk samples is listed in Table 6.1.

Table 6.1 Rice husk samples identification

Sample	Source	Variety	Farm	Mill Type
A	Doho irrigation scheme	Kaiso	Farm 3	Milltop SB30
B	Doho irrigation scheme	Kaiso	Farm 1	Milltop SB30
C	Lira (Abolete)	Super	Abolete	Milltop SB30
D	Doho irrigation scheme	Kaiso	Farm2	Milltop SB30
E	Nuya- Acholi	NERICA-1	Nuya-Acholi	Milltop SB30
F	Lira	Super	Lira	Engelberg
G	Lira	Super	Lira	Engelberg
H	Lira	Super	Lira	Engelberg
I	Lira	Super	Lira	Engelberg
J	Lira	Super	Lira	Engelberg

6.5.3 Methods

6.5.3.1 Protein analysis

The protein contents of the rice husk samples were determined using the Leco TruSpec-N thermochemical analyzer; an instrument that determines nitrogen content of a variety of materials including foods, feeds, oilseeds, fertilizers, meats and oils (Figure 6.1). Replicate samples weighing about 0.120g were placed in aluminum foil cups and weighed on Sartorius CP1245 4 decimal digits weighing scale that was networked to the

Leco analyzer. Sample weights were automatically recorded by the TruSpec software, which controls the machine. The nitrogen contents of the samples were obtained from the analyzer, and were multiplied by 6.25 to obtain the protein content.

Figure 6.1. Leco TruSpec N analyzer

6.5.3.2 Starch analysis

The starch analysis was carried out using Standard AOAC & AACCI methods (AOAC2002.02; AACCI 32-40.01) and the Megazyme reagents kits. The resistant and digestible starch contents of replicates of the samples were determined, and the total starch content was calculated as the sum of the two measurements.

6.5.3.3 Fat analysis

Fat content of the samples were determined using the Soxhlet extractor and petroleum ether based on AOAC Standard 945.16 (AOAC, 1993). Two replicates of the analysis were carried out, just as for the starch and protein analyses.

6.5.3.4 Fourier Transform Infra-Red spectroscopy (FTIR-ATR)

Thermo-Scientific Nicolet-is5 FT-IR equipped with id5 ATR diamond crystal accessory was used for the analysis of the rice husk samples (Figure 6.2). Replicates of the samples were placed on the surface of the prism crystal, and samples were scanned at the IR range of interest between 4000 cm^{-1} to 500 cm^{-1} for 15 seconds with each spectrum that was an average of 64 scans. During the scanning process, the incident beam was introduced into the prism at an angle greater than the critical angle to generate an evanescent wave that absorbs energy at particular regions. This resulted in attenuated energy that is returned to the reflected beam at the exit, and was used to detect and generate the particular IR spectrum of the samples.

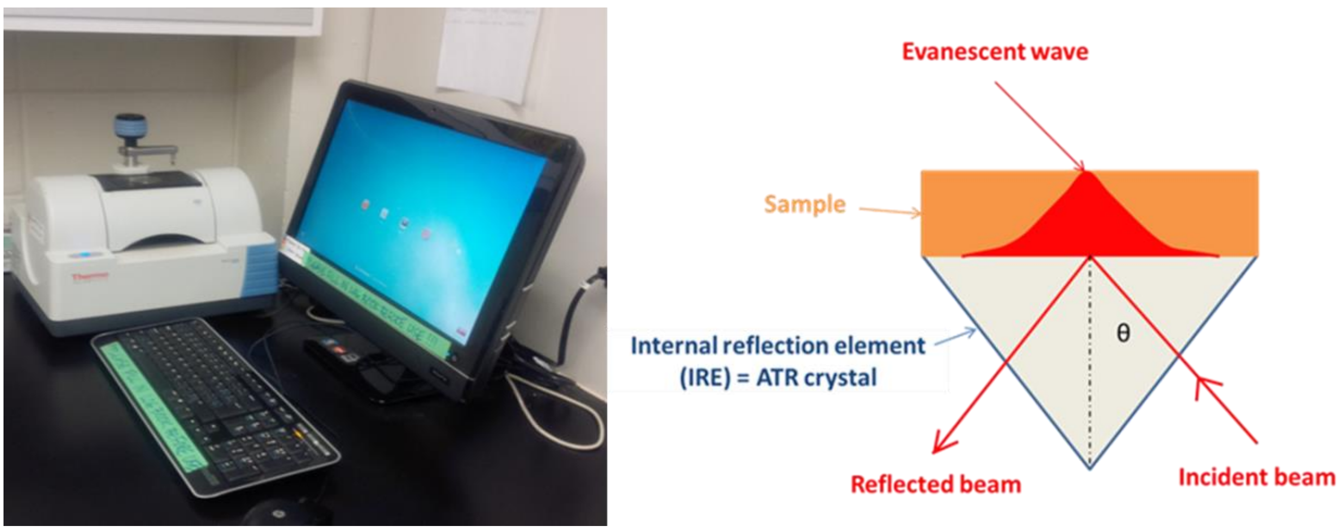


Figure 6.2. FTIR-ATR

6.5.3.5 SEM analysis of rice husk samples

Rice husk samples were studied using Hitachi TM3000 tabletop scanning electron microscope (SEM) at different levels with the objectives of studying the components that made up the rice husk samples. TM 3000 SEM uses charge-up reduction mode at low vacuum level, which increases the presence of gas molecules that ensures the neutralization of excess electron ions on the surface; hence eliminates electron accumulation on the surface of the non-conductive samples due to high vacuum. The sample was irradiated with an electron beam which generates and reflects a characteristic back scattered electron beam (BSE) of the sample, defining the compositional distribution of the sample surface, which was then used to generate the

SEM of the sample (Figure 6.3). This method eliminates the conventional vacuum coating process of non-conductive samples with a thin metal layer, which is time consuming and can interfere with imaging and EDX analysis.

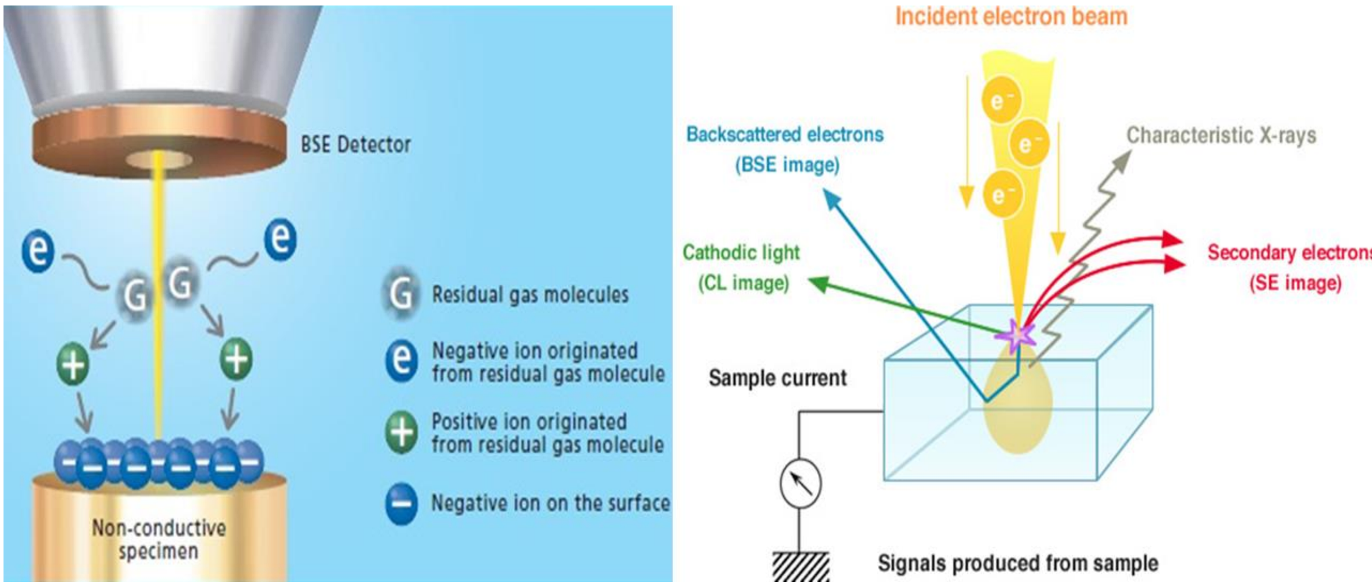


Figure 6.3. TM3000 SEM Low vacuum charge-up reduction mode (TM3000 manual)

6.6 Results and Discussion

6.6.1 Protein analysis

The nitrogen contents obtained from the TruSpec analyzer were multiplied by 6.25 to obtain the protein contents of the rice husk samples (Figure 6.4). The average protein content of the samples was 4.22%.

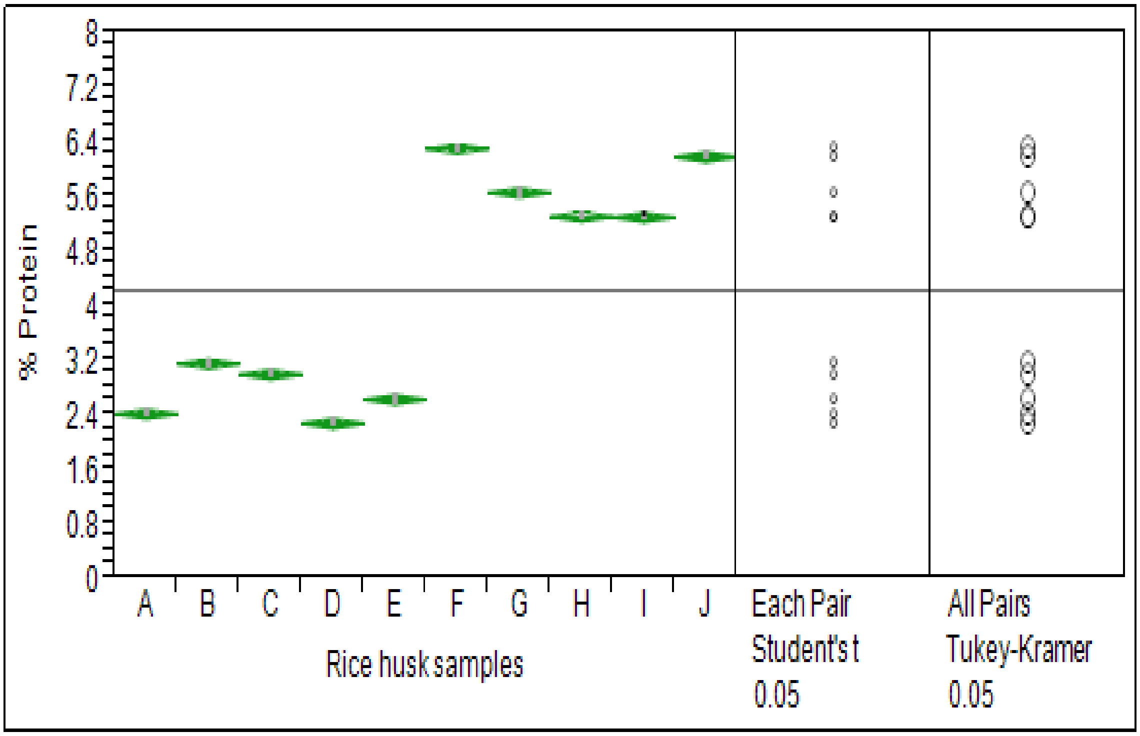


Figure 6.4. ANOVA of protein contents of the rice husk samples

There was a significant difference in protein content between the Milltop and the Engelberg rice husks; with the latter having significantly higher protein contents (Figure 6.5 and Table 6.2).

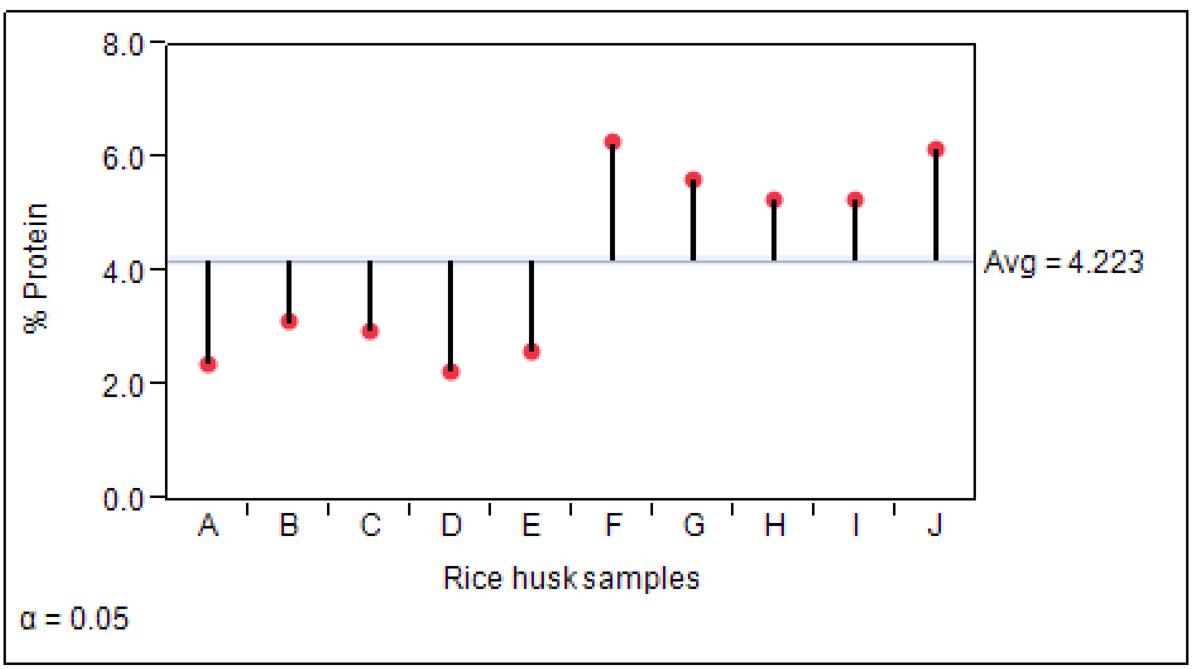


Figure 6.5. Analysis of means of protein contents of the rice husk samples

Table 6.2 ANOVA of protein contents of the rice husk samples

Means for Oneway Anova

Level	Number	Mean	Std Error	Lower 95%	Upper 95%
A	2	2.41500	0.03110	2.3457	2.4843
B	2	3.15000	0.03110	3.0807	3.2193
C	2	2.99500	0.03110	2.9257	3.0643
D	2	2.28000	0.03110	2.2107	2.3493
E	2	2.63000	0.03110	2.5607	2.6993
F	2	6.30000	0.03110	6.2307	6.3693
G	2	5.66000	0.03110	5.5907	5.7293
H	2	5.31000	0.03110	5.2407	5.3793
I	2	5.30000	0.03110	5.2307	5.3693
J	2	6.18500	0.03110	6.1157	6.2543

Std Error uses a pooled estimate of error variance

These findings showed that the protein contents of the rice husks can be classified based on the mill type.

6.6.1.1 Protein analysis of Milltop rice husks

The mean protein contents of the Milltop rice husks samples ranged from 2.28 to 3.15% (Figure 6.6 and Table 6.3).

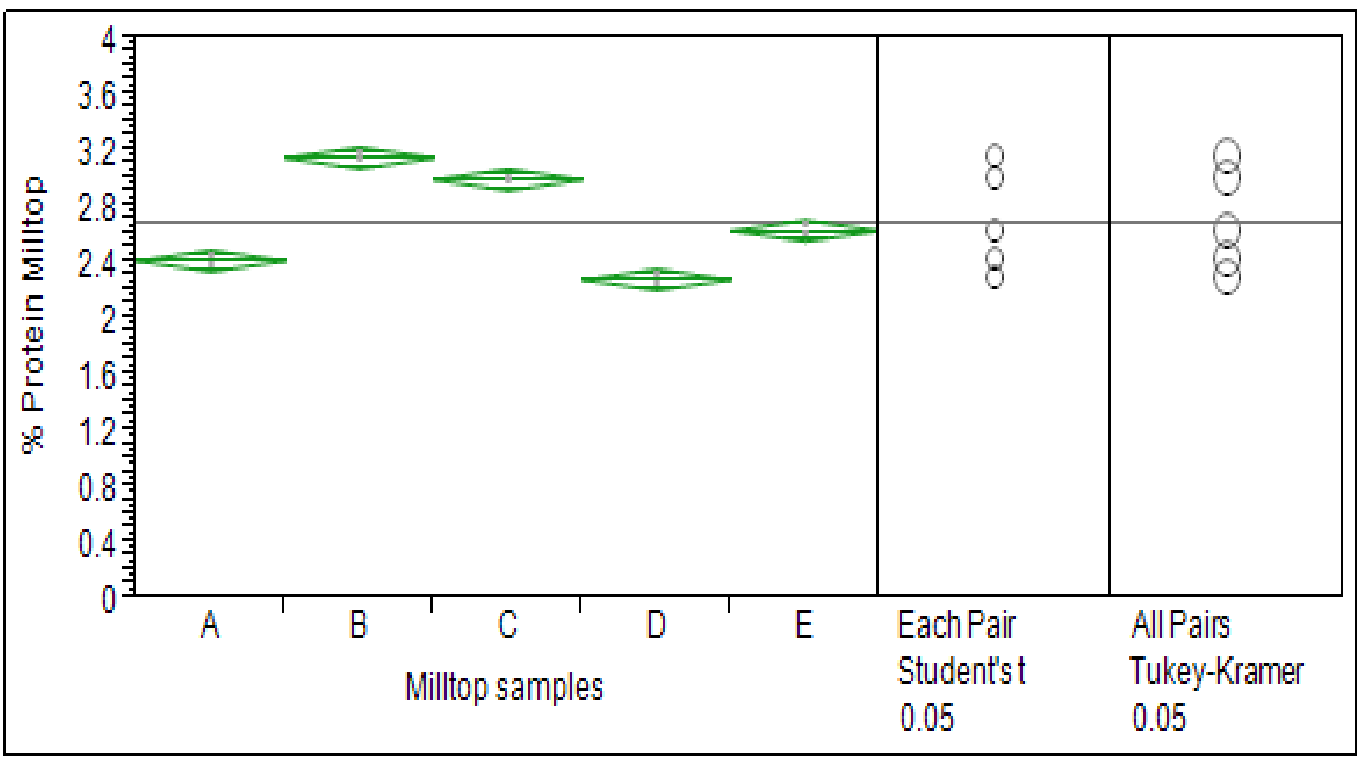


Figure 6.6. ANOVA of protein contents of Milltop rice husk samples

Table 6.3 ANOVA of protein contents of Milltop rice husk samples

Means for Oneway Anova

Level	Number	Mean	Std Error	Lower 95%	Upper 95%
A	2	2.41500	0.02950	2.3392	2.4908
B	2	3.15000	0.02950	3.0742	3.2258
C	2	2.99500	0.02950	2.9192	3.0708
D	2	2.28000	0.02950	2.2042	2.3558
E	2	2.63000	0.02950	2.5542	2.7058

Std Error uses a pooled estimate of error variance

The analysis showed that there was no significant difference in protein content between samples A, D, and E; and also there was no significant difference between samples B and C at α=0.05. Overall it was found that the differences between the protein contents of the Milltop rice husk samples were small and did not depend on variety or region where the rice husks were harvested. The low protein contents of the Milltop could be attributed to the low entrained broken grain contents, and low entrained inner sublayer components including the embryo.

6.6.1.2 Protein analysis of the Engelberg rice husks

The mean protein contents of the Engelberg rice husk samples ranged from 5.31 to 6.30% (Figure 6.7 and Table 6.4).

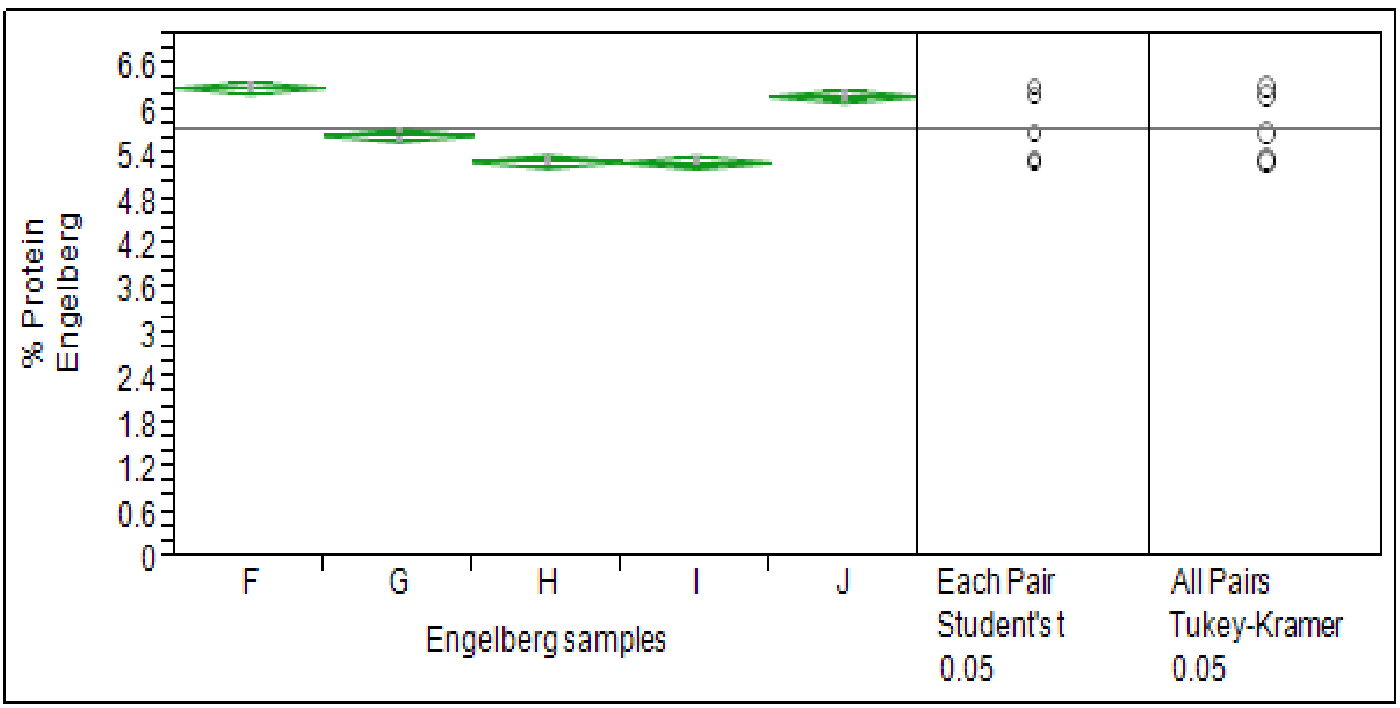


Figure 6.7. ANOVA of protein contents of Engelberg rice husk samples

Table 6.4 ANOVA of protein contents of Engelberg rice husk samples

Means for Oneway Anova

Level	Number	Mean	Std Error	Lower 95%	Upper 95%
F	2	6.30000	0.03263	6.2161	6.3839
G	2	5.66000	0.03263	5.5761	5.7439
H	2	5.31000	0.03263	5.2261	5.3939
I	2	5.30000	0.03263	5.2161	5.3839
J	2	6.18500	0.03263	6.1011	6.2689

Std Error uses a pooled estimate of error variance

The analysis showed that Samples F and J have the highest protein contents with no significant difference between them; and samples H and I have the lowest with no significant difference between them. Overall, it was found that the differences between the protein contents of the Engelberg rice husks were not very high. The high protein contents of J could be attributed to a higher content of immature grains, with partially developed kernel and high content of inner sublayer and the germ. The high protein content of sample F could be attributed to its higher bran content.

6.6.2 Starch analysis

The results provided the total starch of the rice husk contents as the sum of resistant and digestible starch. The total starch contents of the samples are shown in Figure 6.8.

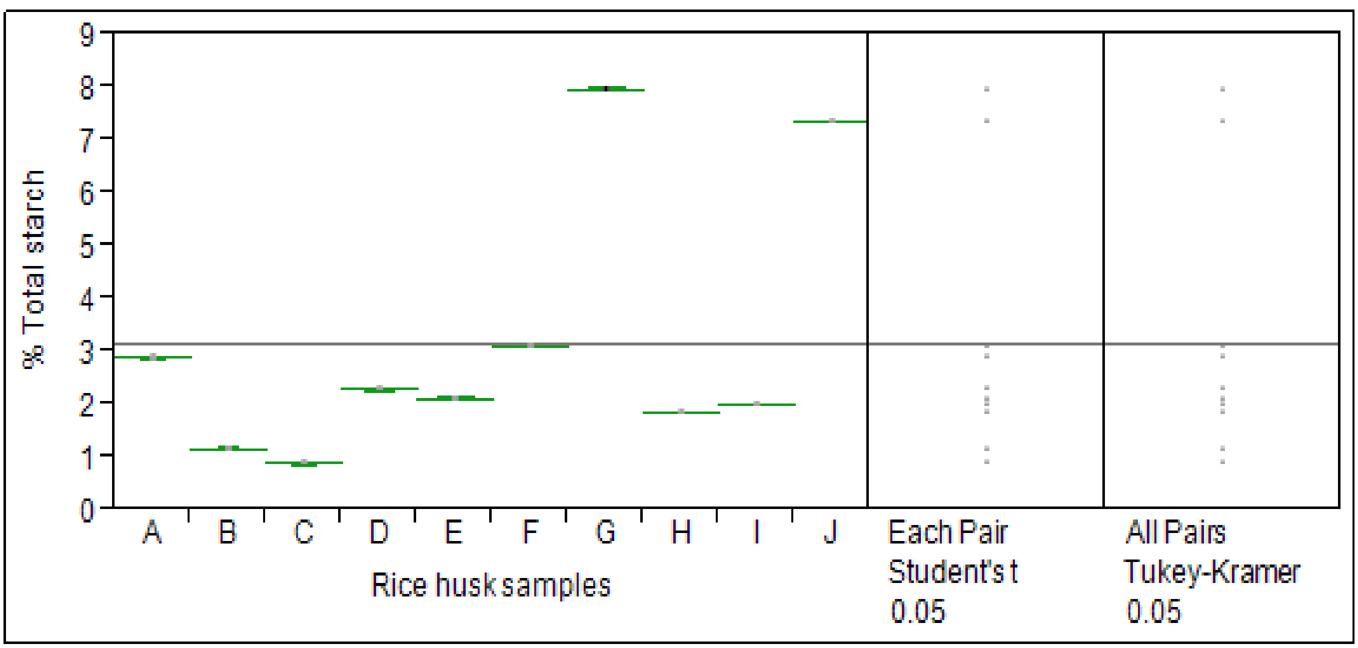


Figure 6.8. ANOVA of starch contents of the rice husk samples

6.6.2.1 Starch analysis of Milltop rice husks

The analysis showed that the Milltop rice husk samples have very low digestible starch with the mean range between 0.08 to 0.27% (Figure 6.9). Most of the starch was found to be resistant starch with a mean range between 0.81 to 2.62% (Table 6.5).

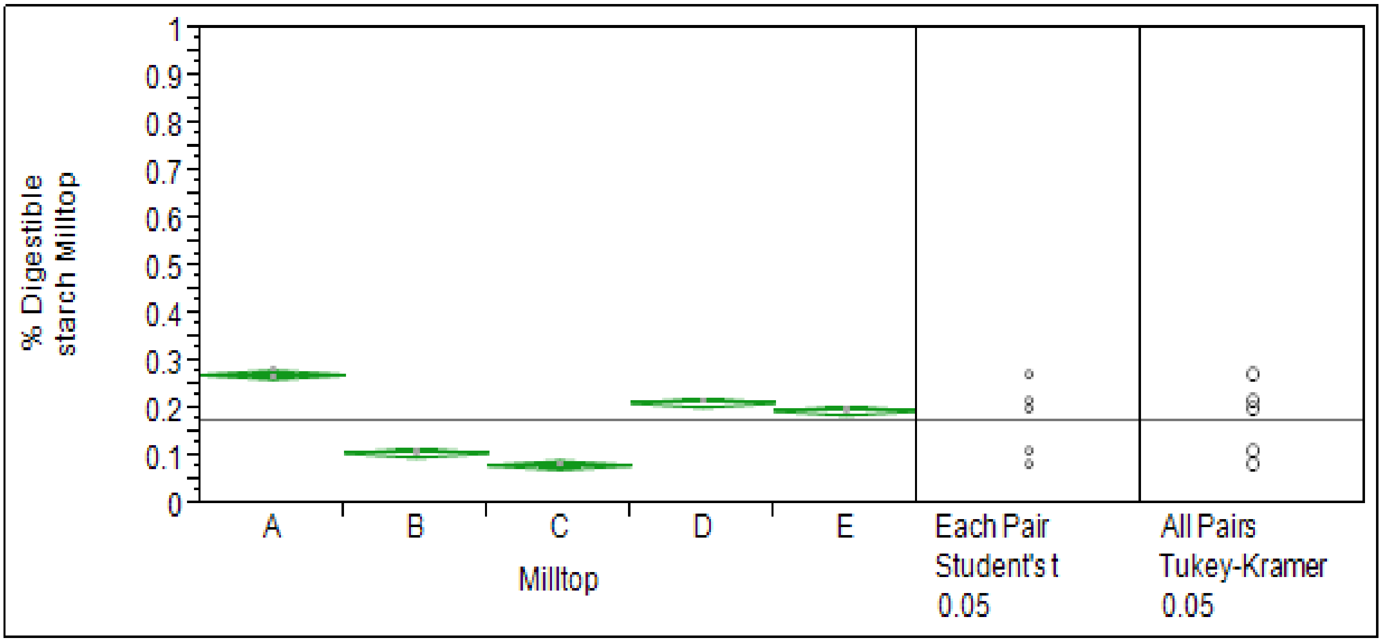


Figure 6.9. ANOVA of digestible starch contents of Milltop rice husk samples

Table 6.5 ANOVA of resistant starch contents of Milltop rice husk samples

Means for Oneway Anova

Level	Number	Mean	Std Error	Lower 95%	Upper 95%
A	2	2.61600	0.00869	2.5937	2.6383
B	2	1.05300	0.00869	1.0307	1.0753
C	2	0.80750	0.00869	0.7852	0.8298
D	2	2.07350	0.00869	2.0512	2.0958
E	2	1.91900	0.00869	1.8967	1.9413

Std Error uses a pooled estimate of error variance

Sample A had the highest total starch content with a mean of 2.7%, while sample C had the lowest starch content with a mean of 0.89%. The pooled average starch content of the Milltop rice husk was 1.87% (Figures 6.10 & 6.11). The variation of starch contents between the Milltop rice husk samples may be likely due the contents of entrained sublayer components and broken kernels within the rice husks (Figure 6.12).

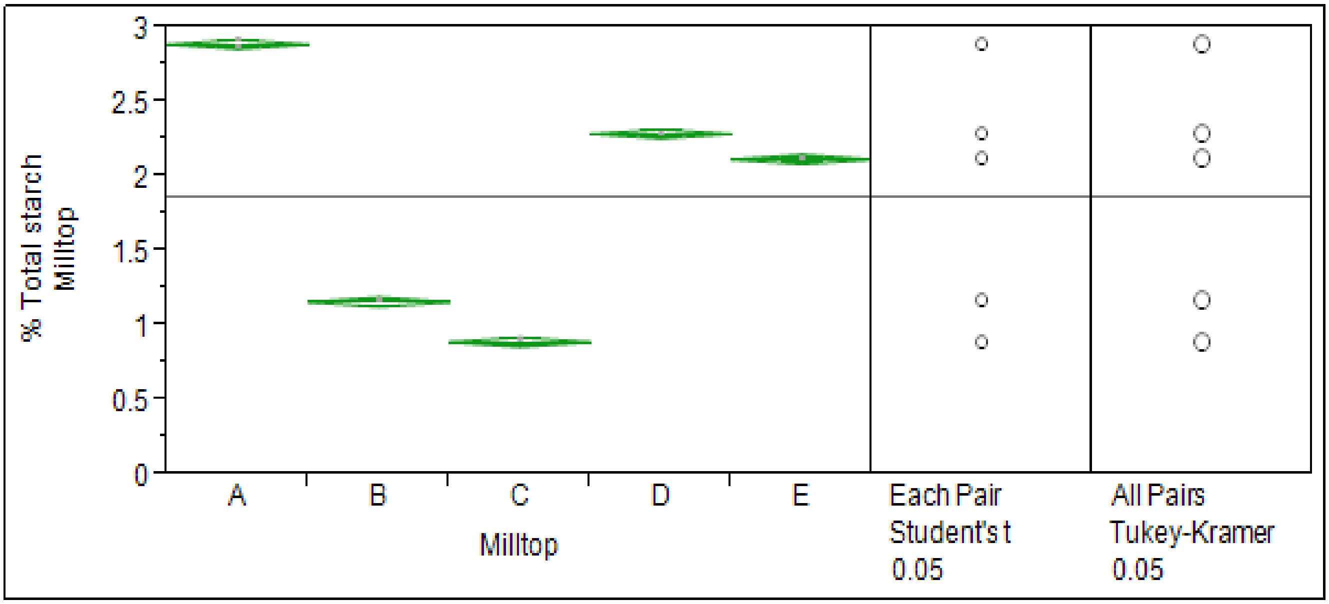


Figure 6.10. ANOVA of total starch contents of the Milltop rice husk samples

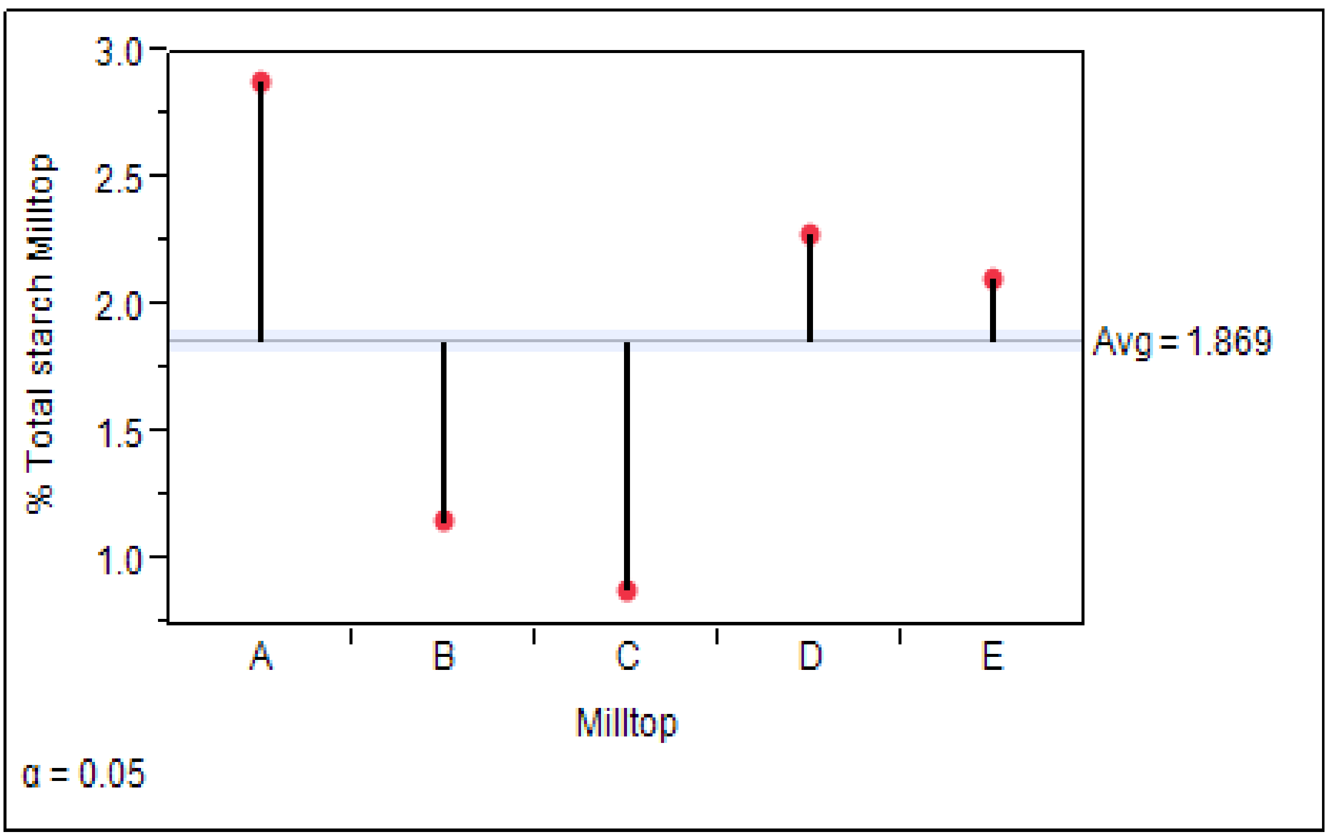


Figure 6.11. Analysis of means of total starch contents of the Milltop rice husk samples

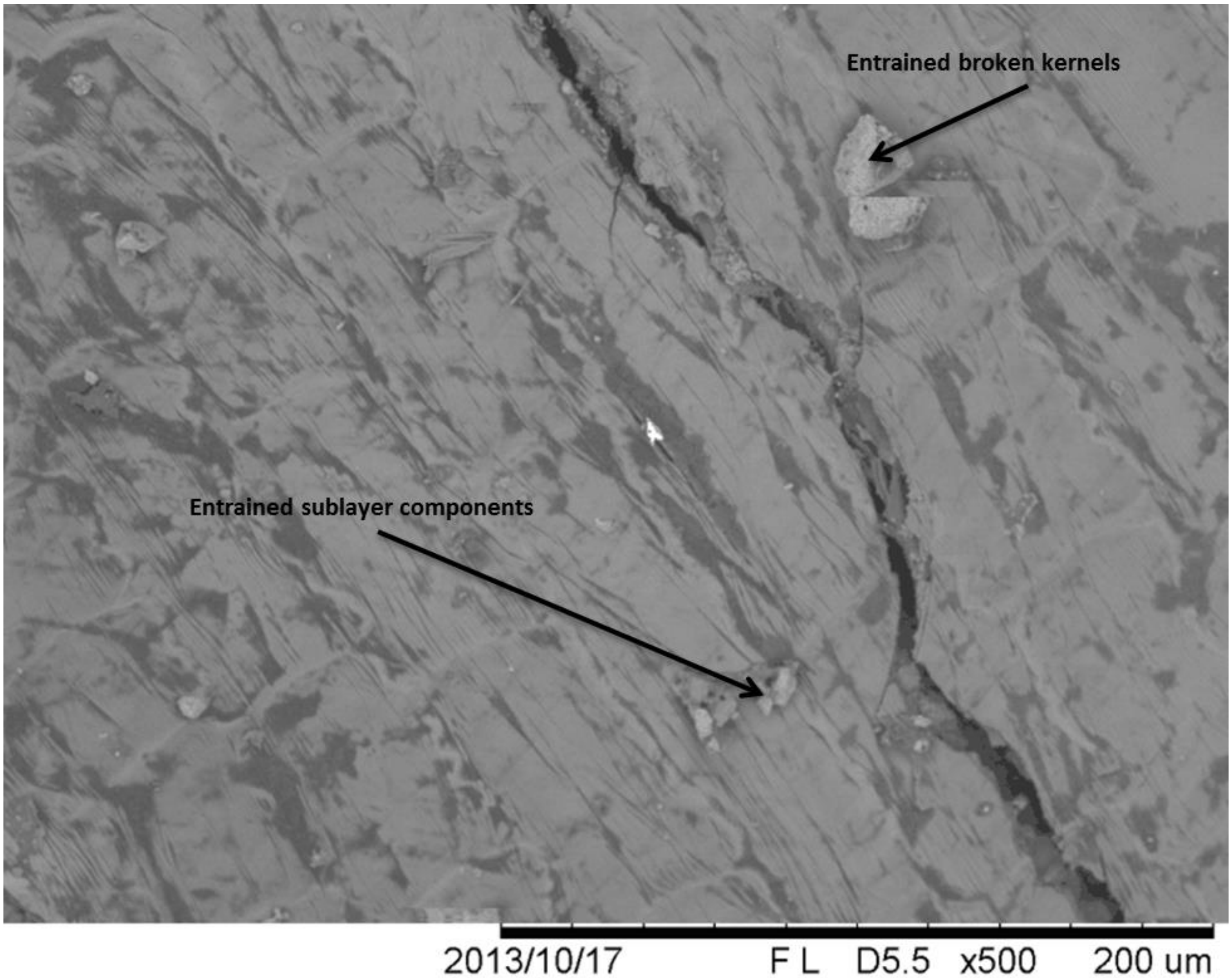


Figure 6.12. SEM imaging of the entrained broken kernels and sublayer components in the Milltop rice husk samples

6.6.2.2 Starch analysis of the Engelberg rice husks

The digestible starch content of the Engelberg rice husk was also found to be very low. However, it was higher than that of the Milltop, and ranged between 0.17 to 0.74% (Figure 6.13). The resistant starch contents of the Engelberg rice husks were found to be also much higher than that of the Milltop rice husk samples, with a pooled average of 4.04% (Figure 6.14).

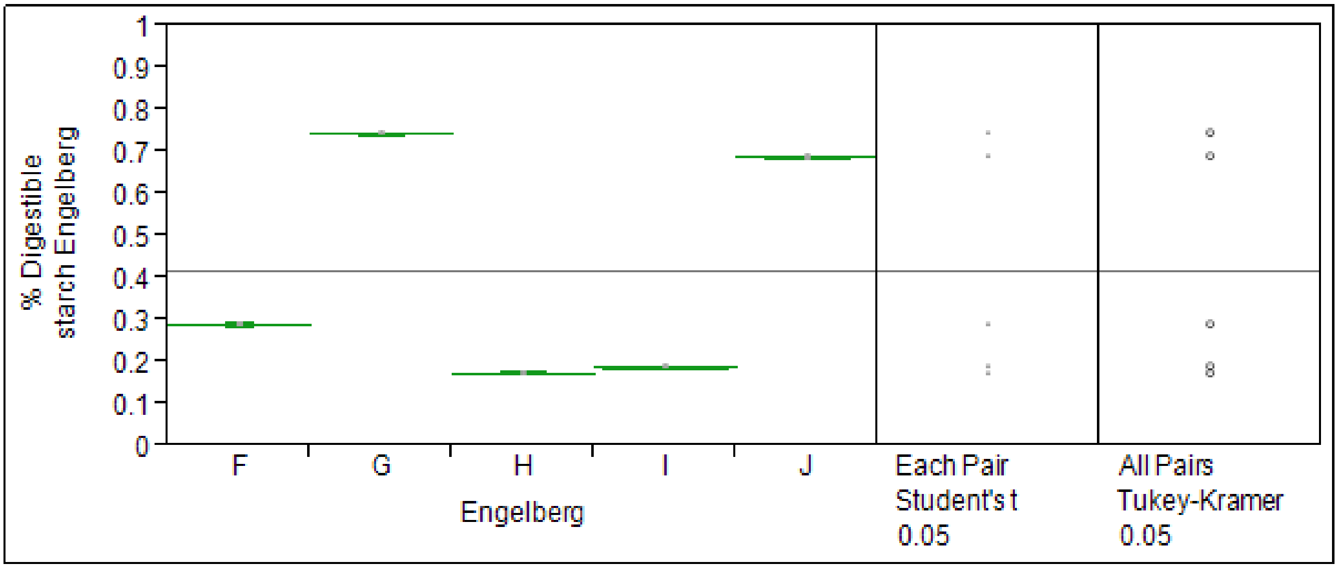


Figure 6.13. ANOVA of digestible starch contents of Engelberg rice husk samples

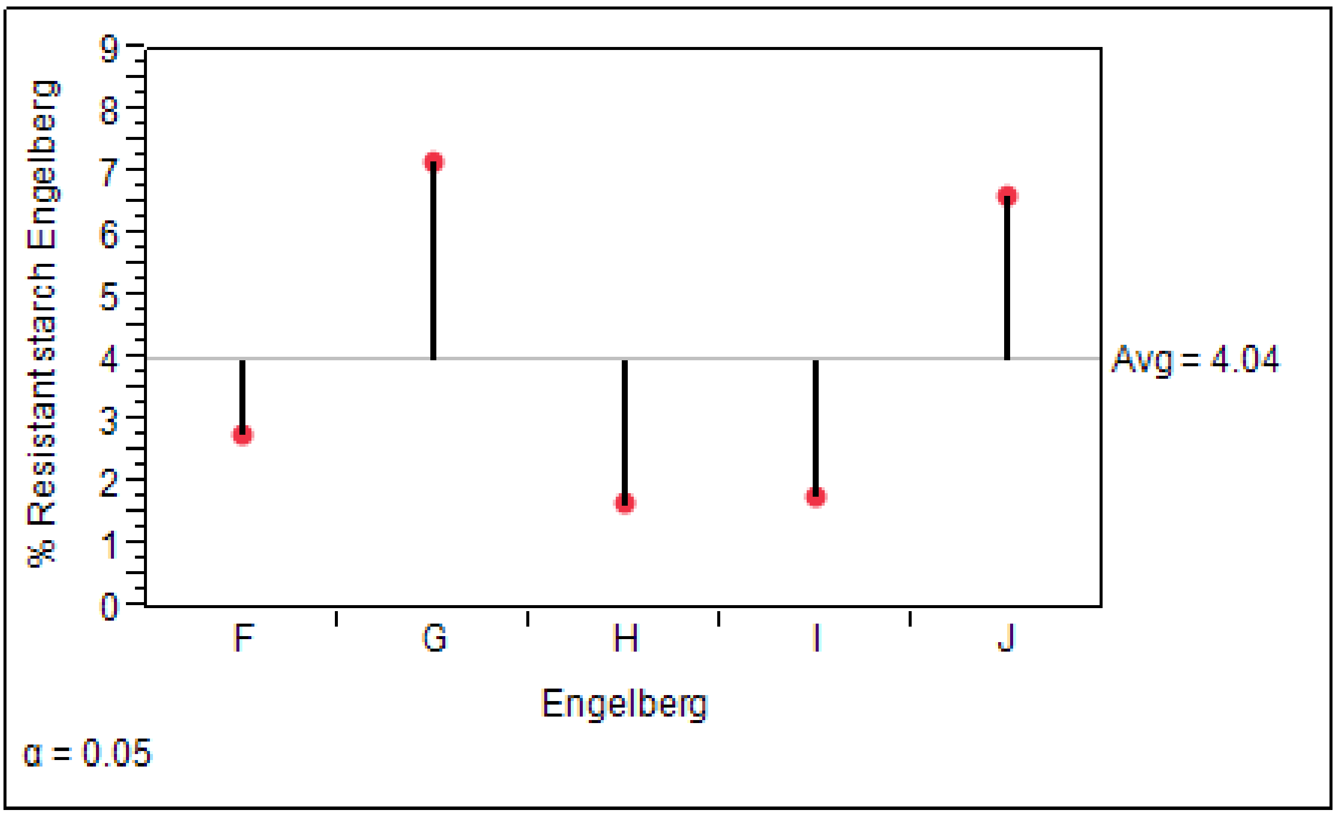


Figure 6.14. ANOVA of resistant starch contents of Engelberg rice husk samples

The mean total starch content of the Engelberg rice husk samples ranged between 2.00 to 7.97% with a pooled average of 4.46% (Figure 6.15 and Table 6.6).

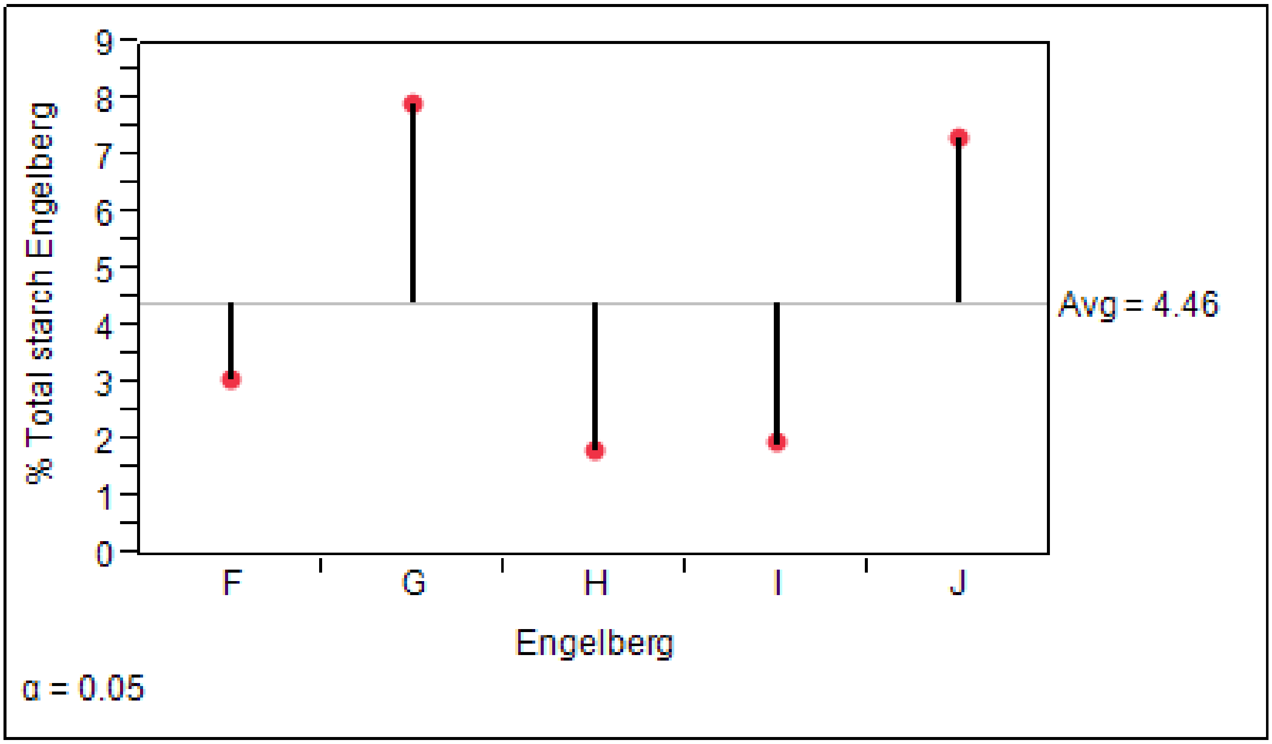


Figure 6.15. Analysis of means of total starch contents of Engelberg rice husk samples

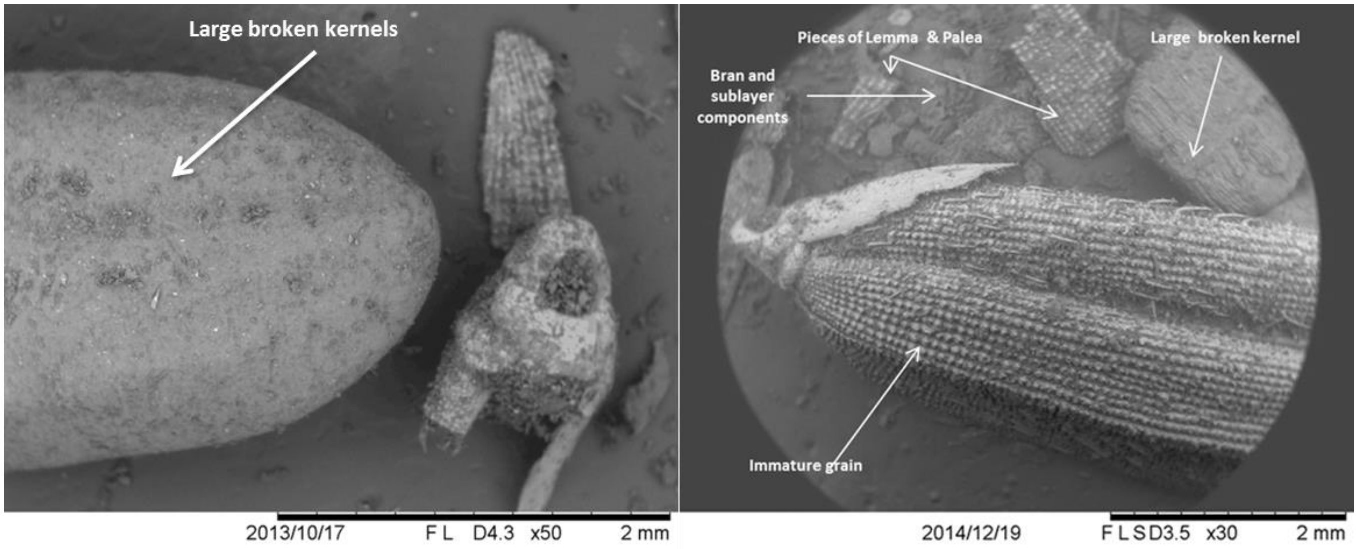
Table 6.6 ANOVA of total starch contents of Engelberg rice husk

Means for Oneway Anova

Level	Number	Mean	Std Error	Lower 95%	Upper 95%
F	2	3.10300	0.00211	3.0976	3.1084
G	2	7.96600	0.00211	7.9606	7.9714
H	2	1.85500	0.00211	1.8496	1.8604
I	2	1.99500	0.00211	1.9896	2.0004
J	2	7.35750	0.00211	7.3521	7.3629

Std Error uses a pooled estimate of error variance

Samples G and J were found to have the highest starch content with mean starch contents of 7.87 and 7.36%, respectively. Physical analysis by SEM imaging has shown that the sample G has a high content of broken kernels, and sample J to have a high amount of immature grains (Figure 6.16).



(a) Large broken kernels in sample G

(b) Immature grains in sample J

Figure 6.16. SEM imaging of the entrained broken kernels and sublayer components in the Engelberg rice husk samples

6.6.3 Fat analysis

Fat content of the Engelberg rice husks ranged between 1.65 to 4.16%; and the fat content of the Milltop rice husk samples ranged between 0.29 to 0.81% (Figure 6.17 and Table 6.7). The Engelberg samples have much higher fat content, likely due to the high quantity of sublayer components entrained in the rice husk samples. On the other hand, for the Milltop husk samples, their major components were the lemma and palea that have just traces of fat.

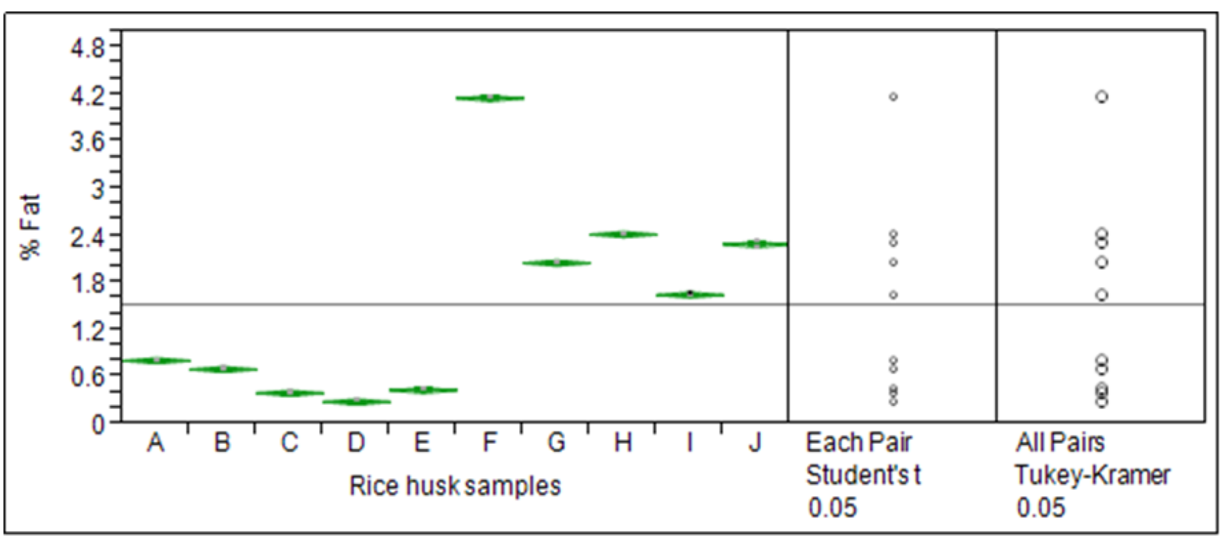


Figure 6.17. Fat contents of the rice husk samples

Table 6.7 ANOVA of Fat contents of rice husk samples

Means for Oneway Anova

Level	Number	Mean	Std Error	Lower 95%	Upper 95%
A	2	0.81300	0.01582	0.7778	0.8482
B	2	0.70250	0.01582	0.6673	0.7377
C	2	0.39950	0.01582	0.3643	0.4347
D	2	0.28850	0.01582	0.2533	0.3237
E	2	0.43500	0.01582	0.3998	0.4702
F	2	4.15800	0.01582	4.1228	4.1932
G	2	2.05850	0.01582	2.0233	2.0937
H	2	2.42350	0.01582	2.3883	2.4587
I	2	1.65200	0.01582	1.6168	1.6872
J	2	2.29450	0.01582	2.2593	2.3297

Std Error uses a pooled estimate of error variance

6.6.3.1 Fat analysis of Milltop rice husks

The Milltop rice husk samples have very low fat contents with a pooled average of 0.53% (Figure 6.18 and Table 6.8). Samples A and B were found to have the highest fat contents with average fat contents of 0.81 and 0.70% respectively. Sample D had the lowest fat content of 0.39%. Sample C and E, have fat contents of 0.40% and 0.44% respectively, with no significant difference in fat contents.

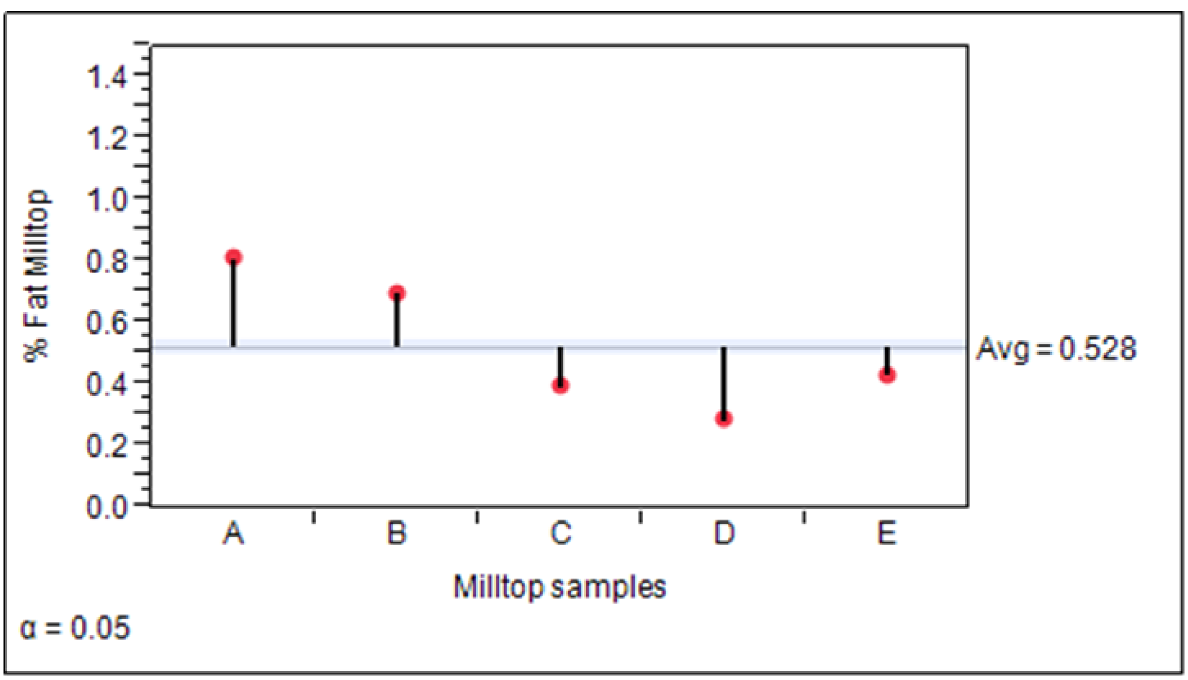


Figure 6.18. Analysis of means of fat contents of Milltop rice husk samples

Table 6.8 ANOVA of Fat contents of Milltop rice husk samples

Means for Oneway Anova					
Level	Number	Mean	Std Error	Lower 95%	Upper 95%
A	2	0.813000	0.00749	0.79374	0.83226
B	2	0.702500	0.00749	0.68324	0.72176
C	2	0.399500	0.00749	0.38024	0.41876
D	2	0.288500	0.00749	0.26924	0.30776
E	2	0.435000	0.00749	0.41574	0.45426

Std Error uses a pooled estimate of error variance

The higher fat contents of samples A and B may likely be due to the higher content of entrained sublayer particles in these two rice husk samples. Further analysis of the postharvest processes including milling process could reveal the efficiencies of these processes.

6.6.3.2 Fat analysis of Engelberg rice husks

The Engelberg rice husks have high fat contents with a pooled average of 2.52% and mean range of 1.65 and 4.16% (Figure 6.19 and Table 6.9). Sample F had a significantly higher fat content than all the rice husk samples tested while sample I had the lowest fat content. The ratio of the amount of the fatty sublayer components, the broken kernel contents, and the non-fatty outer layer components including the lemma, palea, and trichomes would likely be the key factors that determined how much fat the samples contained.

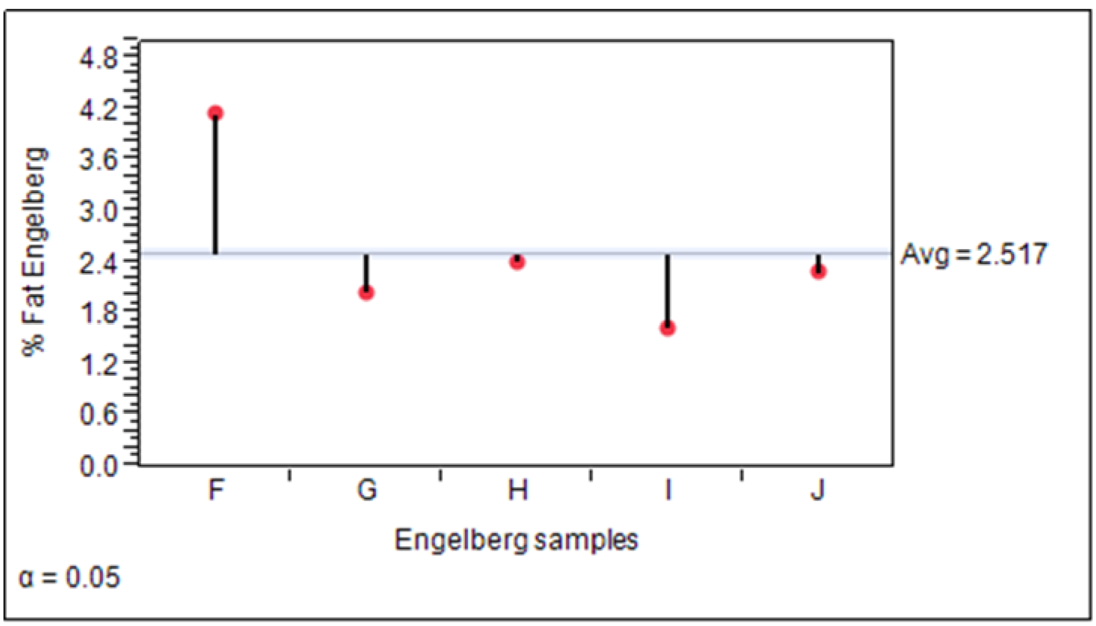


Figure 6.19. Analysis of means of fat contents of Engelberg rice husk samples

Table 6.9 ANOVA of Fat contents of Engelberg rice husk samples

Means for Oneway Anova

Level	Number	Mean	Std Error	Lower 95%	Upper 95%
F	2	4.15800	0.02107	4.1038	4.2122
G	2	2.05850	0.02107	2.0043	2.1127
H	2	2.42350	0.02107	2.3693	2.4777
I	2	1.65200	0.02107	1.5978	1.7062
J	2	2.29450	0.02107	2.2403	2.3487

Std Error uses a pooled estimate of error variance

6.6.4 FTIR-ATR of rice husk samples

The FT-IR of both the Engelberg and the Milltop rice husk samples were similar in many regions of the spectra with the exception of some bands, where higher contents of component peaks were masked by higher presence of other components that were represented by adjacent shared group peaks (Figure 6.20).

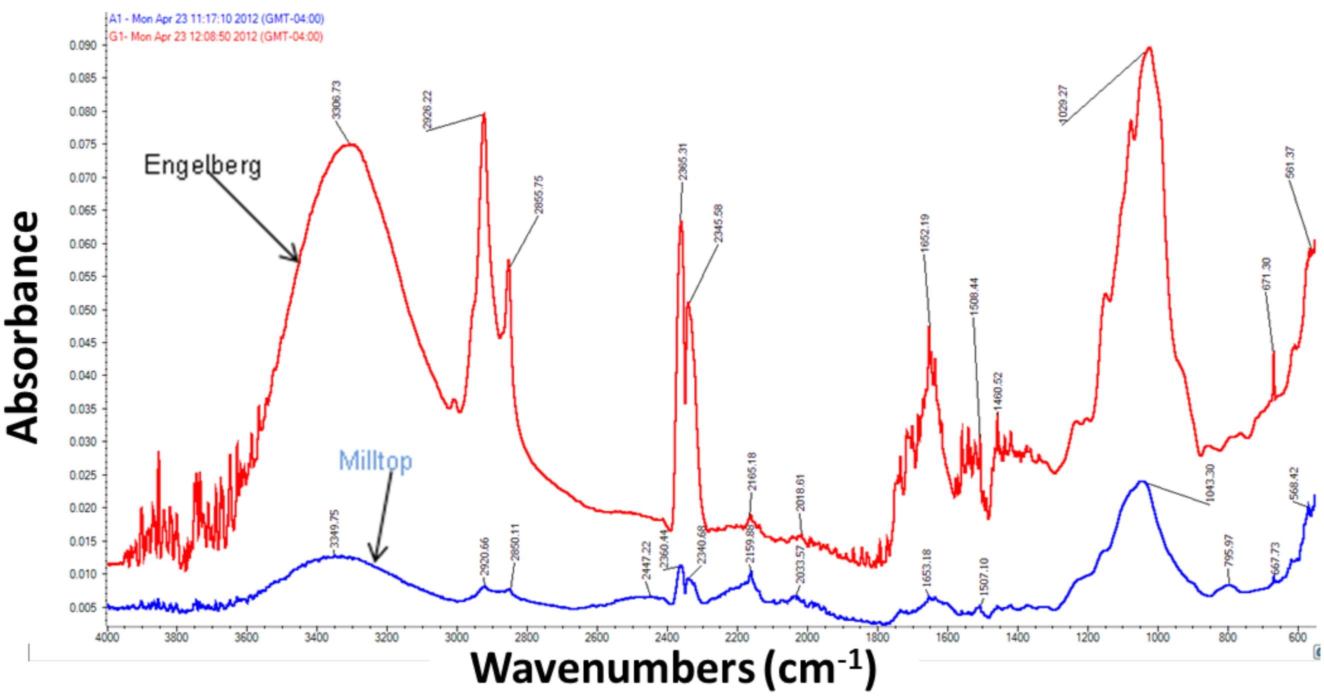


Figure 6.20. Comparison of FT-IR spectra of Engelberg and Milltop rice husk samples

All the rice husk samples have a broad peak at the high frequency range of 3700-3100 cm^{-1}, representing the OH stretching bands of alcohols, phenols, and carboxylic acids. The absorptions were above and below 3000 cm^{-1}, indicative of the presence of both saturated (non-aromatic) and unsaturated or cyclical hydrocarbon moieties. Strong band between 1000 and 650 cm^{-1} confirmed that both samples have alkenes or aromatic structures. Sharp bands near 725 and 1440 cm^{-1} were indicative of linear chains containing 4 or more CH_2 groups (Lambert et al., 2011). Peaks observed at 2359 and 2340 cm^{-1} indicated the presence of triple bond carbon to carbon and triple bond carbon to nitrogen respectively (Anwar et al., 2011). The peaks between 950 and 900 cm^{-1} were indicative of glycosidic linkages (Kizil et al., 2002), while the peaks between 1165 to 1158 cm^{-1} were confirming the presence of amylose and cellulose (Nikonenko et al., 2002).

The peaks observed at 1238, 1315, and 1504 cm^{-1} were indicative of C-O of guaiacyl ring, C-O of syringyl ring, and aromatic skeletal vibrations respectively; all of which are indicative of the presence of lignin (Zhou et al., 2011). The peaks observed around 2323, 1100, 890, and 800, were indicative of Si-C stretching, Si-O-Si stretching, Si-OH bending, and Si-O bending respectively; confirming the presence of Silica in all the rice husk samples (Kamath and Proctor, 1998; Kalapathy et al., 2000; Shokri et al., 2009).

6.6.4.1 FTIR analysis of the Milltop rice husk samples

FT-IR analysis showed that the Milltop rice husk samples have generally the same peaks, with the level of absorbance as the only major differences between them. Samples C and E have highest absorbance in most of the bands of the FT-IR spectra (Figure 6.21). Sample A had the lowest absorbance in most of the bands, with the exception of the region between 2300 and 1850 cm^{-1} band. This was possibly due to higher contents of sublayer particles and broken kernels entrained in the rice husk sample, resulting in higher starch, protein, and fat contents. This finding confirmed what was observed during the starch, protein, and fat analysis of the Milltop rice husk samples.

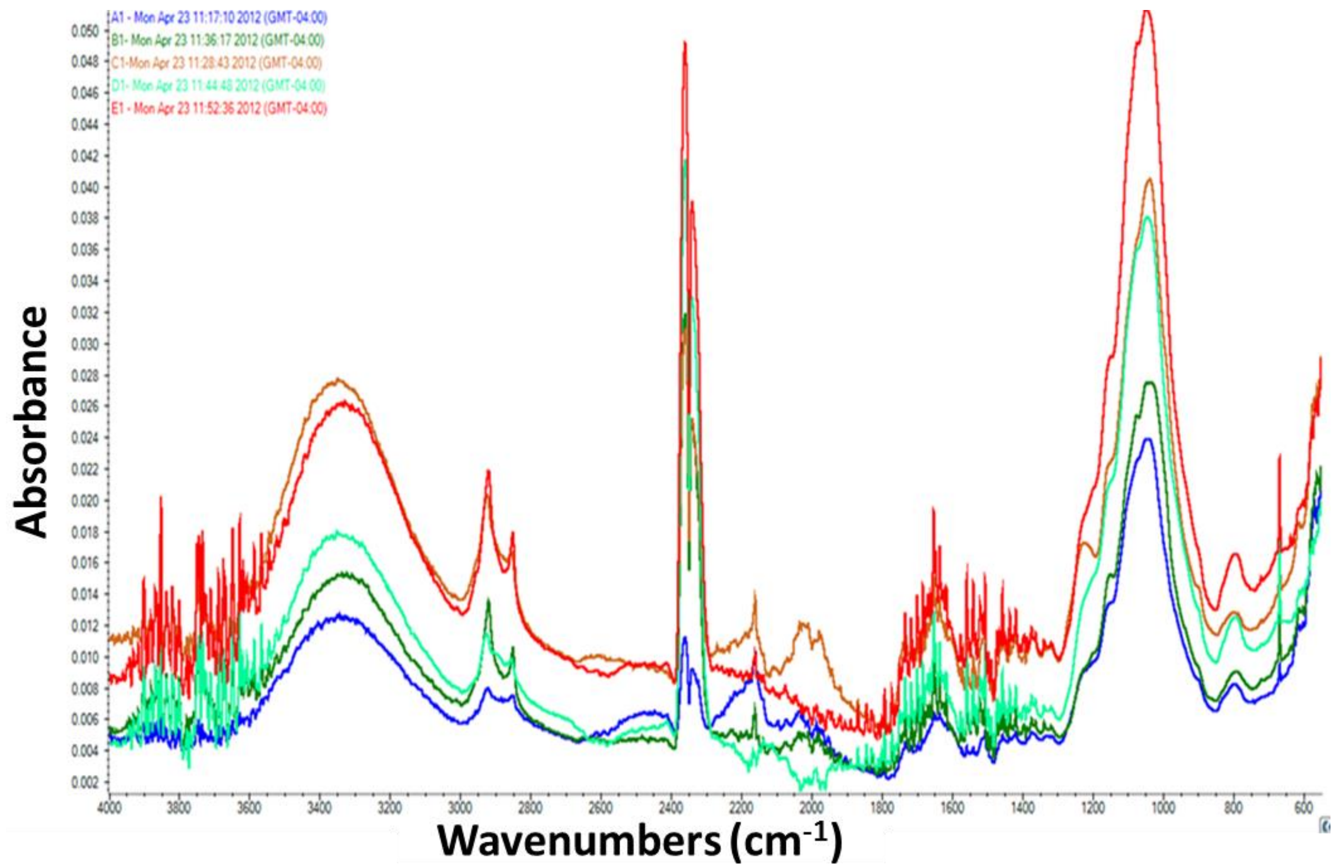


Figure 6.21. FTIR spectra of Milltop rice husk samples

6.6.4.2 FTIR analysis of the Engelberg rice husk samples

FT-IR analysis revealed that the Engelberg rice husks have absorbance at all the characteristic peaks (Figure 6.22). The Engelberg rice husk samples spectra have unique characteristics. One of the key characteristics of the Engelberg rice husk spectra were the absorbance ratios between the OH peak around 3300 cm^{-1} peak and the peak that occurred at 2900 cm^{-1}. For all the Engelberg rice husk samples the absorbance at 2930 cm^{-1} was much higher than the OH peak that occurred at 3300 cm^{-1}. Also a unique peak around 3000 cm^{-1} differentiated the Engelberg from the other rice husk samples. These unique characteristics may be the result of higher sublayer constituents in the Engelberg produced husk, which resulted in higher starch, fats, and proteins within the Engelberg husk samples.

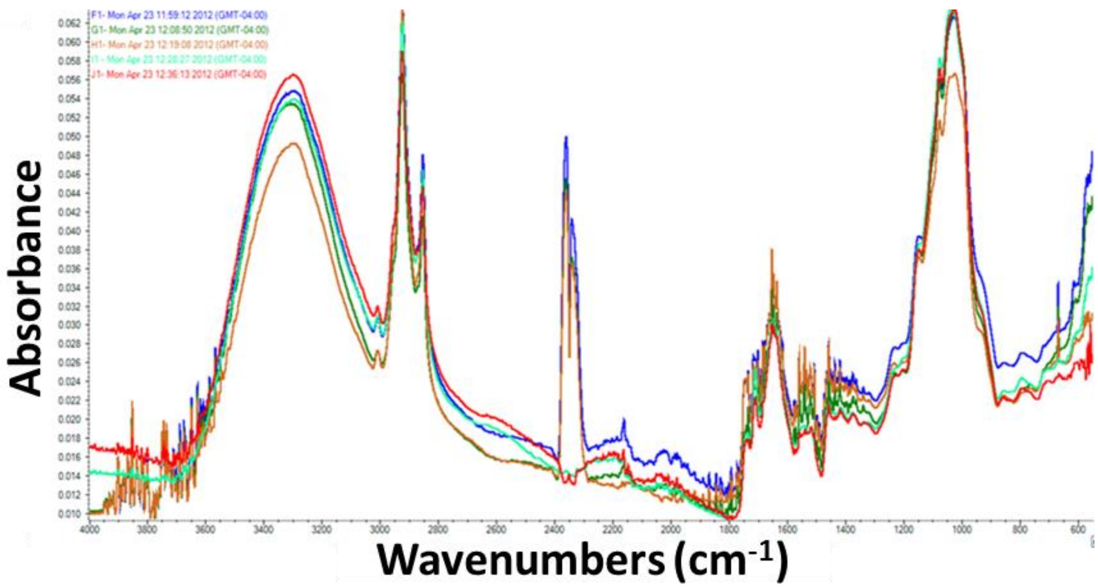


Figure 6.22. FTIR spectra of Engelberg rice husk samples

Sample J had a unique FT-IR spectrum compared to all the other Engelberg samples (Figure 6.23). The sample had highly defined peaks; and did not exhibit peaks in some regions where the other Engelberg rice husks have high peaks, especially at around 2365 and 2345 cm^{-1} which were indicative of lack of presence of triple bonds C≡C and C≡N, respectively. This could be possibly due to the high contents of immature grains in sample J indicative of the possibility that the rice paddy was not fully matured when it was harvested.

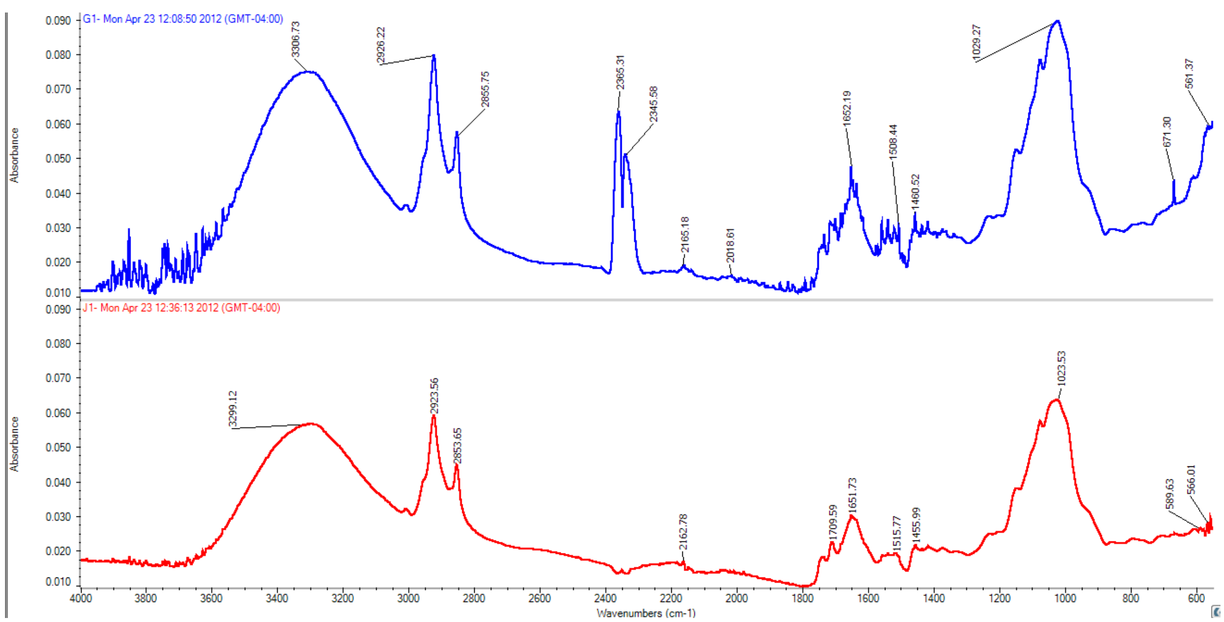


Figure 6.23. Unique FT-IR spectrum of sample J compared to other husk samples

6.7 Conclusions

The chemical characterization of the Engelberg and Milltop rice husks showed that the Engelberg samples have higher contents of inner sublayer components that resulted in higher proximate compositions of protein, fat and starch. The Milltop rice husk samples contained more of the outer shells of lemma and palea and thus had higher FT-IR absorbance ratio of the peaks that represented silica. The Milltop produced husk also had insignificant proximate amounts of protein, fat, and starch compared to the Engelberg rice husks. The FT-IR of the two rice husk groups were found to be similar; the key difference being the different absorption levels indicative of the levels of the key proximate components of the samples. Some unique characteristics of the Engelberg samples spectra observed was the presence of a peak at 3000 cm^{-1} for all the samples, which was not present or obvious in the spectra of the Milltop samples. The spectra of the Engelberg samples showed that the OH broadband, that peaked at 3300 cm^{-1}, was also found to be lower than a common peak observed on all the samples at around 2925 cm^{-1}; differentiating it from the Milltop samples whose OH broadband peaks were found to be higher than the peak around 2925 cm^{-1}. These unique spectral characteristics clearly identified and classified the Engelberg and the Milltop samples. FT-IR of sample J of the Engelberg rice husk samples stood out due to the lack of peaks at 2365 cm^{-1} and 2345 cm^{-1}, as well as, due to clearer and lower number of peaks which is indicative of the lower presence of certain proximate components. The uniqueness of sample J can possibly be due to its high content of immature grains, and the possibility that sample J paddies were harvested before full maturity and ripening.

6.8 Recommendations

The results obtained showed that the quantity of the key proximate components including protein, fat, starch, and silica were what differentiated the Engelberg from the Milltop rice husks chemical characteristics. Therefore, the two rice husks can either be used individually, or preferably as a blend to develop a standard feedstock that can be densified into briquettes and pellets that can be used as fuel for a thermochemical energy conversion system. The blending will not only reduce the need for additional binders, but will also provide an opportunity for a standard rice husk fuel for thermal energy converters; increasing the sustainability of rice production, with due consideration to the triads of sustainability that include social, economic, and environmental perspectives.

6.9 Contribution of this research

This research has established the characteristic FT-IR spectra, identifying key components, for the two most abundant rice husks in sub-Saharan Africa and the developing world. With the results of this research, these rice husks and their blends can be utilized as biofuel feedstock in the regions where they are abundant.

6.10 Limitation of study

The findings of this research were able to differentiate and identify the chemical characteristics of the Engelberg and the Milltop rice husks based on the ten samples studied**.**

Connecting text to Chapter VII

The thermochemical characterization of Engelberg and Milltop rice husk provided important information on the high heating value (HHV), and physical and chemical characteristics of the rice husk ash. An effective method of determination of the HHV of the rice husk is an important contribution to biomass research. The comparison of the Engelberg and Milltop rice husk thermochemical properties has not been carried out before. Important findings of this research included the fact that, although the two rice husks have some quantitative component differences, the products of complete thermochemical conversion in the form of rice husk ash were the same. The ashes were composed of pure silica with trapped carbon atoms in silica matrix and very small impurities as the SEM and FT-IR analyses revealed.

VII Thermochemical characterization of Engelberg and Milltop rice husks

7.1 Abstract

Rice husk is an abundant lignocellulosic biomass from the postharvest processing of rice, with a high potential as a biofuel feedstock. In this study, the thermochemical characteristics of rice husks from the two predominant milling machines (Engelberg and Milltop) used in sub-Saharan Africa including proximate composition and high heating value (HHV) were studied. Effective method of determining the HHV of Engelberg and Milltop rice husk samples using oxygen bomb calorimeter coupled with comparative analysis of bomb calorimeter residuals, proximate ash, and densified pellet impact resistance was developed. HHV of the rice husk samples ranged from 13.49 to 15.98 MJ/kg with a pooled mean of 14.60 MJ/kg and standard deviation of 0.79 MJ/kg; with two distinctive HHV ranges based on the mill type. Milltop rice husk HHV (mean=13.89 MJ/kg and standard deviation=0.25 MJ/kg) were lower than that of Engelberg rice husks (mean=15.33MJ/kg and standard deviation=0.33 MJ/kg). Proximate moisture, ash, volatile, and carbon contents of the rice husk samples based on ASTM standards ranged from 5.07-6.64%, 12.66-24.91%, 62.83-75.99%, and 5.61-14.64% respectively; with respective pooled means of 5.92, 21.20%, 67.32%, and 11.53%. Harvest and postharvest processing were found to have significant effect on the amount of rice paddy components entrained in the rice husk samples; and consequently, on the proximate composition and HHV of the samples. Higher volatile and fixed carbon contents and lower ash contents were found to increase the HHV. The result showed that densification of rice husk at medium pressures, using 15% moisture and hold time of 60 seconds produced pellets with a good impact resistance index which combust completely in the oxygen bomb calorimeter. HHV was correlated to the proximate components to predict HHV of Engelberg and Milltop rice husks based on their proximate components. Prediction models for estimating HHV of the Engelberg and Milltop rice husks showed that quadratic models provided better estimates for both rice husks with R-square values of 0.92 and 0.74 compared to the linear models, which have R-square values of 0.84 and 0.71, respectively. Higher HHV values of the

Engelberg rice husks compared to the Milltop were found to be consistent with the respective higher volatile proximate components, which were found to have the most significant effects on HHV. FTIR and SEM analyses of both Engelberg and Milltop rice husks and their ashes showed that during the thermochemical conversion process, pores and ridges were formed within the silica-lignin matrix as pathways, by the volatilizing of hemicellulose, cellulose, and lignin components exiting the rice husk stable silica structure; which shrank more in the traverse direction than in the longitudinal direction. The FTIR and SEM analyses also showed that there was no significant difference between the physico-chemical composition of the Engelberg and Milltop rice husk ash; a finding that suggests the possibility of designing and building a thermochemical conversion system that can use the two different rice husks with operating physical parameters including particle size distribution, feed rate, and air ratio as possible control parameters. The results also showed that the variety of rice can significantly affect the ash content of the rice husk, as well as, the silica content. Rice varieties with trichomes and more solid cone shape outer structures have higher silica and ash contents. However, it was found that entrained grain and sublayer components reduced the ash content, while entrained immature grain content increased the ash content of the rice husks.

7.2 Introduction

Rice husk is one of the most abundant lignocellulosic biomass by-products of agricultural postharvest processing. In order to utilize it as an alternative renewable energy source, its thermochemical characteristics need to be determined. Evaluation of the thermochemical characteristics of rice husk is crucial for the design and operation of the thermochemical reactors such as gasifiers, pyrolysis reactors and direct combustion stoves (Ghaly & Mansaray, 1999; Antal & Varhegyi, 1996; Ergundenler & Ghaly, 1992; Bining & Jenkings, 1992). Complete understanding of the proximate analysis of rice husk based on postharvest processing methods and the variety of rice husk is important in determining the range of thermochemical parameters for design, development and operation of any energy conversion system to ensure flexibility. Rice husk is mainly composed of cellulose, hemicellulose and lignin (Mansaray and Ghaly, 1999). The proportions of these constituents in rice husk vary to some extent between varieties and postharvest processing methods which may influence its thermochemical characteristics. Key parameters that are used to assess the thermochemical reaction properties of the biomass include the proximate composition of the biomass, and the heating value of the biomass. Proximate composition is used to determine the moisture, ash, volatile, and fixed carbon contents of the biomass based on American Standards of Testing Material (ASTM). Heating value of a biomass is an important characteristic that determines its viability as a bioenergy feedstock. The two main methods of determining heating value are either by measurement or prediction (Demirbas, 1997; Parikh, 2005; Sheng, 2005; Shen et al., 2012). Bomb calorimetry is an effective experimental measurement method for determining the high heating value (HHV) of biomass, and correlation estimate based on proximate component on a dry basis is an effective predictive method for HHV determination.

Thermochemical properties of biomass are based on the analysis of the thermal degradation reaction process of the components of biomass with respect to time, temperature, and pressure increase, in a reactive or non-reactive gaseous medium (e.g. oxygen, nitrogen, argon, helium, etc.). Multi-component devolatilization experiments have shown that weight loss of biomass during the thermochemical conversion is comprised of parallel reactions of pseudo-components or zones that coincide with the decomposition of hemicellulose (223-325 °C), cellulose (325-375 °C), and lignin (250-503°C) (Di Blasi, 2008). It was found that higher heating rates and high degradation temperatures result in reaction overlap with simultaneous devolatilization of the three components (Shafizadeh, 1985; Di Blasi, 2008).

Thermal degradation of rice husk in an oxygen environment, observed both using evolved gas analysis (EGA) and thermogravimetric analysis (TGA) has shown that the hemicellulose component of the rice is the first one to volatize followed by the volatilization of the cellulose. Lignin degradation was found to be slower, occurring over a wider temperature range (Mansaray and Ghaly (1997); Bahari (2012)). Bahari (2012) carried out evolved gas analysis (EGA) of rice husk and found that oxygen absorption at lower temperatures in the low temperature oxidization (LTO) regimes was more than carbon oxides formation, and corresponded to hemicellulose decomposition; medium temperature oxidization (MTO) regimes corresponded to cellulose devolatilization and combustion of degraded volatile hemicellulose components; and lignin volatilization peaked at highest temperatures during the high temperature oxidization (HTO) regime at 350 – 380°C. Mansaray and Ghaly (1997) carried TGA experiments with rice husk in oxygen atmosphere and reported that the thermal degradation of rice husk depends on the proportions of cellulose, hemicellulose, and lignin components present in the rice husk. They reported hemicellulose decomposition in the range of 150 – 350 °C, cellulose decomposition in the range of 275 to 350°C, and lignin decomposition in the range of 250 to 500 °C.

Bharadwaj (2002) studied the microstructural transformation of rice husk particles during thermochemical conversion, and observed that there were virtually no change in size and shape of the particle upto 200°C, and then there was a rapid shrinkage between 200 to 400 °C, after which the shrinkage became slower and stopped after 900°C. These physical observations were consistent with the results of the respective TGA and EGA analyses of Masanray and Ghaly (1997), and Buhari (2012). Bharadwaj et al., (2004) observed that radial shrinkage of rice husk particle was significantly larger than the longitudinal shrinkage and the aspect ratio (L/D) increased from initial value of 2.19 to 3.23; and concluded that the inert silica skeleton resists high temperatures and was strong and stable up to 1500°C. They also found that the hemicellulose, cellulose, and lignin components were preferentially devolatilized in geometrically arranged pores and channels. The shrinkage pattern can be further explained by microstructural analysis of the rice husk structure, which showed that the lemma and palea are made up of roughly rectangular particles bound to form a rigid structure with longitudinally aligned silica fibres regularly interspaced in a matrix consisting of cellulose, hemicellulose, and lignin (Figures 7.1 & 7.2). Bharadwaj et al. (2004) suggested that the structure of rice husk is similar to a composite material with silica tubes filled with cellulose material constituting the strong-phase and a matrix consisting of lignin.

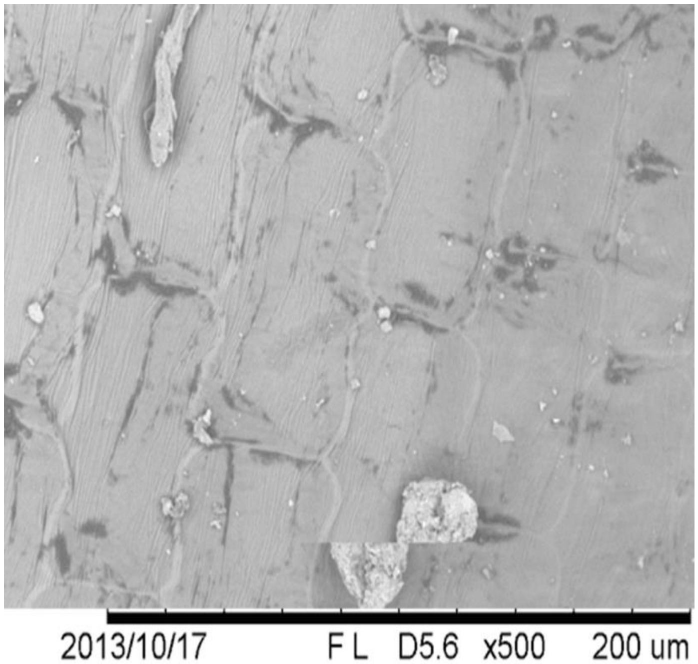


Figure 7.1. SEM of rice husk particle showing silica microstructure in a lignin matrix

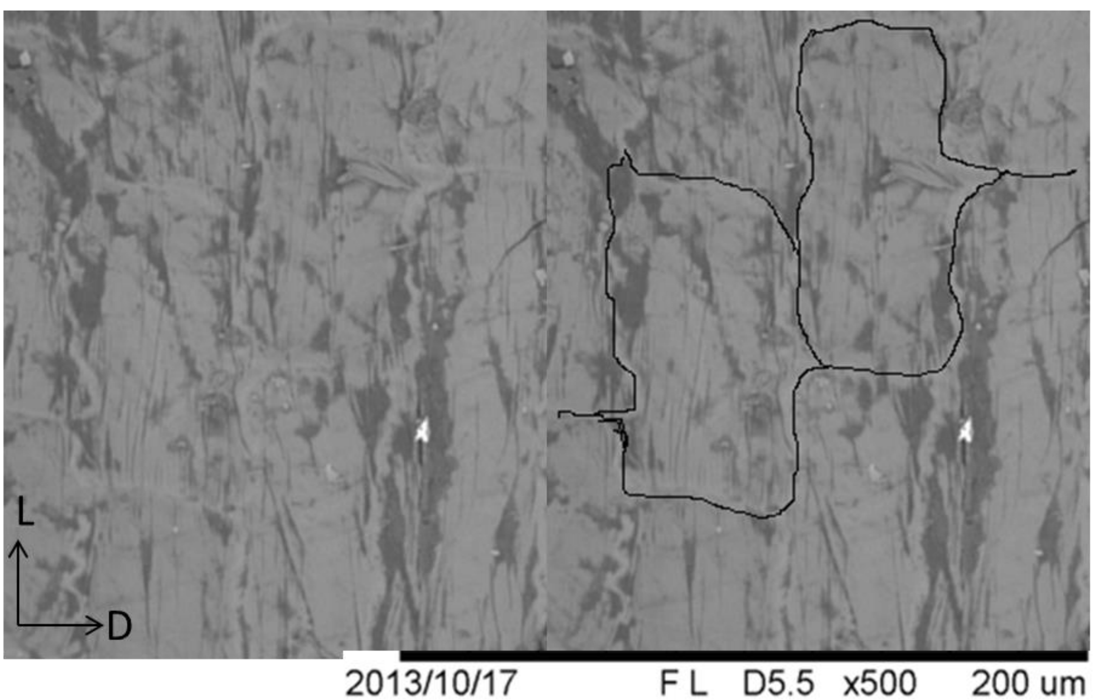


Figure 7.2. SEM of rice husk particle microstructure showing longitudinally aligned silica fibres

FTIR and SEM analyses of rice husk (RH) and its ash (RHA) are important methods of assessing the thermochemical characteristics of the rice husk, and physicochemical characteristics its ash (RHA). FTIR spectra of the RH and RHA of the samples will show the components of the rice husk (RH) that volatized during the thermochemical conversion processes; as well as, the chemical components that constitute the ash (RHA). SEM analysis of RH and RHA will show the physical transformation that the rice husk undergoes during the thermochemical conversion process. The RHA physicochemical characteristics are important in determining design parameters for both the reactor and the ash handling system.

Biomass combustion in a pressurized oxygen atmosphere is a complex dynamic reaction process that can be characterized by three groups of simultaneous and competing reaction regimes: Low temperature oxidation (LTO), medium temperature oxidation (MTO), and high temperature oxidation (HTO) (Bahari, 2012). These regimes are based on temperature and involve chemical reactions that are quite different; but occur across overlapping temperature ranges and are dependent on activation energy levels, rate of diffusion of reactants, and rate of reaction between components that translate into particle to particle ignition rate. The LTO regimes occur at temperatures <300° C, involving mostly, the diffusion of oxygen molecules into the volatile components that are released as gaseous mixtures. In LTO regime, oxygen is consumed to produce carboxylic acids, aldehydes, ketones, alcohols and hydroperoxides with carbon oxides formations. LTO reactions are kinetic control reactions rather than diffusion control reactions due to the fact that oxygen diffusion to hydrocarbons is faster than the oxidation process. This is explained by the fact that diffusion control reactions are governed by collision frequency, where the formation of products is faster than the diffusion of reactants. Since LTO reactions are kinetic control reactions, the energy levels control the reaction pathways of the product mixtures, and their reversibility is based on the activation energy (Fassihi et al., 1984; Solomon, 1988; Bahari, 2012). LTO reactions may cause spontaneous ignition of the oxidized gaseous mixtures released within the inner core of the biomass that may contribute to disintegration of loose or poorly compacted biomass; resulting into spillage in the case of the bomb calorimeter test, thus affecting the gross calorific value measurement. Spillage is a condition where part of the sample spills out of the test dish resulting in only partial combustion of the rice husk samples. Spillage may also occur during pressurization of loosely packed biomass. Spillage can be determined by comparing the bomb calorimeter residuals to the proximate ash content (dry basis) of the rice husk. In a bomb calorimeter experimental process, once the ignition fuse is activated at the surface of the pellet, the temperature rises rapidly with simultaneous LTO, MTO, and to a lesser extent HTO reactions occurring at the surface of the pellet. This increases the temperature and pressure of the core that results in ignition of the released oxidized hydrocarbons and core particles within the pellets that are undergoing the LTO reactions (Figures 7.3 & 7.4). The core ignition could cause the pellet core to disintegrate, if the bonding between particles is weak, resulting in some of the particles spilling out of the dish into the bottom of the bomb calorimeter. When that occurs after the experiment, some un-combusted rice husk particles are usually collected at the bottom of the bomb vessel, resulting in inaccurate measurement of the calorific value of the rice husk. MTO occurs at temperatures above 300°C and is mainly caused by oxidation of the product of pyrolysis producing carbon oxides. In the excess oxygen environment of a bomb calorimeter, any light hydrocarbon produced by the LTO regime may immediately undergo MTO reactions (Fassihi, 1984; Kisler, 1995; Bahari, 2012). The solid residue usually undergoes HTO at higher temperatures. HTO is generally exothermic with heterogeneous reactions that involve the combustion of solid residue deposited by pyrolysis and starts at temperatures between 316-340 °C depending on the biomass (Alexander et al., 1962; Dabbous and Fulton, 1974; Bahari, 2012). HTO oxygen combustion is nearly equal to carbon oxides production (Fassihi et al., 1984; Kisler and Shallcross, 1997; Bahari, 2012). In the case of a bomb calorimeter, these three regimes will occur very fast and will overlap. Lower particle size increases devolatilization of rice husk particle to gaseous components. Natarajan and Sundaram (2009) reported that rice husk gas yield during pyrolysis increased from 32.31 to 43.26% when particle size was decreased from 1.8mm to 0.15 mm. Therefore, grinding the rice husk to below #60 (<0.250 mm) ensures the production of densified rice husk pellets with increase in sub-particle fibre (see Figures 7.1 & 7.2) surface area for bonding during densification, as well as, a smaller silica-fibre sub-particle composite that will devolatilize effectively during the bomb calorimeter test with effective transition during the three oxygenation reaction regimes; as the pellet macrostructure shrinks to form a solid silica ash matrix composite.

A stable pellet can withstand the reaction processes in a bomb calorimeter. Bomb calorimeter reactions start at the surface by the ignition fuse, initiating the three progressive regimes of oxidation process (starting with the LTO reactions, then the MTO reactions, and finally the HTO reactions); and simultaneous pyrolysis of the biomass. Propagation of pressure and reaction temperature fronts (as shown in Figures 7.3 and 7.4) from the surface of the pellet to its core is highly affected by biomass pellet structure. The pellet temperature and pressure increased with time during the reaction processes, with development of higher temperatures and pressures at the core (Di Blasi, 1998; Di Blasi, 2008).

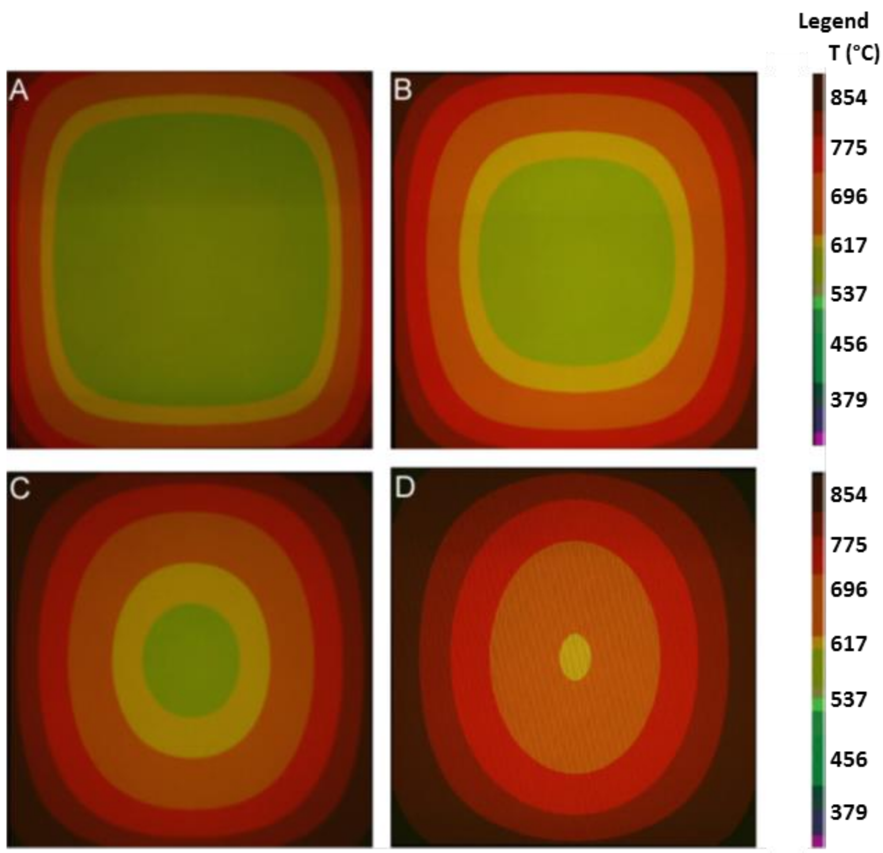


Figure 7.3. Color maps of biomass particle core temperature exposed to T=900 °C with respect to time; A=31s, B=63s, C=93s, D=125s (Di Blasi, 1998; Di Blasi, 2008)

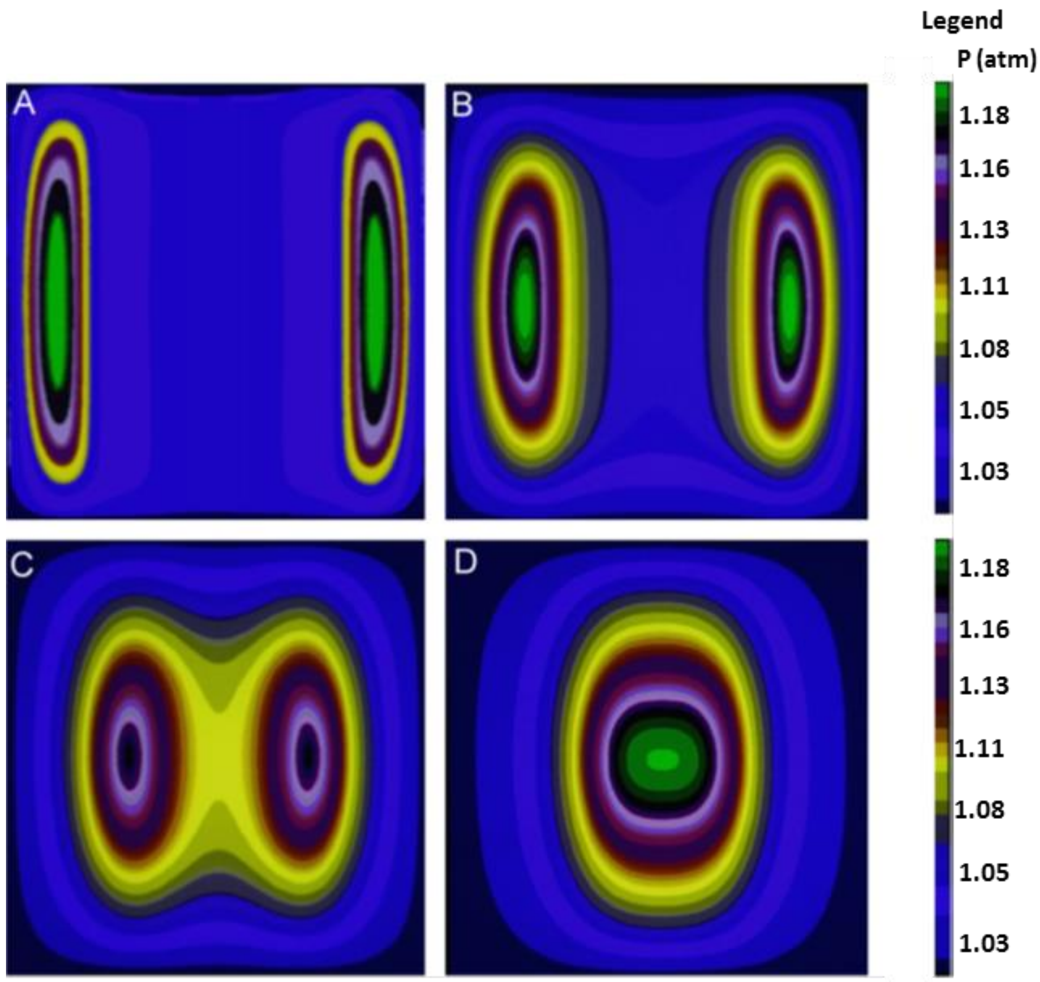


Figure 7.4. Color maps of biomass particle core pressure exposed to T=900°C with respect to time: A=31s, B=63s, C=93s, D=125s (Di Blasi, 1998; Di Blasi, 2008)

Effective densification of rice husk can produce a stable and friable pellet with strong microscopic and macroscopic inter-particle bonding. The key parameter that can be used to determine the friability of the rice husk pellet, which will predict its resistance to breakage during a high pressure combustion process, is its impact strength or its impact resistance (ASTM, 2006). The impact strength of densified rice husk and other biomass can be attributed to the microscopic and macroscopic bonding characteristics between particles (Kaliyan and Morey, 2010). Densification at medium and high pressures can increase the impact resistance of biomass. Factors that may affect the impact strength include particle size distribution, bulk density, particle density, sphericity, porosity, binder characteristics, chemical composition, moisture content, and die pressure during densification (Mani et. al., 2005; Kaliyan and Morey, 2010). Biomass residues are often available as loose particles with low bulk density and are difficult to analyse further as such. In order to test such biomass in an oxygen bomb calorimeter, the biomass needs to be densified into a pellet. However, biomass such as rice husk is difficult to densify without the utilization of binders. The utilization of binders or other additives (adjuvants) can help to ensure complete combustion of rice husk which adds value to the process, since most binders will contribute their own energy value to the system they are meant to bind, thus in order to help in the selection of a binder, its own energy value needs to be known separately from the energy value of the biomass. To avoid changing the composition and the heating value of the biomass samples, water is the best densification binder for a bomb calorimeter test, since the densified pellet can easily be dried to remove the water. The densified pellets also need to be dried to ensure proper ignition and combustion during the test. Figures 7.3 & 7.4 (above) show how high temperatures and high pressures develop within the core of the pellet during thermochemical conversion process, which could lead to disintegration of a pellet. Densification at the lowest die pressures by using hold time as a parameter is a simple and viable technique of obtaining pellet samples that can withstand the high temperatures and pressures that can develop within the pellet core in the bomb calorimeter. Uniform particle size distribution, particle size and shape are important in thermochemical conversion processes (Ghaly and Al-Taweel, 1990). Shen et al. (2012) investigated the heating value of rice husk using an oxygen bomb calorimeter with benzoic acid which has a known heating value, and is usually used for the calibration of bomb calorimeters as a binder and a combustion adjuvant, and they reported higher high heating values (HHV) for rice husk compared to other methods of measurements.

Determination of the proximate composition (dry basis) of the rice husk samples also provides important information for comparative analysis and empirical prediction of HHV. The biomass thermochemical conversion process can be characterized and predicted based on its proximate composition (dry basis) namely: volatile, fixed carbon, and ash contents of the biomass. This has led many researchers to empirically correlate and predict higher heating value (HHV) of biomass based on its proximate components (Cheng & Azevedo, 2006; Parikh et al., 2005; Yin, 2011; Nhuchchen & Abul Salam, 2012).

Grinding the rice husk samples to a particle size that passes through standard sieve size #60 (0.250 mm) can ensure a uniform particle size distribution. To produce such pellets without adding a binder (except water) requires the determination of the effects of die pressure and hold time on the impact strength of the pellets. In this experiment, water was used as a binder. Comparing the ash content (dry basis), obtained using ASTM3174-04 standard, to the bomb calorimetry residuals will help determine if spillage has occurred, or whether there was complete combustion of the rice husk samples in the bomb calorimeter; validating the higher heating value obtained during the test.

7.2.1 Objectives

The overall objectives of this study were to investigate the thermochemical properties of the Engelberg and Milltop mills rice husks. The specific objectives of this research were:

1. To study the proximate compositions of Engelberg and Milltop rice husks including: moisture, ash, volatile and fixed carbon contents.
2. To study the thermochemical conversion properties of Engelberg and Milltop rice husks and their ash using FT-IR and SEM analyses.
3. To study the high heating value (HHV) of the Engelberg and Milltop rice husks.
4. To develop an effective method for the determination of the high heating value (HHV) of rice husks using an oxygen bomb calorimeter based on the densified rice husk pellet physical resistance, and comparative analysis of bomb calorimeter residuals to proximate ash.
5. To develop predictive models by correlating high heating value (HHV) to the proximate analysis components of the Engelberg and Milltop rice husks.

7.3 Materials and Methods

7.3.1 Materials

Ten rice husks samples identified with letters A to J from the sub-Saharan African country of Uganda were used for these experiments (Table 7.1). The rice husks were obtained from two rice processing units, the Milltop and the Engelberg rice dehuskers.

Table 7.1 Rice husk samples

Samples	Source	Variety	Farm	Mill type
A	Doho irrigation	Kaiso	Farm 3	Milltop
B	Doho irrigation	Kaiso	Farm 1	Milltop
C	Lira	Super	Abolete	Milltop
D	Doho irrigation	Kaiso	Farm2	Milltop
E	Nuya-Acholi	NERICA-1	Nuya-Acholi	Milltop
F	Lira	Super	Lira	Engelberg
G	Lira	Super	Lira	Engelberg
H	Lira	Super	Lira	Engelberg
I	Lira	Super	Lira	Engelberg
J	Lira	Super	Lira	Engelberg

The rice husk samples were ground using a Brinkmann Restch mill (Figure 7.5) to produce a uniform particle size which passes through #60 (0.250 mm) standard sieves. The ground rice husk samples were mixed to ensure homogeneity.

Figure 7.5. Top view of Brinkmann Restch mill with the two front shakers

The bomb calorimeter setup includes a Parr 1341 bomb calorimeter coupled to a Parr 6772 microprocessor based calorimetric thermometer that was networked via a D-Link router to a computer used for the determination of the high heating value (HHV) experiments (Figure 7.6).

Figure 7.6. Bomb calorimeter networked via a D-Link router

A four decimal digital scale (measured accuracy to 0.0001g), Sybron-Thermolyne muffled furnace (Figure 7.7), and Isotemp air furnace were used for weight measurement and proximate analysis of the samples respectively. A manual hydraulic jack and a piston-die setup were used for the densification process (Figure 7.8).

Figure 7.7. Sybron-Thermolyne muffled furnace

Figure 7.8. Harco manual hydraulic press equipped with pressure gauge

Fourier transform infrared spectroscopy (FT-IR) and Scanning Electron Microscopy (SEM) were carried out using a Thermo Scientific Nicolet iS5 FT-IR equipped with attenuated total reflectance (ATR) (Figure 7.9), and Hitachi tabletop SEM TM3000 (Figure 7.10), respectively.

Figure 7.9. Thermo Scientific Nicolet iS5 FT-IR equipped with ATR

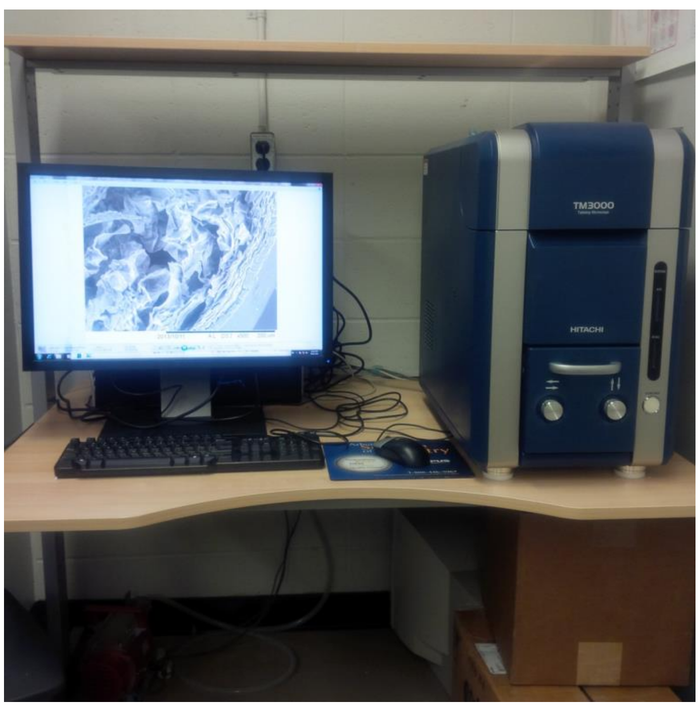


Figure 7.10. Hitachi tabletop SEM TM3000

7.3.2 Methods

7.3.2.1 Proximate analysis

Proximate analysis of fuels provides quantification for moisture, volatiles, fixed carbon and ash. Moisture contents of the rice husk samples were determined using American Society of Agricultural and Biological Engineers standards (ASABE, 2006); and volatiles, fixed carbon and ash were determined using American Standards of Testing Materials standards for gaseous fuels, and coal and coke (ASTM, 2006). Muffled furnace (SYBRON-Thermolyne), desiccators, crucibles, and a high accuracy digital scale were used for these analyses. Three replicate measurements were made for each.

7.3.2.1.1 Moisture analysis

The moisture content was determined using the American Society of Agricultural and Biological Engineers (ASABE) standard S358.2 (ASABE, 2006a) for biomass materials such as the rice husk which are highly volatile. This method is similar to ASTM 3173-03 (ASTM, 2003). Triplicate samples of the rice husk were oven dried at 103±2°C for at least 24 hours and the samples were weighed until a constant weight was obtained.

7.3.2.1.2 Ash content

The ash content was determined based on the ASTM 3174-04 method (ASTM, 2004). Three replicates of 1.0g of the samples were placed in a crucible at a temperature of 750±10°C for 1 hour. The crucibles were then removed and placed in desiccators to cool, and then weighed to determine the ash content (ASTM, 2006; Panwar et al., 2011).

7.3.2.1.3 Volatile matter

ASTM D-3175-07 procedure was used to determine the volatile matter. Three replicates weighing about 1.0g of the samples in covered crucibles were placed in a muffled furnace maintained at 950 ± 10°C for 6 min. Then, the crucibles were removed and placed in desiccators, and weighed after cooling. The amount of volatile matter in the biomass is the weight loss on a dry matter basis (ASTM 2006; Panwar et al., 2011).

7.3.2.1.4 Fixed carbon

The fixed carbon was the weight of the solids left in the crucible after the ASTM D-3175-07 minus the ash obtained from the ASTM 3174-04 experiment. It was calculated as a percentage, by subtracting the ash content and the volatile matter content from 100% (Mansaray and Ghaly 1997; ASTM standard 2006; Panwar et al. 2011).

7.3.2.2 Thermochemical analysis of rice husk and rice husk ash using FT-IR and SEM

The Engelberg and Milltop rice husk samples and their proximate ash were studied using FT-IR and SEM to study their thermochemical and thermophysical characteristics, as well as, to study the thermochemical conversion processes and physical transformation that took place during the reduction processes that converted the rice husks (RH) to rice husk ashes (RHA).

7.3.2.2.1 FTIR-ATR analysis of rice husk and rice husk ash

The rice husk samples and their proximate ash were studied using a Fourier transform infra-red spectrometer equipped with attenuated total reflection equipment (FTIR-ATR), in order to identify the chemical groups and compare the ash to the rice husk samples. In the FTIR-ATR, the samples were held in close contact with the prism called the internal reflective element (IRE) that has a higher refractive index than the samples. When, an incident beam (IR) was introduced into the prism, at an angle greater than the critical angle (θ_C), which is defined by the ratio of the refractive index of the IRE (n_1) and the refractive index of the samples (n_2), as described by Equation 7.1; an evanescent wave with amplitude exponential decay as described by Equation 7.2 that extended into the samples was generated (See Figure 6.2, page 165),

$$\theta_C = \sin^{-1}\left(\frac{n_2}{n_1}\right) \tag{7.1}$$

$$E_C = E_O\, exp(-\gamma z) \tag{7.2}$$

In equation 7.2, E is the amplitude in the sample at a depth z, γ is a constant that is dependent on penetration depth, and E_o is the amplitude at the surface of the sample (at z=0). The evanescent wave absorbed energy in some regions, and its intensity was altered. The attenuated energy was returned to the IR beam as it existed at the opposite end of the crystal to the detector of the spectrometer and was used to generate the IR spectrum of each the samples (Gosh 2010; Setnicka, 2005).

Triplicates of the samples were scanned at the infra-red range of interest between 4000 cm^{-1} to 500 cm^{-1} for 15 seconds with the production of a spectral diagram that was an average of 64 scans.

7.3.2.2.2 SEM analysis of rice husk and rice husk ash

The rice husk samples and their proximate ash were studied using Hitachi TM3000 tabletop scanning electron microscope (SEM) at different levels with the objective of studying the surface and sub-surface structures of the rice husks (RH) and their ash (RHA). In order to avoid the electron accumulation on the surface of the non-conductive specimen due to high vacuum SEM, referred to as the charge-up phenomenon, the T3000 uses charge-up reduction mode, using a low vacuum level, that increases the presence of gas molecules which can collide with the electron beam to generate positive ions and electrons (negative), ensuring neutralization of excess electron ions on the specimen surface (See Figure 6.3, page 166).

This method eliminates the conventional vacuum coating process of the non-conducting sample with a thin metal layer, which is time consuming and can interfere with imaging and EDX analysis. Structure of the ashes (RHA) of both the Engelberg and Milltop samples were analyzed to investigate structural changes after thermochemical conversion processes, as well as, possible pore formations as the volatiles and combustibles escaped during the thermochemical conversion process.

7.3.2.3 Densification experiments

Densification was carried out using a manual hydraulic press equipped with a pressure gauge. The rice husks were ground by a Restch mill to obtain homogeneous particle sizes that passed through a #60 (0.250 mm) standard sieve. Rice husk samples were densified using a piston and die at a medium pressure of 42.5 MPa, moisture content of 15%, and holding times (dwelling times) of 20, 40, and 60 seconds. The densified rice husk pellets were oven dried at 103±2°C for 24 hours before the impact tests were carried out.

7.3.2.4 Rice husk impact test

The impact strength of the rice husk samples was determined using ASTM standard method D440-86 (ASTM, 2002). Triplicate pellets of the densified rice husk samples (densified at hold times of 20, 40, and 60 seconds) were dropped 1.83 meters on a concrete floor and the impact resistance index was determined using the following relation:

$$Impact\ Resistance\ Index\ (IRI) = \frac{\mathbf{100xN}}{\mathbf{n}} \qquad (7.3)$$

Where N= total number of drops and n=total number of pieces. The objective of this test was to determine the resistance to disintegration of the pellet as a result of immediate impact; therefore, the method used by Richards (1990), and later by Panwar et al. (2011) was used based on the ASTM D-440-86(2002) standards. Each pellet was dropped twice and after the first drop, all the pieces that weighed less than 5% were not dropped for a second time (Richards, 1990; Panwar et al., 2011).

7.3.2.5 Bomb calorimetry

The bomb calorimetry tests of the samples were carried out using densified pellets of the samples that have the highest impact resistance based on the impact tests. The bomb calorimeter (Parr 1341) was calibrated using 1.0000 g of standard benzoic acid pellet with energy value of 26.45 MJ/kg (6318.4cal/g). After standardization, corrections for fixed acid (value=41.868 J (10 cal)), fixed sulphur (value=0.0), and fixed fuse (value =62.802 J (15 cal) accounting for the energy value of the ignition fuse, were programmed into Parr 6772, as specified by the manufacturer. The high heating value (HHV) was automatically calculated by the microprocessor control Parr 6772 and the report was accessed via a D-Link router that was connected to the computer. The high heating value (HHV) was measured as the heat of thermochemical conversion processes, based on the change of temperature, the mass of the sample, and the specific heat capacity value of the bomb (determined during the calibration test by combustion of the standard benzoic acid pellet), using the ASTM D5865-04 (ASTM,

2004) standard method. The pellets were combusted in the bomb calorimeter at a high pressure (3.0 MPa) oxygen environment using the microprocessor based Parr 6772 and 1341 bomb calorimeter setup to obtain a HHV of the rice husk samples (Figure 7.6 above). The weights of the combustion residues from the tests were compared to the proximate ash contents (ASTM 3174-04) of the rice husk samples to determine if full combustion had taken place during the bomb calorimetry tests.

7.3.2.6 Bomb calorimetry residual analysis

Bomb calorimeter residuals include the solid ash and the wiped content from the bomb vessel, which includes ash, other combustion products (including soot) and any content of the original sample that had spilled in the bomb vessel and did not volatize during the combustion process. Comparing bomb calorimeter residuals to the proximate ash content gives the indication of the spillage and incomplete combustion that had occurred during the bomb calorimeter oxidation process. Weighed and dried delicate task wipers (Kimwipes EX-L) were used to wipe the inside of the bomb to recover any soot and spillage that might have occurred. These and the bomb dish containing the combusted solid ash were dried in a forced-air oven to obtain the dry weight of the residuals. The dried weight of the residuals was determined as percentages of the pellets' original weight for comparative analysis with the proximate ash.

7.3.2.7 Statistical analysis

Statistical analyses including ANOVA, Tukey-Kramer, and Student's t, analyses were carried out using JMP10 statistical software.

7.4 Results and Discussion

7.4.1 Proximate analysis of rice husk samples

The proximate analysis of the ten rice husk samples from sub-Saharan Africa that were analyzed clearly showed how postharvest processing affects the proximate composition of rice husk (Tables 7.2-7.5). Engelberg rice husks (samples F-J) were found to have generally higher volatile contents, lower ash contents, and lower fixed carbon contents than the Milltop mill rice husks samples (samples A – E). The proximate components observed were also found to be comparable to the study carried out by Mansaray and Ghaly (1997) on characterizing six rice husk samples.

7.4.1.1 Moisture content

The mean moisture content of rice husk samples ranged from 5.08 to 6.64 %, with a pooled average moisture content of 5.92% (Figure 7.11 and Table 7.2). The Milltop rice husk samples (samples A - E) had higher variability of moisture content with an average moisture content of 6.01% and standard deviation of 0.57, than the Engelberg samples (samples F - J), which had an average moisture content of 5.80% and standard deviation of 0.20), although the samples were stored in the same environment. This observation may be due to the moisture absorption characteristics, and the different initial moisture contents of the rice husks.

Table 7.2 Moisture contents of rice husk samples

Moisture content (%)							
Sample	**Number**	**Mean (%)**	**Std Dev (%)**	**Std Err Mean**	**Minimum**	**Maximum**	**Median**
A	3	6.47	0.02	0.01	6.45	6.49	6.46
B	3	5.87	0	0	5.87	5.87	5.87
C	3	5.34	0.46	0.26	5.07	5.87	5.08
D	3	6.12	0.92	0.53	5.06	6.65	6.64
E	3	6.24	0.34	0.2	6.04	6.63	6.04
F	3	5.93	0.09	0.05	5.88	6.03	5.89
G	3	6.03	0.16	0.1	5.89	6.21	5.98
H	3	5.66	0.01	0	5.65	5.66	5.66
I	3	5.85	0	0	5.85	5.85	5.85
J	3	5.54	0	0	5.54	5.55	5.54

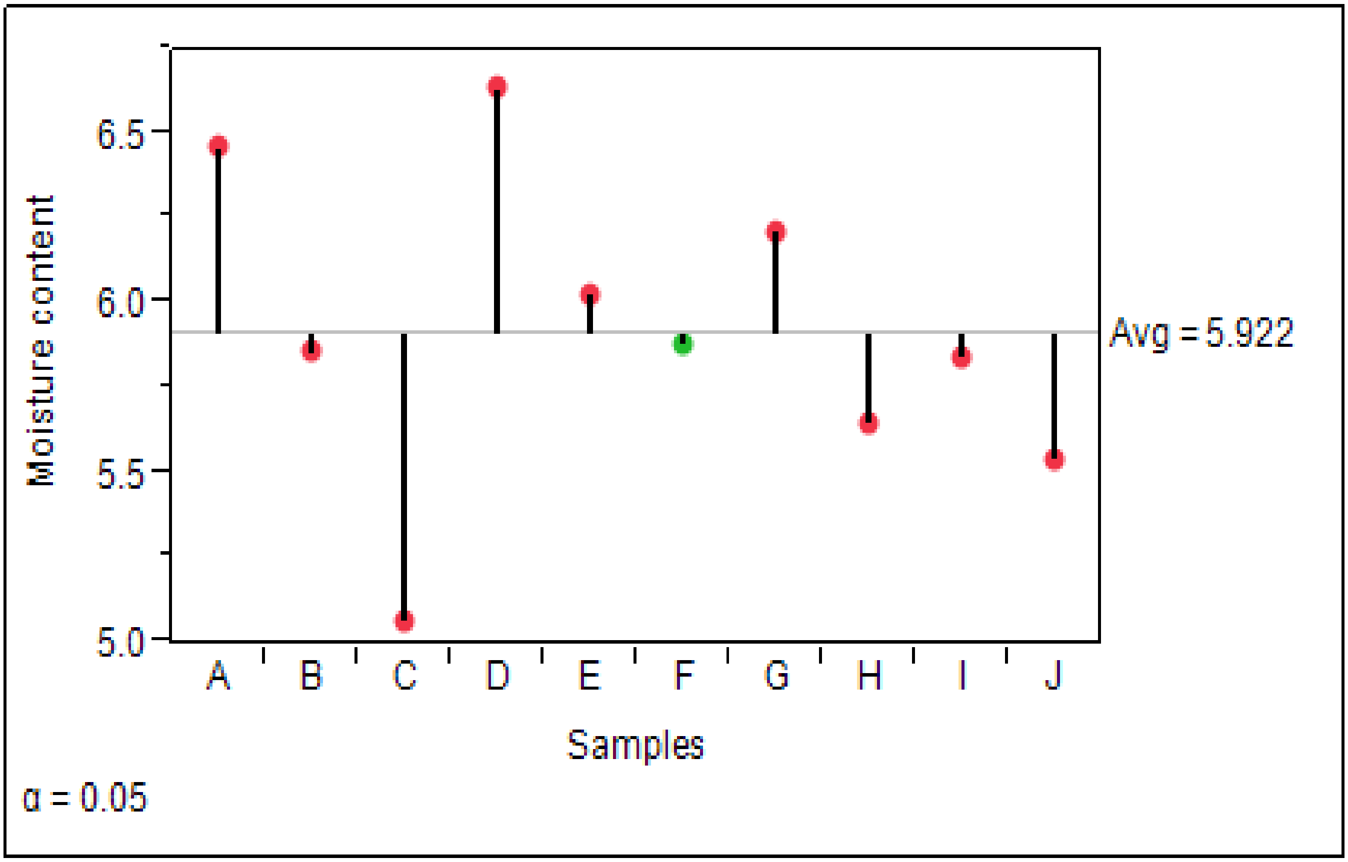


Figure 7.11. Moisture content (%) of rice husk samples

7.4.1.2 Ash content

Ash content of the rice husk samples ranged from 12.66 to 24.91%, with a pooled mean of 21.20% and SE=0.42. Significant differences in ash content between the rice husk samples were observed (Figure 7.12 and Table 7.3). From the results it was observed that the ash contents of the Milltop rice husk were significantly higher than that of the Engelberg rice husk, except for the case of sample J. The reason for high ash content of sample J compared to the other Engelberg samples was further investigated using FT-IR and SEM, which revealed that sample J had higher immature grain content.

Table 7.3 Ash contents of rice husk samples

Ash content of samples (% dry basis)							
Sample	**Number**	**Mean**	**Std Dev**	**Std Err Mean**	**Minimum**	**Maximum**	**Median**
A	3	23.67	0.81	0.47	22.98	24.56	23.48
B	3	21.34	1.61	0.93	19.71	22.93	21.38
C	3	24.88	0.65	0.37	24.13	25.29	25.21
D	3	23.7	0.07	0.04	23.63	23.76	23.72
E	3	21.92	0.93	0.54	20.91	22.75	22.09
F	3	20.17	0.73	0.42	19.58	20.99	19.93
G	3	12.74	0.25	0.14	12.55	13.02	12.66
H	3	19.48	0.37	0.21	19.18	19.89	19.36
I	3	20.38	0.18	0.1	20.19	20.55	20.39
J	3	23.76	0.28	0.16	23.5	24.05	23.73

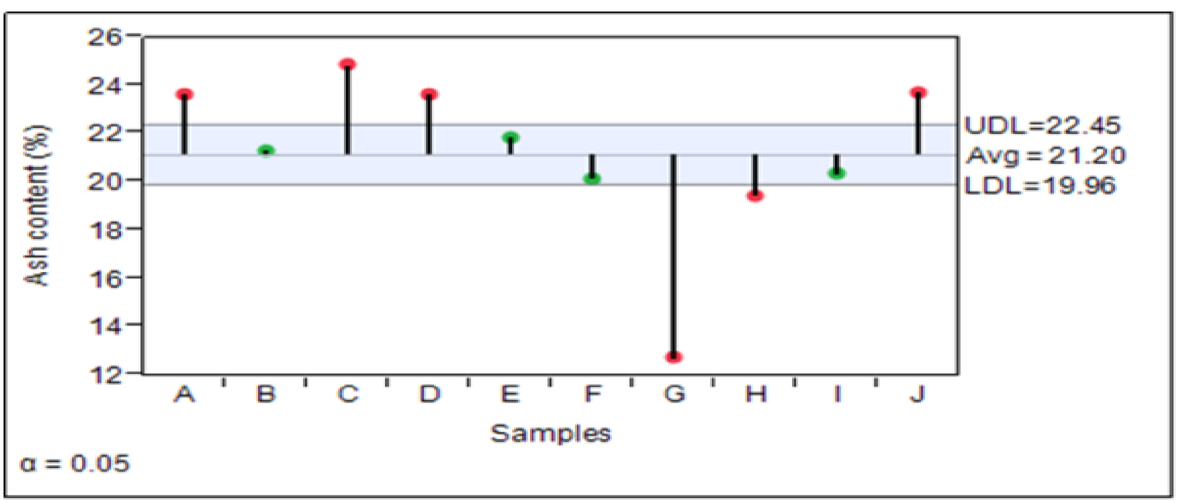


Figure 7.12. Ash content based on ASTM 3714-04 Standard

Analysis of the ash content of the Engelberg rice husks showed that the average ash content of the samples was 19.30%, with a range of 12.74 to 24.45%. Analysis of means showed that sample G had the lowest ash content and sample J had the highest. ANOVA, Student's t Tukey-Kramer, and Hsu's MCS at α=0.05, showed that there were no significant difference among the means of the ash contents of samples F, H, and I; however, it was found that sample G and sample F were significantly below and above the lower and higher decision limits of the analysis of mean, respectively (Figures 7.13 & 7.14). This led to a physical analysis of the rice husk samples, which showed that sample G had the highest broken rice content, and sample J had the highest immature grain content.

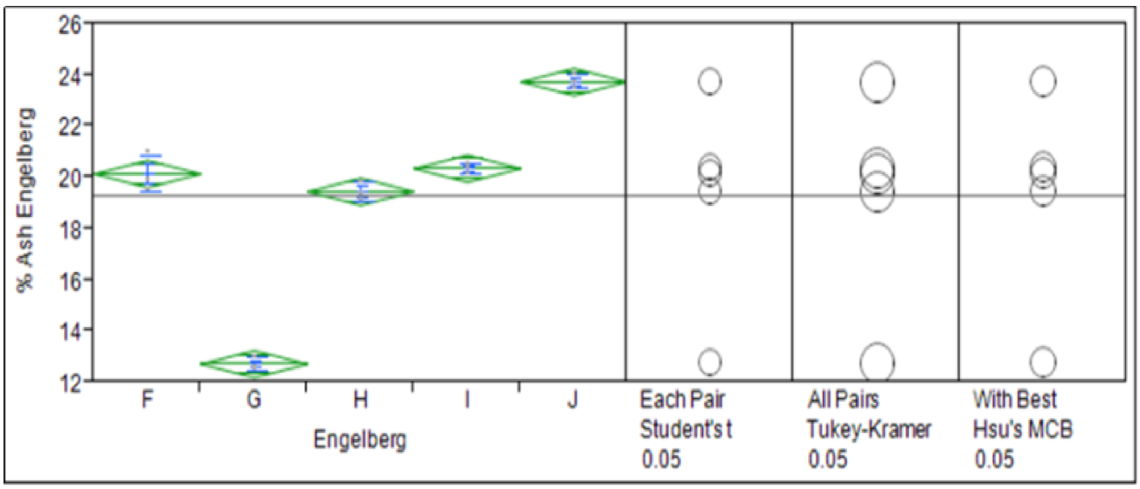


Figure 7.13. Ash content of the Engelberg rice husk

Figure 7.14, shows the ANOVA, Student's t Tukey-Kramer, and Hsu's MCS at α=0.05 of the ash content of the Milltop rice husk. The results showed that there was no significant difference between the means of the Milltop rice husk samples. The mean of the samples was 23.10%, with a range of 21.34 to 24.90%. The ash contents of the Milltop rice husk were significantly higher than that of the Engelberg, since its major component was the high silica containing outer shell (lemma & palea) of the rice paddy with only a very small quantity of the inner aleurone and subaleurone layer components, fewer broken rice, and small amount of entrained immature paddies.

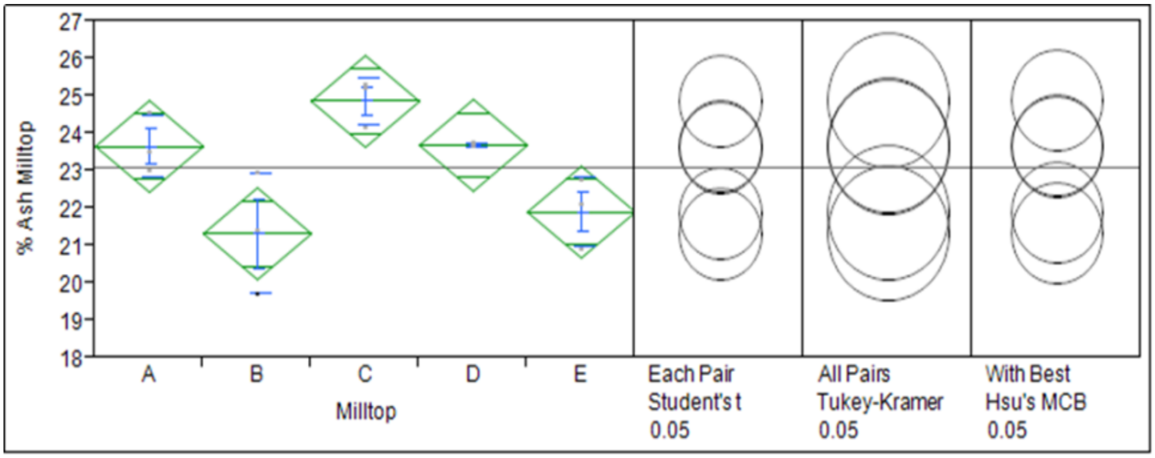


Figure 7.14. Ash content of the Milltop rice husk

7.4.1.3 Volatile matter content

Volatile components of the rice husk samples ranged from 62.83 to 75.99% with a pooled mean of 67.32%. Analysis of the mean (ANOM) showed that the Milltop rice husks were below or close to the mean, while the Engelberg were above the mean (Figure 7.15 and Table 7.4).

Table 7.4 Volatile contents of rice husk samples

Volatile content of samples (% dry basis)							
Sample	**Number**	**Mean**	**Std Dev**	**Std Err Mean**	**Minimum**	**Maximum**	**Median**
A	3	63.72	0.35	0.2	63.47	64.12	63.58
B	3	65.93	0.6	0.34	65.52	66.61	65.65
C	3	63.69	0.58	0.34	63.02	64.07	63.99
D	3	63.72	0.99	0.57	62.83	64.79	63.53
E	3	67.38	0.19	0.11	67.23	67.6	67.32
F	3	68.16	0.47	0.27	67.77	68.68	68.02
G	3	74.36	1.47	0.85	73.14	75.99	73.95
H	3	68.69	1.38	0.8	67.74	70.27	68.06
I	3	67.26	0.05	0.03	67.23	67.31	67.23
J	3	70.32	0.57	0.33	69.75	70.89	70.31

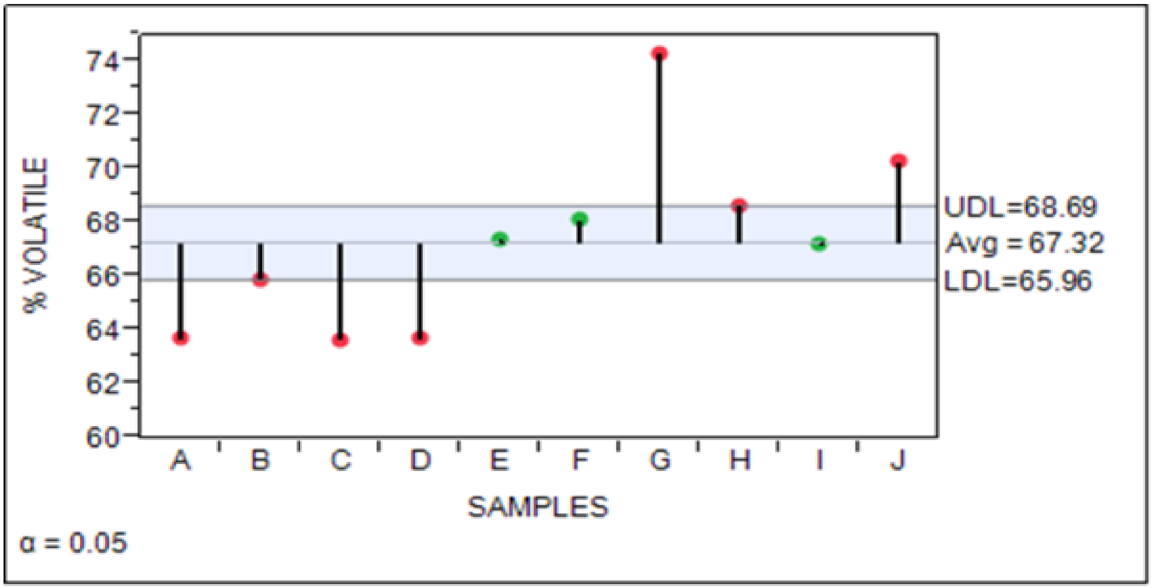


Figure 7.15. Volatile contents of the rice husk samples

Volatile components of the Engelberg rice husk samples ranged from 67.77 to 75.99%, with a mean of 69.76%, and standard deviation of 2.72%. The observed mean of the Engelberg was higher than the pooled mean (Figure 7.15). ANOVA, ANOM, Student's t Tukey-Kramer, and Hsu's MCS at α=0.05, of the volatile component of the Engelberg rice husk showed that sample G had the highest volatile component and was significantly higher compared to the other Engelberg rice husk samples (Figure 7.16). Further analysis revealed that the high volatile component of sample G could be based on its high content of entrained broken rice compared to all other samples. The high broken rice content observed could be attributed to inefficient postharvest processing that may include parboiling, drying and milling conditions. Sample J was also found to be higher than samples F, H, and I, which could be attributed to the higher immature grains content resulting from the inadequate timing of harvesting, and probably difficult growing condition issues.

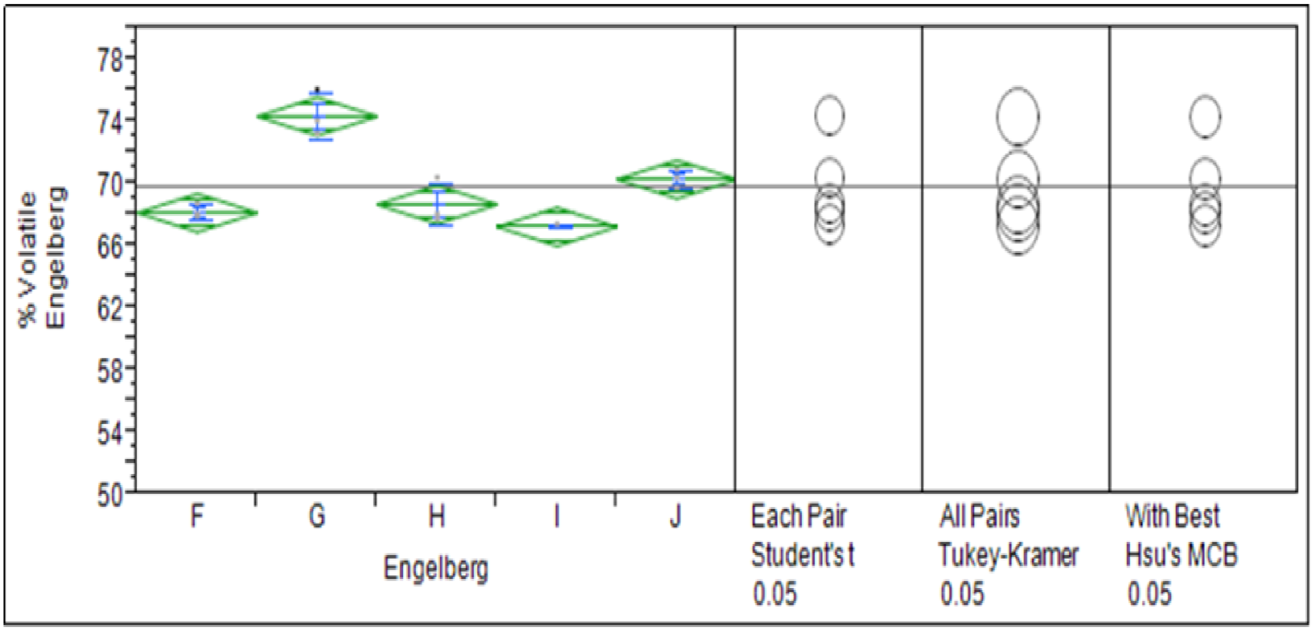


Figure 7.16. Volatile contents of the Engelberg rice husk samples

The range of the Milltop rice husk was 62.83 to 67.60%, with a mean of 64.89% and standard deviation of 1.65%. Volatile components of the Milltop rice husk samples were lower than the pooled mean and even the lower decision limits (UDL) obtained from the analysis of mean (ANOM), with the exception of sample E which was found to be significantly higher than all the other Milltop samples (Figure 7.17).

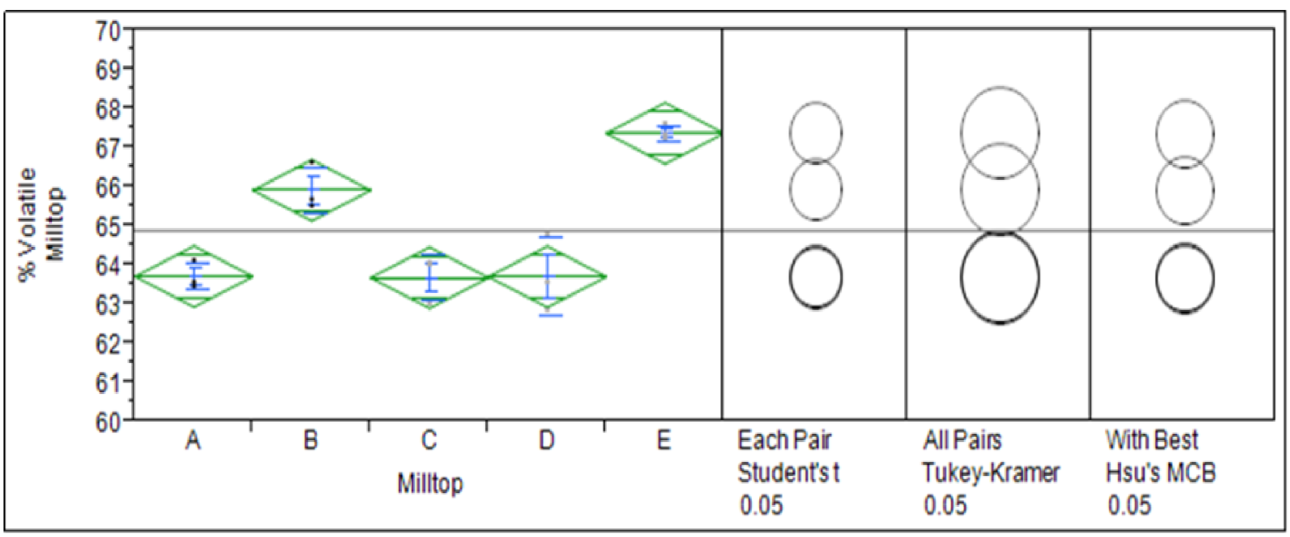


Figure 7.17. Volatile contents of the Milltop rice husk samples

The difference between volatile component of sample E and the other Milltop rice husks could be attributed to variety characteristics. The sample was a NERICA variety, while the others were the Super and Kaiso varieties. SEM analysis showed that sample E which is a NERICA had the most rigid structure and is thicker compared to the other samples (Figure 7.18). The rigid structure might have led to more of the sub-aleurone inner layer components being retained within the shell. The other samples were thinner and with cracks, likely due to the milling pressure.

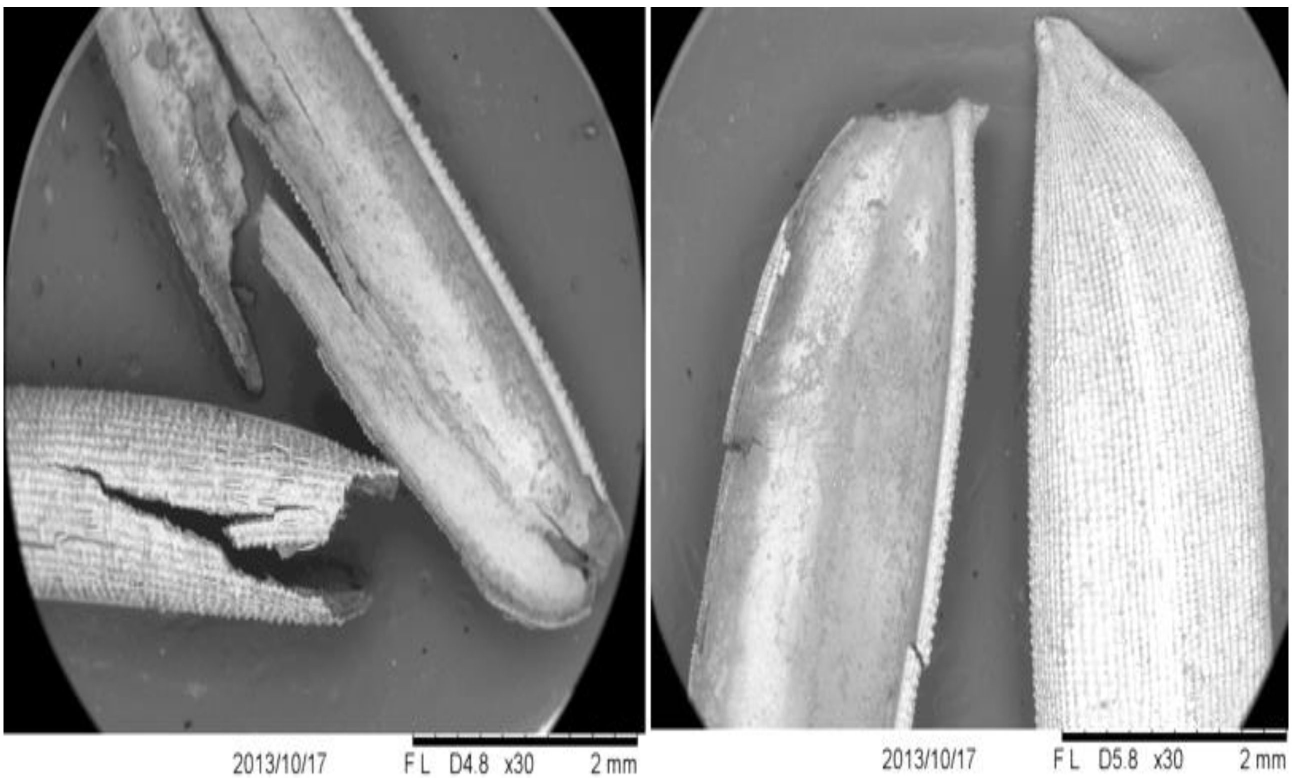


Figure 7.18. SEM of samples A (left) and E (right) of the Milltop rice husks

7.4.1.4 Fixed carbon content

Fixed carbon components of the rice husk samples ranged from 5.61 to 14.64%. The carbon contents of all rice husk samples fell within the decision limits with the exception of sample J which had the lowest carbon content (Figure 7.19 and Table 7.5).

Table 7.5 Fixed carbon contents of rice husk samples

Fixed carbon content of samples (% Dry basis)							
Sample	**Number**	**Mean**	**Std Dev**	**Std Err Mean**	**Minimum**	**Maximum**	**Median**
A	3	12.6	0.76	0.44	11.97	13.44	12.4
B	3	12.73	1.67	0.96	11.55	14.64	12.01
C	3	11.43	0.69	0.4	10.64	11.88	11.77
D	3	12.58	0.99	0.57	11.49	13.41	12.84
E	3	10.7	0.78	0.45	9.93	11.49	10.68
F	3	11.68	1.2	0.7	10.33	12.65	12.05
G	3	13.41	0.41	0.24	13.03	13.84	13.35
H	3	11.83	1.73	1	9.84	12.9	12.76
I	3	12.37	0.19	0.11	12.22	12.58	12.3
J	3	5.92	0.52	0.3	5.61	6.52	5.64

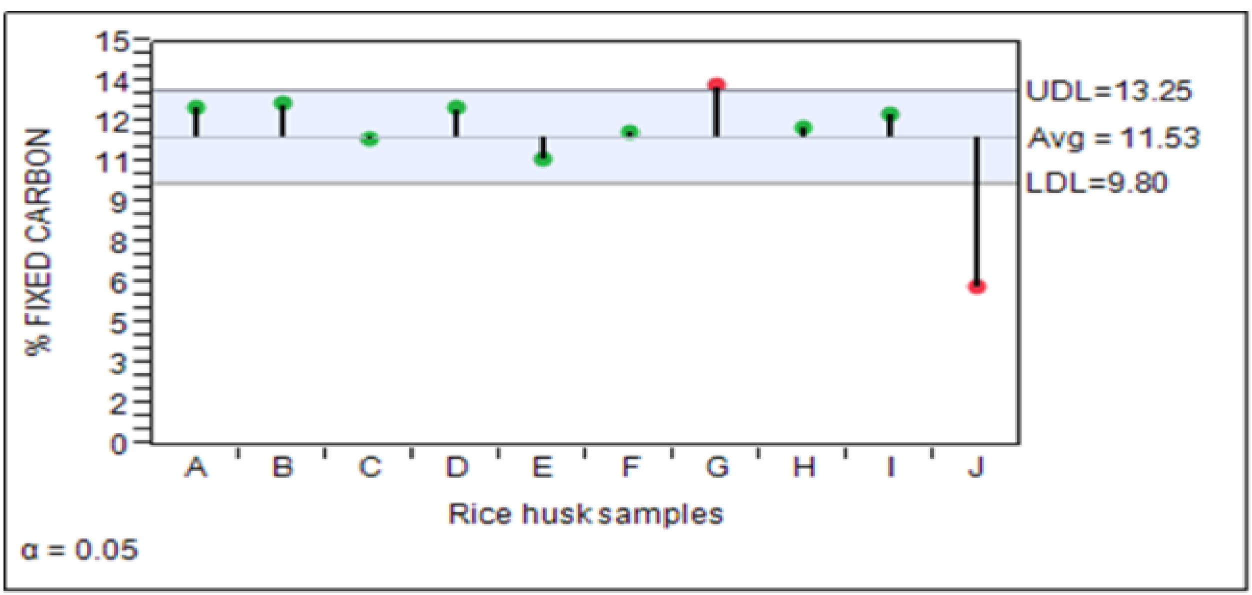


Figure 7.19. Fixed carbon contents of the rice husk samples

The fixed carbon of the Milltop rice husk was higher with little variability between samples (Figure 7.20). This may be due to the higher content of the rough outer shell that is composed of high carbon-silica composites.

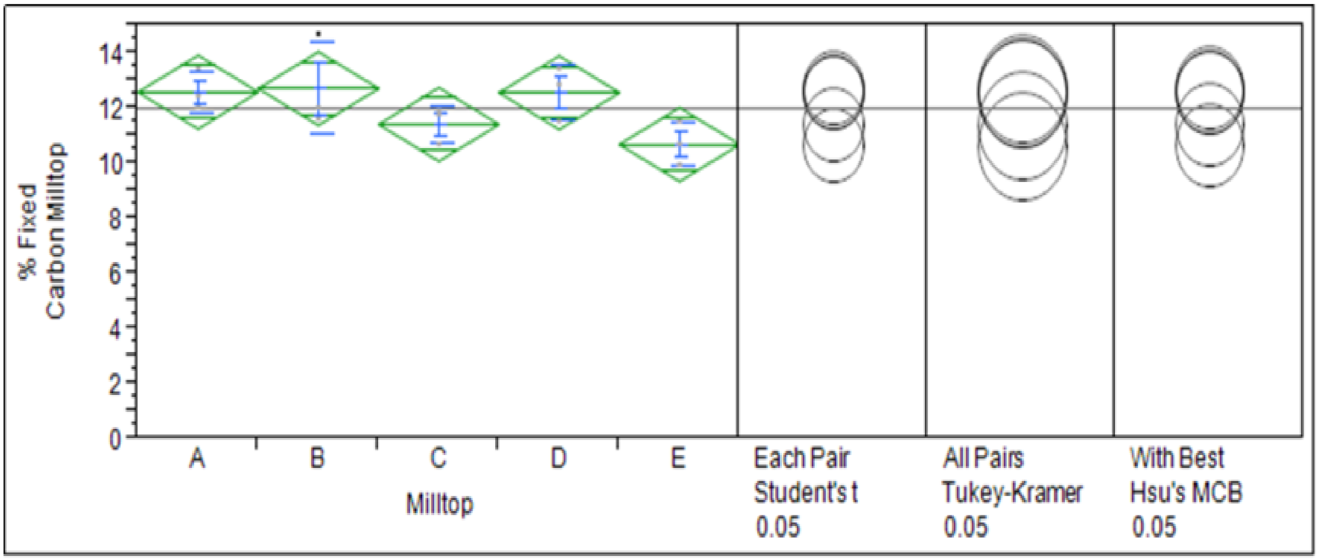


Figure 7.20. Fixed carbon contents of the Milltop rice husk samples

However, for the Engelberg samples the variability was significant with sample J having significantly lower fixed carbon content. ANOM pooled mean was 11.53%, with upper (UDL) and lower (LDL) decision limits of 13.25% and 9.80%, respectively (Figure 7.21).

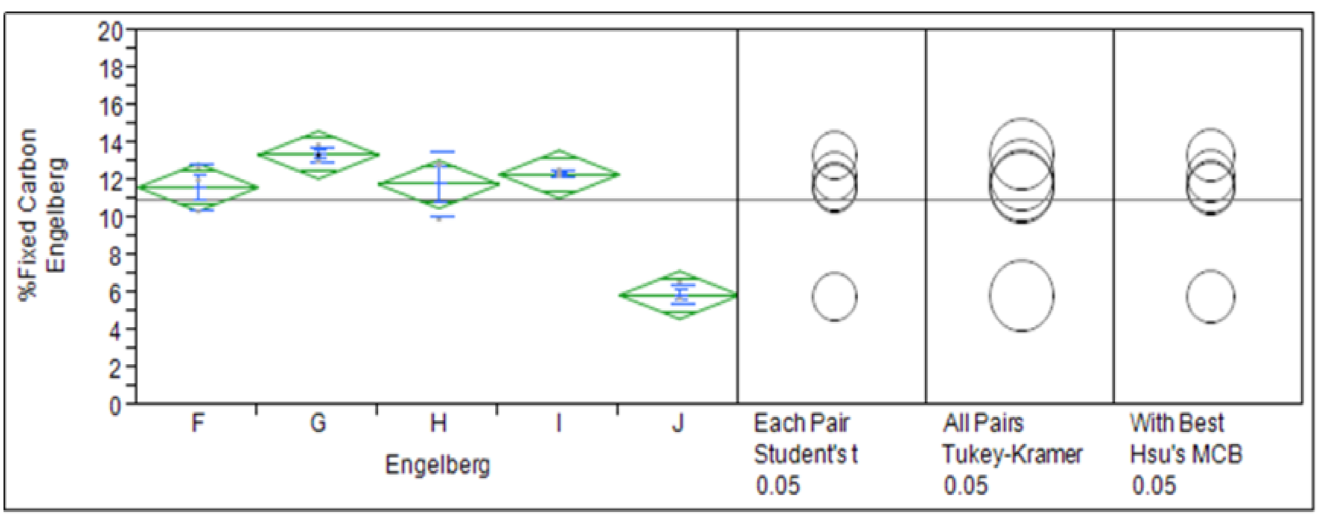


Figure 7.21. Fixed carbon contents of the Engelberg rice husk samples

7.4.2 Thermochemical analysis of rice husk (RH) and rice husk ash (RHA) using FTIR and SEM

These analyses showed that the energetic and volatile components of the rice husk samples including cellulose, hemicellulose, and the lignin volatilize during the thermochemical conversion process, leaving a high silica ash with the same physical structure as the original rice husk samples.

7.4.2.1 FTIR-ATR analysis of rice husk and rice husk ash

FTIR spectra of both the Milltop rice and Engelberg rice husk samples (Figures 7.22 & 7.23) showed that the lignocellulosic components of the rice husk, including hemicellulose, cellulose, and lignin were vaporized leaving an almost pure silica structure that can be identified with Si-O bending at 800 cm^{-1}, Si-OH stretching at 879.68cm^{-1}, Si-O-Si stretching at 1083cm^{-1}, C-O bending at 1632.46 cm^{-1}, Si-C stretching at 2323.03 cm^{-1}, and OH stretching at 3357.47 cm^{-1} (Kamath and Proctor, 1998; Kalapathy et al., 2000; Shokri et al., 2009). The carbon vibrations observed at 1632.46 cm^{-1} and 2323.03 cm^{-1} were due to the stretching of the carbon atoms that were trapped between the silica lattice (Bharadwaj, 2002; Shokri et al., 2009). During his investigation, Bharadwaj (2002) found that not all the carbon atoms of the rice husk were combustible because some of the carbon atoms were trapped in the silica lattice of the ash. In this investigation, based on the comparative analysis of the RH and RHA FTIR spectra of the Engelberg and Milltop rice husk samples, the existing trapped carbon atoms could be attributed to the carbon components of the lignin matrix which is cross-linked with the silica tubes suggested by Bharadwaj (2002). During the HTO regime of the thermochemical conversion process, most of the carbon atoms in the lignin matrix were thermochemically converted except the ones that were cross-linked with the silica tube components; identified in the RHA spectra as a peak at 2320 cm^{-1}. The OH component at 3357.47 cm^{-1} may be due to moisture absorption of the ash from the atmosphere, and the possible mineral impurities that may have the OH bond. The clear higher silica ash content and lower volatile contents of the Milltop rice husk can be seen in Figure 7.22 by the high peak of the Si-O-Si stretching and Si-O bending on the spectra of the rice husk (RH) samples. This is less obvious in the spectra of the

Engelberg RH samples because of the high contents of entrained broken kernels and bran.

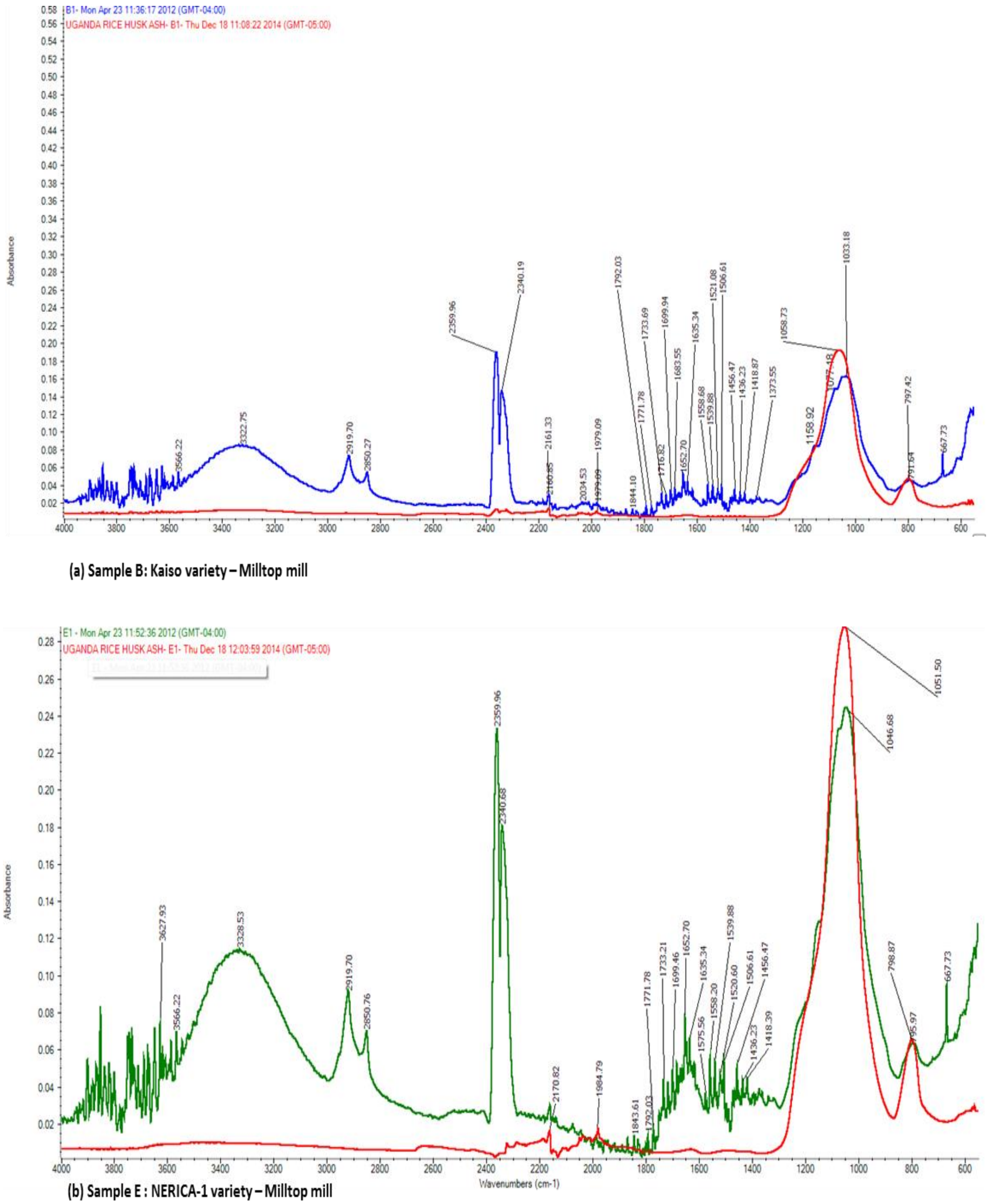


Figure 7.22. FT-IR spectra of (a) Kaiso, and (b) NERICA-1 Milltop rice husks (RH) and their ash (RHA)

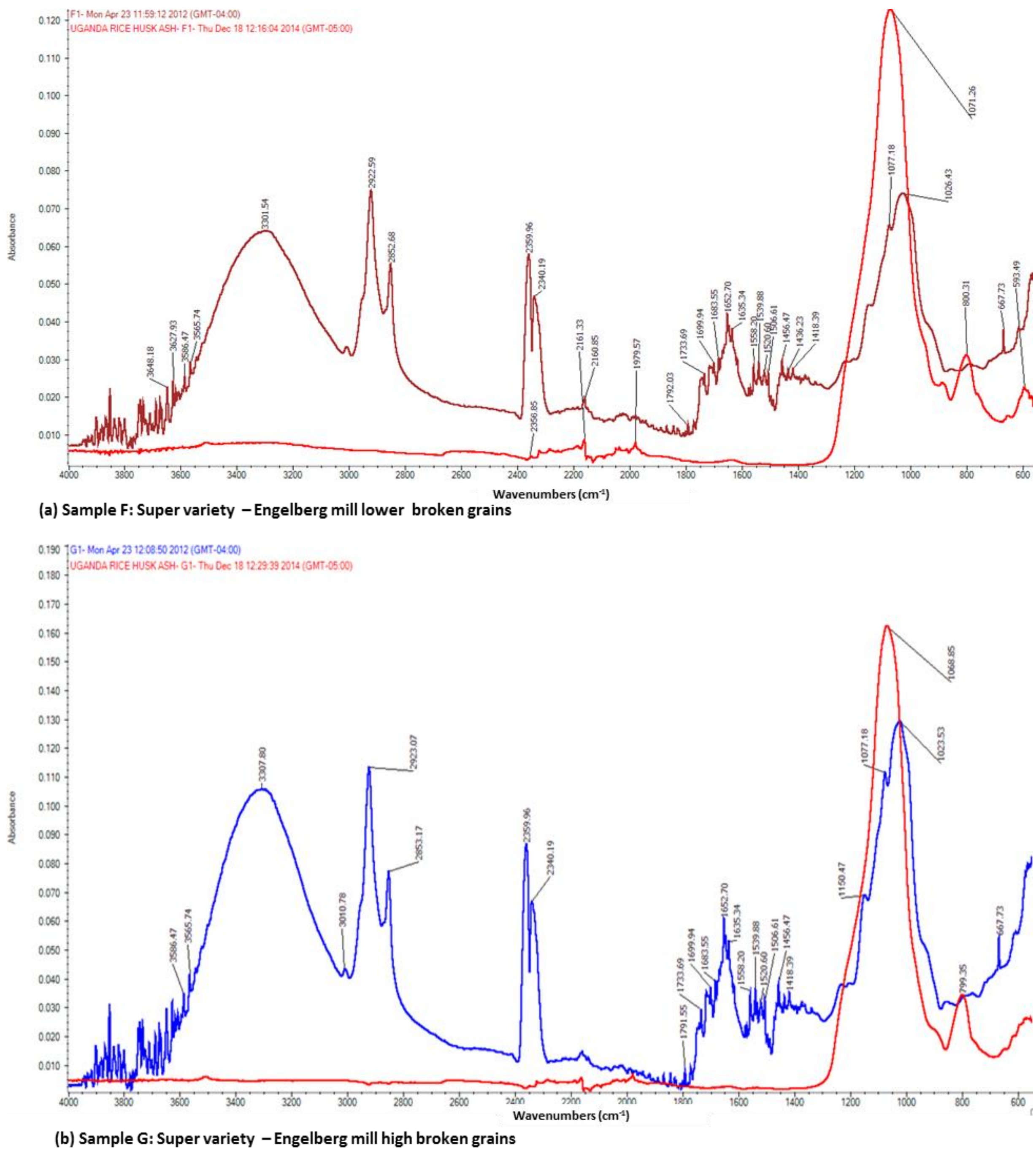


Figure 7.23. FT-IR of Engelberg rice husk (RH) and their ash (RHA) with (a) high broken grains and (b) lower broken grains

Figures 7.24 & 7.25 shows that the rice husk ash of both the Milltop and Engelberg were composed of pure silica with very small carbon silicate impurities due to the carbon that is trapped in the silica lattice. The carbon atoms from the FT-IR spectra showed that the trapped atoms were in the form of C-O (1632.46 cm^{-1}) and Si-C (2323.03 cm^{-1}) bonding in the Si-O-Si lattice. These important findings further explained why these carbon atoms do not participate in the thermochemical conversion processes, as was previously observed by Bharadwaj (2012), when he studied these processes using confocal laser scanning microscopy (CLSM). The other impurities observed were metal silicates at around wave numbers of 2160 and 1980 cm^{-1}.

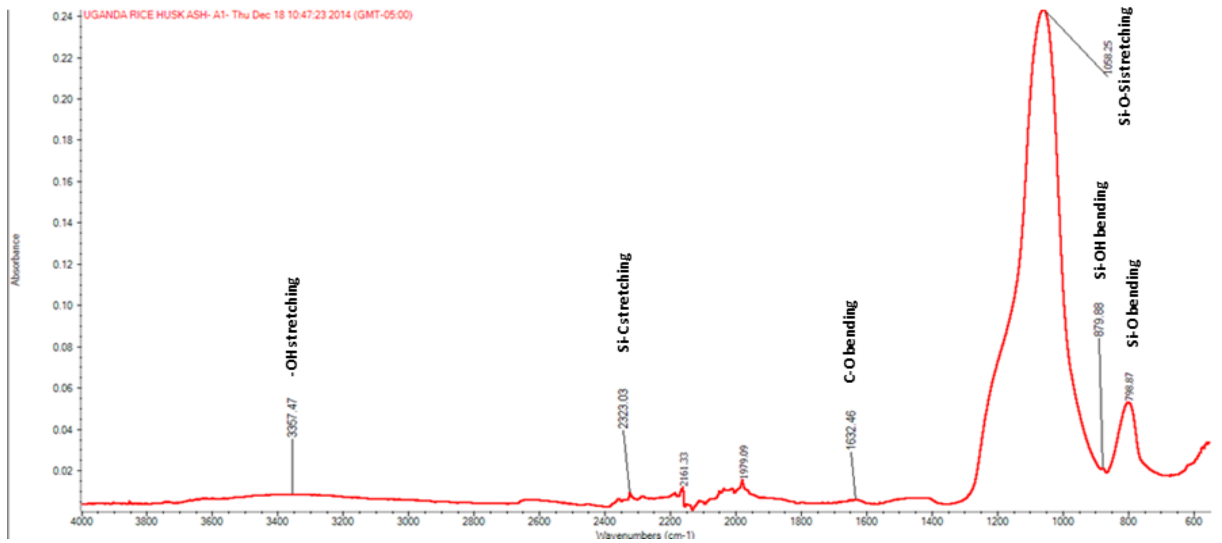


Figure 7.24. FT-IR spectra of the Milltop rice husk ash (RHA)

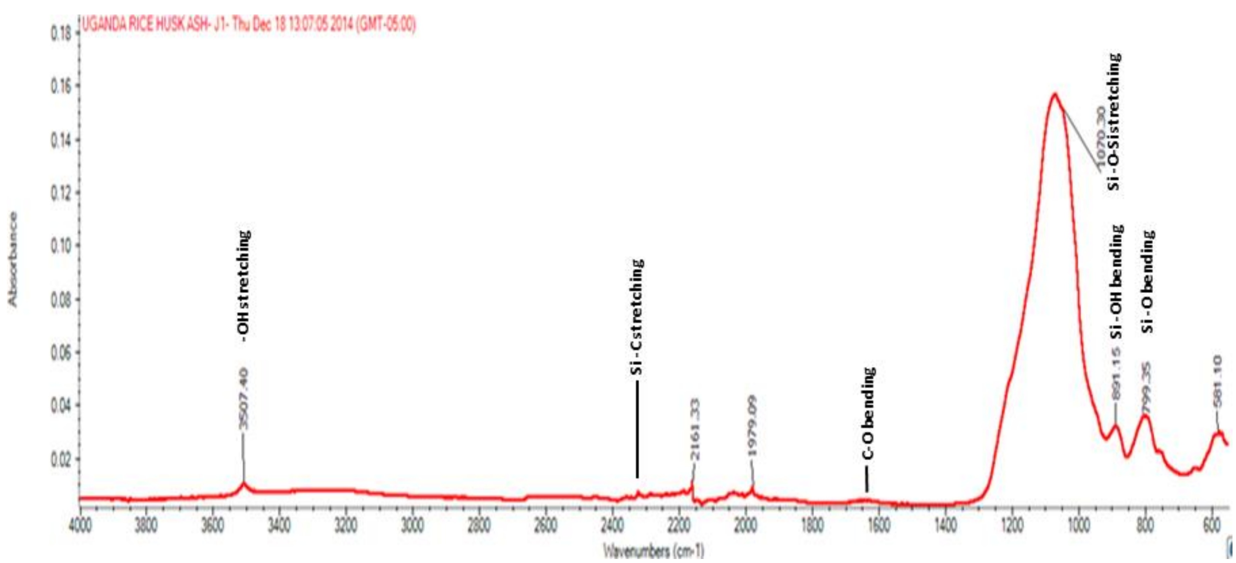


Figure 7.25. FT-IR spectra of the Engelberg rice husk ash (RHA)

The RHA spectra (Figure 7.26) of both the Engelberg and Milltop rice husk samples were similar to the spectra of the thin film silicon dioxide obtained by Shokri et al. (2009) using metal organic based plasma enhanced chemical vapor deposition (PECVD) method at low temperature. These important findings showed that RHA of the Engelberg and Milltop rice husk ash of the samples were almost pure silica and can be used as important feedstock for industrial applications.

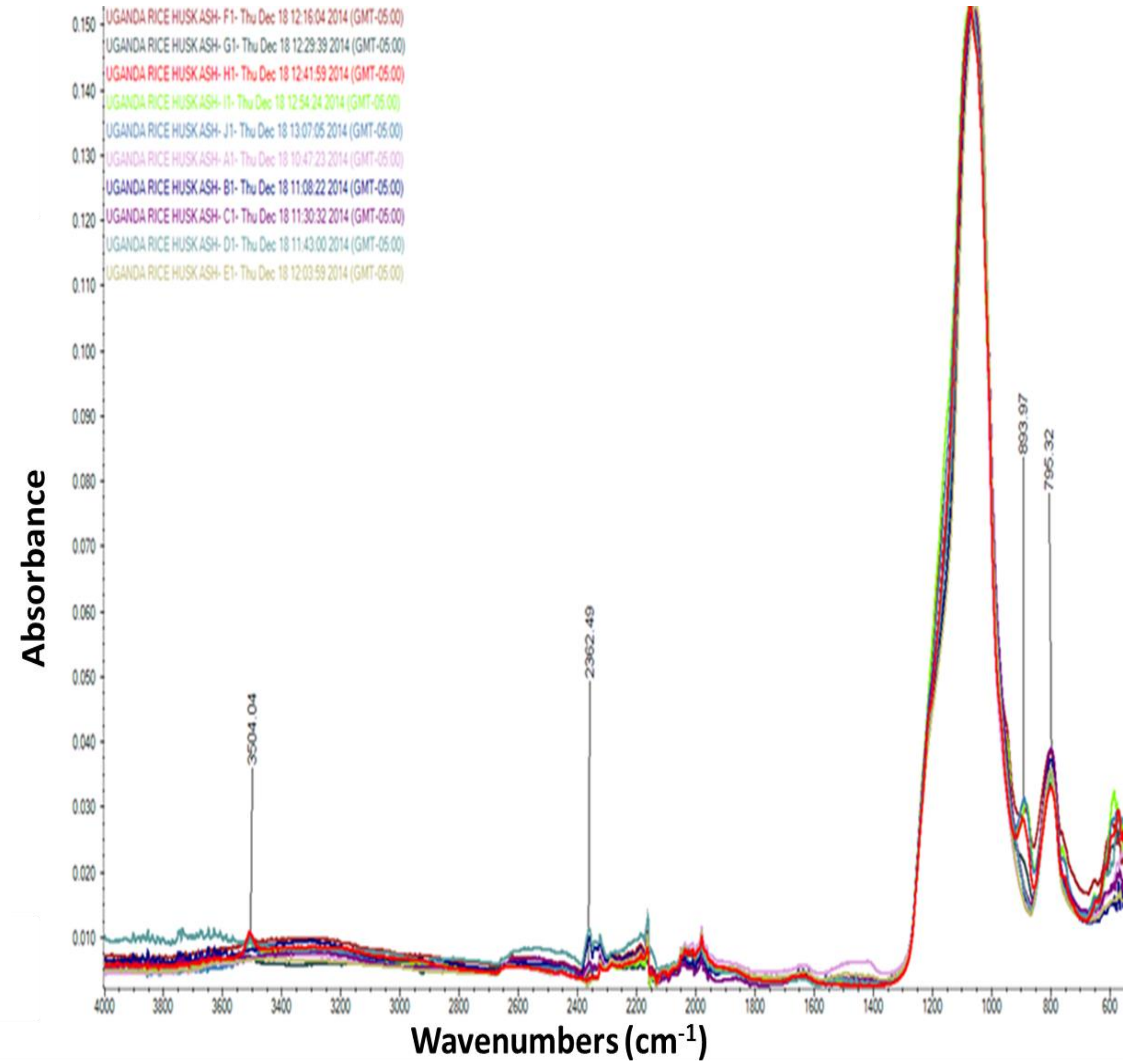


Figure 7.26. Comparative analysis of the Engelberg and Milltop RHA

7.4.2.2 SEM analysis of rice husk ash (RHA) and rice husk (RH)

The most important findings of the research were the similarities of the ashes of the Milltop and Engelberg rice husk samples. Based on the SEM analysis, it was found that both the Milltop and Engelberg rice husks shrank without skeletal deformation with more significant shrinkage in the traverse direction than the longitudinal. The analysis showed that the outer and the inner structures of the rice husk did not change, instead, the region of the sublayers that contained the pericarp and the bran layers were hollow pores with all the non-silica components diffused through the pores during the thermochemical decomposition process (Figure 7.27).

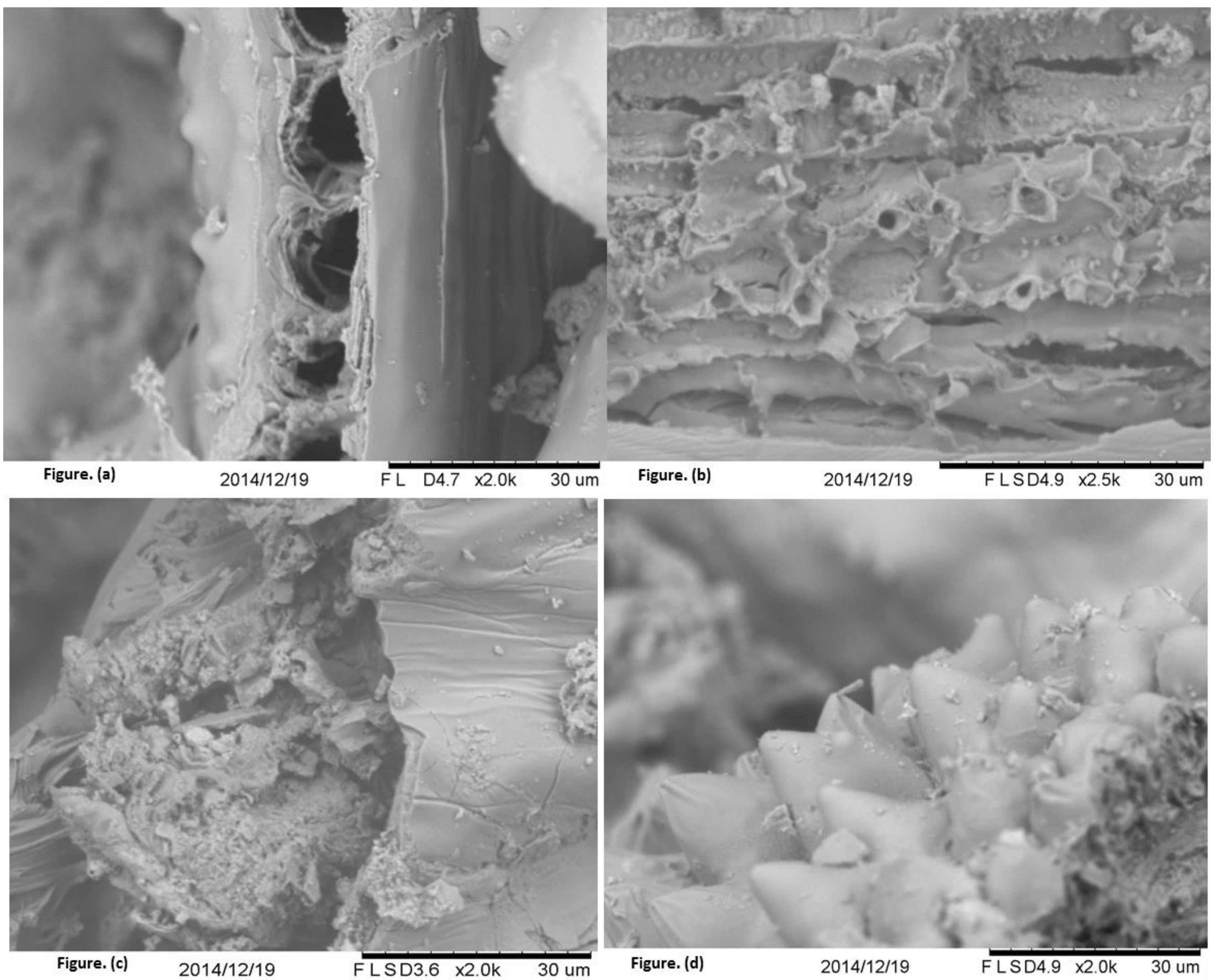


Figure 7.27. Rice husk ash (RHA): sublayer (a), pores (b), Inner (c) & outer (d) surfaces

Bharadwaj et al. (2004) reported similar results with the rice husk shrinking, and the aspect ratio going from 2.19 to 3.23. The shrinkage of rice husk (RH) when it is thermochemically converted to rice husk ash (RHA) is obvious from the following figures (Figures 7.28-7.32). The traverse shrinkage was found to be more than the longitudinal shrinkage. Comparison of the inner component of the RHA to RH of the Milltop showed that the silica structure did not change; the only observation was that the smooth inner surface changed to produce ridges and pores and also shrank more in the traverse direction than in the longitudinal direction, as the lignocellulose component of the rice husk volatized (Figure 7.28). From this figure it can be seen that the shrinkage was more than 3 times in the traverse direction.

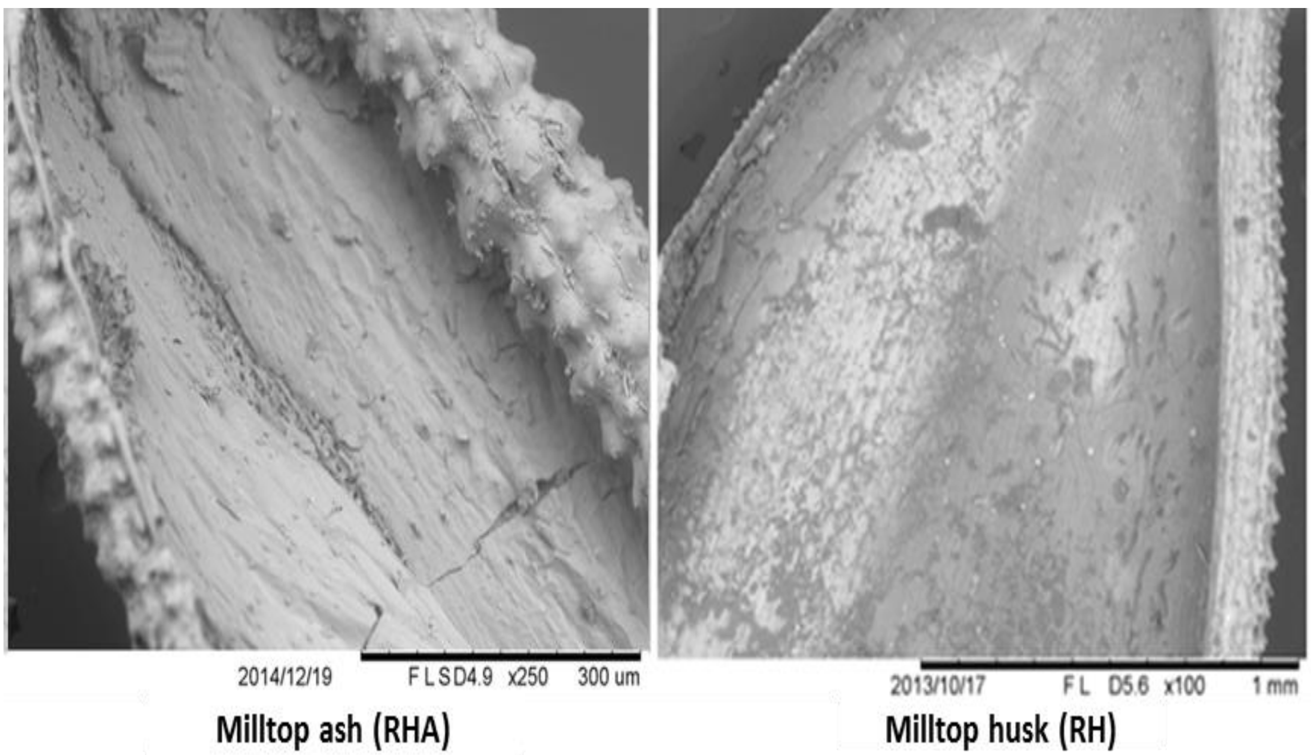


Figure 7.28. SEM of inner surface of the Milltop RHA (left) and RH (right)

Figure 7.30 showed that the needle–like structure hardly shrank during the thermochemical conversion process. This could be due to the fact that it is a structure that is made up of high silica matrix that functions as a defensive structure, protecting the paddy. These findings further signify the protective function of the outer layer and importance of the silica structure of the rice paddy. These findings further confirm the discussion by Epstein (2009), that many plants including rice, armour themselves with solid hydrated amorphous silica incorporated into the cell walls to form structures such as trichomes, spine, and thorns as physical defence against pests.

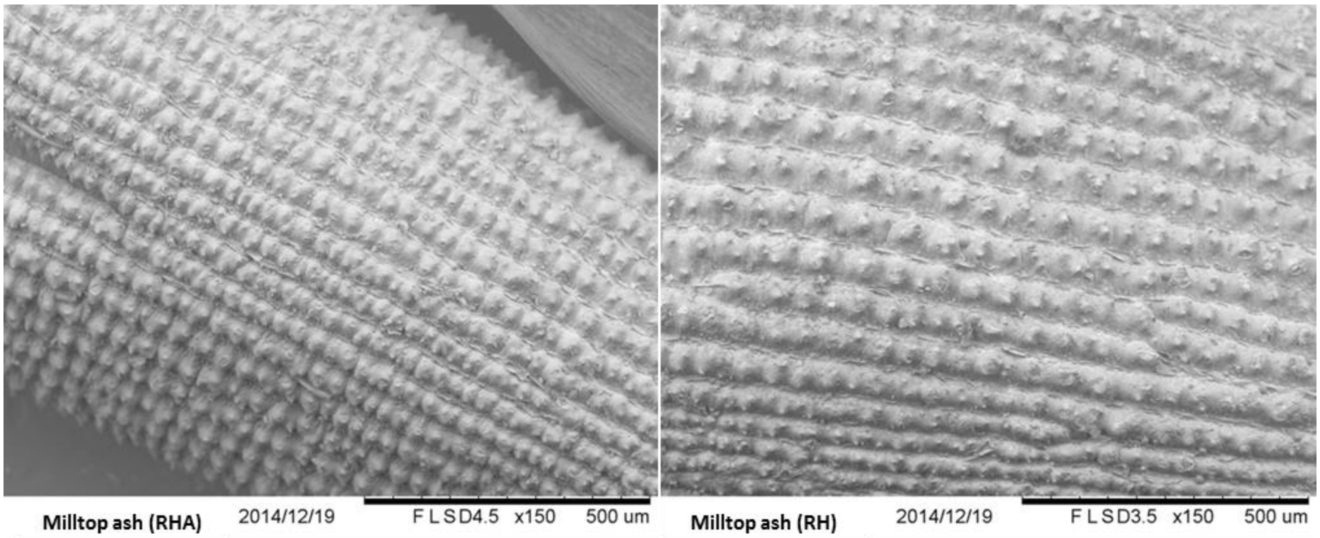


Figure 7.29. SEM of outer surface of the Milltop RHA (left) and RH (right) of a variety without long protruding trichomes

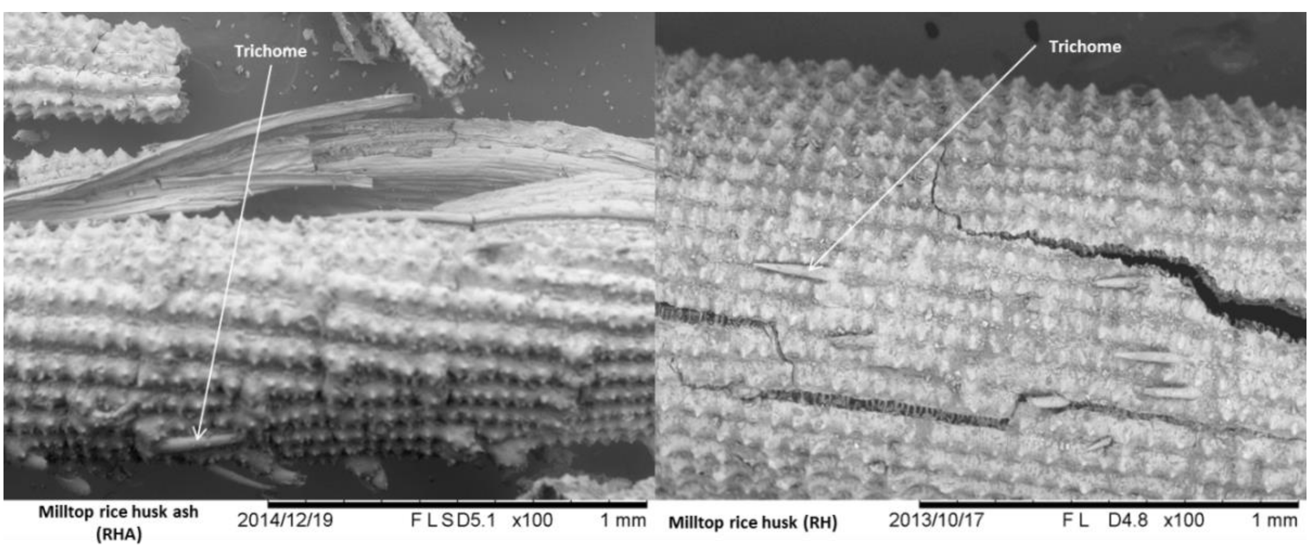


Figure 7.30. SEM of outer surface of the Milltop RHA (left) and RH (right) of a variety with long protruding trichomes

In the case of the Engelberg rice husk samples it was found that the components which included bran, broken rice, and immature grain were all volatized during the thermochemical conversion process producing silica structured rice husk ash (RHA), that resembles the broken components of the Milltop RHA, which essentially was composed of the silica structure of the lemma and palea of the rice husk (Figures 7.31 & 7.32). Figure 7.31 shows, that the trichomes of the Engelberg rice husk, which were intact with the outer surface components during the milling process, stayed attached to the components during the thermochemical conversion process. The SEM results also showed that the Engelberg rice husk from rice varieties that have trichomes have high needle silica structures as a result of the thermochemical conversion process. The result also showed that the trichomes did not shrink during the thermochemical conversion process. This further confirmed that the trichomes are biomass structures that have higher silica content than any other component of the rice husk. Thus, for both the Engelberg and the Milltop rice husks, the varieties that have trichome structures will result in higher ash content and silica contents. Proximate ash analysis confirmed that both the Kaiso and Super varieties (Figure 7.33) have long trichomes which contributed among other things, such as entrained immature grains in the samples, to their high ash content. Although the NERICA-1 variety (sample E) rice husk shown in Figure 7.29, has a larger solid-silica lemma and palea structure, it has lower ash than most of the Kaiso and super varieties, because it does not have the high silica needle-like trichomes (see also Figures 7.12, 7.14 and Table 7.3).

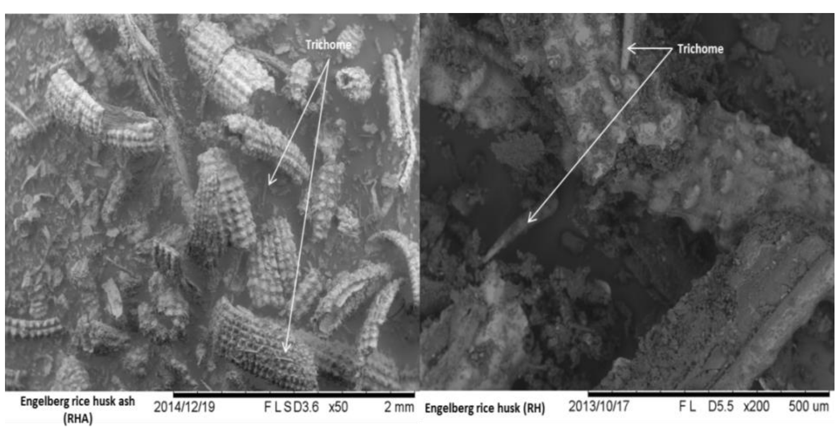


Figure 7.31. SEM of the Engelberg RHA (left) and RH (right) for the super variety showing the trichomes in both RHA and RH

Figure 7.32. SEM of Engelberg RHA (left) and RH (right) for the super variety

One interesting result observed from comparing the RH and the RHA of both the Engelberg and Milltop rice husks was that although the physicochemical characteristics of the two rice husks were different, the physicochemical characteristics of their ashes (RHA) were the same. The only difference between the Engelberg and the Milltop RHA was the sizes of the solid silica structures, which were relative to the original sizes of the structures before the thermochemical conversion process. This is an important finding that showed that the physical characteristics of rice husk ash (RHA) are the same except for the particle sizes which can be easily predicted based on the original particle size analysis of the rice husk, especially when that is coupled with the SEM of the rice husk. Hence in designing ash handling system for both the Engelberg and Milltop rice husk the key factor that needs to be considered is the particle size of the original rice husk lemma and palea, which is the silica-based protective structure of the rice paddy. Coupled with proximate composition data and heating values of the rice husks, operating design parameters for a reactor to thermochemically convert both rice husks to bioenergy can be determined.

7.4.3 Densification experiments

Stable pellets were obtained for all the rice husk samples at all holding times (Figure 7. 33). This made it possible to carry out the impact test for all the rice husk samples at all the three holding times.

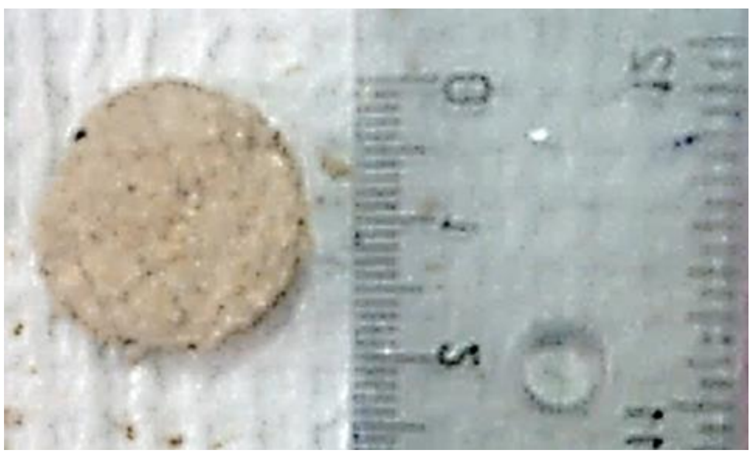


Figure 7.33. Densified rice husk pellet for bomb calorimeter test

7.4.4 Effects of hold time on impact resistance of pellets

The impact resistance at a holding time of 20 seconds showed that there were significant differences between the impact resistances of the rice husk samples (Figure 7.34). When the holding time was increased to 40 seconds, differences were still observed but they were not as significant (Figure 7.35). At hold time of 60 seconds, there were no differences in impact resistance between the samples (Figure 7.36).

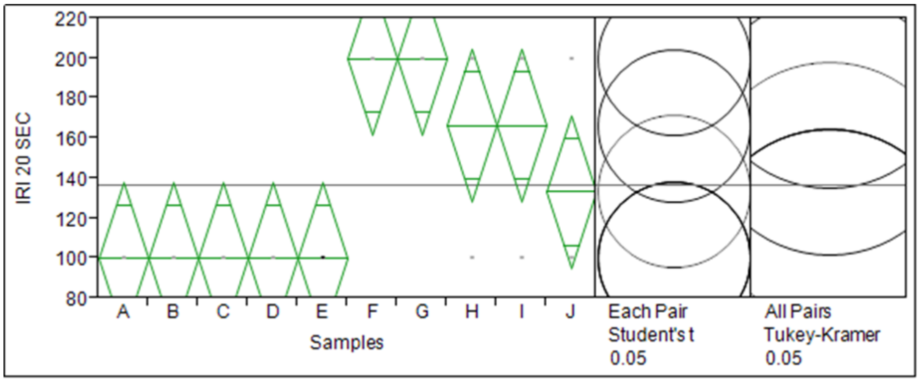


Figure 7.34. Impact resistance analysis of rice husk samples at 20 seconds hold time

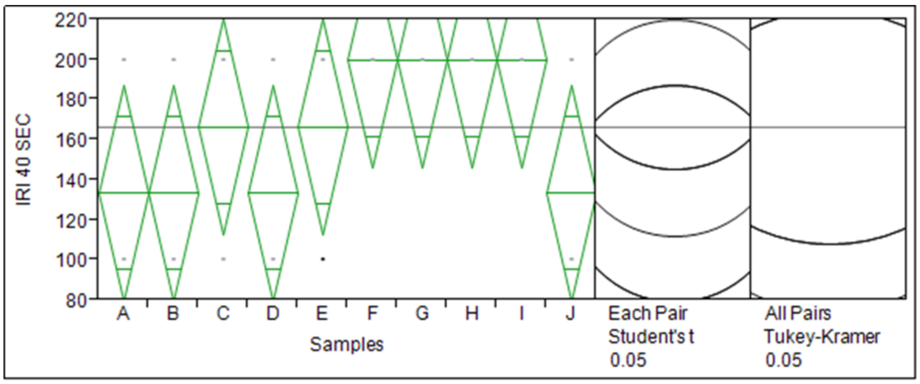


Figure 7.35. Impact resistance analysis of rice husk samples at 40 seconds hold time

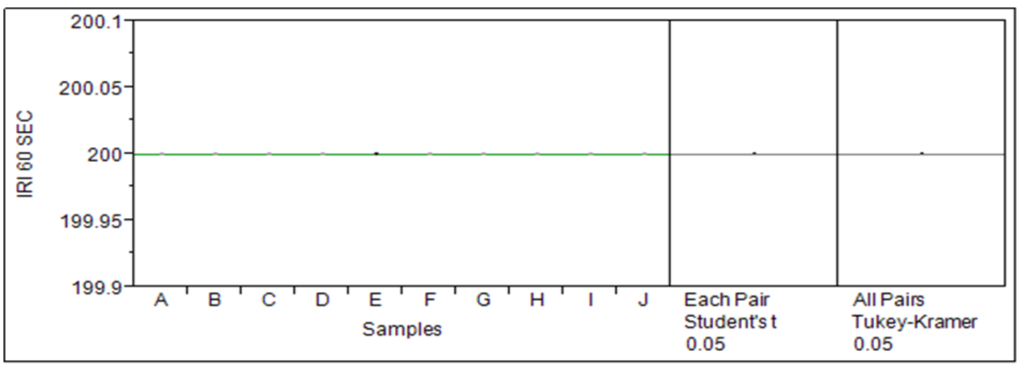


Figure 7.36. Impact resistance analysis of rice husk samples at 60 seconds hold time

7.4.5 Bomb calorimetry

Densified rice husk pellets at die pressures of 42.5 MPa and holding time of 60 seconds proved to have sufficient bonding between particles and rice husk structure to withstand the thermochemical reactions. The pellet shrank without disintegration as the hemicellulose, cellulose, and lignin devolatilized and combusted, resulting in a rigid ash that remained in the bomb calorimeter's experimental dish without spillage, as shown in Figure 7.37. It appeared that the cellulose, hemicellulose, and lignin volatilized leaving the solid silica structure with pores where the volatilized components were. The results were similar to those obtained by Bharadwaj et al., (2004) who studied gasification of a single rice husk particle. An important observation in these experiments was how effective densification enabled the individual silica structures of the rice husk particles to shrink together and form a silica macro-structure. The solid bridges formed during the densification process might have contributed to the formation of the stable silica macro-structure.

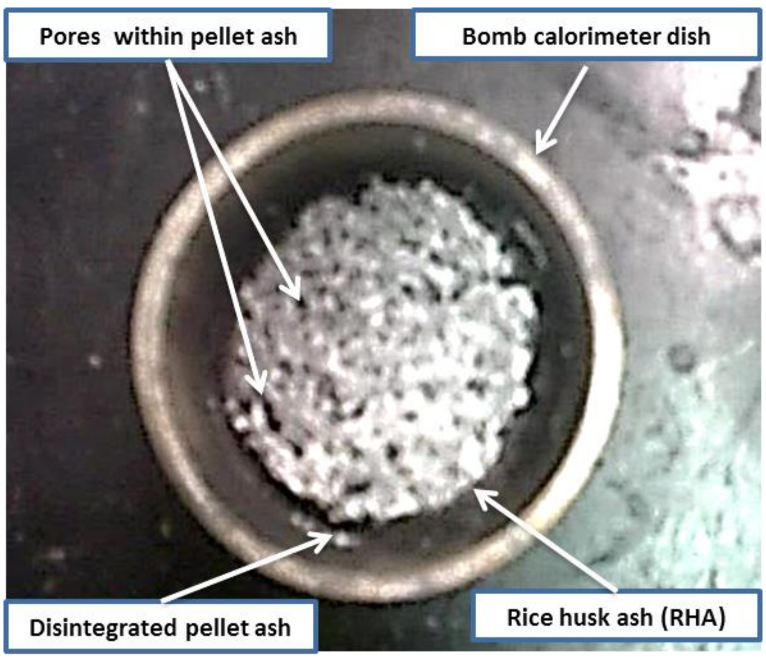


Figure 7.37. Stable pellet shrank to form solid ash in bomb calorimeter dish without spillage with pores within the silica-macrostructure

Bomb calorimeter results showed two distinct high heating values (HHV) for the rice husks which ranged from 13.49 to 15.98 MJ/kg with a pooled mean of 14.60 MJ/kg and standard deviation of 0.79MJ/kg. The results showed that postharvest processing methods, such as type of milling machine, significantly distinguished the two groups (Figure 7.38). The Milltop rice husk samples (A-E) have lower HHV that ranged from 13.49 to 14.24 MJ/kg, with a pooled mean of 13.89 MJ/kg and standard deviation of

0.25 MJ/kg (Figure 7.39). However, the Engelberg rice husk samples (F-J) have higher HHV that ranged from 15.00 to 15.98 MJ/kg and have a pooled mean of 15.33MJ/kg with a standard deviation of 0.33 MJ/kg (Figure 7.40). The Engelberg rice husks samples have higher contents of broken rice, immature grains, and bran (aleurone and subaleurone components of the rice paddy including the embryo), compared to the Milltop rice husks. Thus, the HHV of rice husk is affected by the presence of rice bits, immature grains, and bran.

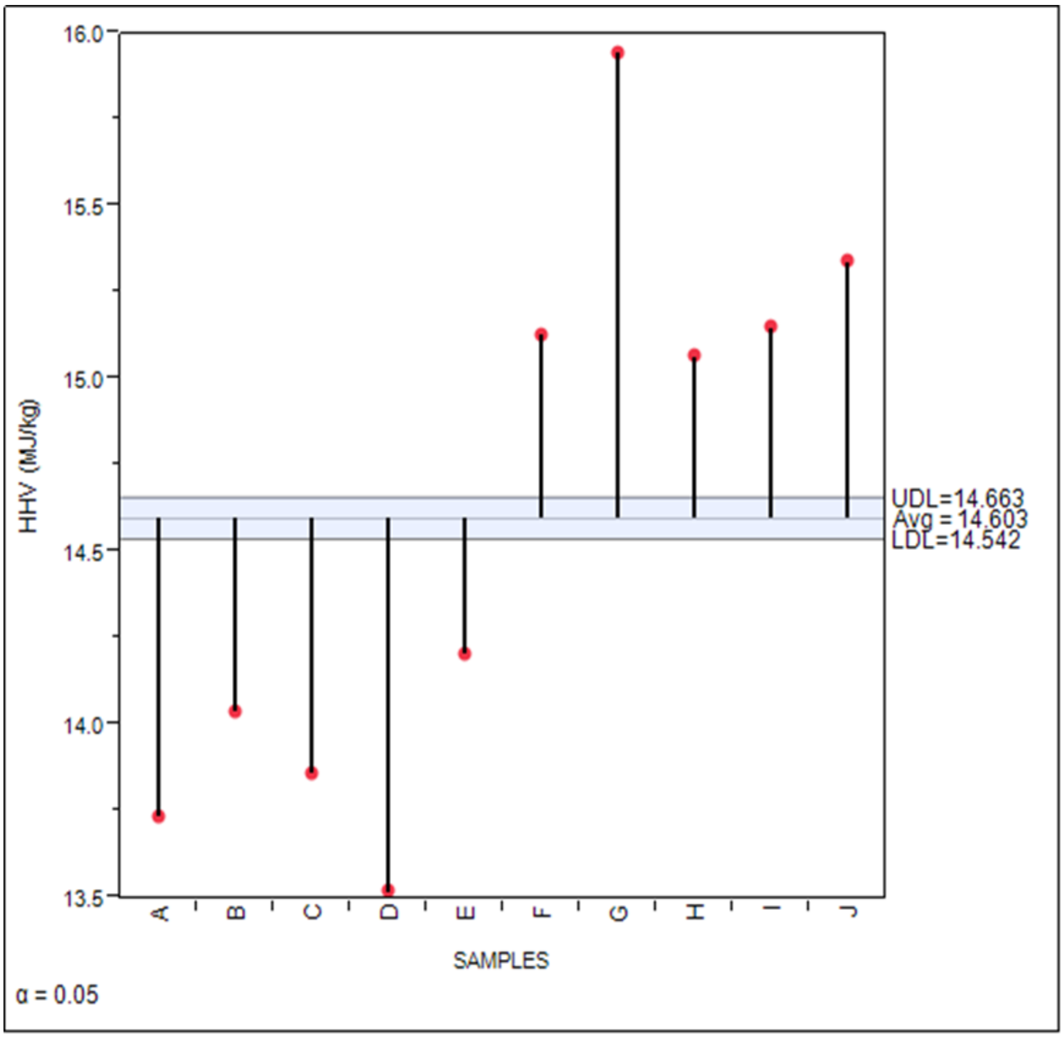


Figure 7.38. Rice husk gross calorific values (HHV)

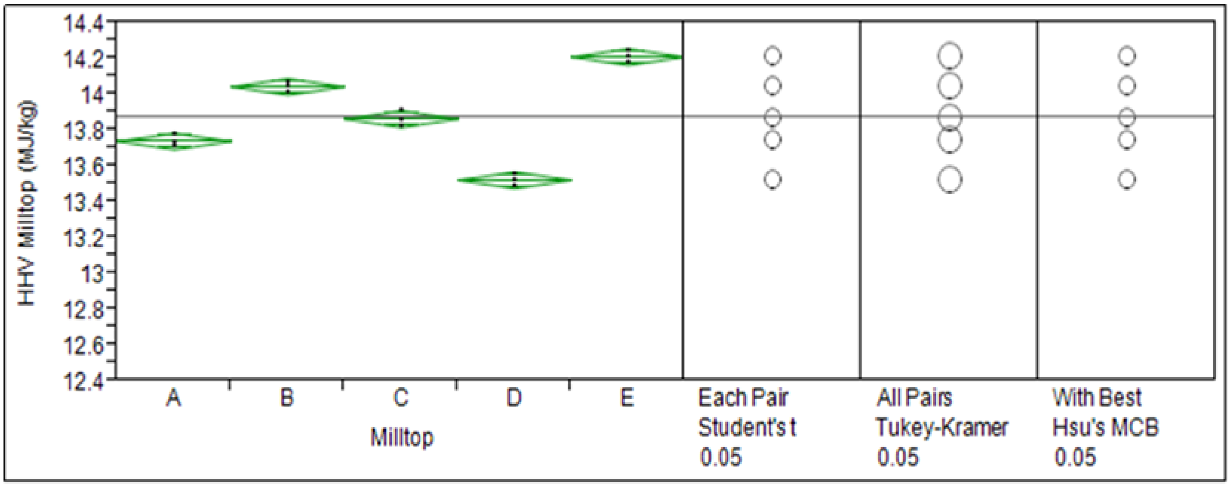


Figure 7.39. HHV of the Milltop rice husk samples

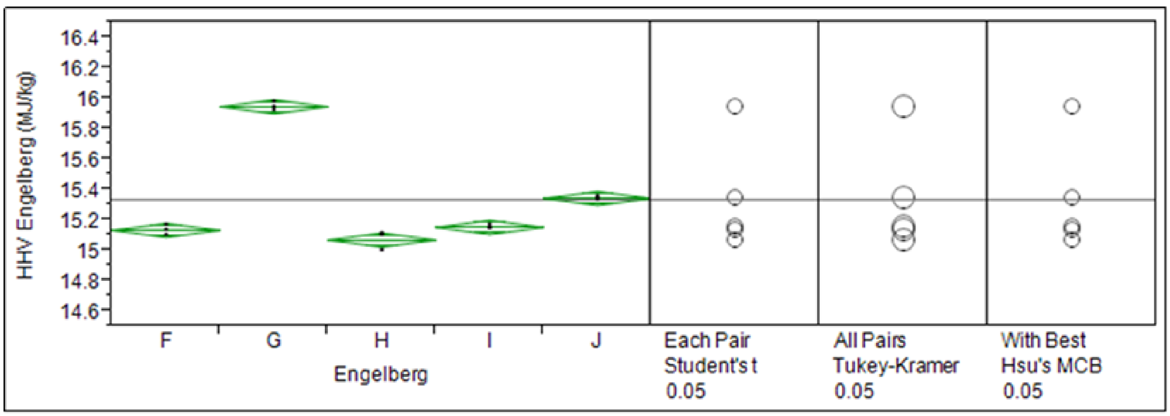


Figure 7.40. HHV of the Engelberg rice husk samples

7.4.5.1 Bomb calorimeter residual analysis

The bomb calorimeter residuals include the solid ash and the wiped content from the bomb vessel, which includes the ash, other combustion products (including soot) and any content of the original sample that had spilled into the bomb vessel. Comparing bomb calorimeter residuals to the proximate ash content gives the indication of spillage and incomplete combustion that had occurred during the bomb calorimeter oxidation process. Weighed and dried delicate task wipers (Kimwipes EX-L) were used to wipe the inside of the bomb to recover any soot and spillage that might have occurred. These and the bomb dish containing the combusted ash were dried in a forced-air oven to obtain the dry weight of the residuals (Figure 7.41). The ANOVA test showed that there was a significant difference between the means of the residual samples similar to that of the ash samples for the different samples tested.

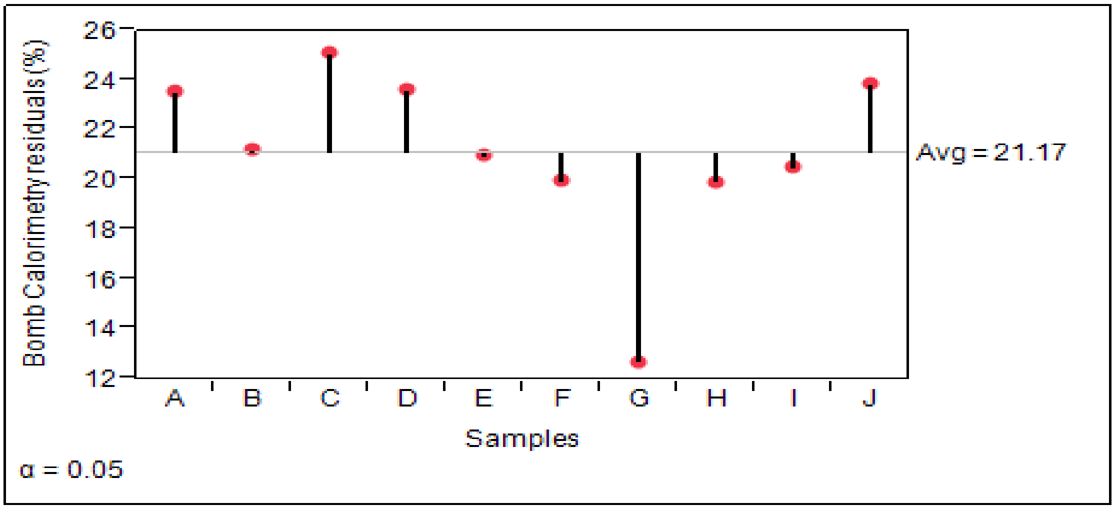


Figure 7.41. Bomb calorimeter residuals analysis of means at α=0.05

7.4.5.2 Comparison of proximate ash to bomb calorimeter residuals

Comparative analysis between the ash content and bomb calorimetry residuals of the samples showed that there was no statistical significance between the two values (Figures 7.42, 7.43 & Table 7.6). This confirms complete combustion during the oxygen calorimetry tests.

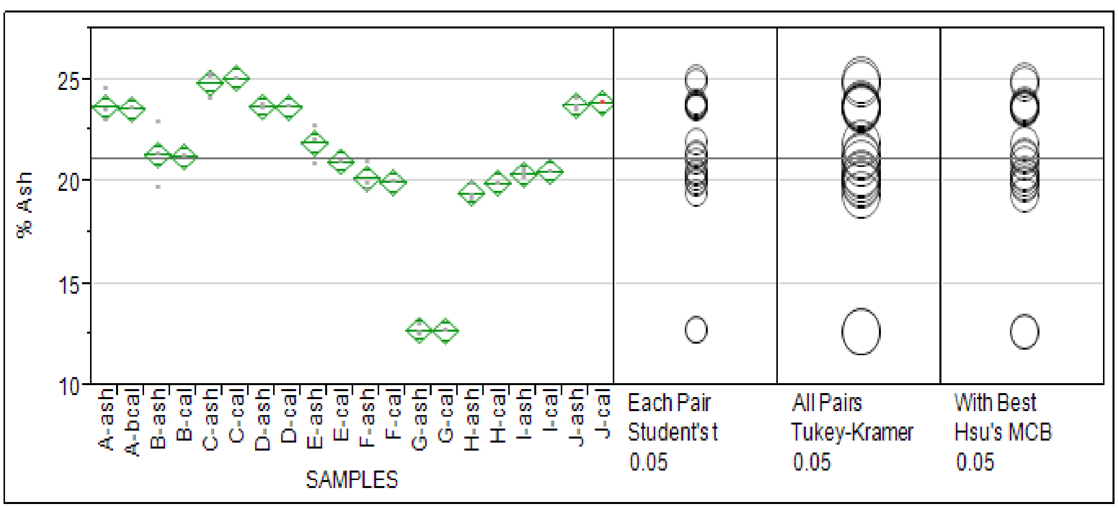


Figure 7.42. One way ANOVA of ash for ASTM 3174-04 ash and bomb calorimeter residual analysis

Table 7.6 LSD statistical analysis report for the comparison

Connecting Letters Report

Level									Mean
C-bcal	A								25.110000
C-ash	A								24.876667
J-bcal		B							23.890000
J-ash		B							23.760000
D-ash		B							23.703333
A-ash		B							23.673333
D-bcal		B							23.660000
A-bcal		B							23.580000
E-ash			C						21.916667
B-ash			C	D					21.340000
B-bcal			C	D					21.250000
E-bcal				D	E				21.010000
I-bcal				D	E	F			20.520000
I-ash					E	F			20.376667
F-ash					E	F	G		20.166667
F-bcal						F	G		19.980000
H-bcal						F	G		19.960000
H-ash							G		19.476667
G-ash								H	12.743333
G-bcal								H	12.710000

Levels not connected by same letter are significantly different.

Individual comparisons between ash analysis (ASTM 3174-04) and bomb calorimeter residual analysis of the samples further confirmed that there was no significant difference between the two (Figure 7.43).

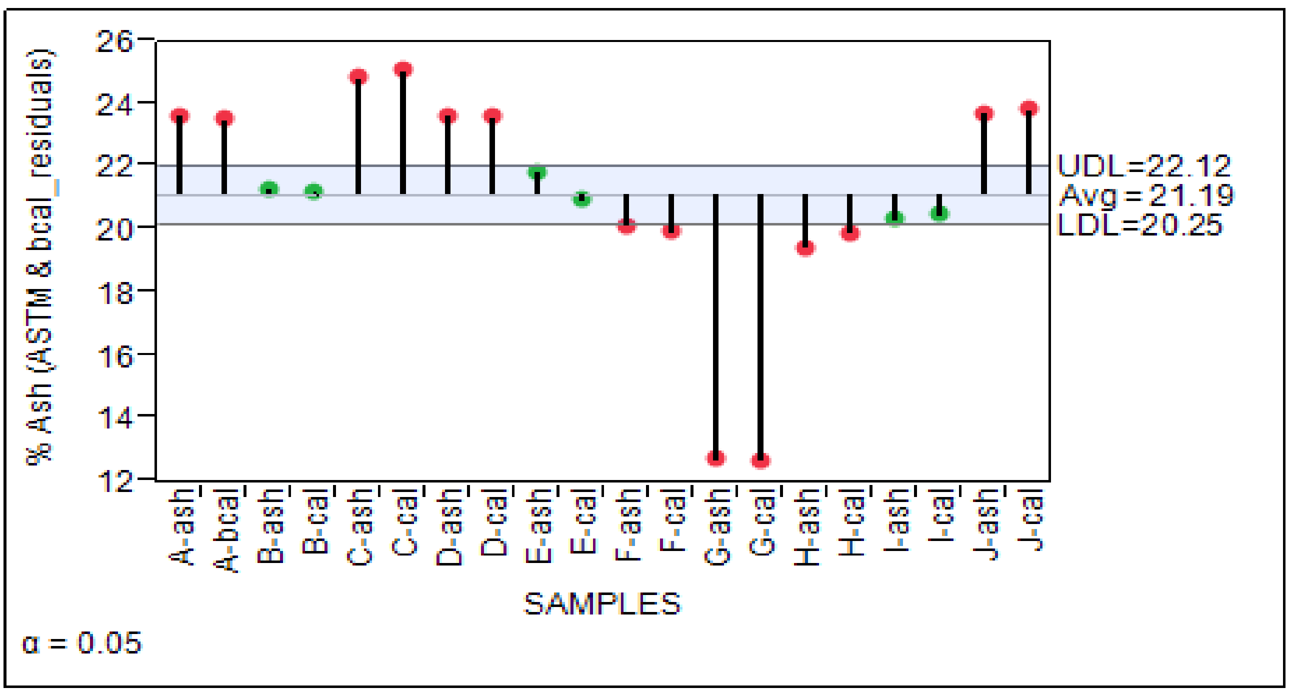


Figure 7.43. Comparative analysis between ASTM determined ash and bomb calorimeter residual

7.4.6 Correlation of high heating value (HHV) to proximate compositions

High heating values (HHV) of biomass have been estimated by several researchers (Cheng & Azevedo, 2006; Parikh et al., 2005; Yin, 2011; Nhuchchen & Abul Salam, 2012) by correlating these values to proximate components including ash, volatile, and fixed carbon contents. From the results obtained, it has been identified that lower ash and higher volatile contents and high fixed carbon have significant effects on high heating value (HHV).

Linear models of the HHV of the Engelberg and Milltop rice husk samples gave a model based on proximate components of volatile and fixed carbon with R-square values of 0.84 and 0.71, respectively (Figures 7.44 & 7.45).

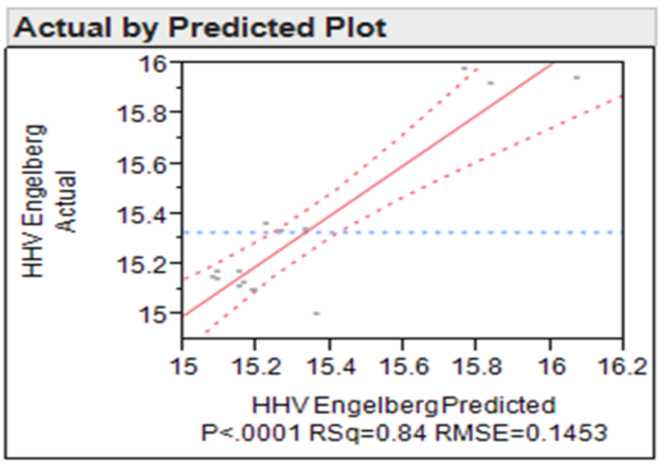


Figure 7.44. Linear predicted model plot for Engelberg rice husks

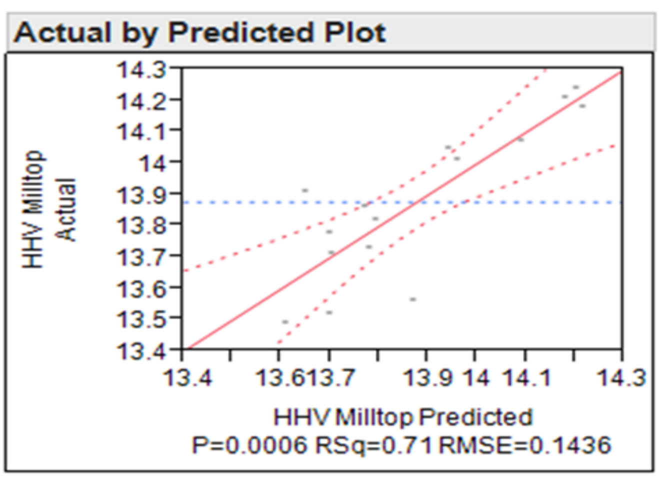


Figure 7.45. Linear predicted model plot for Milltop rice husks

The Linear model parameter estimates of both the Engelberg and Milltop rice husks showed that the volatile component was the most significant factor on the HHV as shown in Tables 7.7 & 7.8.

Table 7.7 Parameter estimates for the Engelberg linear model

Parameter Estimates				
Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	7.4285792	1.005842	7.39	<.0001*
% Volatile Engelberg	0.1096131	0.01428	7.68	<.0001*
%Fixed Carbon Engelberg	0.0230572	0.013638	1.69	0.1167

Table 7.8 Parameter estimates for the Milltop linear model

Parameter Estimates				
Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	6.0514828	1.903778	3.18	0.0079*
% Volatile Milltop	0.1228061	0.025887	4.74	0.0005*
% Fixed Carbon Milltop	-0.012008	0.035221	-0.34	0.7390

The quadratic models predicted the HHV of the Engelberg rice husk with an R-square value of 0.92 and the Milltop with an R-square value of 0.74 giving a better estimate of the HHV based on proximate volatile and fixed carbon components (Figures 7.46 & 7.47). Figures 7.48 & 7.49 show the quadratic model plots of the effect of volatile and fixed carbon contents of the rice husk samples on the high heating values (HHV) of the Engelberg and Milltop rice husks respectively.

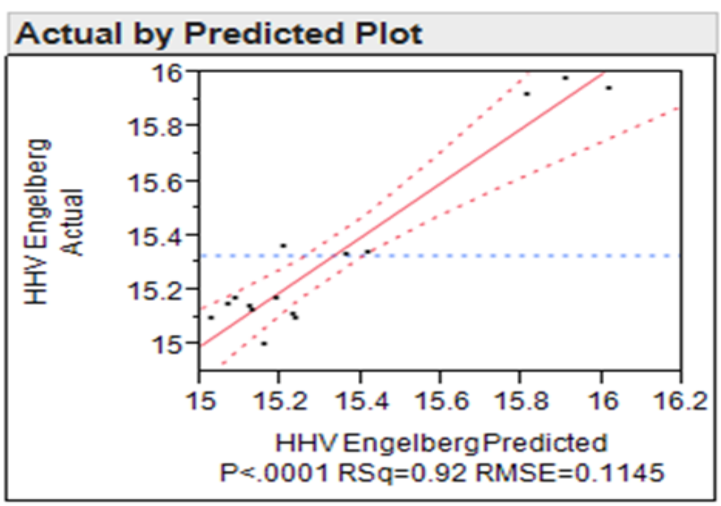


Figure 7.46. Quadratic predicted model plot for the Engelberg rice husks

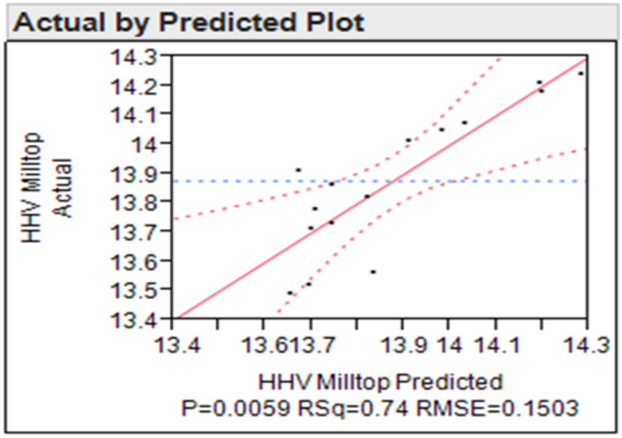


Figure 7.47. Quadratic predicted model plot for the Milltop rice husks

The parameter estimates of the quadratic model of the Engelberg rice husk showed that the volatile components are highly significant at the linear level, but not as significant at the quadratic level. The fixed carbon was found to be highly significant at both linear and quadratic levels (Figure 7.48 & Table 7.9).

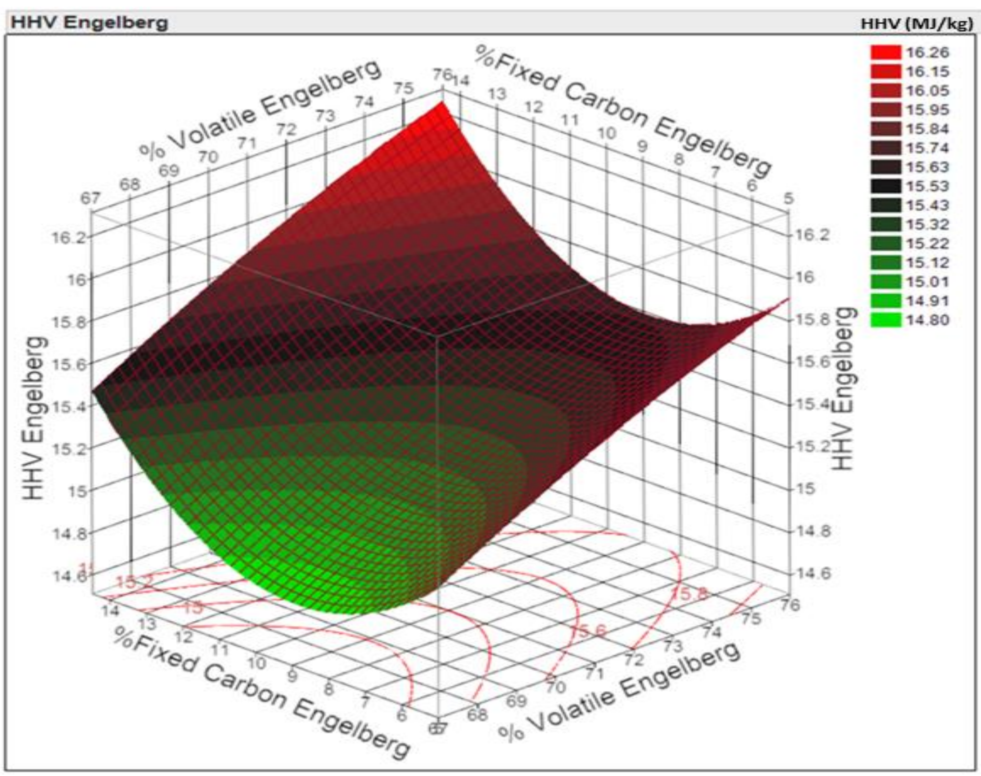


Figure 7.48. Quadratic model plot for the Engelberg rice husks

Table 7.9 Parameter estimates for the Engelberg quadratic model

Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	7.4877592	1.504227	4.98	0.0006*
% Volatile Engelberg	0.0958412	0.021246	4.51	0.0011*
(% Volatile Engelberg-69.756)*(% Volatile Engelberg-69.756)	-0.00237	0.00641	-0.37	0.7194
%Fixed Carbon Engelberg	0.0917094	0.026734	3.43	0.0064*
(%Fixed Carbon Engelberg-11.0413)*(%Fixed Carbon Engelberg-11.0413)	0.0211178	0.006918	3.05	0.0122*

However, the quadratic model of the Milltop rice husk showed that the most significant factor was the volatile component at the linear level (Figure 7.49 & Table 7.10).

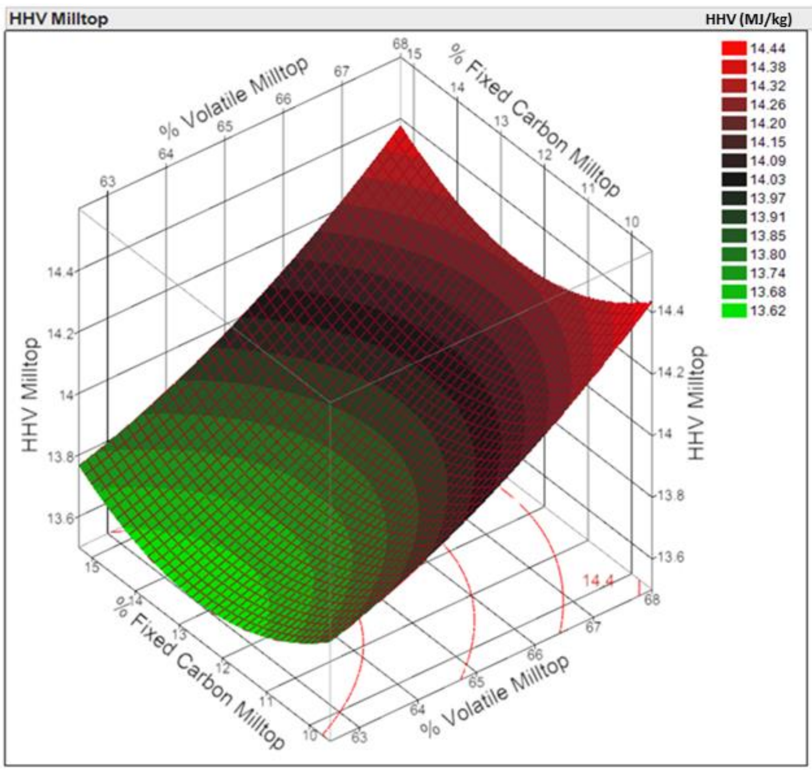


Figure 7.49. Quadratic model plot for the Milltop rice husks

Table 7.10 Parameter estimates for the Milltop quadratic model

Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	7.3500932	2.405025	3.06	0.0121*
% Volatile Milltop	0.1046652	0.033396	3.13	0.0106*
(% Volatile Milltop-64.8887)*(% Volatile Milltop-64.8887)	0.0097709	0.021001	0.47	0.6517
% Fixed Carbon Milltop	-0.026559	0.042388	-0.63	0.5450
(% Fixed Carbon Milltop-12.0093)*(% Fixed Carbon Milltop-12.0093)	0.0207714	0.024127	0.86	0.4094

7.5 Conclusions

The results of this study showed that the heating value of rice husk from different postharvest processing methods can be determined effectively using a bomb calorimeter by prior densification of the husk at a medium pressure of 42.5 MPa with a holding time of 60 seconds, at 15% moisture content, and a particle size distribution that is below the #60 (0.250 mm) sieve. The result also showed that the impact resistance between the rice husk samples at 20 seconds dwelling time is significantly different among the samples. However, when the dwelling or holding time was increased to 40 seconds and above the impact resistance index (IRI) was not statistically different, although there were variations between the IRI of individual samples. When the hold time was increased to 60 seconds, the IRI of all the samples was found to be the same. This observation may be as a result of the spring back effect; likely at 60 seconds, the particles bonding in all the samples had reached their maximum densification (Mani et al., 2006). Therefore, the pellets spring back to maximum densification position after the hold pressure was released. Proximate moisture, ash, volatile, and carbon contents of the rice husk samples based on ASTM standards were: 5.07-6.64%, 12.66-24.91%, 62.83-75.99%, and 5.61-14.64% respectively; with respective pooled means of 5.92, 21.20%, 67.32%, and 11.53%. The respective means for the proximate components (moisture, ash, volatile and fixed carbon contents) of the Engelberg and Milltop rice husks were: 5.80% (Std Dev=0.20) & 6.01% (Std Dev=0.57); 19.30% (Std Dev=3.74%) & 23.10% (Std Dev=1.56%); 69.76% (Std Dev=2.72%) & 64.89% (1.65%); and 11.04% (Std Dev=2.85%) &12.01% (Std Dev=1.21%). Harvest and postharvest processing were found to have significant effect on the amount of rice paddy components entrained in the rice husk samples; and consequently, on the proximate composition and HHV of the samples. Prediction models for estimating high heating values (HHV) of the Engelberg and Milltop rice husks developed based on their proximate compositions showed that quadratic models for both rice husks provided better estimates with R-square values of 0.92 and 0.74 than the linear models, which have R-square values of 0.84 and 0.71, for the Engelberg and Milltop rice husks respectively. HHV values of the Engelberg rice husks (15.07-15.95 MJ/kg; Pooled SE =0.021) were found to be higher than the Milltop rice husks (13.52-14.21 MJ/kg; Pooled SE=0.021), consistent with the volatile proximate components, which were found to have the most significant effects. The analysis of the results showed that lower ash, higher volatile component and higher fixed carbon increase the HHV of both the Engelberg and Milltop rice husk samples. FT-IR and SEM analyses of the rice husk showed that there was no significant difference between the physical and chemical characteristics between the Engelberg and the Milltop rice husk ash (RHA), except for the particle sizes which are related to the original particle sizes of the rice husk (RH). These important findings need to be considered during the design of rice husk thermochemical conversion and ash handling system, and could make it possible for one system to utilize both the Engelberg and the Milltop rice husks as fuel feedstock, with the adoption of standard particle size distribution of the rice feedstock that the system would use. However, for a multi-feedstock system, the high volatile components of the Engelberg and the lower ash contents need to be factored into the systems design. FT-IR spectra of all the rice husk ash samples showed that they were almost pure silica with very small impurities that included the trapped carbon component in silica matrix. It can also be concluded that rice varieties with needle-like trichomes will have higher ash content than the ones without, because the trichomes have a higher silica or ash content than the other components of the rice husk. The local rice varieties for the sub-Saharan region have the protective trichomes as a defence mechanism, while the hybrid NERICA varieties developed by AfricaRice have a more solid cone on the lemma and palea structure as their defensive structure both resulting into higher ash contents, but the trichomes silica content is much higher than that of the lemma and palea which resulted in the local variety having a higher ash content.

7.6 Recommendations

The result showed that rice husk obtained from the Milltop milling machines have lower contents of broken grains and very little paddy components of the aleurone and sub-aleurone layer; while the Engelberg rice husk have higher contents of broken grains, bran, as well as, immature grains. The presence of these extra components was found to have contributed to the higher HHV of the Engelberg rice husks compared to the Milltop rice husks. The Milltop multistage milling process, involves separation and removal of most of these components with the objective of utilizing them as food feedstock rather than waste. However, at the small rural and medium sub-urban scale levels in sub-Saharan Africa, these products usually become waste or lower grade animal feed due to lack of bran stabilization equipment and programs. Thus, from a food processing perspective, the Milltop rice mill is a better mill compared to the Engelberg mill, because it provides better yields, with less broken rice; as well as, it separates other co-products that, if properly recovered, could be effectively used as feedstock for animal feed processing. However, the Engelberg rice husk, when available, has higher energy value than the Milltop rice husk, making it a more attractive energy feedstock. In sub-Saharan Africa, regional, economic and machine availability are the major factors that determine what type of rice mill is used. In Uganda, of the total of more than 600 rice mills (small and large scale), the majority are Engelberg and Milltop (JAICAF, 2010). The Engelberg mills are most common in the eastern part, while the Milltop dominates in the western region of the country due to historical backgrounds (JAICAF, 2010). Sakurai et al. (2006) carried out a research on miller clusters in Ghana and reported that the majority of the millers use either Engelberg or Milltop and concluded that the suburban miller clusters are more quality conscious due to competition than their rural counterparts. Hence, they have higher tendency of adopting the higher technology Milltop (or other one pass milling machines) than their rural counterparts. Bakari et al., (2012) found that the majority of the machines used by the medium and small scale rice processors in the Upper Benue river basin in North Eastern Nigeria were the Engelberg type machines. Therefore, from a postharvest processing perspective, whenever possible, Milltop rice husk with a bran stabilizing equipment should be used. However, on the energetic perspective, the Engelberg rice husk is a better biofuel feedstock than the Milltop. It has lower ash content, and higher volatile components than the Milltop rice husk, and thus has higher HHV. The SEM and the FT-IR analyses of this research have revealed that there were no significant differences between the chemical and physical characteristics of the Engelberg and the Milltop rice husk ash except for particle size distribution. This is an important finding that suggests the possibility of designing and developing a dual feedstock thermochemical conversion system that will utilize both the Engelberg and Milltop as energy feedstock with in-built operating parameters for effective conversion and ash handling. Although beyond the scope of this research, it is recommended that further research on a thermochemical conversion system that will utilize both rice husks as a fuel feedstock be carried out. This will make sure that all rice husks produced in the regions where both the Engelberg and Milltop rice husk mills operate are used as valuable energy feedstock. The purity of the silica of the rice husk ash provides another important opportunity for increasing the sustainability of postharvest rice processing by utilization of both the rice husk and the rice husk ash, as biofuel feedstock and industrial material feedstock, respectively. It is also important that the regional and global rice institutes such as AfricaRice and IRRI, continue the development of hybrid rice varieties with the focus of producing a rice paddy that not only produces high yield milled rice, but also co-products that can be utilized as feedstock for bioenergy, animal feed, and products for industrial applications; as this will increase the sustainability of global rice production, as well as, mitigate the global challenge of climate change by reducing the demand of firewood from the ecologically important trees that protect the region from desertification.

7.7 Contribution to knowledge

This research has shown that, not only harvest and postharvest processing affect the thermochemical conversion characteristics of rice husk, but the rice variety also plays an important role. Therefore, research on how variety affects thermochemical conversion of rice husk should be an important research component in the development of hybrid rice varieties that are suitable for every ecological condition, in order to ensure sustainability of rice production, considering the triads (Social, Economic, and Environment) that sustainability entails.

VIII General Summary and Conclusions

8.1 General conclusion

Sustainable food processing in sub-Saharan Africa is one of the most important factors that will ensure food security, poverty alleviation, environmental security, and self-sufficiency in that region, because for the food to be processed sustainably the social, economic, and environmental criteria of the processes need to be considered. Rice processing is energy intensive and produces large amount of waste by-products such as rice husk which accounts for more than 20% of the rice paddy by weight, and as a waste, endangers the ecosystems and the health of the rural communities. Engelberg and Milltop mill-processed rice husks are the most abundant and the most unused by-products of rice processing in sub-Saharan Africa. Utilization of rice husk as a biofuel alternative to firewood, and the improvement of conventional methods of rural rice processing will greatly increase the sustainability of rice processing in sub-Saharan Africa. Raw rice husk in its simple form has low energy density and is difficult to handle, thus in order to increase its viability and adoption by the community as biofuel alternative, it needs to be densified using low energy techniques that the local community can adopt. However, the characteristics of produced rice husk differ, and they especially depend on the milling method used. Hence, characterization of the most abundant rice husk in the region is an important step towards the utilization of this biomass as a biofuel feedstock.

In this study, the current conventional methods of rice processing at the rural small and medium scale levels were studied, and methods on how to improve the existing methods by utilization of waste heat from the diesel engines driving the mills, utilization of solar energy for pre-soaking, modification of the conventional stove to increase efficiency, and the utilization of rice husk as alternative to firewood were investigated. The utilization of rice husk as a thermal energy source alternative to firewood was further studied, by studying the effect of process parameters on densification characteristics of rice husk and characterization of the most abundant rice husk waste in the sub-Saharan region – the Engelberg and the Milltop mill-produced husks.

Utilization of waste heat from the diesel engines that drive the milling machines was found to be an effective method of increasing the sustainability of rice processing. It was found that the Listeroid engine, chosen by the rice processors due to its simplicity and availability of spare parts and technicians that are familiar with it, is an appropriate prime-mover and offers the opportunity to use the waste heat for both pre-drying and pre-soaking of the rice, simultaneously. This unique investigation has revealed the potential of the Listeroid machines for increasing energy efficiency and sustainability. The dual-barrel configuration is ideal for both pre-drying and pre-soaking of the rice paddy. The cold barrel temperature reached 40.64°C in 62 minutes and hot barrel temperature simultaneously reached an average temperature of 70.2°C ideal for both drying and pre-soaking of paddy.

Active solar heating is attractive but will be too expensive and less likely to be adopted by the local parboilers. The solar system was able to reach the temperature required for parboilers of rice for about two and half hours at the later part of the day. However, this could be improved by simple modification of techniques and the use of more advanced hand tools which is beyond the scope of this research. Also, the optimization of the collector and circulation system may increase the temperature reached; but, at a prohibitive cost and will also require use of advance manufacturing technology that may not be locally appropriate at this time. The RATE (Research Appropriate Technology and Education) theme, which is based on the development of appropriate technology, and using locally available tools and raw materials, as well as, educating both the fabricators of processing equipment and the end users – the food processors; proved to be an effective method of mobilizing the local sheet metal workers and the rice parboilers to develop appropriate technology based on the local inputs, and to increase the awareness of the locals on improving output-based technology development and utilization of recycled materials to increase sustainability. One potential economic issue observed, is the local cost and availability of the component such as aluminium sheet, paint, insulation, glass, copper pipe; and labour cost of construction of a full-scale solar thermo-syphon system. The availability of the low cost scrap material is limited and purchasing new material was expensive. Regional infrastructure and private – public partnership to ensure effective collection of scrap material will reduce cost and increase availability of raw materials.

Modification of the stove by development of a cover significantly increased the efficiency of the stoves. The average time for heating the water barrel on the open conventional stove to 70 °C was about 50 minutes; while the time for heating the same amount of water to the same temperature under the same environmental condition for the covered stove was about 37.2 minutes. Application of the RATE theme to develop a cover based on the input of the rice parboilers and technical capability of the local tradesmen was successful.

The utilization of rice husk as an alternative to firewood was found to be the most sustainable, as well as, the most cost effective method for increasing the sustainability of rice processing because it is free, and by reducing the consumption of firewood, it increases environmental sustainability. The rice husk is free, with potential environmental hazard if not utilized; and a version of the existing stoves has already been adopted for saw dust. The local sourcing of the stoves helps to provide jobs for the craftsmen, the stove sellers, as well as, help in increasing the environmental sustainability by reducing the use of firewood and fossil fuel. The boiling water test showed a polynomial relationship between water temperature and time of heating. The developed conical insert ensured combustion after ignition of the rice husk, with possibly multiple thermochemical conversions, occurring within the stove. The appropriateness of the technology by the ease and willingness of the locals to adopt it makes it one of the most promising technologies for the small scale parboilers. The RATE theme proved to be an effective method for engaging both the stove fabricators and the end-users for adopting the stove. The local technicians and domestic stove users are familiar with the stove without the developed conical insert for adapting the use of the stove with saw dust. However, the low bulk density issue and low energy density of the rice husk as well as, the practical size limitation of the stove will restrict its utilization for the medium size parboilers. Characterization of the rice husk will be an important step for making rice husk an alternative fuel for rice processing. Densification will resolve the bulkiness and low energy density issues; making the study of the effect of process parameters on densification of rice husk important. The physical, chemical, and thermochemical characteristics will also enable the development of an optimum stove for all scales of rice parboiling.

The effect of process parameters on densification of rice husks using locally available binders and a manual hydraulic press at medium pressures showed that at the optimum moisture content of 15.19%, die pressure, binder type, and binder ratio have significant effects on water permeability and the densities of the briquettes produced. Densified rice husk bound with paraffin wax, whole *Afzelia africana* aril, and gum Arabic (*Acacia senegal*) were found to be more hydrophobic than the ones with de-oiled *Afzelia africana* aril and groundnut shell. Comparative analysis of the high lipid whole *Afzelia africana* aril bonded briquettes and the de-oiled *Afzelia africana* bonded briquettes ($P<0.05$) led to the conclusion that the lipid content of binders improved the hydrophobic characteristics of the briquettes, but reduced their density. The analysis of all the results showed that a durable rice husk briquette can be produced at medium die pressure of 53.25 MPa, binder ratio of 6.35%, and an optimum moisture content of 15.19%. This was found to be the saddle point where an increase in die pressure and binder ratio would positively affect water absorption/permeability and densities of the briquettes.

Physical analysis of the rice husk showed that the Engelberg rice husk is significantly different from the Milltop rice husk ($P<0.05$). Analysis of the rice husk samples showed that the Milltop rice husks have significantly higher geometric diameters with 95% of the samples by weight, retained by Standard sieve #20 (0.850 mm). While the Engelberg rice husks were much smaller with 95% of the particles by weight were retained by sieve #100 (0.150 mm). The Milltop rice husks were also found to be less dense than the Engelberg rice husks with much lower bulk and particle densities. The Engelberg and the Milltop rice husk samples are two significantly different groups based on that, predictive models of the particle size distribution of the two rice husks were developed with R-square values of 0.82 and 0.86 respectively.

Chemical analysis of the Engelberg and Milltop rice husks showed that the Milltop samples have lower amount of proximate starch, protein, and fat compared to the Engelberg samples. The FT-IR spectra of the two rice husks showed that they have unique characteristics, which defined them as two distinctive groups; with the key differences being the quantity of proximate components, which was confirmed by the results observed during the starch, protein, and fat analyses of the samples.

Thermochemical characteristics of the Engelberg and the Milltop rice husks were studied. Proximate analysis of the rice husk samples showed that the ash content of the Milltop rice husks was significantly higher than that of the Engelberg. The Engelberg samples were found to have significantly higher volatile component and high heating value compared to the Milltop samples. High heating value predictive models developed for the Engelberg (R-square =0.92) and the Milltop (R-square=0.72) samples showed that the proximate volatile and fixed carbon contents have significant effects on the high heating value of the rice husk samples. FT-IR and SEM analyses of the samples showed that although the physical and chemical characteristics of the rice husk samples differ, the physical and chemical characteristics of the rice husk ashes of the two samples were the same. The rice husk ashes of both samples were pure silica with trapped carbon-silicate components in the silica matrix, with very little impurities.

8.2 Summary of the contributions to knowledge

One of the most important contributions that this research made was the development of the Research Appropriate Technology and Education (RATE) theme proposed and used during this research investigation. RATE will enable the sub-Saharan African region to increase sustainability of rice and other agricultural production, by engaging the community of craftsmen, postharvest processors, local government skill acquisition centres, and educational and research institutions to work together in developing sustainable appropriate technology based on the end-user needs. This research further studied simple methods of improving the conventional methods of parboiling to increase energy efficiency and environmental sustainability. Three non-conventional thermal energy systems including: Utilization of waste heat from diesel engines, a solar thermal thermosyphon system, and a rice husk stove were developed and tested based on the RATE theme to determine their viability and acceptance by the rice post-harvest processors in the region.

Several researchers have studied the physical, chemical and thermochemical characteristics of rice husk and other biomass at various conditions (Mansaray and Ghaly, 1997; Sokhansanj et al., 2005, Ndazi et al., 2007; Mani et al., 2006; Bharadwaj et al., 2004; Wannapeera et al., 2008; Bahari, 2012). However, there has not been any study carried out to characterize and compare the rice husks and the rice husk ash, of the two major milling machines (Engelberg and the Milltop) used in sub-Saharan Africa. The findings from this research provided the necessary information on the characteristics of the two most abundant rice husk groups in rural sub-Saharan Africa that can be used to adopt the rice husk waste as an alternative to firewood.

The determination of the optimum moisture content for the densification of rice husk, and the possibility of using the five binders (gum Arabic, *Afzelia africana* aril (whole), *Afzelia africana* (deoiled), groundnut shell, and paraffin wax), for medium die pressure densification is an important contribution. These findings will encourage low energy densification of rice husk at the rural level in sub-Saharan Africa. The findings will not only make rice husk an alternative to firewood, but they will also provide employment for youths, hence meeting all the criteria of the triads of sustainability. The findings which show that rice husk briquettes can be produced at low energy usage as both an energy alternative to firewood, as well as, potential manure absorbing bedding for animals, are also very important contributions. One key issue of rice production in the sub-Saharan region is lack of fertilizer; this research opens up a research avenue for lightly densified rice husk as a manure collecting mechanism in the sub-Saharan region and other rice producing regions.

The physical parameters and models that define these two groups of rice husks were defined and developed. There has not been any research to date comparing the physical characteristics of these two rice husks. The research result of this study will motivate the equipment designers to work to utilize simultaneously the two rice husks as fuel feedstock.

This research has established the characteristic FT-IR spectra, identifying key components, for the two most abundant rice husks in sub-Saharan Africa and the developing world. The research also identified the unique FT-IR spectra of rice husk with high amount of immature grains. FT-IR and SEM analyses showed that although the chemical composition of the two rice husk differ quantitatively, the proximate ash of the two rice husks were the same. With the results of this research, these rice husks and their blends can be utilized as biofuel feedstock in the regions where they are abundant.

This research has shown that, not only harvest and postharvest processing affect the thermochemical conversion characteristics of rice husk, but the rice variety also plays an important role. Therefore, research on how variety affects thermochemical conversion of rice husk should be an important research component in the development of hybrid rice varieties that are suitable for every ecological condition, in order to ensure sustainability of rice production, considering the triads (Social, Economic, and Environment) that sustainability entails.

8.3 Recommendation for future research

Improvement of the conventional methods and development of new methods using the RATE theme proposed in this research will increase the sustainability of rural rice processing. The adaptation of the RATE by NEPAD and the leaders of sub-Saharan African region; and its implementation in their agricultural development program will increase sustainability of agricultural production. Development of skill acquisition centres that train farmers, postharvest processors, and the local tradesmen that fabricate agricultural equipment; and collaboration with research institutions including the local Universities to develop and design the equipment for the farmers and processors (which defines RATE) is very important for increasing sustainable agricultural production at the small (rural) and medium scale levels. Since this sector is a potential employer for the local youth and rural community, it will not only help in providing food security, but will also help in reducing poverty, and minimizing social insecurity, that most regions of sub-Saharan Africa are experiencing. Although this research was based on the objective one and objective two of the Millennium Development Goals (MDG's), which focus on the eradication of extreme poverty and hunger, and environmental sustainability, respectively; it went further in determining how to effectively engage all parties within the local community to participate for economic, social, and environmental benefit of the entire society. The research paves the way for the 17 Sustainable Development Goals (SDG's) proposed by the UN to end poverty, fight inequality and injustice, and tackle climate change by 2030.

Coincidentally, the region where this research was carried out - the upper Benue river basin of North Eastern Nigeria is currently undergoing security, and instability issues. These issues can highly be attributed to the extreme poverty, lack of appropriate policies and programs to alleviate hunger, and the ineffective methods that were used to improve economic, social, and environmental sustainability in the region. The research findings can be used as a basis for public-private partnerships, as well as, sustainability research to ensure full implementation of the United Nation's SDG's regarding food production and sustainability, in the sub-Saharan African region.

The fact that there are two regions of absorption or permeability dependant on process parameters is an opportunity for multiple applications of rice husk briquettes. Higher density rice husk produced at higher densification pressures can be utilized as fuel feedstock, while briquettes with the highest water absorption/permeability can be an attractive bedding that can be used not only to provide comfort to animals, but also a means of manure absorption mechanism that can later be easily spread in the field mixed with soil to improve soil fertility.

The physical characterizations of the Milltop and Engelberg rice husks have shown that the two rice husks have unique characteristics that define them as separate groups. The parameters developed in this research will be important tools for designing of handling, densification, and thermochemical equipment. Particle analysis of the rice husk samples revealed important pre-harvesting and post-harvest processes issues that ultimately could have affected rice kernel yield. The utilization of this research procedure using Standard sieves #10 and #20 for the Milltop, sieves #20 and # 35 for the Engelberg will be valuable during quality assessment of rice production.

Sieves #10 and #20 can be related to the flowability of the Milltop samples due to the presence of structures such as trichomes, and the existence of breakages of the rice husk outer shells due to milling gap, variety characteristics, or other conditions that could be defined by further investigations. For the Engelberg rice husk, sieves #20 and #35 could be used to investigate whether there were pre-harvesting and post-harvesting processing issues. High retention by sieve #20 for the Engelberg could indicate the existence of larger particles, which can be correlated to high contents of large broken rice kernels or high content of immature grains; which can both be attributed to pre-harvesting and post-harvesting sub-optimal processes.

The unique method of HHV determination for rice husk samples investigated and presented in this research will contribute in the development of Standards ASABE or ASTM that will incorporate the impact test as well as, the bomb calorimeter residual analysis to increase accuracy of HHV determination for biomass using bomb calorimetry. Most of the adopted standard especially regarding the ASTM were based on fossil fuel such as coke and coal. The growth of renewable fuel as alternative to fossil fuel to mitigate climate change will further motivate research on standards more specific to biomass similar to what was carried out in this research.

Although beyond the scope of this research, it is recommended that further research on thermochemical conversion systems that will utilize both rice husks as fuel is carried out. This will enable the communities where both the Engelberg and Milltop milling machines are used to convert the entire rice husk to valuable energy feedstock. The purity of the silica of the rice husk ash provides another important opportunity for increasing the sustainability of postharvest rice processing by utilization of both the rice husk and the rice husk ash, as biofuel feedstock and industrial material feedstock, respectively. It is also important that the regional and global rice institutes such as AfricaRice and IRRI, continue the development of hybrid rice varieties with the focus of producing a rice paddy that not only produces high yield milled rice, but also co-products that can be utilized as feedstock for bioenergy, animal feed, and industrial applications; as this will increase the sustainability of global rice production, as well as, mitigate the global challenge of climate change by reducing the demand of firewood from the ecologically important trees that protect the region from desertification.

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