

ADDIS ABABA UNIVERSITY  
ADDIS ABABA INSTITUTE OF TECHNOLOGY  
SCHOOL OF CHEMICAL AND BIO ENGINEERING



UPGRADATION OF THE ENERGY CONTENT OF RICE  
HUSK THROUGH CHEMICAL TREATED TORREFACTION

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## DECLARATION

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## ABSTRACT

*Despite all its advantages biomass has some shortcomings that often create difficulties in its wide scale use as an energy source. Compared to the other fuels like coal, biomass has a higher oxygen content, lower calorific value, lower energy density, lower bulk density, higher hygroscopic nature, and higher moisture content. Thus, biomass faces some technical challenges in the energy conversion systems. Torrefaction process is the partial pyrolysis of biomass carried out under atmospheric pressure in a narrow temperature range of 200°C to 300°C, under an inert environment which yields higher solid yield than the pyrolysis. Torrefaction of biomass significantly changes its physical and chemical properties like moisture content, density, grinding ability, pelletability, hydrophobicity, Calorific value, proximate and ultimate composition, and storage. The objective of this study is to examine the torrefaction process of lignocelluloses biomass the rice husk produced in Ethiopia by chemical treated torrefaction process. Three torrefaction temperatures 200°C, 250°C and 300°C, three holding times 20, 40 and 60min and three acid concentrations 0.75, 1.50 and 2.25g/l will be considered from the literature value 0.25 -2.5% concentration of sulfuric acid. Design-Expert 7.0.0 three-level-three-factor BBD was applied for experimental design and statistical analysis of results. The result showed a significant net reduction of the volatile matter content, mass yield, moisture content, bulk density and atomic oxygen content with the increasing torrefaction temperature and reaction time, the atomic carbon content, higher heating value, fixed carbon content and energy density were found to increase with higher torrefaction temperatures and time in both dry and chemical treatment . Torrefaction temperature and holding time had a significant effect on torrefaction process of the rice husk. From the thermo gravimetric analysis, torrefaction peaks were observed at temperatures between 200°C-300°C. The FTIR shows peaks appearance of a result of the degradation of the rice husk functional group. Therefore, the torrefied biomass becomes is found to lie a significant fuel sources which has the potential to replace the fossil fuel. The chemical treated torrefaction yields better result and increase the energy density.*

**Keyword:** *dry, calorific value, pyrolysis and torrefaction.*

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## LIST OF ABBREVIATIONS AND SYMBOLS

DSC	Differential scanning
AAIT	Addis Ababa Institute of Technology
ANOVA	Analysis of Variance
TGA	Thermo Gravimetric Analysis
YE	Energy yield
CV	Calorific value
LHV	Lower heating value
HHV	Higher heating value
H <sub>2</sub> SO <sub>4</sub>	Sulfuric acid
MJ	Mega joule
EMC	Equilibrium moisture content
d a f	Dry ash free basis
Kg	Kilogram
O <sub>2</sub> /c	Oxygen to carbon ratio
W/W	Weight by weight
Wt. %	Weight percent
ASTM	American Society for Testing and Material
BBD	Box -Bhenken Design

## 1. INTRODUCTION

Biomass is a primary type of renewable energy, which is expected to be important energy source in the coming years. Of the different non-conventional energy sources available, wind, solar, tidal, and nuclear, biomass is the widely available and carbon neutral renewable energy. The net carbon emissions resulting from the burning of biomass is zero. (Poudel and sea, 2014). Owing to the increasing impact of traditional energy usage on global climate patterns and the environment, stakeholders are turning their attention to renewable energy sources.

Researchers reported that fossil fuels have been continuously consumed in the 21<sup>st</sup> century and contributed to the climate change like global warming. Therefore, new energy which can be renewable and friendly with environment is the priority concerned (Bergman and Kiel, 2005). Biomass is expected to play a major role in the transition to renewable or sustainable energy production (Lee, 2012). Woody and herbaceous biomasses are regarded as ligno cellulose biomass, because their major organic mass fraction consists of cellulose, hemicellulose and lignin (Chen and Kuo, 2011).

Bioenergy can be generated in different ways. It can be converted to a value-added liquids and gaseous products such as ethanol, synthesis gas, or bio-oil, or it can generate electricity via direct combustion, or gasification. Bioenergy is produced from organic materials, which are any form of biomass such as food crops, organic wastes, and forestry products (Chad, 2012).

Ethiopia has an abundant of forest resources, and these resources can provide a considerable amount of bio-based energy, however, utilizing these sources presents problems. Existing infrastructure for generating energy uses low moisture and oxygen content fuels, such as coal. The major challenge is either adapting this infrastructure to accommodate lower quality Biomass fuel, which can be very costly, or creating a biomass product that can be utilized in a current steam generation or gasification plant. It is for this reason that methods to upgradation the biomass are being explored. Torrefaction is a treatment process for biomass, which is to reduce oxygen content and moisture absorption and increases the energy content.

Torrefaction is a thermo-chemical pretreatment process using biomass within a narrow temperature ranging from 200°C to 300°C (Du et al., 2014). Torrefaction process provides an alternative Bioenergy resource since it increases energy density and reduces transport cost.

Torrefaction increases the energy density of biomass and stimulates its carbon/oxygen and carbon/hydrogen ratios. Due to charring of biomass and cracking of volatiles, the amount of fixed carbon in biomass increases after torrefaction. The amount of fixed carbon increase after the torrefaction due to the conversion of hemicelluloses into more thermally stable compounds (Pelaez., 2014). Reported that the energy density increases with torrefaction temperature since carbon/oxygen and carbon/hydrogen ratios increase with rising temperatures. (Bridgeman et al., 2008) . Found that torrefaction reduces the ignition time for both char and volatiles. Upon torrefaction, biomass loses various compounds with high oxygen and hydrogen contents such as moisture (water), CH<sub>3</sub>OH, and carbon dioxide. This is particularly beneficial for gasification of biomass which contains a large amount of oxygen (Prins et al., 2006).

Many researchers have observed different types of biomass (bamboo, rice husk, or wood) which have low mass yield at longer residence time, (Bergman et al., 2005) found a small decrease in the reactivity due to the increase in the fixed carbon. This meant that torrefied biomass could require a longer combustion time for the complete reaction than the raw biomass. In this study, selected biomass feed stock typical lignocellulose biomass; the rice husk produced in Ethiopia is torrefied. The effect of dry and chemical treated torrefaction pretreatment on the fuel properties of biomass was examined, in this study.

The heart of the torrefaction technology is the concept of reactor. In the development of the torrefaction system, knowledge is important to obtain a good insight into the mechanisms of torrefaction at fundamental level. Torrefaction is a complex process which involves many physical and chemical processes such as heat transfer, moisture evaporation, decomposition kinetics, heat of torrefaction, pressure build up in the solid, changes in material properties all in relation with torrefaction temperature.

## 1.2 Statement of the Problem

The price of oil and gas as well as the energy crisis are continuously increasing; there is a growing demand for the energy which is environmental friendly and less expensive. Biomass is one of the choices among these kinds of energy resources. A wide variety of biomass can be used as raw material for the production of energy such as waste wood chips, agricultural crops and animal waste. In this respect, biomass is one of the most promising energy sources in the immediate future (Basu, 2014). Agricultural and forestry biomass residues can be utilized for energy conversion system by the process of gasification, pelletization, briquetting, direct combustion, or co-firing processes. In Ethiopia, enormous amount of agricultural and forestry biomass residues such as, coffee husk from coffee processing industry, barley husk from brewery factory, rice husk from rice mill/farmers and sawdust which are utilized inefficiently in open fire, land fill occupying for storage or if dumped to environment, this causes environmental pollution and contaminate waters but they can be used as a major source of fuel in energy recovery system if appropriate technology is applied (Dawit, 2012). Despite all its advantages, biomass has some shortcomings that often create difficulties in its wide scale use as an energy source. Compared to other fuels like coal, biomass has higher oxygen content, lower calorific value, low energy density, lower bulk density, higher hygroscopic nature, and higher moisture content. Thus biomass faces some technical challenges in energy conversion systems (Daya, 2008). Low bulk density of raw biomass causes storage and handling problems. It also reduces the energy density of biomass that in turn increases the volume of biomass feed into a conversion system to produce a given amount of power (Arias, 2008). Higher oxygen content reduces the heating value and thereby makes it a lower-grade fuel. Higher oxygen content is responsible for producing large volume of flue gas during combustion that requires much bigger size of plants and auxiliary equipment (Van der Stelt, 2011). Therefore, biomass torrefaction has emerged as a promising technology to fulfill the aforementioned problems of biomass raw materials as well as to reduce significantly the volume of biomass waste generated. This research develops a torrefaction process for rice husks to improve Bioenergy properties.

## **1.3 Objectives**

### **1.3.1 General Objective**

The general objective of this research was to upgradation the energy content of the rice husk through the torrefaction process.

### **1.3.2 Specific objectives**

The specific objectives are:

1. To characterize the physico-chemical properties of the raw material through ultimate and proximate analysis.
2. To assess the effect of dry and chemical treated torrefaction on the mass yield, specific energy, energy density, and chemical properties of raw materials.
3. To find the influence of reaction temperature, residence time, energy density, mass yield, on the properties of torrefied raw materials.
4. To characterize the physico-chemical properties of the torrefaction material through ultimate and proximate analysis.
5. To assess the effect of biomass torrefaction on hydrophobicity property

### **1.4 Scope of the study**

The scope of this research is to study the torrefaction process and parameters that affect the torrefaction process in order to increase the energy density of rice husk. To obtain the best torrefied product and characterize the same. And to analyze the calorific value of the product.

### **1.5 Significance of the study**

The significance of this study obtains the torrefied produce that benefits the house hold and industrial application on further briquetting, pelletization, gasification, or co-firing applications.

## 2. LITERATURE REVIEW

### 2.1 Overview of biomass

Biomass (ranging from woody biomasses to agricultural crop biomasses) can be defined as the organic material produced from solar energy by the process of photosynthesis. The atmospheric carbon dioxide is fixed in the form of biomass as the primary product of photosynthesis in the terrestrial and aquatic regions of earth (Sule, 2012). Biomass is considered as the most abundant resources and is used as feedstock of fuel in its solid, liquid and gaseous forms and chemicals, through different process methods of process. (Basu, et al 2013 ).Reported that the most common utilization of biomass for energy is the direct combustion, followed by gasification, carbonization, pyrolysis and torrefaction. The production of transportation fuel from biomass through pyrolysis, transesterification, fermentation, and gasification-based synthesis is also gaining commercial importance.

The major agricultural cereal crops grown in Ethiopia are maize, rice, wheat, barley, teff, millet and sorghum. They are cultivated in highland and mid-highland areas with the exception of sorghum which also grows in the lowlands. Rice is cultivated in many parts of the country, and the predominant potential areas are:-West Central highlands of Amhara Region (Fogera, Gonder Zuria, Dembia, Takusa and Achefer), North West lowland areas of Amhara and Benshangul Regions (Jawi, Pawi, Metema and Dangur); Gameblla regional state (Abobo, Etangworedas by utilizing rain forest and irrigation); South and South West Lowlands of SNNPR (Beralee, Weyito, Omorate, Gura Ferda, Menit); Somali Region (Gode); South Western Highlands of Oromia Region (Illuababore, East & West Wellega and Jimma Zones) (Teshome and Dawit, 2011). The rice production grows from year to year, which means the availability of rice husk also increase.

### 2.2 Biomass Properties

The use of any biomass for the conversion to energy carriers will be affected by the values of its physicochemical properties. These values will not only determine these conversion process but in general the investment evaluation, as a whole. The dependence of these properties on the various biomass resources which they come from is great and the in-depth understanding of them is essential before the thermochemical conversion process can be considered (Miao, 2015). In general, the most important properties of the biomass are the following: Moisture content, ash content, volatile matter

content, heating value, bulk density, alkali metal content and halogen ion content (in particular Chlorine). In this study, alkali matter content and halogen ion content was not taken into account during analysis.

### **2.2.1 Biomass for Energy Generation**

With growing energy demand and emerging environmental issues, new and clean energy sources are being explored to avoid the possible damages from global warming and climate change. Biomass is widely distributed around the world, and it is often available at a relatively low price. It could therefore become the world's important renewable energy resource. Biomass can help replace fossil fuels in transportation and power generation sectors because it has the ability of producing biofuels such as biodiesel, methanol, and hydrogen through the Fischer-Tropsch Synthesis process (Ptasinski, 2008). However, some of its inherent limitations like low energy density, fibrous nature, and hygroscopic nature, use of biomass for energy generation has so far been restricted. Currently, co-firing technology has gained wide acceptance for reducing fossil fuel consumption and corresponding emissions in thermal power plants by replacing a part of fossil fuel with biomass. But the share of biomass in the mix has been limited to 5-10%. Higher percentage is not economically feasible unless the properties of biomass are upgraded (Van der Stelt, 2011).

Higher moisture content of raw biomass has a significant negative impact on the bioenergy production and its consumption chain. Though moisture adds some benefits in biological conversion methods, it remains as one of the major obstacles for thermochemical conversion. At the same time, higher moisture also decreases the overall gasification temperature, resulting in a lower gasification efficiency and higher tar formation. Most biomass on the other hand also shows a greater tendency to undergo natural decomposition. This alters the physical, chemical, and microbiological properties and degrades the fuel quality (Tumuluru, 2011). Hygroscopic nature is another major drawback of biomass. Though biomass can be dried before its use, the hygroscopic nature makes it to reabsorb the moisture from the surrounding atmosphere even if it is stored indoors.

### **2.2.2 Biomass composition**

Biomass is composed of lignin, cellulose, hemicellulose, lipids, proteins, simple sugars, starches, water, hydrocarbon, ash etc. Due to the carbohydrate structure, biomass is highly oxygenated with respect to conventional fossil fuels including HC liquids and coals. The combination of high

oxygen and high organic volatile matter in biomass indicates a potential for creating large amounts of inorganic vapors during combustion.

### 2.2.3 Constituents of Biomass Cells

The polymeric composition of the cell walls and other constituents of a biomass vary widely (Bergman, 2005) but they are essentially made of three major polymers: cellulose, hemicelluloses, and lignin.

Cellulose: is the most common organic compound on Earth, and is the primary structural component of cell walls in biomass. Its amount varies from 90% (by weight) in cotton to 33% for most other plants. Represented by the generic formula  $(C_6H_{10}O_5)_n$ , cellulose is a long chain polymer with a high degree of polymerization ( $\sim 10,000$ ) and a large molecular weight ( $\sim 500,000$ ). It has a crystalline structure of thousands of units, which are made up of many glucose molecules. This structure gives it high strength, permitting it to provide the skeletal structure of most terrestrial biomass (Rautiainen, 2014). Cellulose is primarily composed of d-glucose, which is made of six carbons or hexose sugars (Figure 2.1) (Prabir, 2010). Cellulose is highly insoluble and, though a carbohydrate is not digestible by humans. It is a dominant component of wood, making up about 40 to 44% by dry weight.

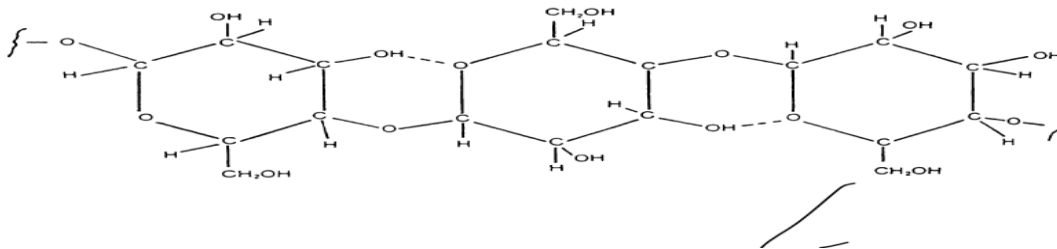


Figure 2.1: Molecular structure of cellulose

Hemicellulose: is another constituent of the cell walls of a plant. While cellulose is of a crystalline, strong structure that is resistant to hydrolysis, hemicelluloses has a random, amorphous structure with little strength (Figure 2.2). It is a group of carbohydrates with a branched chain structure and a lower degree of polymerization ( $\sim 100$ – $200$ ), and may be represented by the generic formula  $(C_5H_8O_4)_n$  (Figure 2.2) (Prabir, 2010) shows the molecular arrangement of a typical hemicellulose molecule.

There is significant variation in the composition and structure of hemicelluloses among different biomass. Most hemicelluloses, however, contain some simple sugar residues like d-xylose (the most common), d-glucose, d-galactose, l-arabinose, d-glucuronic acid, and d-mannose. These typically contain 50 to 200 units in their branched structures. Hemicellulose tends to yield more gases and less tar than cellulose. It is soluble in weak alkaline solutions and is easily hydrolyzed by dilute acid or base. It constitutes about 20 to 30% of the dry weight of most biomass.

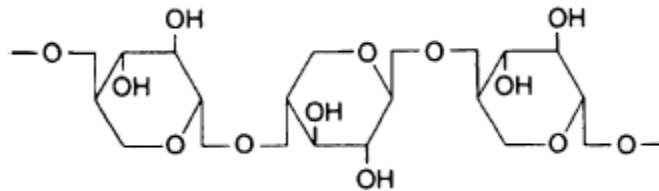


Figure 2.2: Molecular structure of hemicelluloses

Lignin is a complex highly branched polymer of phenylpropane and is an integral part of the secondary cell walls of plants. It is primarily a three dimensional polymer of 4-propenyl phenol, 4-propenyl-2-methoxy phenol, and 4-propenyl-2,5-dimethoxy (Prabir, 2010) shows Figure.2.3.

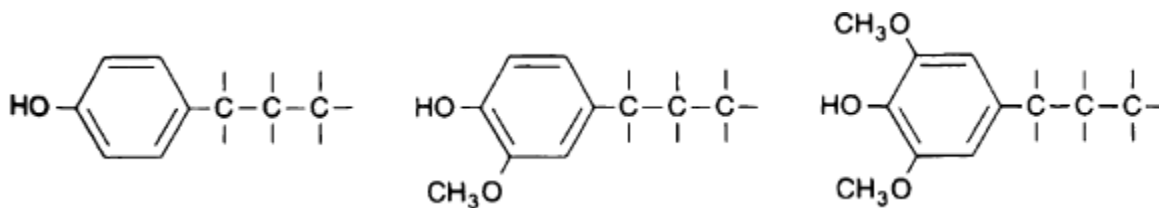


Figure 2.3: Molecular structure of lignin

#### 2.2.4 Biomass Conversion

Pyrolysis: Unlike combustion, pyrolysis takes place in the total absence of oxygen, except in cases where partial combustion is allowed to provide the thermal energy needed for this process. Pyrolysis is a thermal decomposition of the biomass into gas, liquid, and solid. It is three types:

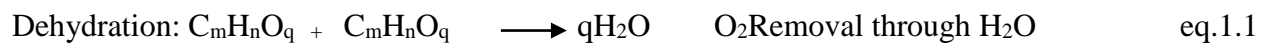
- ✓ Torrefaction, or mild pyrolysis
- ✓ Slow pyrolysis
- ✓ Fast pyrolysis

In pyrolysis, large hydrocarbon molecules of biomass are broken down into smaller hydrocarbon molecules. Fast pyrolysis produces mainly liquid fuel, known as bio-oil; slow pyrolysis produces some gas and solid charcoal one of the most ancient fuels, used for heating and metal extraction before the discovery of coal.

Pyrolysis is promising for conversion of waste biomass into useful liquid fuels. Unlike combustion, it is not exothermic. Torrefaction, which is currently being considered for effective biomass utilization, is also a form of pyrolysis. In this process (named for the French word for roasting), the biomass is heated to 200°C to 300 °C without contact with oxygen. The chemical structure of the biomass is altered, which produces carbon dioxide, carbon monoxide, water, acetic acid, and methanol.

In general, the higher the hydrogen content of a fuel, the lower the vaporization temperature and the higher the probability of the fuel being in a gaseous state. Gasification or pyrolysis increases the relative hydrogen content (H/C ratio) in the product through one the followings means,

Gasification of biomass also involves removal of oxygen from the fuel to increase its energy density. For example equation 1.1 and 1.2 , a typical biomass has about 40% to 60% oxygen by weight, but a useful fuel gas contains only a small percentage of oxygen.



The oxygen is removed from the biomass by either dehydration or decarboxylation. The latter process, which rejects the oxygen through CO<sub>2</sub>, increases the H/C ratio of the fuel so that it emits less greenhouse gas when combusted:

### 2.2.5 Biomass Pretreatment Methods

Above limitations of biomass are hindering the wide-scale use of biomass. This limitation can be reduced to some extent by pretreatment. Pretreatment alters the biomass such that enzymatic hydrolysis of cellulose and Hemicellulose can be achieved more rapidly and with greater yield. Pretreatment also enhance its physical properties making it suitable for use in existing energy conversion systems. Biomass pretreatment methods are classified into five categories: Chemical, Mechanical, Thermal, Hydrothermal, and Biological. These pretreatment methods facilitate biomass conversion process, increasing the economical and environmental viability of biomass use. Only chemical and thermal treatment can be discussed.

**Chemical:** The primary goal of chemical pretreatment is to improve the degradability of cellulose in biomass by removing the lignin and hemicellulose. Common chemical pretreatment techniques are catalyzed steam-explosion, acid, alkaline, ammonia fiber/freeze explosion, organo-solvent, pH-controlled liquid hot water, and ionic liquids pretreatments. In this study acid is used to pretreatment of biomass. It involves the use of diluted acids to break the rigid structure of the lignocellulosic material. The most commonly used acid is dilute sulfuric acid ( $H_2SO_4$ ), which has been commercially used to pretreatment a wide variety of biomass (Torrent, 2011). This chemical pretreatment usually consist of the addition of diluted or concentrated acids (usually between 0.2% to 2.5% w/w) to the biomass followed by constant mixing.

**Thermal:** Thermal pretreatment is a slow heating process in which biomass releases its volatiles. This process modifies the physical, structural, and chemical properties of biomass. Torrefaction, which is a thermal pretreatment method, produces a carbon rich solid product. This process is different from drying because in addition to removal of moisture it involves some chemical transformations within the polymer constituents of the cell wall. These transformations reduce the mechanical strength of biomass, and produce more brittle and less fibrous products. Thermal pretreatment also increases biodegradability of waste biomass in biological conversion process. Thermal treatment enhances the fuel flexibility making wide range of fuels suitable for firing in pulverized coal fired plant. Thermal pretreatment, which mainly refers to the dry torrefaction process (Rentizelas et al., 2009)

## 2.3 TORREFACTION

Dry torrefaction is a thermal pretreatment technique that is used to improve the physical and chemical properties of biomass. Torrefaction is defined as slowly heating the biomass in an inert atmosphere to a maximum temperature of 300 °C (Bergman, 2005), which will result in a solid uniform product with lower moisture and higher energy content when compared to raw biomass.

Various biomass reactions occur during torrefaction, such as devolatilization and carbonization of hemicellulose, depolymerization and devolatilization/softening of lignin and depolymerization, and devolatilization of cellulose. These reactions result in changes in biomass moisture, chemical composition, and energy content. Torrefaction is a partial pyrolysis of biomass which is carried out under atmospheric pressure in a narrow temperature range of 200-300°C and under an inert environment (Acharya, 2013). It produces three major products such as dark color solid products, yellowish color acidic aqueous products, and non-condensable gaseous products.

### 2.3.1 Process stages

The overall torrefaction process can be divided into five steps, such as heating, pre and post drying, torrefaction and cooling. The definitions provided by (Bergman et al., 2005) have been used as a basis to further define the temperature-time stages in torrefaction. Five main stages that have been defined in the total torrefaction process. They are:

- ✓ Initial heating: the biomass is initially heated until the stage of drying of the biomass is reached. In this stage, the temperature is increased, while at the end of this stage moisture starts to evaporate.
- ✓ Pre-drying: at 100°C the free water is evaporated from the biomass at constant temperature.
- ✓ Post-drying and intermediate heating: the temperature of the biomass is increased to 200 °C. Physically bound water is released. During this stage some mass loss can occur as light fractions can evaporate.
- ✓ Torrefaction: during this stage the actual process occurs. The torrefaction will start when the temperature reaches 200°C and ends when the process again is cooled down from the specific temperature to 200°C.

The torrefaction temperature is defined as the maximum constant temperature. During this period most of the mass loss of the biomass occurs.

- ✓ Solids cooling: the torrefied product is further cooled below 200°C to the desired final temperature, which is the room temperature.

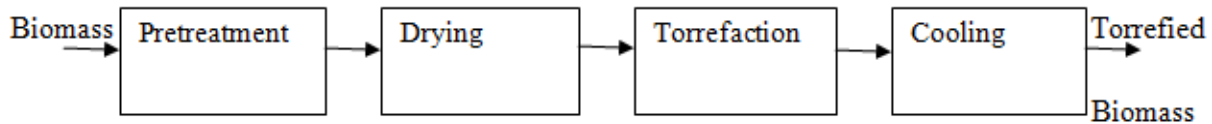


Figure 2.4: Torrefaction and process schemes

Torrefaction, a French word for roasting, changes the chemical and physical properties of raw biomass making it similar to those of char. Torrefaction is usually performed at a low heating rate, which gives higher yield of solid product (Deng,2009). Unlike pyrolysis, the major motivation of torrefaction is maximization of solid yield. Decomposition, devolatilization and depolymerization are three major reactions that occur during the torrefaction process. This process releases condensable hydrocarbon, hydrogen, oxygen, and some carbon content from the biomass in the form of water, carbon monoxide, and carbon dioxide. During the torrefaction process, drying is considered to be more destructive as it breaks inter- and intra-molecular hydrogen, C-O, and C-H bonds. This leads to emissions of hydrophilic and oxygenated compounds, forming a blackened hydrophobic energy dense product. This greatly helps storage of biomass and thereby addresses the problem of seasonal availability of biomass.

Torrefaction of biomass significantly changes its physical and chemical properties like moisture content, density, grind ability, pelletability, hydrophobicity, CV, proximate and ultimate composition, and storage behaviors in terms of off-gassing, spontaneous combustion, and self-heating ( Wang,2015). The main motive of torrefaction is to upgrade the fuel quality of biomass to make it more suitable for thermo-chemical conversion. A torrefied biomass can be used in briquetting, pelletization, gasification, and co-firing thermal power plants (Bridgeman,2008). Torrefaction of biomass destructs tenacity and fibrous structure of biomass, and also increases its energy density.

### 2.3.2 Torrefaction Principles and Conditions

Torrefaction described as: “a thermo chemical process in an inert or limited oxygen environment where biomass is slowly heated to within a specified temperature range and retained there for a stipulated time such that it results in near complete degradation of its hemicelluloses content while maximizing mass and energy yield of solid product.” Torrefaction is early phase of the carbonization or thermal treatment in temperatures of 220°C to 300 °C in holding time one hour or less at atmospheric pressure. Method is the same than in carbonization, but the pyrolysis temperature is lower. Synonyms for torrefaction are roasting, slow- and mild-pyrolysis. Torrefaction can be divided in to three classes according to the temperature light (220 °C), mild (250 °C) and severe torrefaction (280 °C)(Chen and Kuo, 2011). In the torrefaction process hemicelluloses are the most reactive compounds. Lignin and cellulose decomposes in higher temperatures, but the reactions of polymers are overlapping. Lignin is the cementing agent for cellulose fibers holding adjacent cells together. The dominant monomeric units in the polymers are benzene rings. It is similar to the glue in a cardboard box, which is made by gluing together papers in special fashion. Lignin is highly insoluble, in sulfuric acid (Prabir, 2010). Torrefied wood is promising as a renewable fuel for industrial use in coal co-combustion, gasification-combustion and Fisher-Tropsch fuel production or in the small-scale use as barbeque fuel or firelighter. The advantages of torrefaction are improved higher heating value, grind ability and possible hydrophobicity. Technologies used in torrefaction are the same as carbonization (Bergman, 2005).

From this definition, it is easy to derive the three important conditions for a torrefaction process, temperature, acid concentration, and residence time. Some torrefaction studies where the researchers have suggested all different temperature ranges for a torrefaction process. Although their minimum temperatures are different, they have all set their maximum torrefaction temperature at 300°C. A typical torrefaction temperature range is between 200 °C and 300 °C (Bergman,2005).This is mainly due to the following two reasons: the first one is the decomposition temperatures ranges of the three main components of biomass, cellulose, hemicellulose and lignin. Another motivation for choosing this temperature range is to make the biomass lose its fibrous nature such that it is easily grindable, while it is still possible to form it into pellets without binders. These requirements limit the torrefaction temperature range.

The advantages of torrefaction are improved higher heating value, grind ability and possible hydrophobicity. Technologies used in torrefaction are the same as carbonization (Bridgeman,2008). From this definition, it is easy to derive the four important conditions for a torrefaction process, temperature, oxygen concentration, heating rate and residence time. Table 2.1 has depicted some torrefaction studies where the researchers have suggested all different temperature ranges for a torrefaction process. Although their minimum temperatures are different, they have all set their maximum torrefaction temperature at 300°C. A typical torrefaction temperature range is between 200 °C and 300 °C this is mainly due to the following two reasons: the first one is the decomposition temperatures ranges of the three main components of biomass, cellulose, hemicellulose and lignin.

Table 2.1: Torrefaction temperature ranges as suggested by different researchers

Researchers	Temperature range (°C)
Arias et al.[2008]	220-300
Chen and Kuo [2010], Prins [2005]	225-300
Pimchuai et al.[2010], Prins et al.[2006]	230-300
Bergman et al.[2005],Tumuluru et al.[2011]	200-300

Conventional direct heated torrefaction for making tea and coffee beans is carried out under atmospheric conditions; torrefaction of biomass in contrast, is carried out in absence of oxygen. However, some studies (Basu et al., 2013) have shown that it is not essential to have an oxygen-free environment for torrefaction. Presence of a modest amount of oxygen can be tolerated and may even have a beneficial effect on design of commercial torrefier as low concentration of oxygen can be tolerated.

A biomass torrefaction process is traditionally characterized by a low particle heating rate, which is typically less than 50°C/min. Also the reactor residence time (about one hour) of the process is relatively long. This is to ensure that maximization of the solid yield is achieved during the process; a higher heating rate would increase the liquid yield at the expense of solid products as is done for pyrolysis.

### 2.3.3 Torrefaction Process principle

Figure 2.5 is a simple illustration of the torrefaction process, where one unit of biomass (dry wood) is used as input for the process. During torrefaction, the biomass will partly decompose and give off various types of volatiles and gases. Product of this process is referred as torrefied biomass or char.

Thermal treatments happen in the torrefied through (direct) contact of the biomass with the heating medium or heat carrier. The heating medium here could be a hot substance, dry or wet. Dry torrefaction involves heating either by a hot inert gas (like nitrogen) or by indirect heating. The dry torrefaction process is currently being commercialized (Basu, 2008)

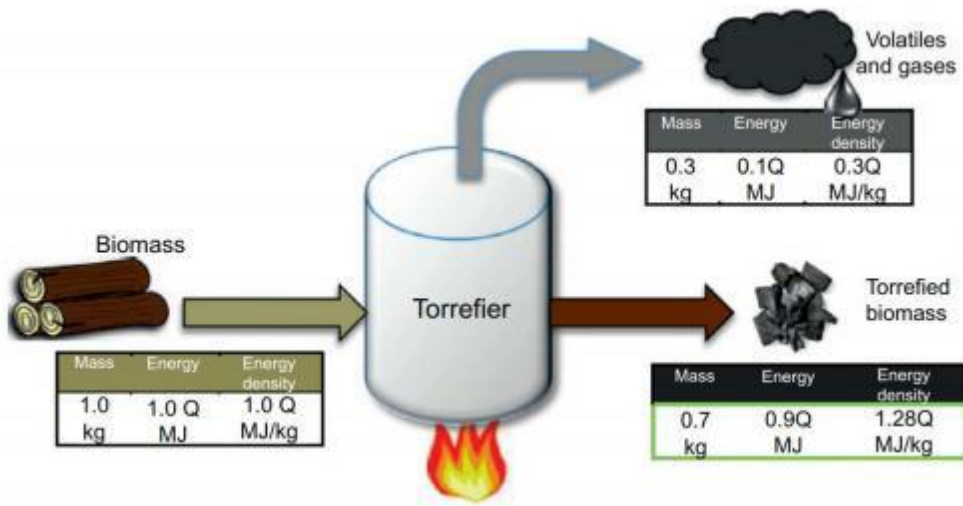
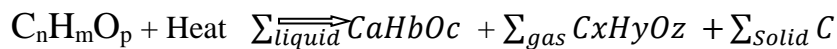


Figure 2.5 Simple illustration of the torrefaction process (Basu, 2008)

The solid carbon as well as the condensed liquid enters the gasification reaction with carbon dioxide, oxygen, or steam to produce combustible or synthetic gas. To illustrate the different reactions we take simple carbon as the feedstock.



When a biomass or other carbonaceous material is heated in a restricted oxygen supply, it is first pyrolyzed or decomposed into solid carbon and condensable and non-condensable gases (Stelt, van der, 2011).

### 2.3.4 Process yields

As mentioned in the previous section, different biomass species react differently to the torrefaction process due to their various compositions. Also the torrefaction temperature is a determining factor for the properties of the torrefaction products. (Bridgeman et al.,2008),conducted several torrefaction mass balance experiments, the data is reproduced in Table 2.2, which provides a summary of torrefaction products' mass and energy yields of three different biomass species, reed canary grass, wheat straw and willow.

It can be concluded from the table that biomass torrefaction has an overall higher energy yield than mass yield; this effect becomes more marked for higher temperature treatments, where the differences between mass and energy yields also become higher. Comparing the differences between species, woody biomass like willow shows higher yields than agricultural residues under the same torrefaction conditions, this is due to the higher volatile matter content in the agricultural residues and the decomposition of extractives and hemicellulose, the main fraction decomposed in the torrefaction temperature range.

Table 2.2: Mass and energy yields, treated at different temperatures and (reaction time of 30 mint) (Bergman,2005)

Biomass	Temperature(°C)			
	230	250	270	290
Reed canary grass				
Mass yield(d.a.f.)	92.6%	84.0%	72.0%	61.5%
Energy yield (d.a.f.)	93.5%	86.6%	77.1%	69.0%
Wheat				
Mass yield(d.a.f.)	91.0%	82.6%	71.5%	55.1%
Energy yield(d.a.f.)	93.5%	86.2%	78.2%	65.8%
Willow				
Mass yield(d.a.f.)	95.1%	89.6%	78.8%	72.0%
Energy yield	96.5%	92.7%	85.8%	79.2%

However, knowledge on the influence of chemicals/ alkali content/chemical properties on torrefaction characteristics are limited. From the search of reviews on torrefaction of rice husk, only dry torrefaction was performed to enhance the energy density of rice husk. But using chemical treatment it is also possible to modify the fiber structure or the lignin components to enhance the energy content of rice husk. And this research focuses on the enhancement of energy density through both dry and influence of chemical treated torrefaction. Many researchers have studied the effect of torrefaction temperature and residence time on the physical and chemical composition. (Suriyati,2013).

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### **2.3.5 Torrefaction product properties**

During torrefaction, three different products are produced: (1) a brown to black solid biomass, which is often used for combustion in a boiler (bioenergy applications), (2) condensable volatile organic compounds comprising water, acetic acid, aldehydes, alcohols, and ketones, and (3) non-condensable gases like CO<sub>2</sub>, CO, and small amounts of methane. The condensable (liquid) can be further divided into four groups which are reaction water produced from thermal decomposition, freely bound water that has been released through evaporation, organics (in liquid form) which consist of organics produced during devolatilization and carbonization, and lipids which contain compounds such as waxes and fatty acids(Tumuluru,2011). The emissions of condensable and non-condensable products are depending on heating rate, torrefaction temperature and time, and biomass composition. The release of these condensable and non-condensable products results in the changes interms of the physical, chemical, and storage properties of biomass. The physical and chemical properties of biomass before and after torrefaction have been analyzed for the following characteristics: (a) mass and energy yield, (b) grindability, (c) particle size and distribution, (d) chemical compositional changes, and (e) hydrophobicity.

### 2.3.6 Effect of Torrefaction Process Parameters

The feedstock and process variables that influence the torrefaction process are (1) feedstock type, (2) particle size, (3) temperature, (4) residence time, and (5) heating rate. (Tumuluru,2011) divide thermal pretreatment regimes into three zones: non-reactive 50 to 150°C, reactive 150–200°C, and destructive drying 200–300°C. According to the study the reactive drying temperature regime is also called deep drying, whereas the destructive drying temperature is called the torrefaction regime. The initial heating of biomass up to 150°C (non-reactive drying zone) removes the unbound water. Increasing the temperature from 150 to 200°C removes most of the bound water by a thermo-condensation process. Furthermore, increasing the temperature to greater 200°C will result in decomposition, devolatilization, and carbonization reactions. Most of the biomass hemicellulose undergoes decomposition reactions, which result in significant changes in color, chemical composition, and physical characteristics.

At temperatures greater 280°C, the process is completely exothermic, which results in significant increases in the production of CO<sub>2</sub>, phenols, acetic acid, and other higher hydrocarbons. During torrefaction, hemicellulose degradation causes the destruction of OH functional groups and will leave the material hydrophobic. The degree of hydrophobicity depends on the torrefaction temperature. Hydrophobicity will help biomass to absorb less moisture during its storage in different environments, therefore making it more stable against fungal and microbial attacks.

Temperature:the yield of solid char, gases and liquids depend strongly on the process conditions; pyrolysis temperature, holding time, heating rate and raw material(Prinset al., 2006). Peak temperature is the highest temperature reached in the carbonization or torrefaction process. High pyrolysis temperatures decline solid yield of char, but increase higher heating value, carbon and ash content(Rautiainen,2014).Torrefaction occurs in the temperature range of 200 to 300°C when the residence time varies between 10 to 45 min, in practice. Increasing temperature and residence time results in higher mass loss of biomass during torrefaction.

Heating rate: Heating rate affects to the yield and composition of charcoal in addition to wood species. Rapid decomposition gives a lower yield of charcoal but greater yield of gases. Effects of prevailing pressure in the process to decomposition of wood have been studied. The studies have shown that pressures above atmospheric pressure effects to exothermic reaction and reaction becomes very violent producing a slight increase in charcoal and gas volume.

Residence time (holding time): Holding time has an impact on solid char yield, higher heating value and carbon content. Increase in holding time decrease the yield of solid char. yield of solid char observed to be approximately 13% higher in holding time of one hour than three hours in temperature of 280°C. Holding time has a slight positive impact on higher heating value and carbon content (Rautiainen, 2014).

Residence time of the feedstock in the reactor is an important parameter for designing reactors. Compared to many other thermo-chemical conversion processes like combustion, gasification or pyrolysis, the reaction time for torrefaction is much longer (about an hour). It is nearly an order of magnitude longer than that for other processes. Such a long reaction time requires the biomass feed to reside within the reactor for very long time. This naturally increases the volume requirement of the reactor for a given output. The residence time has thus a greater impact on the reactor size. For example, length and rotational speed of the screw in a screw type reactor and belt speed in conveyer belt reactor are mainly determined by the required residence time. The residence time also determines the solid space velocity and reactor height of a moving bed torrefied (Daya,2016).

## **2.4 PROXIMATE AND ULTIMATE ANALYSIS**

The proximate analysis shows that the torrefied biomass has higher fixed carbon and lower volatile matter than the original biomass. The higher content of fixed carbon in torrefied biomass is closer to coal. The increase in the fixed carbon was attributed to a partial volatilization, which occurs during torrefaction. The ultimate analysis of torrefied biomass shows that more H and O are released compared to C during torrefaction. Consequently, the atomic ratios of O/C and H/C of torrefied biomass are smaller than that of the raw biomass (Shoulaifar, 2016). Torrefaction process converts complex polymers of biomass into smaller monomers and then the smaller monomer into condensable and non-condensable volatile gases. This transformation alters both proximate and ultimate analyses of the biomass. Torrefaction drives away volatile matter as well as fixed carbon from a biomass due to decomposition and devolatilization reactions. Although the absolute amount of fixed carbon decreases after the torrefaction process, the fraction of fixed carbon in the torrefied biomass increases. However, the fraction of ash, the inert and non-combustible material in biomass increases even more because none of it is driven away during torrefaction. Decrease in volatiles along with the chemical transformation of remaining polymeric components produces a brittle carbonaceous coal like solid torrefied products. The torrefied product would, therefore, have a proximate and ultimate composition different from that of the parent biomass. The change in proximate composition of the torrefied biomass is influenced by both temperature and residence time of torrefaction. Increase in time and temperature reduces the volatile content of biomass (Arias, 2008).

## **2.5 PROPERTIES OF RICE AND RICE HUSK**

Rice husk is a potential material, which is amenable for value addition. The usage of rice husk either in its raw form or in ash form is many. Most research shows that approximately 20 kg of rice husks are obtained from 100 kg rice. Most of the husk from the milling is either burnt or dumped as waste in open fields and a small amount is used as fuel for boilers, electricity generation, bulking agents for composting of animal manure, etc (Bronzeoak, 2003). The exterior of rice husk are composed of dentate rectangular elements, which themselves are composed mostly of silica coated with a thick cuticle and surface hairs.

The mid region and inner epidermis contain little silica (Bronzeoak and Jauberthie,2000) confirmed that the presence of amorphous silica is concentrated at the surfaces of the ricehusk and not within the husk itself. The chemical composition of rice husk is similar to that of many common organic fibers and it contains cellulose 40-50 percent, lignin 25 to 30 %, ash 15-20% and moisture 8- 15 % [Hwang and Chandra, 1997].



(a)

(b)

(c)

Figure 2.6: (a) Polished Rice (b) Un Polished Rice with Husk (c) Rice Husk

After burning, most of the evaporable components are slowly lost and the silicates are left. The typical Properties of rice husk are indicated in Table 2.3. No other plant except since husk is able to retain such a huge proportion of silica in it. Plants absorb various minerals and silicates from earth into their body. Inorganic materials, especially silicates are found in higher proportions in annually grown plants, such as rice, wheat, sunflower, etc, than in long-lived trees. Inorganic materials are found in the form of free salts and particles of cationic groups combined with the anionic groups of fibres into the plants (Basha et al., 2005). A combined study using back scattered electron and X-ray images of the husk showed that the silica is distributed mostly under the husk's outer surface (Stroeven et al., 1999). This confirms the general concept of a soluble form of silica transported through the plant, and concentrated at the outer surface of straw and husk through evaporation, where upon it polymerizes into an opaline cellulose-silica.

Table 2.3: Typical husk analysis [Bronzeoak, 2003]

S.No		Range
1	Bulk density (kg/m <sup>3</sup> )	96-160
2	Length of husk(mm)	2.0-5.0
3	Hardness	5.0-6.0
4	Ash (%)	22.0-29.0
5	Carbon (%)	35
6	Hydrogen (%)	4.0-5.0
7	Oxygen (%)	31.0-37.0
8	Nitrogen (%)	0.23-0.32
9	Sulfur(%)	0.04-0.08
10	Moisture (%)	8.0-9.0

### 2.5.1 Proximate Analysis

The proximate analysis of a material quantifies the percentages of moisture, ash, volatiles, and fixed carbon in the sample. The ash percentage of a sample is the inorganic residue that remains after a sample has undergone complete oxidation. Biomass ash is very high in alkali metals and, as a result, is highly reactive. During combustion, it can react with gases such as sulfur and chlorine to cause slagging, fouling, and corrosion problems. Table 2.3 shows the proximate analysis of some biomass types. Biomass contains a high percentage of volatile matter when compared to coal, which is generally less than 40% by weight. This might be seen as a disadvantage for biomass since the high volatile content is typically accompanied by high oxygen content, which decreases heating value. The high volatile content of biomass may, however, be beneficial when co-firing with coal. Combustion efficiency of the mixture can be increased since the ignition temperature is decreased with the addition of biomass. The volatiles in biomass promote better burnout of the fuel and lower NO<sub>x</sub> emissions.

### 2.5.2 Energy Content

The energy content (or heating value) of a material is the ratio of the enthalpy of complete combustion to the mass of the sample. It is one of the most important parameters for a biomass sample and is used to design Bioenergy systems. Heating value can be defined in two ways, lower and higher heating value. The difference between the two values is the state of the water after combustion: water in vapor phase equal to lower heating value (LHV), water in liquid phase equal to higher heating value (HHV). Lower heating value can sometimes be misleading because it does not include the latent heat of vaporization of the water products, which can produce thermodynamic heating efficiencies greater than 100%. Using higher heating value is practical for energy systems that allow the water in the reaction products to condense, such as in a boiler. The higher heating value is stated in this work and is most commonly used in literature, which typically reports dry HHV values of 16-22 MJ/kg for biomass. As mentioned previously, energy content is strongly related to chemical and physical composition of the biomass and can be estimated by either proximate or elemental analyses data for a range of biomass types (Friedl et al., 2005).

Increasing the torrefaction temperature and residence time will increase the higher heating value (HHV) of biomass. Energy yield based on the heating value and mass yield can be viewed as a measure of the amount of energy loss during torrefaction. Energy yield for woody biomass subjected to torrefaction temperature below 250 °C is above 89%, and decrease to 71-73% as torrefaction temperature increase to 300 °C. Non-woody biomass generally has a lower energy yield compared to woody biomass with a wider spread ranging from 41% to 95% due to the higher variation in volatile matter and hemicelluloses fraction (Torrent.,2011).

The heating value of the biomass is an important property, as it will determine its use in energy applications. An increase in the carbon content as reported from ultimate analysis lead to an increase in the heating value. At higher temperature, the content of C in the solid product increases while the contents of H and O decrease. Calculation of the HHV illustrates the impact that these changes have on the energy content. Table 2.4 shows the heating value together with the ultimate analysis and moisture content of raw and torrefied wheat straw (Torrent, 2011). The energy content of wheat straw torrefied at 290 °C rose by 17% with the highest loss of hydrogen and oxygen content, and the increase in carbon content.

Table 2.4: Ultimate analysis, HHV (dry ash free basis) and moisture content of untreated and torrefied wheat straw (Bridgeman and Jones, 2008)

wheat straw	Torrefaction temperatures				
	Raw	230°C	250°C	270°C	290°C
C	47.3	48.7	49.6	51.9	56.4
H	6.8	6.3	6.1	5.9	5.6
N	0.8	0.7	0.9	0.8	1
O	37.7	36.5	35.6	33.2	27.6
Moisture (%)	4.1	1.5	0.9	0.3	0.8
Heating value (MJ)	18.9	19.4	19.8	20.7	22.6

(Pimchualet al.,2010) reported that the energy density continues to increase with the increase in temperature. The increase in energy density because of greater residence time however was insignificant. Table 2.5 shows the influence of temperature and residence time on the energy density of the torrefied agriculture residue. It can be seen that the increase in energy density varied with the type of fuels investigated.

Table 2.5: Influence of temperature and residence time on the energy density of the torrefied agricultural residue (Pimchualet al.,2010)

		<i>Energy density</i>			
Temperatures(°C)	Time(hr)	Rice husk	Saw dusts	Peanut husk	Bagasse
250(°C)	1	1.11	1.08	1.12	1.36
	1.5	1.12	1.11	1.14	1.38
	2	1.16	1.06	1.23	1.42
270(°C)	1	1.12	1.13	1.27	1.42
	1.5	1.14	1.21	1.27	1.43
	2	1.2	1.22	1.28	1.45
300(°C)	1	1.23	1.31	1.3	1.58
	1.5	1.24	1.35	1.31	1.66
	2	1.24	1.37	1.32	1.62

Water is a major product released by two different mechanisms, firstly during drying when moisture evaporates and secondly during dehydration reactions between organic molecules. The experiments on the individual components of biomass showed that the cellulose particles shrink slightly as they are heated. Unlike cellulose, particles of pectin and xylan show evidences of softening or melting (at the temperatures of 150 °C and 200 °C, respectively), as well as bubble formation as they are heated. The bubbles are formed within the particles, and as the bubbles burst volatile products are released into the gas stream. The torrefied sample lost most moisture and low weight organic volatile components and then the long polysaccharide chains were depolymerized, thus forming a hydrophobic bio-char with a higher energy density than the raw biomass.

### 2.5.3 Solid Product (Mass yield) and Energy Yield

Solid product yield and energy yield are important quantitative and qualitative measures of a torrefaction process. Solid product yield is defined as a ratio of final mass of solid torrefied product to initial mass whereas energy yield is a ratio of final energy in solid product to initial energy content of raw biomass. Both solid product and energy yields are expressed in dry basis or in dry and ash free (d.a.f) basis.

Mass yield: The changes in the content of biomass can be shown by mass loss or mass yield of the biomass during torrefaction, equation 2.1&2.2 (Suriyati, 2013).

$$L_{mass}\% = \frac{(m_i - m_f)}{m_i} \times 100 \quad \text{eq.2.1}$$

Where: L mass is mass loss,  $m_i$  is initial mass of the sample and  $m_f$  is final mass of the sample

$$Y_{mass}\% = \frac{m_f}{m_i} \times 100 = 100 - L_{mass}\% \quad \text{eq.2.2}$$

Where  $Y_{mass}$  is mass yield of torrefied biomass

The final mass and the initial mass are usually provided on a dry basis. In practice, it is not common to provide the mass loss or mass yield of torrefaction on the ash free basis. The mass loss depends on the temperature and residence time. The value of the mass loss varies widely, for instance, it is reported that the mass loss for the wood residues are between 6% and 57% , and particularly 5% to 63% for pine (Shoulafar, 2016), It was proposed that the mass loss from

torrefaction could be correlated to the fuel properties like heating value and Equilibrium Moisture Content (EMC).

Energy yield: The energy yield describes the amount of biomass energy retained in the torrefied biomass. The energy yield is defined as the ratio of the total energy still in the torrefied biomass to the energy content of raw biomass, equation (2.3) (Bergman, 2005).

$$Y_{\text{energy}\%} = \frac{HHV_{\text{torr}}}{HHV_{\text{raw}}} \quad \text{eq.2.3}$$

Where:  $Y_{\text{Energy}\%}$  is percentage energy yield,  $HHV_{\text{torr}}$  is energy content of torrefied product and  $HHV_{\text{raw}}$  is energy content of raw sample. The value of the energy yield, depending on the temperature and residence time, can vary widely. For example, the energy yield for wood residues is reported between 50% to 97% and for pine particularly 52.4% to 99.8%.

#### **2.5.4 Hydrophobicity**

Torrefaction substantially removes both free and bound moisture of biomass. The free moisture inside capillaries of fibers shows surface wetness whereas the bound moisture determines the hydrophilic or hygroscopic (affinity for water) nature of biomass. Though drying could remove the surface moisture as well as some of the bound moisture of biomass, its hydrophilic property makes it regain the moisture from the surrounding air when stored. Equilibrium moisture content (EMC) of raw biomass influences its hygroscopic nature. Lowering the EMC reduces the moisture absorbing capacity and thereby increases the hydrophobicity of biomass. The equilibrium moisture content also depends on the chemical composition and functional groups of biomass (Acharjee et al., 2011). The EMC highly varies with the relative humidity of air. Torrefaction process has a positive effect on humidity uptake from the air. A higher torrefaction temperature also has a favorable influence on hydrophobicity. After 15 min of immersion water absorption in wood pellet is 76% while that of torrefied pellet reduces it to 55%.

#### **2.5.5 Bulk Density**

Bulk density is an important parameter that must be considered when transporting and storing large quantities of biomass. Bulk density is the ratio of the mass of a material to its volume, and it plays a crucial role in the economic analysis of a bioenergy supply chain. Biomass has to be transported from where it is harvested to where it is processed. When transportation vehicles are a given volume, the bulk density can be used to determine the amount of mass that can be moved during transit. The values are used to calculate feedstock cost and estimated transportation costs. If the material is to be stored inside a silo or tank, the bulk density is used to design those

storage containers. (Rentizelas,2009).The logistics for the transportation and storage of biomass for energy purposes are the largest fractions of the overall cost.

### 2.5.6 Equilibrium Moisture Content (EMC)

High moisture is a major characteristic of biomass. Biomass moisture content is defined as the amount of water in the biomass expressed as a percentage of the material's mass. Moisture content has a significant effect on the engineering of the conversion process; either a thermochemical (i.e. combustion) or a biochemical (i.e. Fermentation) process is considered. Actually, it has been estimated that an increase in the moisture content of biomass from 0% to 50% can decrease the heating value by about 66%(Sokhansanj,2011).The moisture content can vary from less than 20% for many of the agricultural wastes, like husks and straws, and up to 70% for switch grass.

Table 2.6: Moisture contents of some biomass (Source: compiled from Kitani and Hall,1989)

Biomass	Corn stalks	Wheat straw	Rice straw	Rice husk	Wood bark	Saw dust	Water hyacinth
Moisture(%)wet basis	40-60	8-20	50-80	7-10	30-60	25-55	95.3

Moisture in biomass could be divided into free water and bound water. Free water is the part of moist that can easily be removed by weak mechanical strains. Bound water is a small proportion in the total moisture which needs extra treatments upon its removal( Halde,1979),distinguished three types of bound water:

**Chemically bound water:** which is attached to solids by strong chemical bindings, and can be removed by thermal drying at a minimum temperature of 105°C.

**Physically bound water:** This can be removed by thermal drying, and is fixed to the solid particles by adsorption or absorption.

**Mechanically bound water:**This is found in both micro- and macro capillaries of capillary-porous bodies. This can be eliminated by strong mechanical strain. Moisture removal techniques applied in this study were oven drying and furnace torrefaction.

Biomass inherently contains moisture, which normally varies between 10-50%. The moisture in biomass causes some problems: increases the storage and handling costs (Miao, 2015), and makes it susceptible to biodegradation during storage.

$$EMC\% = \frac{(M_e - M_d)}{M_d} \times 100 \quad \text{eq.2.4}$$

Where  $M_e$  is the mass of the sample at equilibrium with a humid atmosphere and  $M_d$  is the mass of dry sample. The EMC values for torrefied biomass are lower than raw biomass. This is due to lower hydrophilic characteristic of torrefied biomass. Increasing the torrefaction temperature decreases the hydrophilic characteristic of biomass .

### 3. MATERIALS AND METHODS

#### 3.1 Materials

The equipment's used in this study are tubular Furnace with a stainless steel tubular reactor, a glass reactor, , balance, oven, Muffle furnace, different size conical and Erlenmeyer flasks, beakers and measuring cylinders. Preparation of the rice husk, pyrolysis of the rice husk, washing and characterization of bio-char was done at School of Chemical and Bio Engineering Laboratory, AAIT. The other characterization such as elemental analysis, FTIR, elemental analysis, TGA analysis and calorific value were carried out at faculty of natural science department of chemistry, AratKillo, Ethiopian Geological Survey Organization and Leather Industry Development Institute.

#### 3.2 Methods

Rice husk obtained from local farmers they were air dried to a moisture content of 10-15 % (wet. basis). The husk was then fractionated to remove the large (>4mm) and smaller chippers (<2mm) with the use of vibrating screen separator. After screening, the husk was kept in dry atmosphere for further analysis. The raw and fractionated rice husk is shown in figure 3.1.

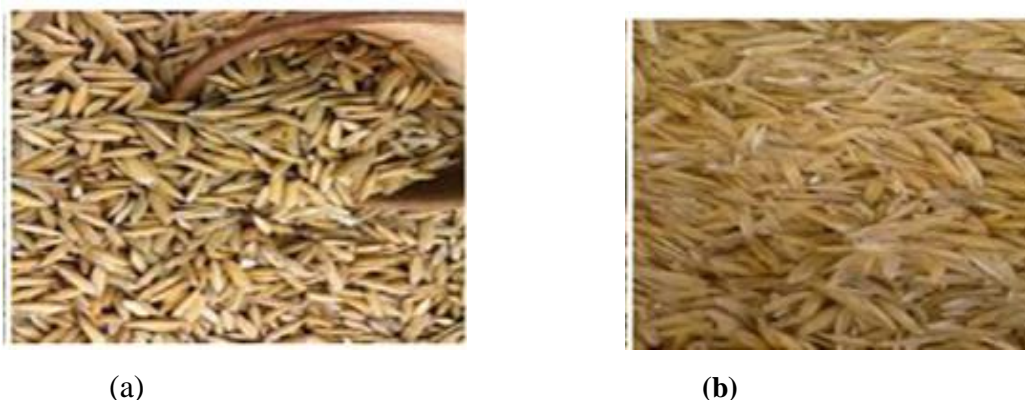


Figure 3.1 : (a) Raw Husk (b) Fractionated Rice Husk

##### 3.2.1 Pretreatment Methods

In this research, some pretreatment steps were adopted before the performing the experiments. These pretreatments were not only needed for determining some basic material properties such as ash and moisture content, but also mandatory for preparing the samples for the experiments. The employed steps were sieving, washing with distilled water (twice), drying, chemical treating

(if chemical treated torrefaction), and samples after pretreatments will be later referred as pretreated biomass.

### 3.3 RAW MATERIAL CHARACTERIZATION

Rice husk from rice producing farmers was selected as feedstock for this study since it is the main agricultural crops in Ethiopia. The selection aims among others to utilize these available resources potential by enhancing the energy density using two methods i.e. chemical and dry torrefaction. Proximate analyses of the raw feedstock and the torified rice husks were performed according to ASTM standards: ASTM E871, ASTM E872, and ASTM D1102 for moisture content, volatile matter, and ash content, respectively. The ultimate (elemental) analysis was performed at Addis Ababa University (AAU) Chemistry department. Ultimate analyses of the samples of fuel on dry basis were determined by an “EA 1112 Flash CHNS-O- analyzer”. In addition, the higher heating value (HHV) was calculated according to a unified correlation proposed by (Daya and Muhammad, 2017) .

### 3.4 Proximate, Ultimate Composition and Energy density

#### 3.4.1 Proximate Analysis

Proximate analysis which is a standardized procedure that gives an idea of the bulk components that make up a fuel was done to determine the average of the percentage volatile matter content, percentage ash content, moisture content and percentage content of fixed carbon of the rice husk obtained from three replicates. The contents were found according to ASTM standards. Mass yield: Mass yield can be calculated from the ratio of torified to raw solids . The mass yield was calculated using the following equations equation 3.1.

$$\text{Mass yield} = \left( \frac{M_f}{M_i} \right) \times 100\% \quad \text{eq.3.1}$$

Where:  $M_f$  is the final mass of biomass after torrefaction;  $M_i$  is initial mass of biomass before torrefaction (raw biomass).

Moisture Content: Moisture content of each sample was found using oven drier and moisture content analyzer by taking sample amount, time and temperature, taken a mass difference before and after drying to the mass before drying, the moisture content was calculated using the following equation 3.2

$$\text{Moisture content\%} = \frac{(M_i - M_f)}{M_i} \times 100 \quad \text{eq.3.2}$$

Where: MC% moisture content of sample,  $m_i$  is initial mass of sample and  $m_f$  is final mass of sample after oven dry

**Volatile Content:** The percentage volatile matter (VM %) was determined by weighing of the dry rice husk sample in a crucible and placing it in an oven until a constant weight was obtained. The sample were then kept in a furnace at a temperature of 550°C for 3hr and weighed after cooling in desiccators. The percentage volatile matter was then calculated using the Equation 3.3.

$$\% \text{ Volatile} = \frac{[M_i] - [M_f]}{[M_i]} \times 100 \quad \text{eq.3.3}$$

Where: % Vol is percentage of volatile content,  $m_i$  is initial mass of sample and  $m_f$  is final mass of sample

**Ash Content:** Ash is the inorganic solid residue left after the fuel is completely burned. Its primary ingredients are silica, aluminum, iron, and calcium; small amounts of magnesium, titanium, sodium, and potassium may also be present. Ash content is determined by ASTM test protocol D-1102 for wood, E-1755-01 for other biomass, and D-3174 for coal. A 15g sample in a standard condition was placed in a muffle furnace with the lid of the crucible removed. Temperature of the furnace is raised slowly from 550 to 575 °C to avoid flaming for 3hrs. Following this, the temperature is increased to 575 °C and kept there until all the carbon is burnt. After that the sample was cooled and weighed. The percentage ash content was determined using the Equation 3.4:

$$\% \text{ Ash} = \frac{[M_{ash}]}{M_i} \times 100 \quad \text{eq.3.4}$$

Where: % Ash is the percentage of Ash content,  $M_{ash}$  is ash mass;  $M_i$  is initial mass of sample

**Fixed carbon content:** The percentage fixed carbon (%FC) was computed by subtracting the sum of % VM and % AC from 100 as shown in the Equation 3.5:

$$\text{FC\%} = 100\% - \text{ASH (DRY)} - \text{VOLATILE MATTER} \quad \text{eq.3.5}$$

Each test was performed in triplicate, and the average was reported. Results were given on a dry basis.

### 3.4.2 Elemental Analysis

Elemental analysis of the biomass samples was performed using an elemental analyzer an EA 1112 Flash CHNS-O- analyzer. Conditions for the ultimate analysis were: Carrier gas flow rate of 120 ml/min, reference flow rate 100 ml/min, oxygen flow rate 250 ml/min; furnace temperature of 900°C and oven temperature of 75°C. A small sample was placed in the analyzer, and results for carbon, hydrogen, and nitrogen content were returned by the analyzer. Helium was used as a carrier gas. Rice husk samples with two repetitions were analyzed for each set of treatment and reported only the average values on a dry basis. Results were corrected for moisture content and reported on a dry basis. Oxygen was calculated by difference eq: 3.6.

$$\text{OXYGEN\%} = \text{CARBON\%} - \text{HYDROGEN\%} - \text{NITROGEN\%} - \text{ASH} \quad \text{eq.3.6}$$

**Energy Content:** Energy content can be described by using higher heating value (HHV) and Lower heating value (LHV). HHV is the most commonly used way of describing energy contents. The HHV from ultimate and proximate analysis of torified biomass was determined by using unified correlation proposed by (Daya and Muhammad, 2017).

$$\text{HHV} = 0.1846\text{VM} + 0.3525\text{FC} \quad \text{eq.3.7}$$

Where: VM is volatile matter and FC is fixed carbon contents

**Energy Density:** Energy yield and Mass yield were used to calculate an energy density for the biomass samples. Torrefaction should be performed after transport to ensure the maximum amount of energy is moved per load. Biomass volume can change and be modeled as a function of moisture content .

$$\text{ED} = \frac{Y_{\text{energy}}(\%)}{Y_{\text{mass}}(\%)} \quad \text{eq.3.8}$$

Where: ED is the energy density,  $Y_{\text{mass}}$  is the percentage mass yield

### 3.4.3 Hydrophobic properties

The equilibrium moisture content (EMC) of a material surrounded at least partially by air is the moisture content at which the material is neither gaining nor losing moisture. The value of the EMC depends on the material and the relative humidity and temperature of the air with which it is in contact. The speed at which it is approached depends on the properties of the material and the speed with which humidity is carried away or towards the material (e.g. diffusion in stagnant air or convection in moving air). Equilibrium moisture content (EMC) can be used as an indicator of the hydrophobicity of a solid. Hydrophobic property of torrefied biomass is examined by water immersion test or by equilibrium moisture contents (EMC) studies (Pimchuai,2010). Both water immersion and equilibrium moisture content test was performed in the study for hydrophobicity analysis. The equilibrium moisture content was analyzed by equilibrium moisture content analyzer.



Figure 3.2: Equilibrium Moisture content analyzer

Equilibrium Moisture Content (EMC), showing the amount of moisture that biomass has absorbed at a specific temperature, pressure and humidity. And the equilibrium moisture content analyzer calculates the EMC using equation 3.9.

$$EMC = \frac{Me - Md}{Md} \times 100 \quad \text{eq.3.9}$$

Where  $M_e$  is the mass of the sample at equilibrium with a humid atmosphere and  $M_d$  is the mass of dry sample. The sample was measured at 79% relative humidity (RH) and temperature of 25°C.

Bulk density: Bulk density is the ratio of the mass of a material to its volume, and it plays a crucial role in the economic analysis of a Bioenergy supply chain. It can be calculated by emersion of a known quantity (mass) of biomass to a known volume of water in graduated cylinder. And, the ratio of mass of biomass to the volume of water displaced is bulk density.

$$\rho = \frac{M}{V} \quad \text{eq.3.10}$$

Where:  $\rho$  is the density of biomass,  $m$  is mass of sample and  $V$  is the volume of water displaced

### 3.5 THERMO GRAVIMETRIC ANALYSIS

Thermal gravimetric analysis (TGA) is a method of thermal analysis in which change in physical and chemical properties of materials measured as a function of increasing temperature (with constant heating rate), or as a function of time (with constant temperature and/or constant mass loss). The TGA instrument (BJ HENVEN Analysis (ATAT2012)) as seen in figure 3.3, it continuously weights and measure the sample as it was heated up to 1000<sup>0</sup>C. The systems consist of a combustor and balance connected to a computer in order to record automatically every 30 second and a thermal meter records data every 1 second. Three samples (raw rice husk, 300<sup>0</sup>C,2.25g/l and 60 min treated, and 300<sup>0</sup>C,1.50 and 40min treated, 300<sup>0</sup>C,0.75 and 20 min) having 5mg weight for each sample were loaded separately. Once the 15-mg sample was loaded to the balance, 20ml/min nitrogen gas was purged to the sample port to create inert atmosphere, the temperature rise was set to 10<sup>0</sup>C/min, and the final temperature was set to 1000<sup>0</sup>C and finally the sample was analyzed. The information that was obtained from TGA is in order to precede further investigation on the effect of torrefaction temperature on the thermal decompositions of the biomass raw materials to observe the torrefaction peaks or to clearly identify thermal degradations of raw biomasses.



Figure 3.3: Thermo gravimetric Analyzer (TGA)

Data Analysis: Microsoft Excel (Microsoft Office 2010) and Design-Expert ® Software (Version 7.0) were used for the statistical as well as graphical analysis. Statistical analysis was performed on the biomass treatment method types (dry and chemical treated torrefaction) separately because of their different natures. The general factorial design was used for statistical analysis.

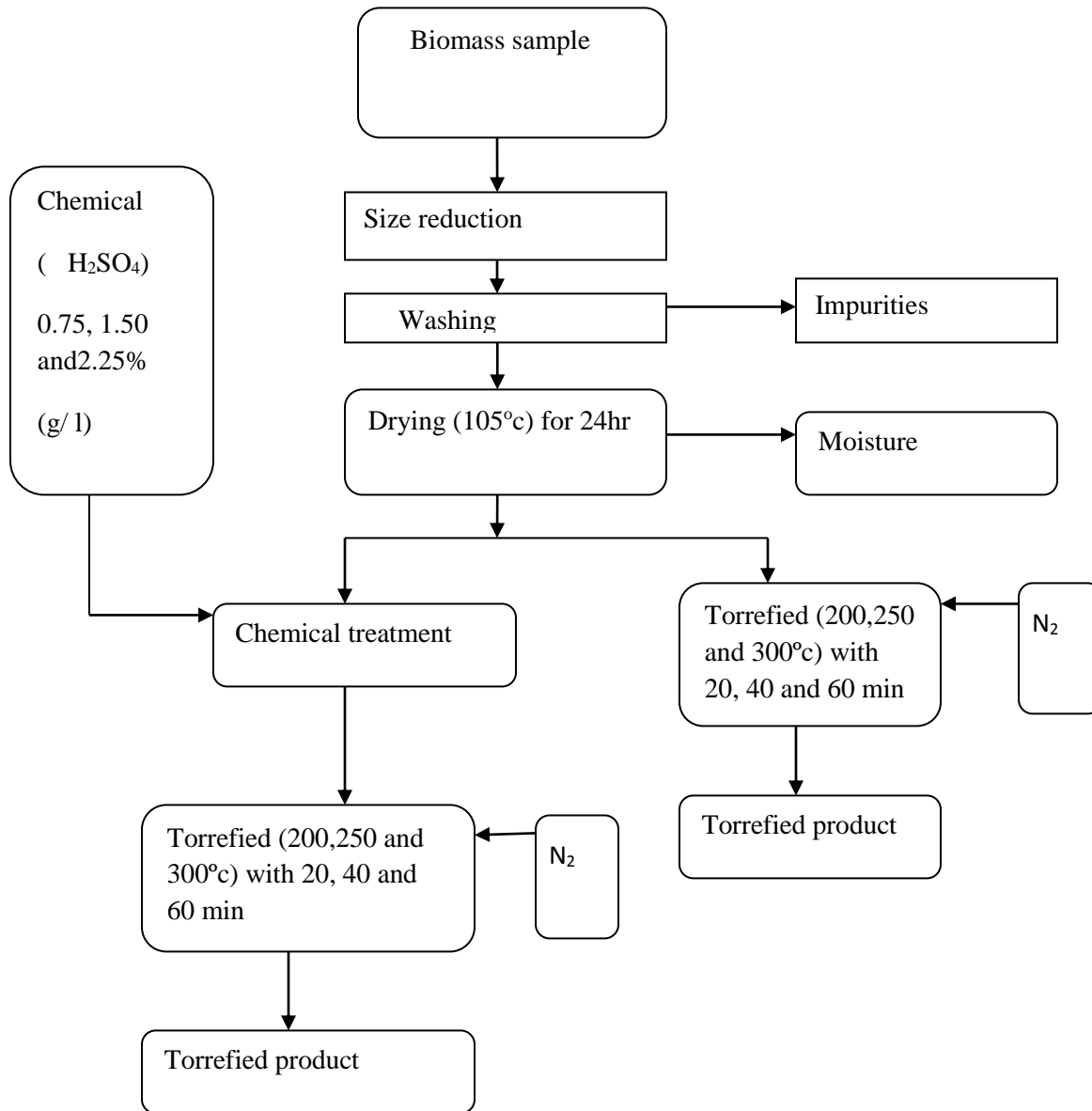


Figure 3.4: General experimental procedure for torrefaction process

### 3.6 EXPERIMENTAL SETUP AND DESCRIPTION

All experiments were carried out in a tubular reactor equipped with a hot plate heater (AM-5250A), nitrogen cylinder, a thermocouple and a pressure gauge. A thermocouple for monitoring the reaction temperature (temperature of the sample and the reactor) is connected to the reactor by which the electrical duty of the heater is controlled manually. The reactor is connected to a nitrogen (99.99% purity) cylinder via a valve to create inert atmosphere. After the samples were placed inside the tubular reactor, it was completely purged with nitrogen gas to remove all oxygen. The furnace/torified reactor was preheated to the desired temperature set point. Treatment time was said to begin when the furnace reached the desired set point. At the end of the treatment time, the biomass samples were pulled from the furnace and immediately placed in desiccators to prevent from moisture exposer and for further treatment and combustion. Once the crucible cooled to room temperature, the samples were weighed and analyzed with the respective test. The experimental set up for the torrefaction experiments are shown in figure 3.4 and the general experimental frame work are shown in Figure 3.5.



Figure 3.5 The experimental set up for the torrefaction experiments

#### 3.6.1 Experiments and Experimental Design

Effect of Temperature: Torrefaction experiments were conducted in the temperature range of 200-300 °C at different value of reaction holding time, acid concentration and different treatments reaction temperature of 200,250 and 300 °C was taken for this study. Effect of time Contact time has an impact on solid yield, higher heating value and carbon content. Compared to

many other thermo-chemical conversion processes like combustion, gasification or pyrolysis, the reaction time for torrefaction much longer (about an hour). Three residence times of 20, 40 and 60 min was considered for the torrefaction experiments. Effect of acid treatment (Chemical torrefaction): The primary goal of chemical pretreatment is to improve the degradability of cellulose in biomass by removing the lignin and Hemicellulose. Chemical pretreatment separates lignin and hemicellulose, and upgrade energy production. Chemical pretreatment also changes the morphological structures. In this study acid was used to pretreat biomass. It involves the use of diluted sulfuric acid to break the rigid structure of the ligno cellulosic materials. Chemical treatment was performed by using 0.75, 1.50 and 2.25% dilute acid from the literature range of 0.25-2.5% to modify the fiber structure of biomass for better energy yield. Since, lignin is highly insoluble, even in sulfuric acid ( Prabir, 2010).

### 3.6.2 Experimental design approach

The experimental design selected for this study was response surface methodology, three-level-three-factor Box-Behnken Design (BHD) and the response variable measured was the percentage of conversion.

3.2: Table Independent variables and levels use in the BHD for upgrading energy

Variable	Unit	LEVELS		
		-1	0	+1
Temperature	°C	200	250	300
Residence time	T (min)	20	40	60
Chemical(H <sub>2</sub> SO <sub>4</sub> )	(g/l)	0.75	1.50	2.25

Below in table the complete experimental design matrix of BHD for the factorial design was shown. The order in which the runs were made was randomized to minimize systematic errors.

Table 3.3: The actual experimental set up for torrefaction process

Std	Run	Factor 1 A:Temperature °c	Factor 2 B:Time (min)	Factor 3 C:Chemical (g/l)
1	5	200.00	20.00	1.50
2	9	300.00	20.00	1.50
3	7	200.00	60.00	1.50
4	6	300.00	60.00	1.50
5	14	200.00	40.00	0.75
6	15	300.00	40.00	0.75
7	3	200.00	40.00	2.25
8	1	300.00	40.00	2.25
9	11	250.00	20.00	0.75
10	2	250.00	60.00	0.75
11	17	250.00	20.00	2.25
12	10	250.00	60.00	2.25
13	12	250.00	40.00	1.50
14	16	250.00	40.00	1.50
15	4	250.00	40.00	1.50
16	13	250.00	40.00	1.50
17	8	250.00	40.00	1.50

## 4. RESULTS AND DISCUSSION

### 4.1 Preliminary Qualitative Assessment

Figure 4.1 shows the surface morphology of fractionated and dry torrefied rice husk. The mass of samples in each of the sample holder were 15g. As can be seen in Figure 4.1, with increasing torrefaction temperature, the surface morphology of the torified rice husk changed significantly, showing a gradually shrinking volume and turning from yellow to brown and then black. The visual difference of the biomass subjected to torrefaction is the color of the samples. Carbonization of the biomass increased with the intensity of torrefaction. (Pelaez et.al., 2014) reported that changes of color might be occurred due to the oxidation of phenolic compounds and the presence of sugars and amino acids during torrefaction process.



Figure 4.1: Effect of Torrefaction temperature on surface morphology of rice husk sample.

Figure 4.2 shows, the surface morphology of chemical treated and torrefied rice husk. As can be seen in the figure, the color had changed gradually from yellow to red and then turned to brown due to oxidation within the environment, finally after torrefaction, changed to deep black. As it has been discussed previously, this is due to the oxidation of phenolic compounds and the presence of sugars with amino acids during torrefaction. The chemical treatment modifies the fiber structure, and dilute sulfuric acid is better used for surface modification, the fiber strictly modified for better carbonization that was the reason for its deep black after torrefaction.



a) Raw Rice husk



b) 0.75% H<sub>2</sub>SO<sub>4</sub>



c) 1.25% H<sub>2</sub>SO<sub>4</sub>



d) 2.25% H<sub>2</sub>SO<sub>4</sub>

Figure 4.2: Effect of Torrefaction temperature a) 200°C and 20min b) 250°C and 40min c) 300°C and 60min on surface morphology of chemical treated and torrefied rice husk sample.

Mass yield: Figure 4.1 shows the effect of torrefaction temperature and time on the solid yield of rice husk for dry torrefaction. From the result, it can be concluded that temperature had significant effect on mass yield than residence time (See Appendix Table A.1 and Table A.4 for dry torrefaction and chemical treated torrefaction respectively). And from Figure 4.3 and 4.4

chemical treated torrefaction shows a great reduction of solid yield. The mass loss of rice husk can be attributed to the release of moisture and volatile matter. During the torrefaction, moisture content released following two mechanisms. The first mechanism was evaporation of moisture content in biomass and the second one was dehydration reaction of organic components of biomass. Torrefaction temperature and torrefaction time had significant effect on mass yield. When the torrefaction temperature was 200°C and 20 min, the solid yield was 97.335% and 82.151% for dry and chemical treated torrefaction respectively. As the torrefaction temperature increased the solid yield decreased in both cases. When torrefaction temperature is higher than 250°C, most of hemicelluloses was decomposed, and the cellulose started to decompose, so the solid yield decreased quickly, at 300°C and 60 min solid yield became 77.410 and 68.411 for dry and chemical treated torrefaction respectively. Increasing torrefaction temperature from 200 to 300°C, the mass yield dropped gradually at the respective treatment time. This illustrates the effect of torrefaction temperature and holding time on the mass yield. This is in compliance with the expected results, since torrefaction involves the loss of both moisture and volatile matter from the sample of biomass.

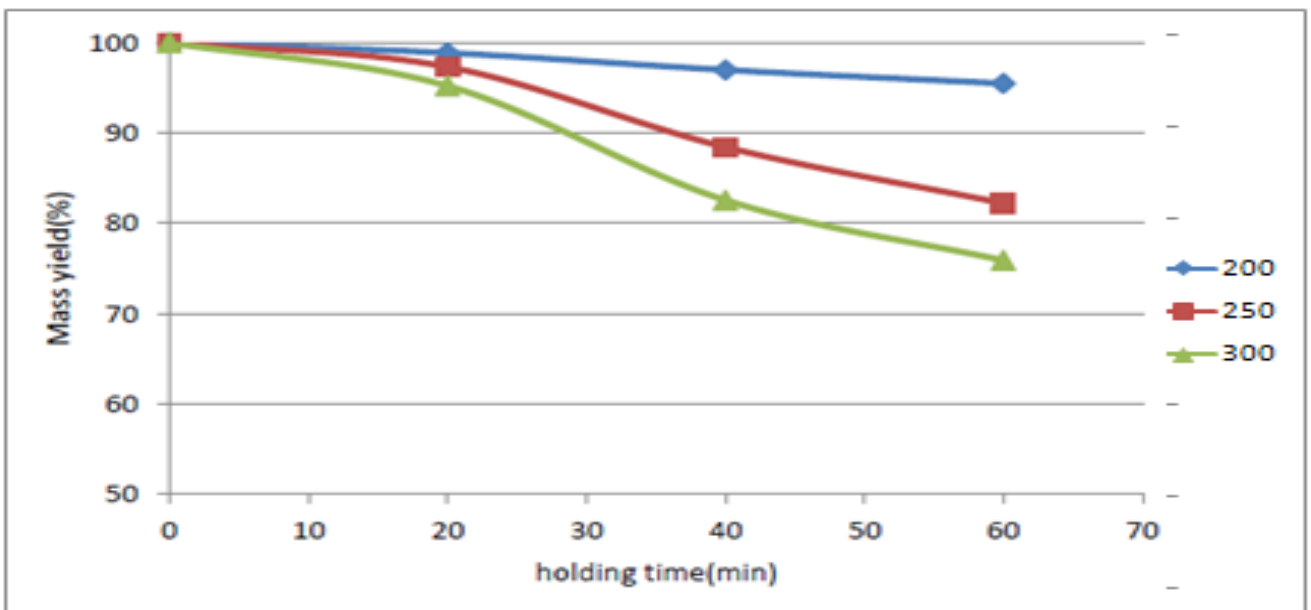


Figure 4.3: Effect of torrefaction temperature and holding time on mass yield of dry torified rice husk

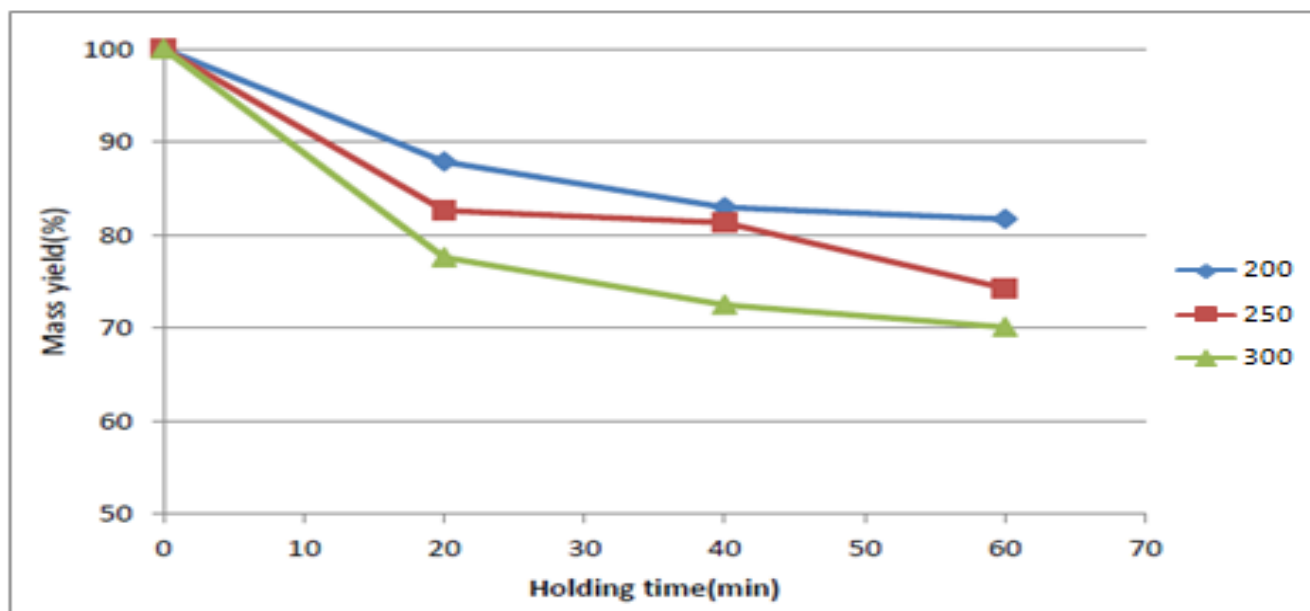


Figure 4.4: Effect of torrefaction temperature and holding time on mass yield of chemical treated torified rice husk

## 4.2 Effect of Torrefaction on Chemical Composition

Proximate and Ultimate Composition: The raw data obtained during the analysis for proximate analysis, ultimate analysis, higher heating values (HHV), energy density and moisture absorption of rice husk with dry and chemical treated torrefaction are listed in the appendix section.

### 4.2.1 Proximate Composition

Equilibrium Moisture contents: The initial moisture content of the raw rice husk was about 8.45% (wet. Basis). After torrefaction, the torrefied samples' moisture content had significantly decreased with the increase in torrefaction temperature and time in both treatment cases. The lowest moisture content observed for dry torrefaction was about 3.35% (w.b.) at 300 °C and a 60-min residence time (Table 4.1). For chemical treated torrefaction it was about 2.93% at 300°C and a 60-min residence time (Table 4.2). The percent decrease observed in moisture content for dry torrefaction was about 27.83% at a specified temperature of 300°C and hold time of 60 min. While a 35.11% decrease was observed for chemical treated torrefaction. A similar trend was observed for other residence times and temperature combinations.

The lower the moisture content of the torrefied biomass is an indicator of the torrefied rice husk became more hydrophobic than the raw biomass. Similar observation had been found in the

study of effect of thermal pretreatment on equilibrium moisture content of ligno cellulosic biomass (Acharji et al., 2011). For ligno cellulose biomass, moisture adheres to the surface of pores in materials and is hydrogen-bounded to the hydroxyl groups of the cell wall components (Chen et al.,2014). The more oxygen in the ligno cellulosic biomass, the greater will be the possibility of forming H bonds with the H<sub>2</sub>O. The ultimate analysis showed that a large amount of oxygen was removed and the hydroxyl groups in the hemicelluloses were broken. The breakdown of these hydroxyl groups after torrefaction results in more hydrophobic torrefied rice husk; thus, the EMC decreased with increasing torrefaction temperature.

Table 4.1: Moisture contents (wet basis) of dry torrefied Rice husk

Temperate(°C)	Time(min)	Moisture content (%)
Raw rice husk(105°C)	Initial	8.45
200	20	5.15
	40	4.04
	60	3.97
250	20	3.75
	40	3.61
	60	3.46
300	20	3.42
	40	3.37
	60	3.35

Table 4.2: Equilibrium Moisture contents (wet basis) of chemical treated torrefied Rice husk

Temperate(°C)	Time(min)	Moisture content (%)
200	20	5.45
	40	4.51
	60	4.11
250	20	3.95
	40	3.73
	60	3.61
300	20	3.33
	40	3.21
	60	2.93

And torrefaction temperature from 250 to 300°C, the moisture content was nearly constant. This is because the moisture adheres on the surface of the biomass as well as bonded moisture reaches nearly equilibrium, generally, temperature and time had significant effect on moisture content.

These values show that the equilibrium moisture content of torrefied rice husk is, at least partly, hydrophobic and consequently cannot reabsorb moisture to the same extent as untreated rice husk (Chen et al.,2014).

Volatile contents:Figure 4.5 shows the effect of temperature and time on volatile matter contents. As it can be seen in figure4.5 volatile content of the torrefaction product shows a noticeable reduction at high torrefaction temperature and time, indicating that high temperature had a noticeable influence on the volatile matter content. For dry torrefaction at lower torrefaction temperature (200°C) and different residence times, the decrease in volatile content in the torrefied biomass was relatively minimal (the maximum decrease was about 1.22% at 60 min with respect to the original value) (Figure 4.5 ). Increasing the torrefaction temperature to 250 and 300°C for the residence time to 60 min reduced the volatile content to about 27.41% and 38.71%. And for chemical treated torrefaction, at lower torrefaction temperature (200°C) and different residence times, the decrease in volatile content in the torrefied biomass was relatively

minimal (the maximum decrease was about 42.28% at 60 min with respect to the original value) (Appendix Table A.6). Increasing the torrefaction temperature to 250 and 300 °C for the same residence time of 60 min, the volatile content reduced to 45.51% and 53.73%. The effect of torrefaction temperature and time showed a more significant effect on volatile content. Similar observation had been found in the study of dry torrefied pin chips (Phanphanic and Mani, 2011) and torrefaction vs. Fuel properties (Chain et al., 2014).

During the torrefaction, as torrefaction temperature increases, some volatile matter was released because of lack of resistance to the respective temperature i.e. some of the volatile matter might escape out at lower temperature while some may resist this temperature. Comparing the results of dry and chemical treated torrefaction of rice husk, it can be seen from Appendix (Table A.5 and Table A.6) with increase in torrefaction temperature, the amount of volatile matter decreased in dry torrefaction is much higher than that of chemical treated torrefaction. Since in chemical treated torrefaction, the chemical structure of biomass could be modified easily than dry torrefaction so that more volatile component may be produced during the chemical decomposition.

**Ash contents:** The ash content in the torrefied material increased with the increase of torrefaction temperature and time (Figure 4.5). The changes in the ash content are mainly due to breakdown of carbon-hydrogen bonds, resulting volatile loss and further concentrating the ash content in the biomass. The highest ash content of about 28.26 % was observed for dry torrefied samples at 300°C and 60 min. The increase was about 70% with respect to the original value/raw rice husk. And for chemical treated torrefaction, the highest ash content of about 31.11% was observed for torrefied samples at 300°C and 60 min which was 98% increases from the original biomass. The increase in the ash content of chemical treated torrefaction with the increase in torrefaction temperature was higher than that of the dry torrefaction.

**Fixed carbon:** Figure 4.5 and Figure 4.6 presents the changes in the fixed carbon content in the rice husk torrefied at different temperatures and residence times for dry and chemical treated torrefaction respectively.

The initial fixed carbon of the raw biomass was 18.06%. Increasing the temperature (dry torrefaction) to 200, 250, 300 °C and a 60-min residence time increased the fixed carbon content to about 20.60%, 22.80%, and 34.57% (an increase of 21%, 87% and 135.44% from its original value). The maximum fixed carbon observed at 300 °C and 60 min was about 31.57% (Figure 4.6). Whereas in chemical torrefaction, increasing the temperature to 200, 250, 300 °C for 60-min residence time increased the fixed carbon content to about 30.85%, 35.42%, and 38.724% (an increase of 122%, 156% and 162% from its original value) and torrefaction treatment at 300°C and 60 min, the fixed carbon content became 40.13 (an increase of 208% from its original value). Therefore, chemical treated torrefaction increases the fixed carbon content even for the lower residence time.

A higher temperature and a longer residence time increased the composition of fixed carbon in torrefied rice husk. The weight percentage of fixed carbon increases significantly with increasing torrefaction temperature due to the carbonization process. The reason behind is that during torrefaction at different temperature, the moisture content and volatile matter removed. So, the composition remained is purely ash and fixed carbon. (Tumuluru et al. 2011) in their review on the torrefaction of biomass, indicate that at temperature higher than 250°C, the biomass undergoes extensive devolatilization and carbonization. These reactions result in the loss of volatiles and an increase in the carbon content. Furthermore, it is observed that the change in the ash content is related to the loss of other biomass components, such as moisture and volatiles. According to (Park et al) 2013, during torrefaction, volatile loss is due to thermal breakdown of carbohydrate fractions, which results in the accumulation of the residual ash after torrefaction. The same authors further indicate that these changes increase the fixed carbon content of the biomass.

Torrefaction increases the energy density of biomass and stimulates its carbon/oxygen (C/O) and carbon/hydrogen (C/H) ratios. Due to charring of biomass and cracking of volatiles, the amount of fixed carbon in biomass increases after torrefaction. The amount of fixed carbon increased after torrefaction because of conversion of hemicelluloses into more thermally stable compounds.

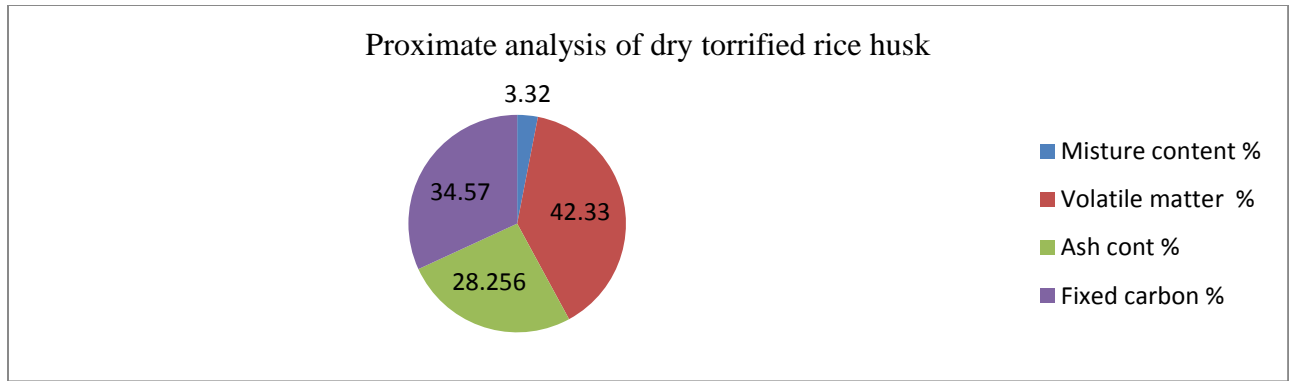


Figure 4.5 Proximate Analysis of Dry Torified Rice Husk

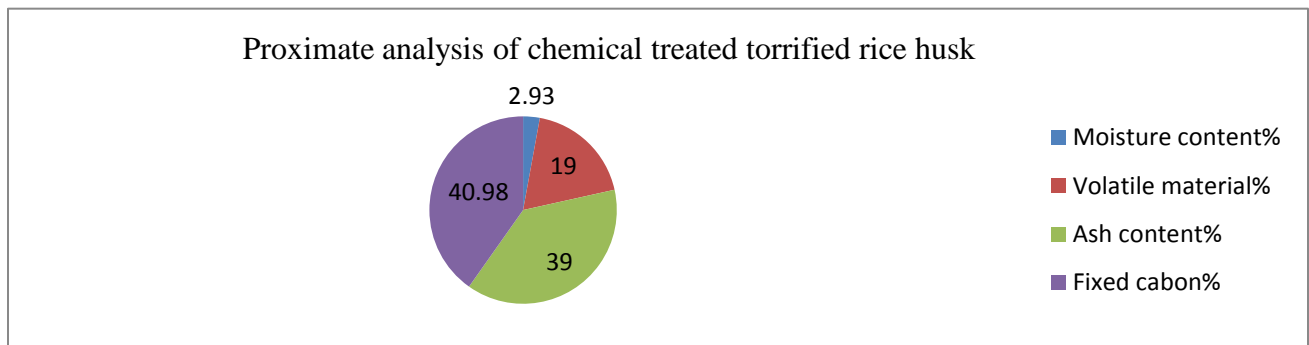


Figure 4.6 proximate analysis of chemical treated torrefied rice husk

#### 4.2.2 Elemental composition

The values presented are the values for ultimate analysis of rice husk samples with dry and chemical treated torrefaction. Percentage of Fixed Carbon (%): The initial elemental carbon in the rice husk sample was about 30.12%. Heating the biomass at 200 to 300<sup>o</sup> C for 20, 40 and 60min residence time increased the elemental carbon content. Increasing the carbonization temperature from 200 to 250<sup>o</sup> C increases the fixed carbon content to 6.05% and 12.78% respectively. Further increases the carbonization temperature to 300<sup>o</sup>C, the carbon content increased to 22.55 % ( see Figure 4.7 and 4.8). And for chemical treated torrefaction, heating the biomass at 200, 250 and 300<sup>o</sup>C and 60 min residence time increased elemental carbon content to 22.75%, 44.10% and 40.98% respectively. It is clear from the data that the increase in elemental carbon is significantly higher at temperatures at high temperature (250 and 300<sup>o</sup>C).

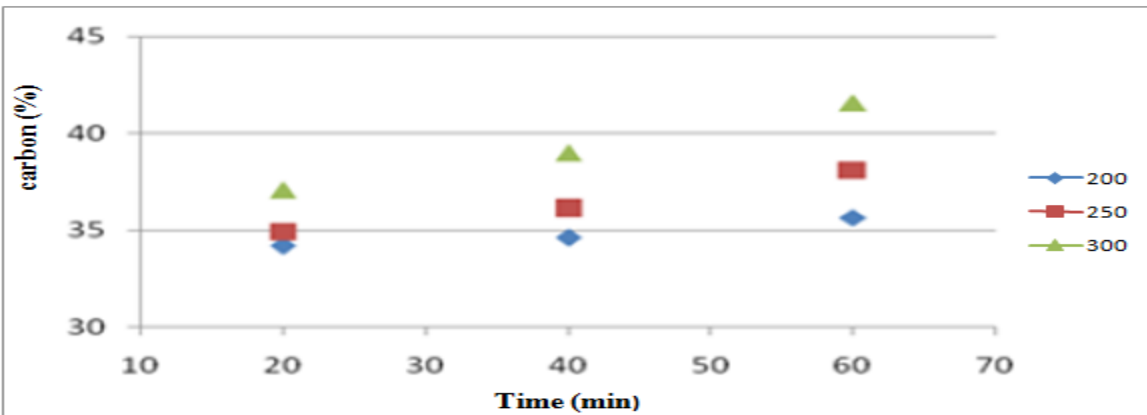


Figure 4.7: Carbon content in dry torrefied rice husk with respect to the torrefaction time

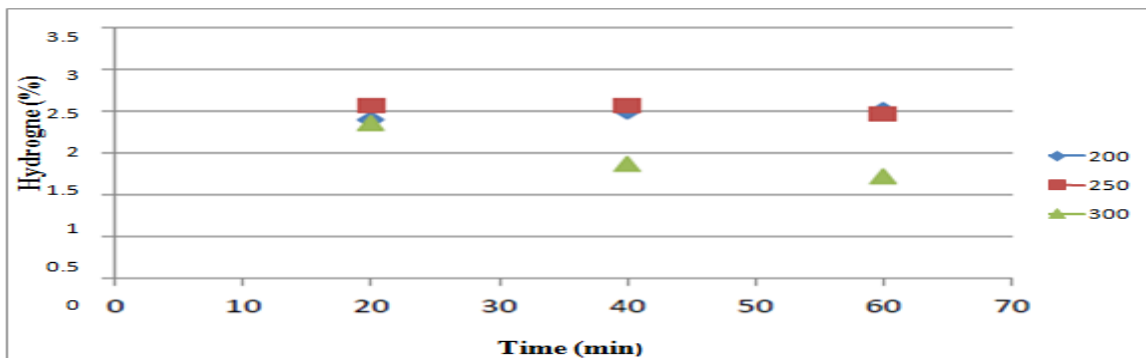


Figure 4.8: Hydrogen content in dry torified rice husk with respect to the torrefaction time and temperature

With increasing torrefaction temperature and torrefaction time, the main elements (C, H, N, S, and O) of rice husk changed to different degrees with both dry and chemical treated torrefaction. As can be seen in Figure 4. 8, the hydrogen content was basically not reduced during the low temperature period of 200°C (at 20, 40 and 60min) to 250°C (at 20min), and a slight decrease was detected at higher temperature from 250°C (40 and 60min) to 300°C (20, 40 and 60 min). This is because hydrocarbons, such as CH<sub>4</sub> and C<sub>2</sub>H<sub>5</sub>, are only released at higher temperatures. Similar results have been reported by Arias et al for eucalyptus (Arias, 2008).

The most obvious change is the contents of carbon and hydrogen (see Figure 4.7 and Figure 4.8). Carbon content gradually increases and the hydrogen content of the torrefied samples underwent a considerable decrease. (Park ,2013)suggested that the changes in carbon and oxygen contents are due to the formation and release of CO<sub>2</sub> and CO during the torrefaction process.

Ultimate composition data indicate that oxygen is reduced during torrefaction and the reduction is increased at higher torrefaction temperatures. In the present study, changes in hydrogen and oxygen were at a higher temperature of 300°C, when compared to torrefaction temperatures of 200°C. During torrefaction, the loss of volatiles, gases, and water also results in a decrease in hydrogen content. The decrease in oxygen and hydrogen content results in increasing the carbon content which lowers the O/C atomic ratio from 1.011 to 0.567 for dry torrefaction and from 1.098 to 0.558 for chemical treated torrefaction. According to (Tumuluru, 2011) torrefaction temperatures higher than 300°C may not be needed, because there is a significant loss of higher energy content of volatile matter. Furthermore, it may increase the relative ash content of the biomass.

**Nitrogen and Sulfur (%):**The initial nitrogen and sulfur content observed for the raw biomass samples were 0.25% and 0.03 % respectively At lower temperatures of 200°C and different residence times, the changes in nitrogen content and sulfur content were nearly constant; however, increasing the torrefaction temperature to 250 and 300°C at 60 min increased the nitrogen content by 0.1% and sulfur content unchanged. The sulfur and nitrogen contents were lower due to torrefaction treatments. The low Sulfur and nitrogen contents in the torrefied sample are welcomed development as there will be minimal release of Sulfur and nitrogen oxides into the atmosphere and that is an indication that the burning of torrefied rice husk biomass examined in this work will not pollute the environment.

### 4.3 FOURIER-TRANSFORM INFRARED SPECTROSCOPY

FTIR Analysis has dramatically improved the quality of infrared spectra and minimized the time required to obtain data. In addition, with constant improvements to computers, infrared spectroscopy has made further great strides. Infrared spectroscopy is a technique based on the vibrations of the atoms of a molecule. An infrared spectrum is commonly obtained by passing infrared radiation through a sample and determining what fraction of the incident radiation is absorbed at a particular energy (Gardette, 2002). The energy at which any peak in an absorption spectrum appears corresponds to the frequency of a vibration of a part of a sample molecule.

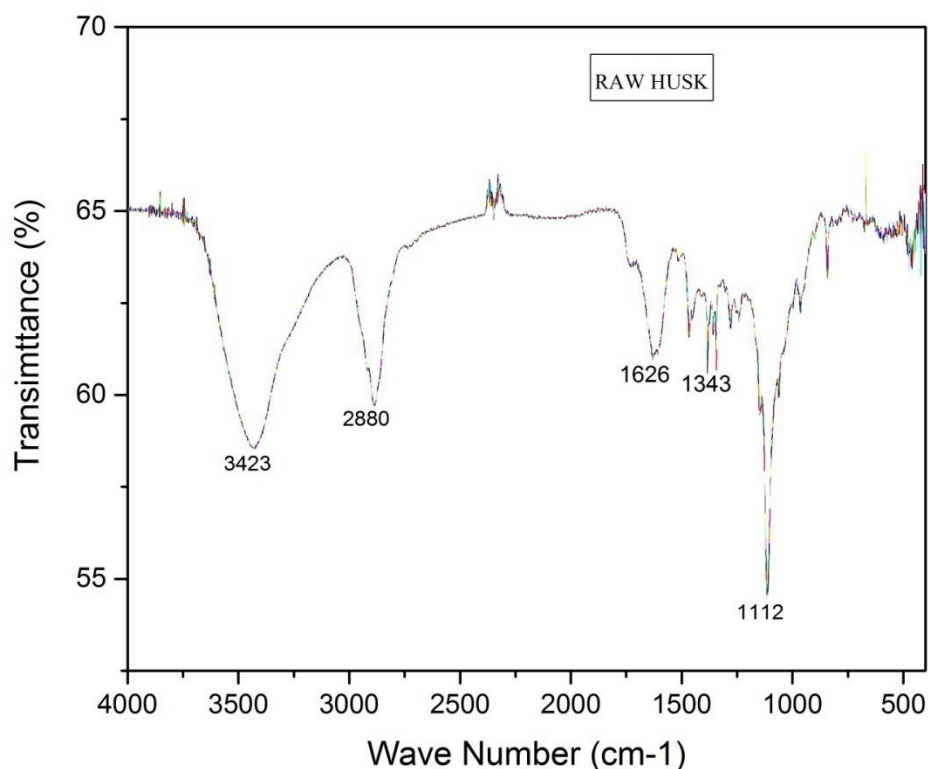


Figure 4.9 Dry Rice Husk with Respect to the Torrefaction Transmittance and Wave Number

The CH<sub>3</sub> bending bands, arising from metal-CH<sub>3</sub> groups, appear in the 1210 to 1180 cm<sup>-1</sup> region in mercury and tin compounds, and at 1170 to 1150 cm<sup>-1</sup> in lead compounds. Aromatic organo metallic molecules show a strong band near 1430 cm<sup>-1</sup>, due to benzene ring stretching for metals

directly attached to the benzene ring. Primary ( $-\text{NH}_2$ ), secondary ( $-\text{NH}$ ) and tertiary (no hydrogen attached to N) amines may be differentiated by using infrared spectra. Primary amines have two sharp N–H stretching bands near  $3335\text{ cm}^{-1}$ , a broad  $\text{NH}_2$  scissoring band at  $1615\text{ cm}^{-1}$ , and  $\text{NH}_2$  wagging and twisting bands in the  $850\text{ to }750\text{ cm}^{-1}$  range. Secondary

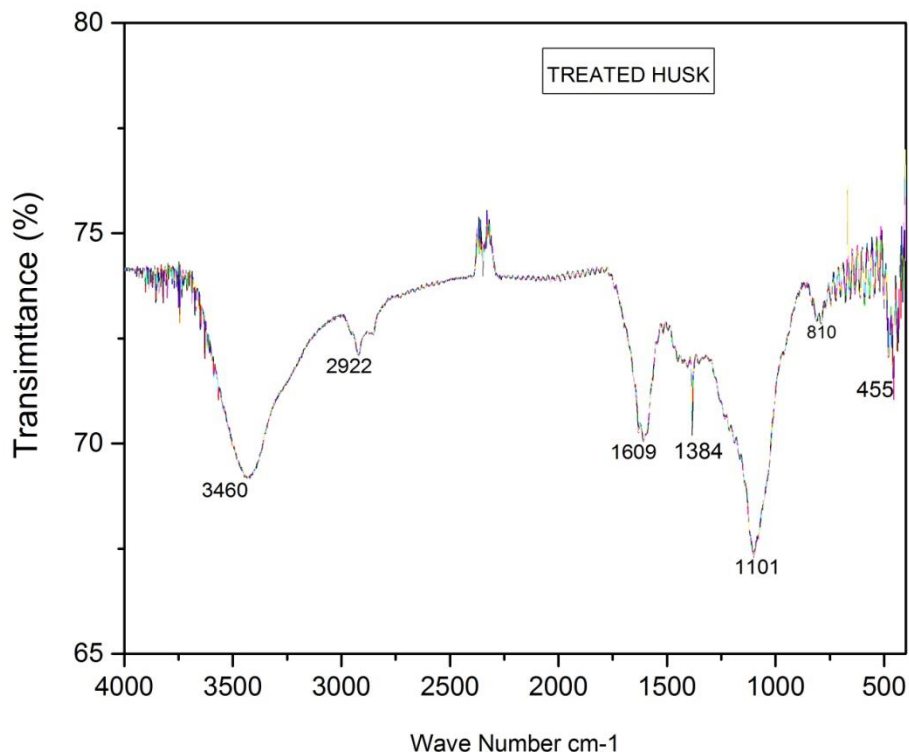


Figure 4.10 Chemical Torrefied Rice Husk with the Torrefaction Transmittance and Wave Number

Amines show only one N–H stretching band at  $3435\text{ cm}^{-1}$  and an N–H bending band at  $1605\text{ cm}^{-1}$ . The N–H wagging band for secondary amines appears at  $455\text{ cm}^{-1}$ . Silicon compounds show characteristic Si–H bands. The Si–H stretching bands appear at  $2250\text{ to }2100\text{ cm}^{-1}$ . The Si– $\text{CH}_3$  band gives rise to a symmetric  $\text{CH}_3$  bending band in the  $1280\text{--}1250\text{ cm}^{-1}$  range. The O–H stretching bands of Si–OH groups appear in the same region as alcohols, i.e.  $3700\text{ to }3200\text{ cm}^{-1}$ . Phosphorus acids and esters possess P–OH groups which produce one or two broad bands in the  $2700\text{ to }2100\text{ cm}^{-1}$  region. The spectra presented in Figure 4.9 and 4.10 shows a trend in the wavenumber shifts for the three complexes compound; the N–H bands shift to lower wave

numbers from N to Si . This indicates that the N–H bond order (bond strength) decreases as the metal–N bond order increases in the stability order mentioned. Therefore the CH<sub>3</sub> groups are appear symmetrical after torified and N<sub>2</sub> group are shifted .The hydrogen bonds of husk were broken down when the chemical were in contact with cellulose, which led to more C–H, C–C, C–OH and C–O–C exposed on the surface; as a result the intensity of these peaks increased (Tong et al., 2013). FT-IR spectra for rice husk torified at 200, 250 and 300°C .Figure 4.9 showed the IR spectrum of the pyrolysis at 200, 250 and 300°C before torrefaction. The band 1750 cm<sup>-1</sup> were C=O stretching vibration peak and 3430 to 2364cm<sup>-1</sup> belonged to O-H stretching vibration peak. In addition to, phenolic C-OH, C=C, C=O,OH stretching vibration, and carboxylic C-OH bending vibration bands appear at 1191cm<sup>-1</sup> 1608cm<sup>-1</sup>, 1750 to 1788cm<sup>-1</sup>, 2928cm<sup>-1</sup>, and 1425cm<sup>-1</sup>, respectively, demonstrating the presence of COOH and phenolic OH groups on the surface of the H<sub>2</sub>SO<sub>4</sub> (Qi et al.,2012). These peaks were seen in spectra showed that there were plentiful of oxygen-containing groups such as phenolic hydroxyl, ester, ether, and carboxylic groups in polycyclic aromatic skeleton. And a band at 3445 cm<sup>-1</sup> is attributable to saturated C-H stretching vibration, showed that the carbonizations complete (Tong et al., 2013).

#### 4.4 HYDROPHOBICITY ANALYSIS

The moisture contents of rice husk were 8.45 and 5.45% for dry and chemical treated torrefaction of rice husk samples respectively, and absorption rates were the highest within the initial two hours for every sample.



Figure 4.11: Hydrophobicity properties of torified rice husk using water emersion test

At 4.12 hours, the moisture contents appeared to be nearly unchanging for each rice husk sample. These unchanging or the minimal changes from 4 to 12 hours, moisture content at 24 hours is considered to be the maximum. Table A.11 and Table A.12 in Appendix section present the moisture absorption of each biomass sample and statistical for both treatments. Statistical analysis in the appendix table shows that torrefaction does significantly decrease moisture absorption.

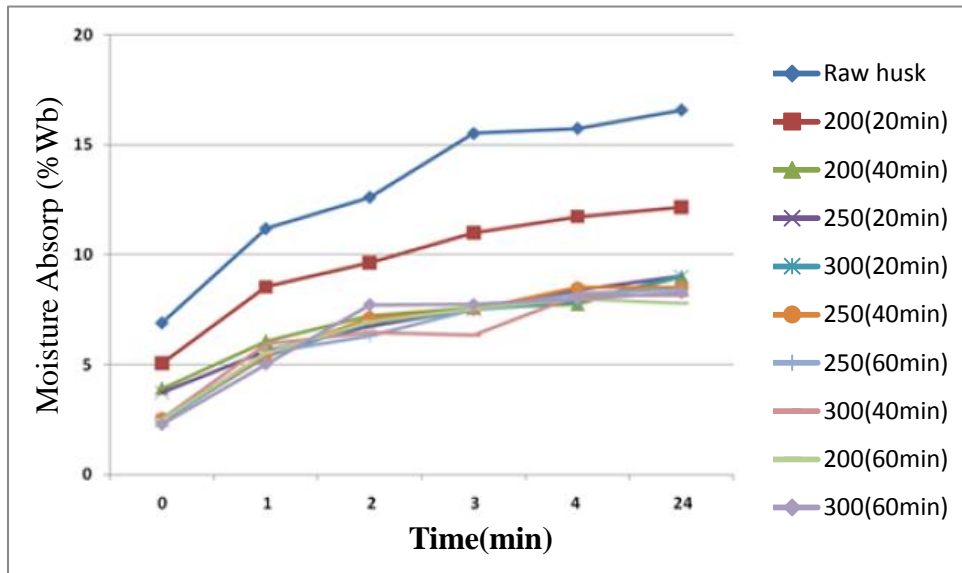


Figure 4.12: Moisture absorption of raw and dry torified rice husk at 25<sup>0</sup>C during 24hr water immersion test

Figure 4.12 presents moisture absorption of raw and dry torrefied rice husk at 25<sup>0</sup>C and 79%RH, it can be seen that the raw rice husk absorbs more moisture than all the torrefied rice husk samples. Again, at increased torrefaction temperature and time, the moisture absorption decreases. Torrefaction temperature of 300<sup>0</sup>C and torrefaction time at 40 and 80min was observed as a small change of moisture that could be absorbed compared to the other treatments. These values show that EMC of torrefied rice husk is hydrophobic and consequently cannot reabsorb moisture to the same extent as untreated raw rice husk. Biomass often has a certain amount of moisture. The moisture content of a fuel has a direct impact on its heating value, market price, as well as thermo chemical utilization. Thus, drying pretreatment is essential before biomass pyrolysis.(Chen and Kuo, 2011). However, the low moisture content of torrefied rice

husk is a major claim made of torrefaction. Figure 4.14 shows the water uptake in weight percentage of dry torrefied biomass during immersion test. As expected, raw biomass has high water absorbance than torrefied biomass. It can be observed from figure; the water absorption drastically decreases upon torrefaction treatment. As the torrefaction temperature increased from 200 to 300°C, there was a drastic decrease in moisture absorption. Since torrefaction removes the hemicellulose fraction in biomass through dihydroxylation and decarboxylation/decarbonylating reactions and consequently, the fractional lignin increases where lignin is known to have little tendency towards water sorption thus making torrefied rice husk hydrophobic .

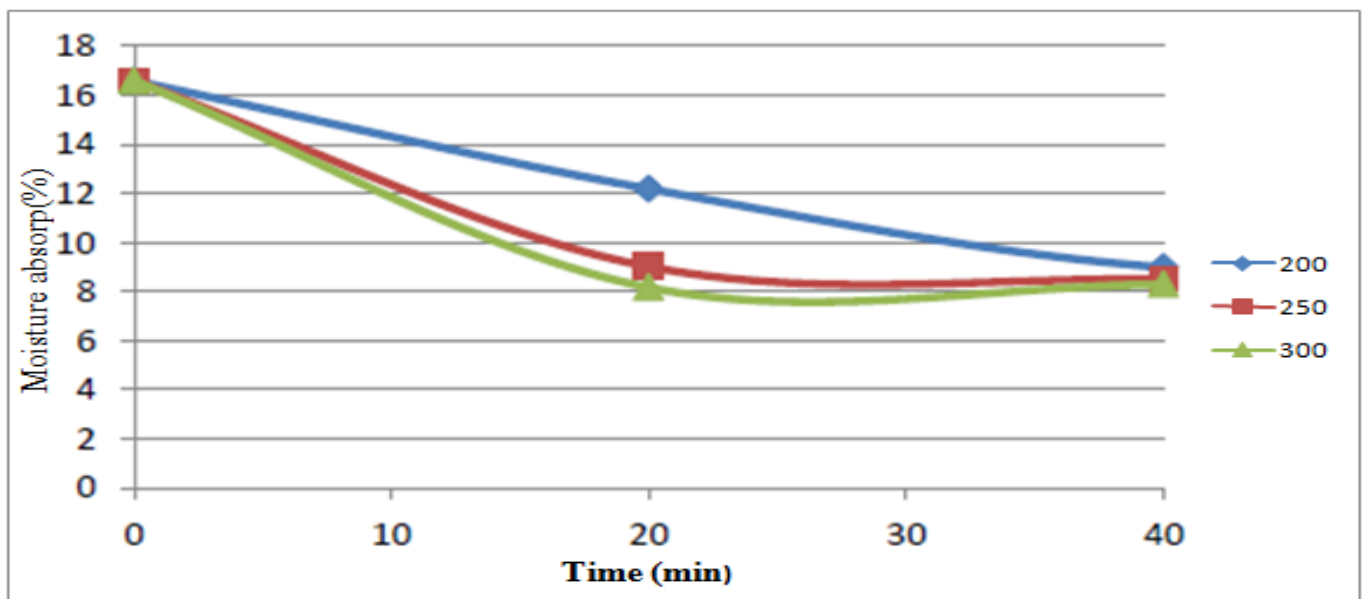


Figure 4.13: Effect of reaction time and torrefaction temperature on moisture absorption

#### 4.5 BULK DENSITY, HHV, AND ENERGY DENSITY

The HHV of the untreated raw Rice husk was found to be 15.96MJ/kg. This was a mean value calculated from three proximate analysis runs. This has been used to calculate the energy yields following torrefaction.

Bulk density: During torrefaction, the bulk density decreases due to the decrease in mass (moisture and volatile matter). The same results were obtained as expected in torrefaction of rice husk at different torrefaction temperature and time. Figure 4.14 and 4.15 shows increasing the

torrefaction temperature and holding time, results a decrease in bulk density of rice husk for both treatment methods in both treatment cases.

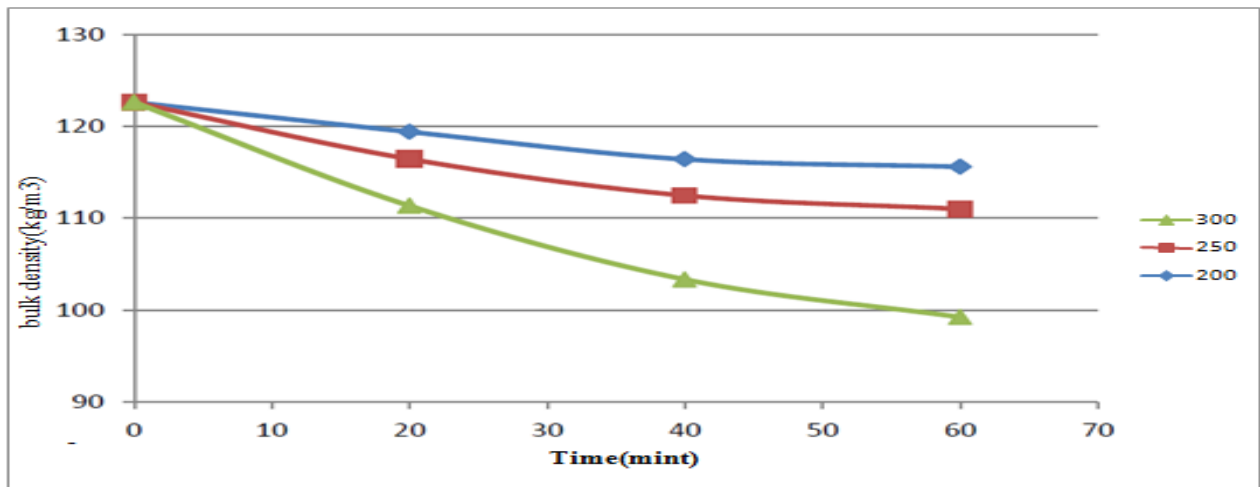


Figure 4-14: Effect of torrefaction temperature and residence time on bulk density of dry torrefied rice husk

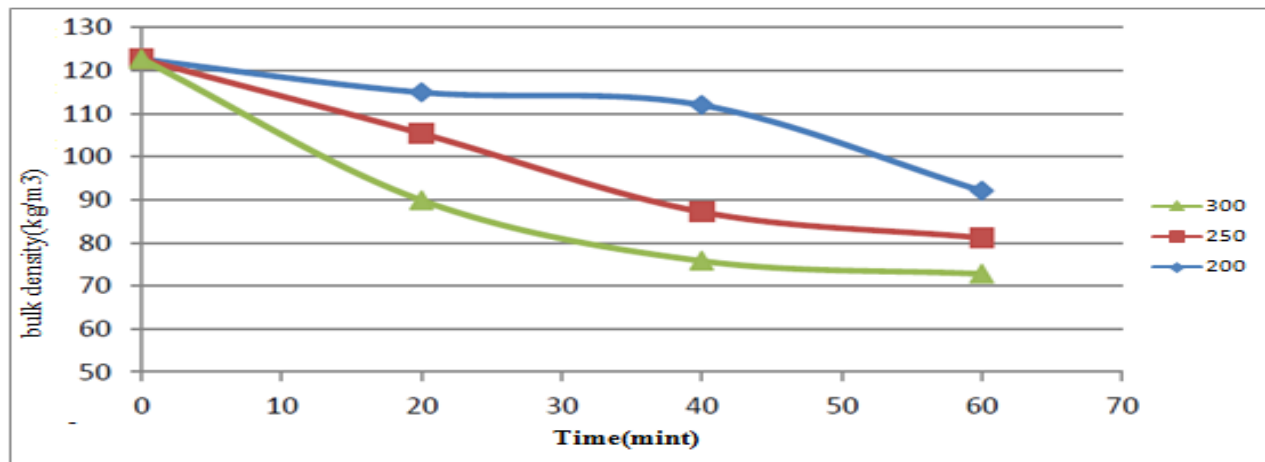


Figure 4-15: Effect of torrefaction temperature and residence time on bulk density of chemical treated torrefied rice husk

Higher heating Value (MJ/kg): As can be seen in Figure 4.16 and Figure 4.17, the HHV of torrefied rice husk noticeably increased with increasing torrefaction temperature and time for dry as well as for chemical treated torrefaction. The increase in heating values of rice husk during torrefaction was comparable with (Chen et al., 2014). Other similar studies for agricultural residues (wheat straw and cotton gin waste and rice husk. More moisture and high oxygen

content are the primary reasons for the low quality of biomass. The decrease in moisture content and increase in the carbon to oxygen ratio improves the HHV of the torrefied rice husk compared to the raw rice husk, which will also help enhance the value of rice husk as a raw material for thermo chemical conversion. So, temperature and time had significant effect on the HHV of rice husk. The increments of energy content for dry (300°C and 60min) and chemical treated (300°C and 60min) was 23.76% and 29.53% compared to the original biomass.

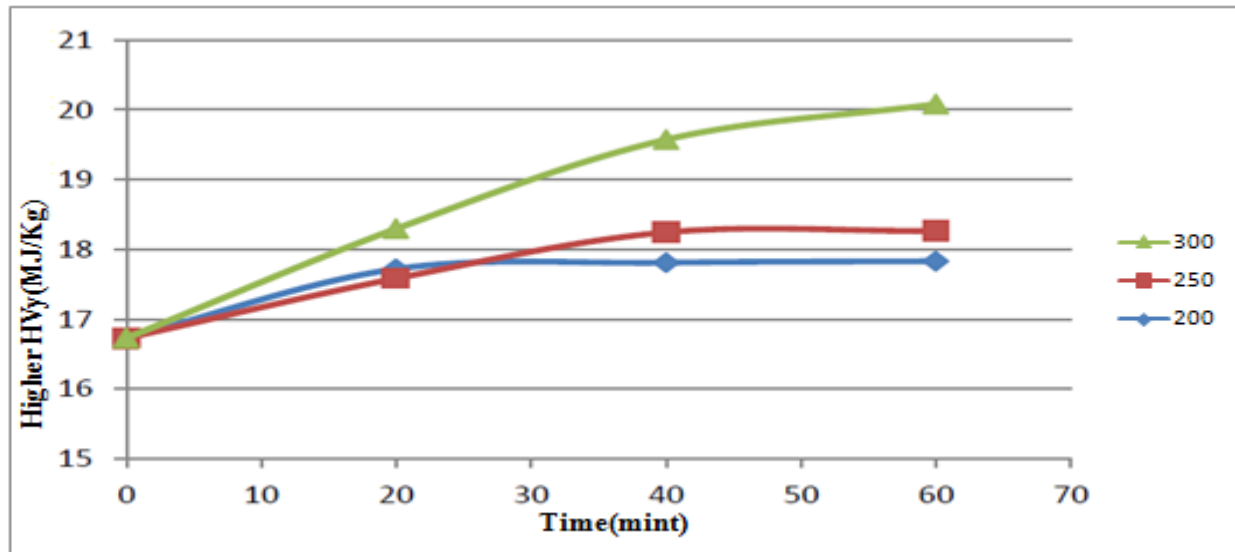


Figure 4-16: Effect of torrefaction temperature and holding time on HHV (Higher heating value ) of dry torrefied rice husk

The increase in the calorific values of the chemically torrefied rice husk could be attributed to the catalysed decomposition of lower energy density components of rice husk; hemicelluloses and cellulose [Sheng and Azebdo,2005]. The chemical torrefaction is able to volatilise these lower calorific components leaving behind the higher calorific lignin fractions.

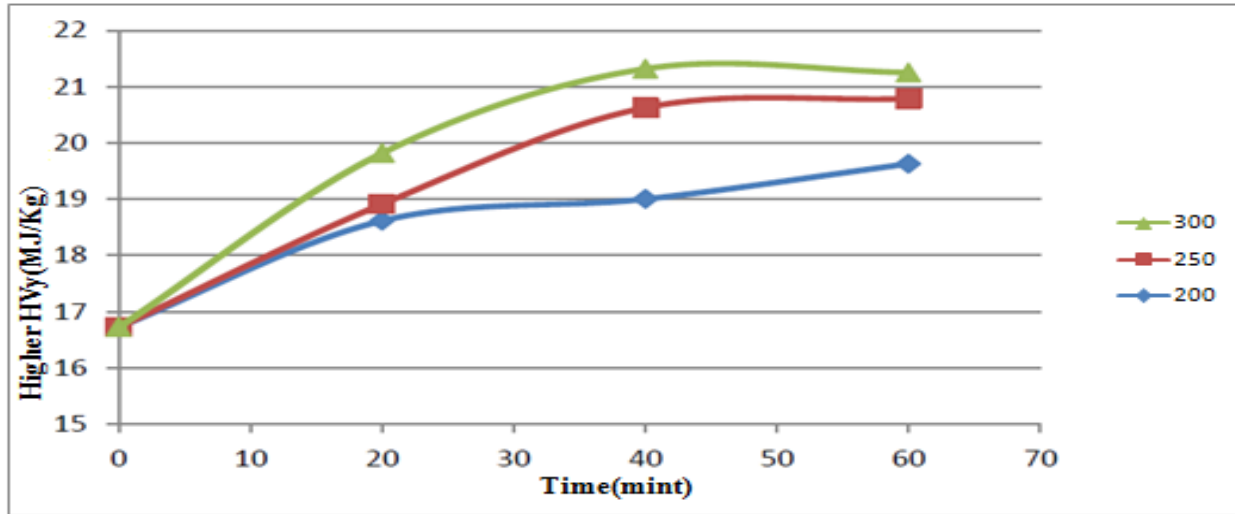


Figure 4-17: Effect of torrefaction temperature and holding time on HHV of chemical treated rice husk

Energy density: The energy density was determined from the ratio of HHV of torrefied product to raw biomass. In line with HHV results, energy density increases for the torrefied biomass according to the increase in temperatures and residence time. The highest energy density yield was obtained with a resident time of 60 min and 300°C for dry torrefaction and 60min and 300°C for chemical treated torrefaction. At those conditions, the energy density of dry and chemical treated torrefied rice husk was 120% and 127.4% respectively. As shown in Figure 4.19 a significant energy density yield was found at temperature between 200 to 300°C. (Bergman et al.,2005) reported that energy density increases with torrefaction temperature because C/O and C/H ratios increase with rising temperatures. Upon torrefaction, biomass loses various compounds with high oxygen and hydrogen contents such as moisture (H<sub>2</sub>O), CH<sub>3</sub>COOH, CH<sub>3</sub>OH, and CO<sub>2</sub>. This is particularly beneficial for gasification of biomass that contains a large amount of oxygen. This is because volatile and moisture content has reduced. The torrefaction process does not remove any part of the fixed carbon and ash content in biomass materials. Therefore, the energy density will be increasing according to temperature and residence time since energy density is proportional to fixed carbon contents.

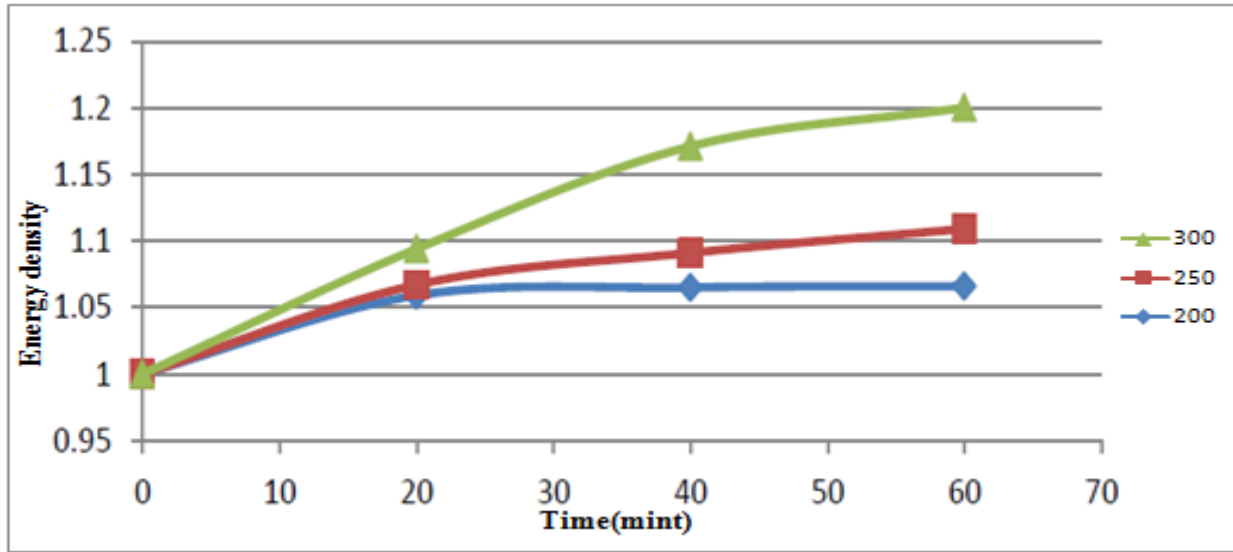


Figure 4.18: Effect of torrefaction temperature and holding time on energy density of dry torrefied rice husk

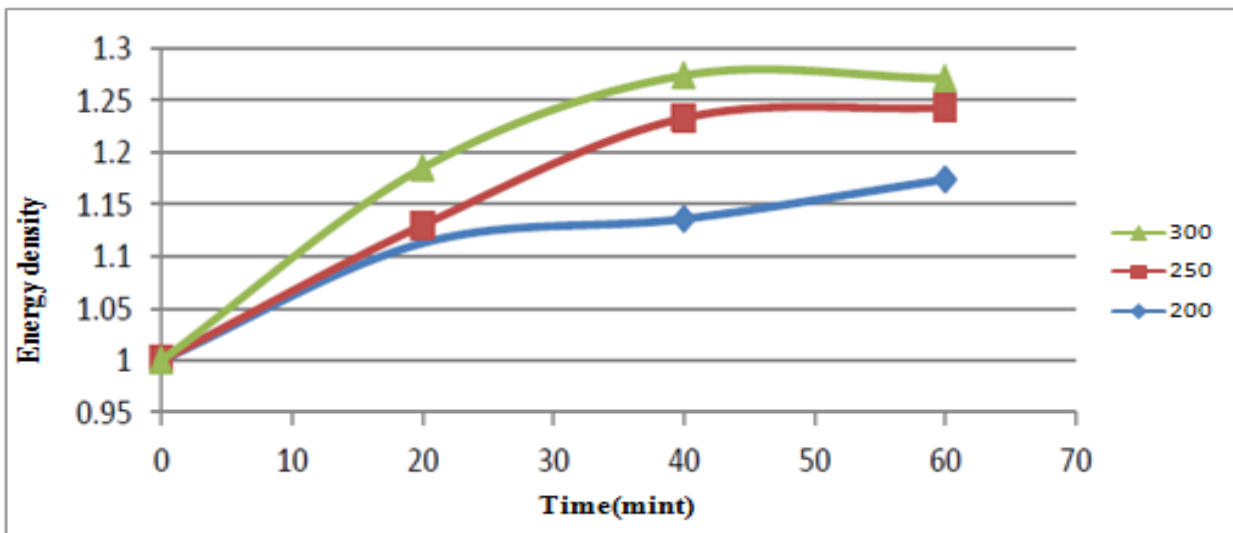


Figure 4.19: Effect of torrefaction temperature and holding time on energy density of chemical treated torrefied rice husk

Figure 4.20 displays the effect of holding time on energy density of chemical treated rice husk for different temperature. As can be seen in the figure, the maximum energy density achieved was when operating the torrefaction process at holding time of 40 min and temperature of 300 °C. The optimal energy density achieved was 120.45% which is about 5.15% higher than energy density obtained from dry torified rice husk. Further increase in torrefaction time will have a

reduction in energy density. Possibly the reason is because there is a significant loss of higher energy content of volatile matter at increased time.

The maximum energy density, higher heating value and fixed carbon contents of dry torrefaction were 1.20, 20.0791 MJ/kg and 34.067% respectively. While the maximum energy density, higher heating value and fixed carbon contents of chemical treated torrefaction were 1.274, 21.248 MJ/kg and 43.733% respectively. This suggested that chemical treated torrefaction process outperform the dry torrefaction process in enhancing the energy density of the rice husk.

#### **4.6 THERMO GRAVIMETRIC ANALYSIS (TGA)**

In order to precede further information on the effect of torrefaction temperature, TGA analysis of raw rice husk, dry torrefied rice husk (300<sup>0</sup>C and 60 min) and chemical treated torrefied rice husk (300<sup>0</sup>C and 40 min) were performed. The result is presented in Figure 4.20, the thermal decomposition of rice husk occurred within the temperature range of 250 to 300<sup>0</sup>C. Peak temperature is the highest temperature reached in the carbonization or torrefaction process. The torrefaction peaks were observed at temperatures between 200 to 300<sup>0</sup>C and pyrolysis process could be measured after 300<sup>0</sup>C. The pyrolysis peaks appeared as the result of the degradation of biomass (Chain et al., 2011). At increasing temperature above 500<sup>0</sup>C, Stage 3 (See Figure 4.20), the final product of the three samples is most importantly ash content and that is why it showed constant. Weight losses observed in TG found to be relevant to the composition of cellulose, hemicelluloses, and lignin fractions in biomass. Hemicellulose, cellulose and lignin peaks of biomass observed at temperatures of 200 to 250<sup>0</sup>C, above 360<sup>0</sup>C, and 500<sup>0</sup>C to 900<sup>0</sup>C respectively. High pyrolysis temperatures decline solid yield, but increase higher heating value, carbon and ash content. Increasing temperature and residence time results in higher mass loss of biomass during torrefaction. Weight change of a sample is recorded as a function of time or temperature and portrayed by a TG curve. As it can be seen in the Figure, different stages of decomposition curves were clearly shown by the vertical lines.

The first stage (temperature below 200<sup>0</sup>C) corresponds to the drying period where light volatiles, mainly water were liberated throughout the procedure. Slight decay of sample weight can be observed as illustrated. In the second stage, devolatilization of condensable products are the major step in all thermo chemical conversion process involving biomass. This step is occurring

at temperature between 200 to 550<sup>0</sup>C, where remarkable slope of the TG curves is observed, corresponding to significant drop in weight of samples due to liberation of volatile hydrocarbon from rapid thermal decomposition of hemicelluloses, cellulose and some part of lignin. At this stage; weights of the tested materials are reduced. This shows that volatile products play a very important part in pyrolysis of biomass materials and product gas composition. In stage three, the sample does not show remarkable weight loss. The slow change of weight could be primarily due to the steady decomposition of the remaining heavy components. As it can be seen in Figure 4.20, the torrefaction peak of the raw rice husk was observed at 300<sup>0</sup>C. While for torrefied product the peak was observed at 250<sup>0</sup>C, and 200<sup>0</sup>C respectively for dry and chemical torrefaction. So, the chemical treated torrefaction reduces the torrefaction peak by 100<sup>0</sup>C comparing to the raw rice husk and it reduces the temperature by 50<sup>0</sup>C to dry torrefaction. Remember that the fractionated rice husk, the optimum sample from the dry torrefied product (300<sup>0</sup>C and 20min) and the chemical treated torrefied product (300<sup>0</sup>C and 40 min) were used for the thermo gravimetric analysis (TGA) analysis.

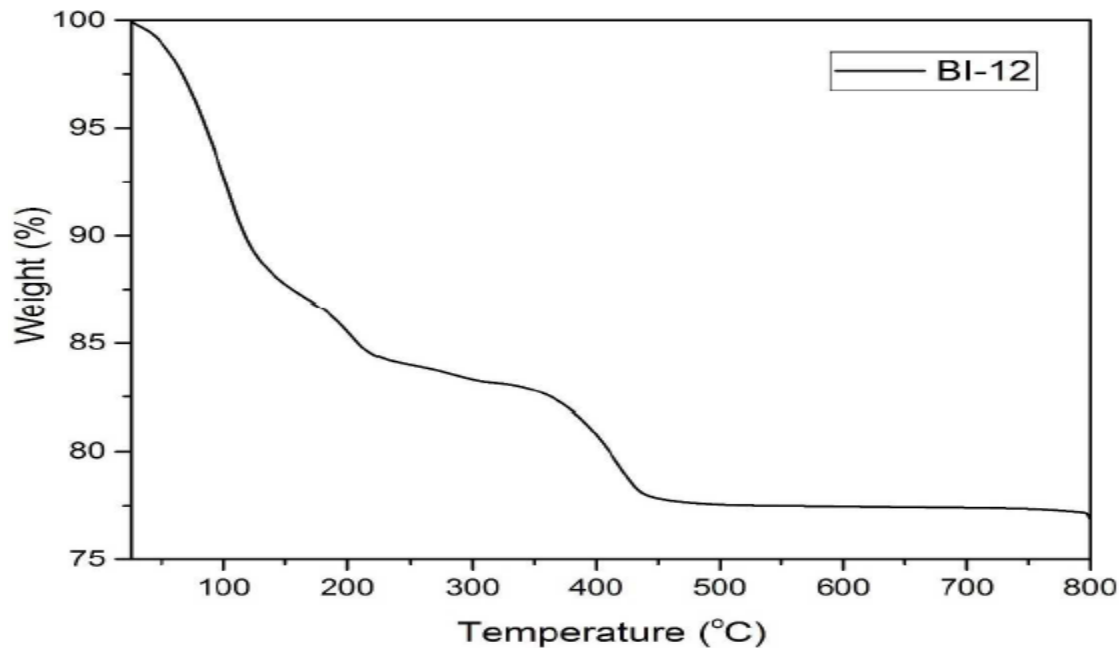


Figure 4.20: The Thermo gravimetric Analysis (TGA) curves of rice husk

During torrefaction the weight loss of biomass comes primarily from the decomposition of its hemicellulose constituents. Hemicellulose decomposes mostly within the temperature range 150 to 280°C, which is the temperature window of torrefaction. Lignin, the binder component of biomass, starts softening above its glass-softening temperature (~130°C), which helps densification (pelletization) of torrefied biomass. Unlike hemicellulose, cellulose shows limited devolatilization and carbonization and that too does not start below 250 °C (Stelt, van der, 2011). Thus, hemicellulose decomposition is the primary mechanism of torrefaction. At lower temperatures (<160 °C), as biomass dries it releases H<sub>2</sub>O and CO<sub>2</sub>.

### **4.7 MODEL FITTING AND RESPONSE SURFACE METHODOLOGY**

The regression coefficients of the model for each response are presented in Table below while results of the analysis of variance (ANOVA) are summarized in Table 4.3. According to particularly high value of coefficient of multiple determinations ( $R^2$ ) for yield (0.9951) (Table 4.3) model equation provides good representation of experimental values.

Moreover, for the response, mathematical model was statistically acceptable due to significant regression for the model ( $p < 0.05$ ) (Table 4.4). Lack of fit testing confirmed adequacy of fitting experimental data to a second-order polynomial model, where p-value for lack of fit was insignificant ( $p > 0.05$ ) (Table 4.4). Therefore, as suggested by ANOVA it can be concluded that Eq.4.1 would be able to adequately describe behavior of yield of torrefied husk.

Table 4.3 Box-Behnken experimental designs with predicted and experimentally obtained values of torified carbon yield.

Response	Temperature °C	Time (min)	Chemical Connection g/l	Yield of torified rice husk		
				Actual result	Predict result	Residual
1	200	20	1.5	81.25	81.81	-0.56
2	300	20	1.5	78.33	78.83	-0.50
3	200	60	1.5	85.23	84.73	0.50
4	300	60	1.5	69.33	68.77	0.56
5	200	40	0.75	87.15	86.11	1.04
6	300	40	0.75	75.76	74.78	0.98
7	200	40	2.25	83.44	84.42	-0.98
8	300	40	2.25	75.76	76.80	-1.04
9	250	20	0.75	82.57	83.92	-1.54
10	250	60	0.75	80.99	82.46	1.54
11	250	20	2.25	80.99	81.03	0.48
12	250	60	2.25	80.99	80.53	-1.47
13	250	40	1.5	83.44	82.46	-1.47
14	250	40	1.5	83.44	82.46	0.98
15	250	40	1.5	83.44	82.46	0.98

### 4.7.1 Effect of Individual Process Variables

As shown in Figures below the percentage of yield is significantly affected by reaction temperature, acid and residence time. It can be seen from the figure that with increasing reaction temperature until it reaches its center value would result in increasing in the percentage of yield, the percentage of conversion then starts to drop as the temperature tends to increase above the center limit. Such behavior could be attributed to the following reasons.

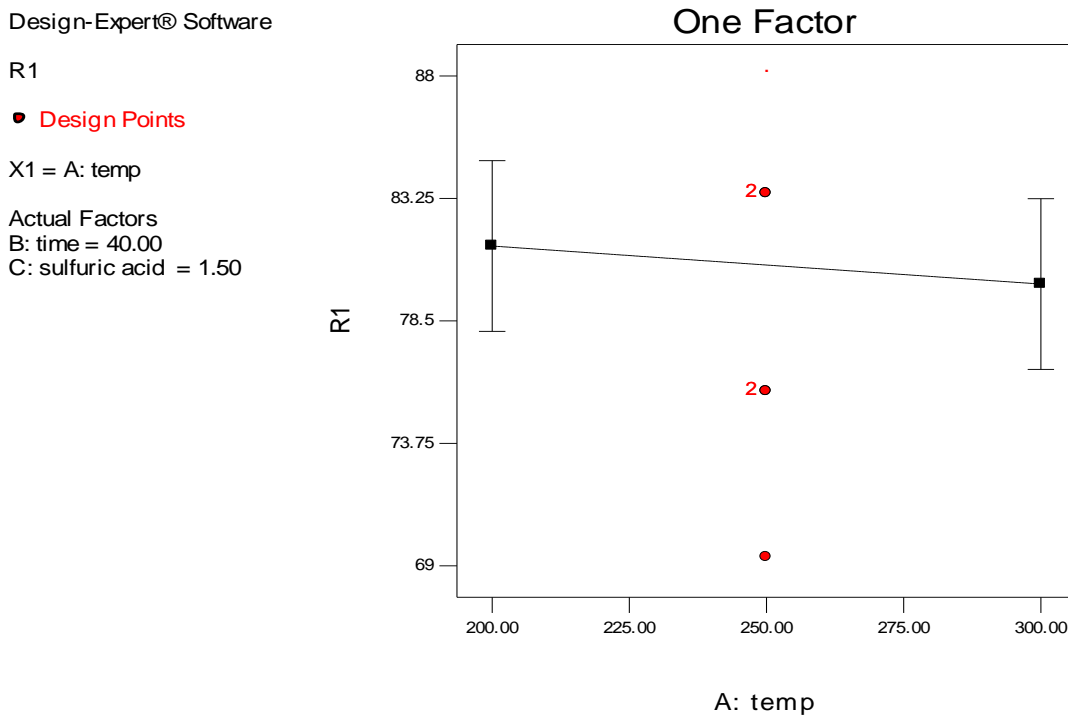


figure4.21: Percentage of yield versus temperature

In the three cases, temperature increase the value of fixed carbon is increase, but the other effect is decreases like moisture. In the case of time also when the time is increases the fixed carbon is increases. In the case of sulfuric acid the concentration is increases also the fixed carbon is increases, in general when it camper in three factor in figure 4.21 and 4.22 has the value is highly effective, that means the value of yield is increases.

Design-Expert® Software

R1

● Design Points

X1 = C: sulfuric acid

Actual Factors  
A: temp = 250.00  
B: time = 40.00

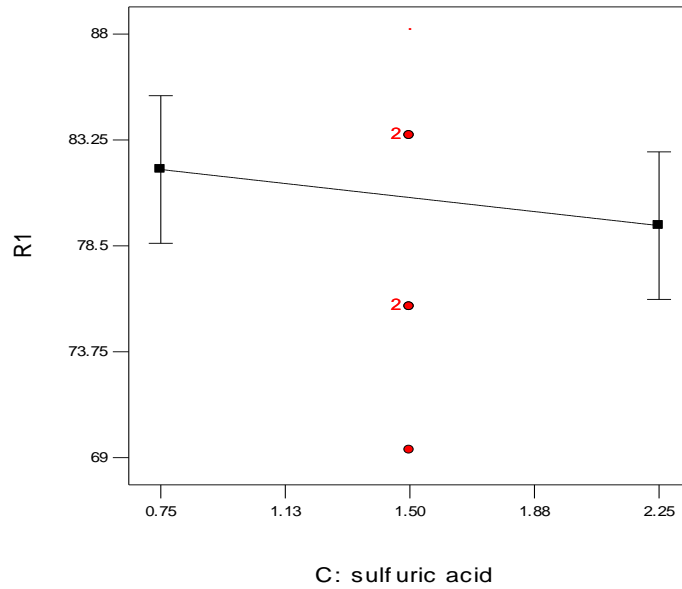


figure4.22: Percentage of yield versus sulfuric acid

Design-Expert® Software

R1

● Design Points

X1 = B: time

Actual Factors  
A: temp = 250.00  
C: sulfuric acid = 1.50

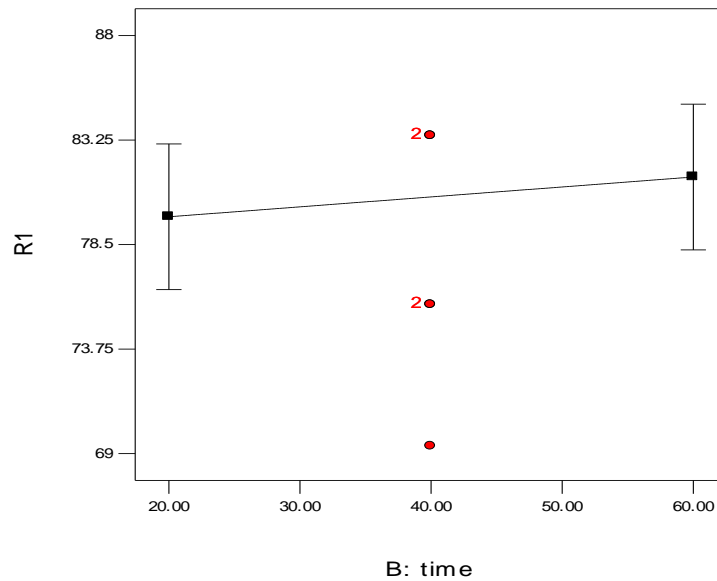


figure4.23: Percentage of yield versus resident time

#### 4.7.2 Development of Regression Model Equation

The model equation that correlates the response (conversion of yield) to the torrefaction process variables in terms of actual value after excluding the insignificant terms was given below. The predicted model for percentage of degree of conversion in terms of the coded factors is given in equation 4.1.

$$\begin{aligned} \text{Yield of Torrified Carbon} = & 120.28037 + 1.60068*A - 6.51031*B + 24.95250*C + \\ & 0.055467*A*B + 0.17373*A*C + 1.93950*B*C - 0.123512*A^2 - 1.42662*B^2 - \\ & 34.46200*C^2 \end{aligned} \text{Eq.4.1}$$

Where A= Temperature, B= Time, C= chemical concentration

The model was tested for adequacy by analysis of variance. The regression model was found to be highly significant with the correlation coefficients of determination of R-Squared, adjusted R-Squared and predicted R-Squared having a value of 0.9869 0.9694 and 0.8970 respectively. The quality of the model developed could be evaluated from their coefficients of correlation. The value of R-squared for the developed correlation is 0.9869. It implies that 98.69% of the total variation in the percentage of conversion is attributed to the experimental variables studied. The graph of the predicted values obtained using the developed correlation versus actual values is shown in Figure 4.24. The results in Figure 4.24 demonstrated that the regression model equation provided a very accurate description of the experimental data, in which all the points are very close to the line of perfect fit. This result indicates that it was successful in capturing the correlation between the torrified carbon process variables to the percentage of conversion.

The adequacy of the model was further checked with analysis of variance (ANOVA) as shown in, based on a 95% confidence level, F – value is a test for comparing model variance with residual (error) variance. If the variances are close to the same, the ratio will be close to one and it is likely that any of the factors have a significant effect on the response with the P – value less than 0.05. It is calculated by model mean square divided by residual mean square. Here The Model F-value of 56.52 implies the model is significant. There is only a 0.01% chance that a "Model F Value" this large could occur due to personal error.

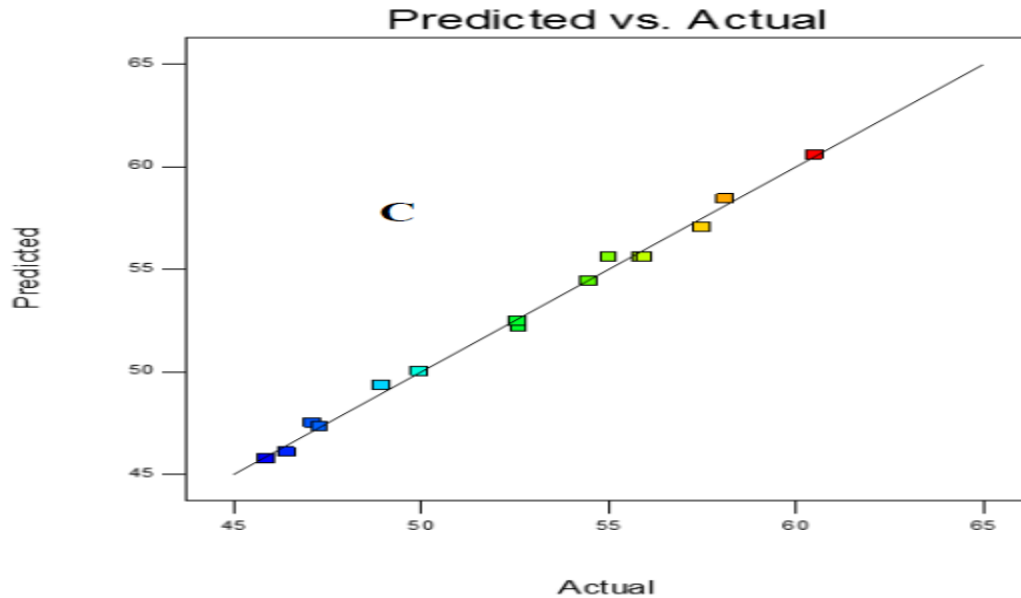


Figure 4.24 Predicted versus actual percentage conversion of the torrefied carbon

The Table 4.4 below shows Analytical variance The Model F-value of 13.00 implies the model is significant. There is only a 0.14% chance that a "Model F-Value" this large could occur due to noise. Values of "Prob > F" less than 0.0500 indicate model terms are significant. In this case A, B, A<sup>2</sup>, B<sup>2</sup>, AB are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), model may improve your model. The "Lack of Fit F-value" of 1.92 implies the Lack of Fit is not significant relative to the pure error. There is a 26.73% chance that a "Lack of Fit F-value" this large could occur due to noise. Non-significant lack of fit is good -- we want the model to fit.

Box and Behnken proposed three level designs for fitting response surfaces. These designs are formed by combining 2<sup>k</sup> factorials with incomplete block designs and 3 center points was employed in the optimization study, a total of 15 experiments were conducted.

Table 4.4: Analysis of Variance (Partial Sum of Squares)

Source Model		Sum of squares	DF	Mean square	F value	Prob>F	
		294.20	9	32.69	13.00	0.0014	Significant
	A	179.46	1	179.46	71.38	<0.0001	
	B	25.49	1	25.49	10.14	0.0154	
	C	0.053	1	0.053	0.021	0.8888	
	A <sup>2</sup>	17.59	1	17.59	7.00	0.0332	
	B <sup>2</sup>	14.90	1	14.90	5.93	0.0451	
	C <sup>2</sup>	0.052	1	0.052	0.021	0.8896	
	AB	42.12	1	42.12	16.75	0.0046	
	AC	3.44	1	3.44	1.37	0.2803	
	BC	9.30	1	9.30	3.70	0.0958	
Residual		17.60	7	2.51			
Lock fit		10.40	3	3.47	1.92	0.2673	Not significant
Pure error		7.20	4	1.80			
Cor total		311.80	16				

### 4.7.3 Effect of interaction of torrefied Process Variables

Based on the analysis of variance, torified reaction was significantly affected by various interactions between the process variables. This result demonstrated that the advantage of using BHD surface response for experimental data analysis in capturing the interaction between variables that affects the torrefaction. In addition to the interaction effect, significant individual process variables that affect the process reaction temperature.

Effect of interaction Process Variables: As shown in Figure 4.25 below the percentage of conversion is significantly affected by temperature. It can be seen from the figure that with increasing reaction temperature until it reaches its center value would result increasing in the percentage of conversion, the percentage of conversion then starts to drop as the temperature tend to increase above the center limit. Such behavior could be attributed to the following reasons. Increasing temperatures favored the formation of sulfuric acid. In order to precede further information on the effect of torrefaction temperature, analysis of variance of raw rice husk, dry torrefied rice husk (300<sup>0</sup>C and 60 min) and chemical treated torrefied rice husk (300<sup>0</sup>C, 2.25 g/l and 40 min) were performed. This resulted in a more rapid torrefaction rate, but also in higher temperature it resulting higher carbonized.

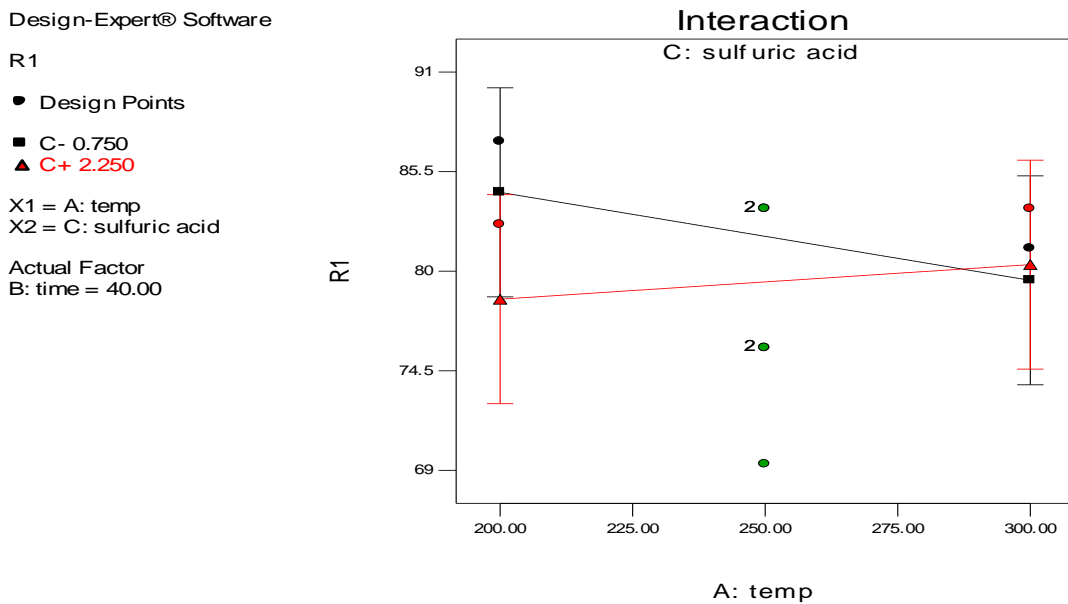


Figure 4.25 Percentage interaction of chemical with temperature

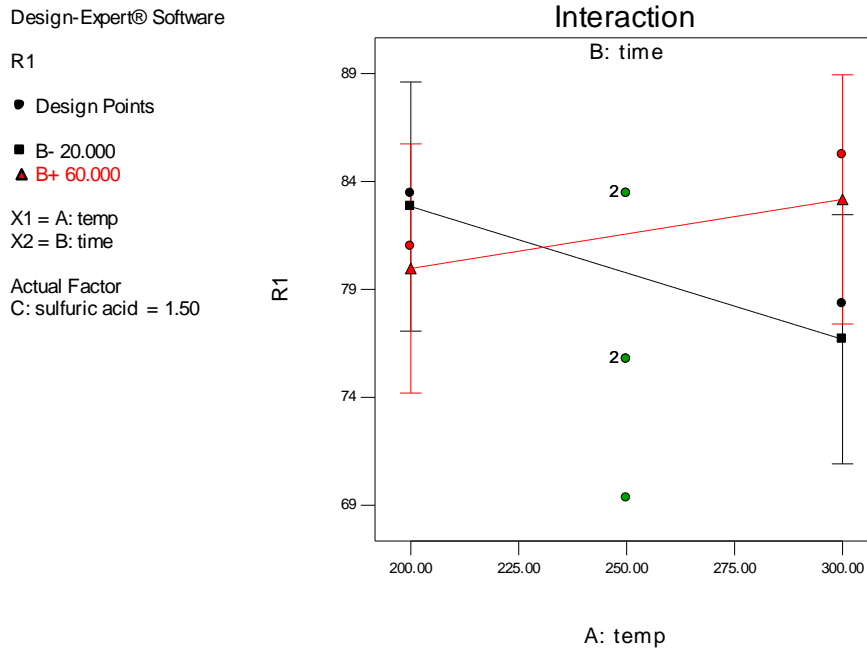


Figure 4.26 Percentage of interaction of temperature with resident time

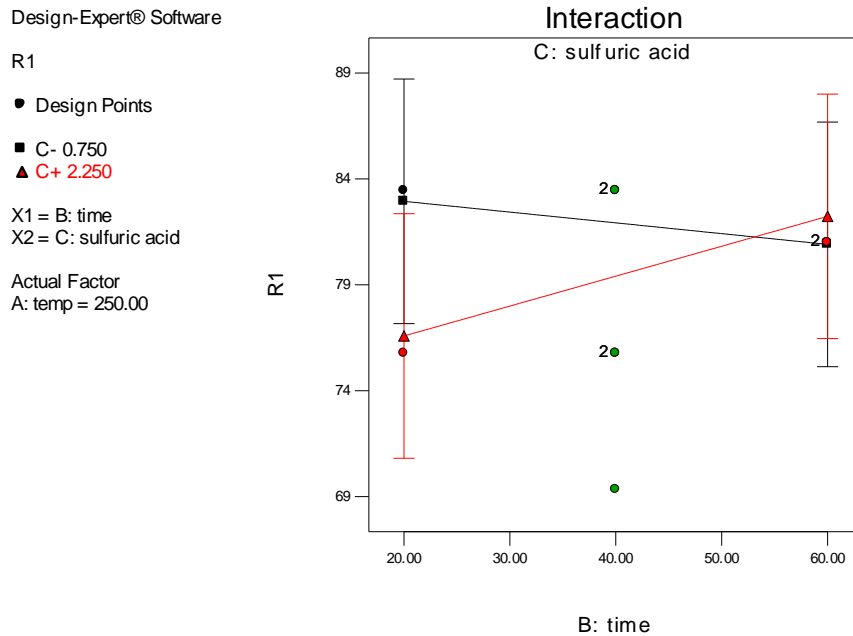


Figure 4.27 Percentage of interaction of chemical with resident time

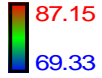
The most common way to summarize the results of a central composite design experiment is in the form of a response surface plot and via response contours plot.

The process variables were found to have significant interaction effects chemical with temperature interaction. Figure 4.26 and Figure 4.27 shows the interaction between torified temperature and amount of sulfuric acid, and time amount of carbonized on percentage of conversion respectively. Generally, an increase in amount of temperature is found to increase the percentage of torified carbon conversion. This similar explanation given in the previous section. From the three interaction effects shown in the figures and contours at lower range of torified carbon a temperature of the start point and center point, always resulted in the percentage of conversion higher than when using lower or higher temperature and higher or lower resident time. The above observations can easily be explained as higher catalyst loading and medium torified temperature will drive the reaction forward and goes to maximum value which results in efficient carbon value of the product.

Another notable observation is that at higher range of chemical sulfuric, the observations showed that using a combination of higher upgrading, higher amount of carbon temperature is significant, beneficial in increasing the percentage of conversion. This is because at this process conditions, higher amount of chemical and temperature is already sufficient to push the rice husk forward to more carbenized. This phenomena is further supported by the fact that resident time is the most significant process variable that affect the percentage of conversion as indicated by the highest F – value in the ANOVA as shown in Table 4.4 above. The Response Surface Methodology (RSM) was used to optimize the conditions of conversion for upgrading rice husk and to understand the interaction of the factors affecting the torrefaction production. Figure 4.28 and Figure 4.29 show surface plots between the independent and dependent variable for fixed parameters.

Design-Expert® Software

R1



X1 = A: temp  
X2 = C: sulfuric acid

Actual Factor  
B: time = 40.00

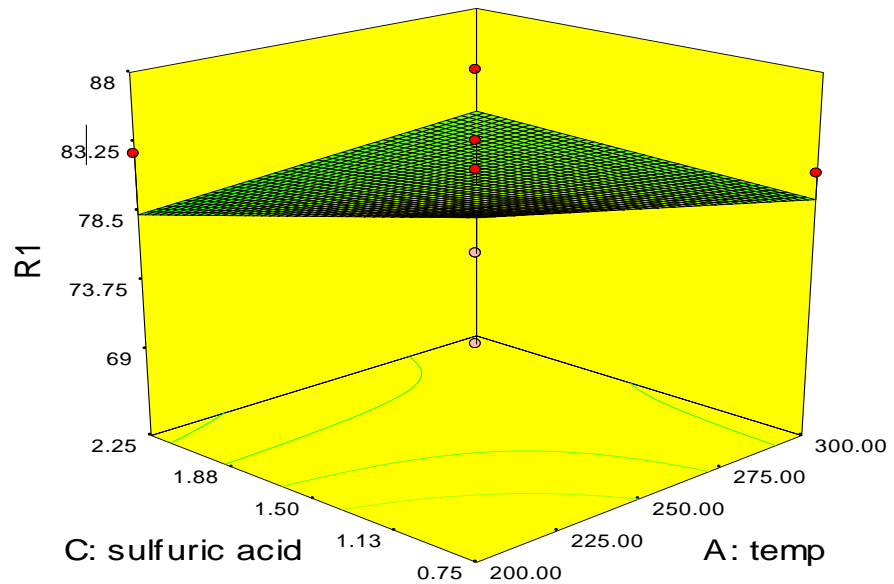


Figure 4.28: Surface plot of the interaction effect of torrefied temperature and amount of chemical concentration versus percentage of conversion

Design-Expert® Software

R1



X1 = A: temp  
X2 = C: sulfuric acid

Actual Factor  
B: time = 40.00

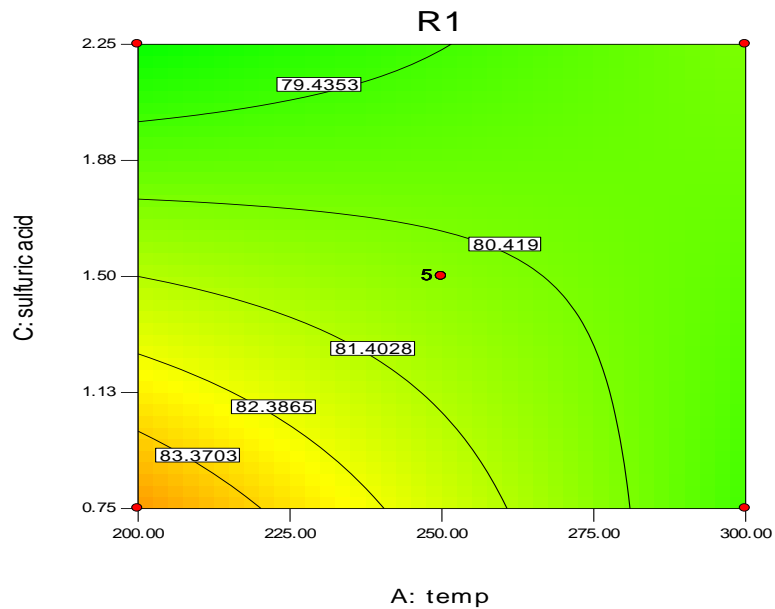


Figure 4.29: Contour plot of the interaction effect of torrefied temperature and amount of chemical concentration with percentage

## 5. Conclusions and Recommendation

### 5.1 Conclusion

Dry and chemical treated torrefaction of rice husk was performed to enhance the energy contents or the Bioenergy property of rice husk. From the results obtained by the torrefaction of rice husk, a net reduction of the volatiles content, mass yield, moisture content, bulk density and atomic oxygen content correlate with increasing torrefaction temperature and reaction time, while atomic carbon content, higher heating value(HHV), fixed carbon content and energy density increase with higher torrefaction temperatures and time in both treatment cases. A mild torrefaction treatment of 300<sup>0</sup>C at 60 min and 300<sup>0</sup>C at 40 min is found to be the optimal torrefaction conditions for improving the heating value (calorific value), energy density and Hydrophobicity characteristics of rice husk. Torrefied rice husk became brittle and fragile, and showing gradual shrinking volume and turning from yellow to brown and then black in both treatments. From the TGA analysis, torrefaction peaks were observed at temperatures between 200<sup>0</sup>C to 300<sup>0</sup>C and the pyrolysis peaks appeared as a result of the degradation of rice husk. From the dry and chemical treated torrefaction treatments, the chemical treated torrefaction yields better result and increase the energy density. The energy density of dry torrefied product was 102.4% and that of chemical treated torrefaction was enhanced to 110.5%.

## 5.2 Recommendation

In the laboratory experimental equipment like Gas flow rate, acid composition and particle size was fixed in this study. But, they have significant effect on the energy density of biomass. By optimizing the nitrogen gas flow rate, acid composition and the biomass particle size. If those equipment well available, the energy density can be enhanced better. Effective design of Torrefayer will enhance much better the energy density yield of biomass. So, by designing actual torrefayer with better heat source (Automatic controller heat source) should be recommended for better temperature control, so that heat can be distributed equally throughout the sample and more biomass can be torrefied.

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**APPENDIX A: CALCULATION OF PHYSICAL AND CHEMICAL PROPERTIES**

Table A.1: Mass Yield for Dry Torrefaction Treatments of Rice Husk

Temp( <sup>o</sup> C)	Time (min)	Run	$\frac{\text{Mass of solids}(g)}{\text{Initial Final}}$		Yield solid	Mean
200	20	1	15	14.700	98.880	97.335
		2	15	14.699	97.600	
		3	15	14.200	98.000	
	40	1	15	13.670	97.000	97.536
		2	15	13.560	97.011	
		3	15	14.580	98.500	
	60	1	15	13.670	97.000	97.312
		2	15	14.870	98.530	
		3	15	12.680	96.500	
250	20	1	15	14.900	89.700	86.670
		2	15	13.500	86.990	
		3	15	12.650	85.990	
	40	1	15	13.560	86.980	85.340
		2	15	12.780	86.090	
		3	15	11.660	84.060	
	60	1	15	13.170	82.090	80.990
		2	15	13.450	80.900	
		3	15	12.670	81.001	
300	20	1	15	14.120	86.780	87.330
		2	15	13.340	87.800	
		3	15	14.330	88.650	
	40	1	15	14.340	80.440	82.160
		2	15	11.230	82.500	
		3	15	10.450	83.780	
	60	1	15	12.380	81.340	80.410
		2	15	10.340	80.000	
		3	15	10.140	79.890	

Table A.2: Bulk Densities (Dry Basis) of Dry Torified Rice Husk

Temp( <sup>o</sup> C)	Time(min)	Run	bulk Density (g/cm <sup>3</sup> )	Mean
Raw Rice husk  200	20	1	120.500	120.410
		2	119.680	
		3	122.200	
	40	1	121.550	118.530
		2	119.660	
		3	121.610	
	60	1	119.770	117.220
		2	120.870	
		3	119.980	
250	20	1	14.900	115.435
		2	117.510	
		3	118.750	
	40	1	117.560	112.984
		2	116.780	
		3	117.650	
	60	1	116.770	110.230
		2	116.450	
		3	109.971	
300	20	1	114.120	105.110
		2	115.940	
		3	115.830	
	40	1	114.640	98.780
		2	111.230	
		3	113.150	
	60	1	107.080	90.990
		2	99.400	
		3	95.540	

Table A.3: Bulk Densities (Dry Basis) of (0.75, 1.50 And 2.25%) Chemical Treated Torified Rice Husk

<i>Temp(<sup>o</sup>C)</i>	Time(min)	Run	bulk Density (g/cm <sup>3</sup> )	Mean
Raw Rice husk	20	1	121.500	120.310
		2	119.680	
		3	121.200	
200	40	1	119.550	118.330
		2	118.660	
		3	117.610	
	60	1	119.770	119.220
		2	120.870	
		3	119.980	
	20	1	114.900	115.435
		2	116.510	
		3	114.750	
250	40	1	112.560	112.984
		2	109.650	
		3	107.640	
	60	1	110.670	110.230
		2	111.350	
		3	109.971	
	20	1	95.210	93.110
		2	93.960	
		3	91.380	
300	40	1	85.770	85.780
		2	84.320	
		3	86.220	
	60	1	73.080	72.990
		2	72.450	
		3	71.220	

Table A.4: Mass Yield for Torrefaction Treatments of (0.75, 1.50 And 2.25%) Chemical Treated Rice Husk

Temp( <sup>o</sup> C)	Time (min) Yield	Run	<i>Mass of solids(g)</i>		solid	Mean
			<i>Initial</i>	<i>Final</i>		
200	20	1	15	13.700	79.853	82.151
		2	15	13.699	80.600	
		3	15	13.200	86.000	
	40	1	15	13.670	87.000	87.153
		2	15	13.560	88.011	
		3	15	13.580	88.500	
	60	1	15	13.670	87.000	85.312
		2	15	13.870	88.530	
		3	15	13.680	86.500	
250	20	1	15	13.900	78.700	76.570
		2	15	13.500	76.990	
		3	15	13.650	75.990	
	40	1	15	13.560	76.980	75.440
		2	15	13.780	76.090	
		3	15	13.660	74.060	
	60	1	15	13.170	77.890	77.990
		2	15	13.450	77.900	
		3	15	12.670	77.665	
300	20	1	15	12.120	78.780	72.330
		2	15	12.340	66.802	
		3	15	12.330	68.653	
	40	1	15	12.340	83.440	75.576
		2	15	11.230	72.500	
		3	15	10.450	70.780	
	60	1	15	11.380	68.340	69.411
		2	15	10.340	70.000	
		3	15	10.140	69.890	

Table A.5: Ash and Volatile Contents (Dry Basis) of Dry Torrefied Rice Husk

<i>Temp(°C)</i>	Time (min)	Run	volt (%)	Avg	Ash (%)	Avg	
Dry Rice Husk	20	1	70	69.333	22.60	22.366	
		2	70		21.50		
		3	68		23.00		
	200	40	1	73	67.333	24.55	24.183
			2	65		25.00	
			3	64		23.60	
		60	1	63	66.00	23.67	24.056
			2	67		24.30	
			3	68		24.20	
250		20	1	62	63	24.55	23.88
			2	61		23.67	
			3	66		23.57	
	40	1	69	63.33	22.33	23.67	
		2	67		24.43		
		3	54		23.44		
	60	1	60	56.33	24.65	24.53	
		2	55		24.73		
		3	54		23.87		
300	20	1	52	52.33	24.86	23.57	
		2	54		23.54		
		3	51		23.90		
	40	1	54	52	24.99	25.45	
		2	53		25.66		
		3	49		26.22		
	60	1	44	42.33	28.56	28.256	
		2	42		27.21		
		3	41		29.53		

Table A.6: Ash and Volatile Contents (Dry Basis) of (0.75, 1.50 And 2.25%) Chemical Treated Torrefaction

Temp( <sup>o</sup> C)	Time (min)	Run	volt (%)	Avg	Ash (%)	Avg	
Dry Rice Husk	20	1	75	71	14.60	12.366	
		2	70		11.50		
		3	68		13.00		
	200	40	1	65	65	17.55	14.183
			2	67		15.00	
			3	63		13.60	
		60	1	56	52.33	18.67	14.056
			2	45		14.30	
			3	56		14.20	
		20	1	45	46.66	19.55	13.88
			2	47		13.67	
			3	48		13.57	
	250	40	1	51	45.33	20.33	13.67
			2	46		14.43	
			3	39		13.44	
		60	1	44	39	21.65	20.53
			2	38		22.73	
			3	35		17.87	
20		1	30	32	23.86	22.57	
		2	32		22.54		
		3	34		21.90		
300	40	1	30	26.33	24.99	21.45	
		2	25		19.66		
		3	24		18.22		
	60	1	22	19	31.56	31.11	
		2	20		32.21		
		3	15		30.53		

Table A.7: Energy Content and Energy Density of Dry Torrefaction of Rice Husk

Temp( <sup>o</sup> C)	Time (Min)	Run	HHV (MJ/KG)	Mean	Energy density	Mean	
Dry Rice Husk	20	1	18.654	18.721	-		
		2	18.756		-		
		3	18.897		-		
	200	40	1	19.453	19.532	1.206	1.242
			2	19.569		1.203	
			3	19.790		1.225	
		60	1	20.453	20.854	1.204	1.250
			2	20.645		1.208	
			3	20.907		1.254	
250		20	1	21.621	21.781	1.259	1.122
			2	21.890		1.203	
			3	21.987		1.214	
	40	1	22.673	22.331	1.125	1.161	
		2	22.371		1.289		
		3	22.221		1.187		
	60	1	22.661	22.421	1.032	1.032	
		2	22.561		1.034		
		3	21.341		1.032		
300	20	1	23.098	23.171	1.235	1.161	
		2	23.442		1.032		
		3	23.145		1.320		
	40	1	24.445	24.315	1.189	1.271	
		2	24.125		1.299		
		3	24.654		1.304		
	60	1	34.548	34.57	1.402	1.402	
		2	34.745		1.401		
		3	34.881		1.405		

Table A.8: Energy Content and Energy Density of (0.75, 1.50 And 2.25%) Chemical Treated Torrefaction of Rice Husk

Temp( <sup>o</sup> C)	Time (Min)	Run	HHV (MJ/KG)	Mean	energy density	Mean
Dry Rice Husk  200 A    250    300	20	1	18.654	18.721	-	
		2	18.756		-	
		3	18.897		-	
	40	1	19.453	19.532	1.206	1.142
		2	19.569		1.203	
		3	19.790		1.225	
	60	1	30.453	30.854	1.204	1.150
		2	30.645		1.208	
		3	30.907		1.254	
	20	1	21.621	21.781	1.259	1.122
		2	21.890		1.203	
		3	21.987		1.214	
40	1	22.673	22.331	1.125	1.161	
	2	22.371		1.289		
	3	22.221		1.187		
60	1	35.661	35.421	1.032	1.032	
	2	35.561		1.034		
	3	35.341		1.032		
20	1	23.098	23.171	1.235	1.161	
	2	23.442		1.032		
	3	23.145		1.320		
40	1	24.445	24.315	1.289	1.351	
	2	24.125		1.399		
	3	24.654		1.504		
60	1	38.548	38.724	1.612	1.632	
	2	38.745		1.641		
	3	38.881		1.654		

Table A.9: Moisture Contents (Wet Basis) of Dry Torified Rice Husk

<i>Temp</i> ( <sup>0</sup> C)	Time (Min)	Run	Moisture content (wt% db)	Mean	
Dry Rice Husk	20	1	13.654	13.112	
		2	13.756		
		3	13.897		
	200	40	1	9.453	9.543
			2	9.569	
			3	9.790	
		60	1	10.453	9.120
			2	8.645	
			3	7.907	
	20	1	8.621	7.431	
		2	6.890		
		3	6.987		
250	40	1	6.673	5.750	
		2	5.371		
		3	4.221		
	60	1	5.661	4.654	
		2	3.561		
		3	4.341		
	20	1	3.098	3.127	
		2	3.442		
		3	3.145		
300	40	1	2.445	2.314	
		2	2.125		
		3	4.654		
	60	1	3.408	3.324	
		2	3.455		
		3	3.231		

Table A.10: Moisture Contents (Wet Basis) of (0.75, 1.50 And 2.25%) Chemical Treated Rice Husk

<i>Temp</i> <sup>(°C)</sup>	Time (Min)	Run	Moisture content (wt%db)	Mean	
Dry Rice Husk	20	1	9.154	8.935	
		2	9.056		
		3	8.597		
	200	40	1	9.453	9.543
			2	9.569	
			3	9.790	
		60	1	10.453	9.120
			2	8.645	
			3	7.907	
250	20	1	8.621	7.431	
		2	6.890		
		3	6.987		
		40	1	6.673	5.750
			2	5.371	
			3	4.221	
		60	1	5.661	4.654
			2	3.561	
			3	4.341	
300	20	1	3.098	3.127	
		2	3.442		
		3	3.145		
		40	1	2.445	2.314
			2	2.125	
			3	4.654	
		60	1	2.990	2.290
			2	2.140	
			3	1.550	

Table A.11: Moisture Absorption of Dry Treated Rice Husk

Temp( <sup>o</sup> C)	Time (Min)	Moisture (%)				Mean	
		Initial	1hr	4hr	24hr		
Dry Rice Husk	20	9.154	11.243	14.768	14.985	13.324	
		9.056	10.857	12.543	12.663		
		8.597	10.034	13.457	13.213		
	200	40	9.453	11.685	14.824	14.992	13.667
			9.569	10.231	11.341	13.443	
			9.790	9.980	10.335	11.664	
		60	10.453	9.663	10.437	13.443	12.848
			8.645	8.436	9.543	11.673	
			7.907	8.243	10.654	13.430	
	250	20	8.621	7.745	8.365	10.663	12.745
			6.890	7.324	9.540	12.354	
			6.987	6.340	7.845	13.231	
40		6.673	6.103	8.940	10.467	9.764	
		5.371	6.054	7.662	9.822		
		4.221	5.923	6.961	8.521		
		5.661	5.543	6.773	8.413		
		3.561	5.321	7.745	9.661		
		4.341	5.026	8.431	10.642		
60		3.098	4.685	6.430	7.312	8.982	
		3.442	4.765	7.459	9.311		
		3.145	4.932	5.320	8.125		
	2.445	4.954	6.442	7.327			
	2.125	4.723	5.329	8.940			
	4.654	4.236	5.015	6.241			
300	40	2.990	4.056	6.160	7.342	7.213	
		2.140	4.190	7.231	7.532		
		1.550	4.214	6.931	7.332		
	60	2.990	4.056	6.160	7.342		
		2.140	4.190	7.231	7.532		
		1.550	4.214	6.931	7.332		

Table A.12: Moisture Absorption of (0.75, 1.50 And 2.25%) Chemical Treated Rice Husk

Temp( <sup>o</sup> C)	Time (Min)	Moisture (%)				Mean
		Initial	1hr	4hr	24hr	
Dry Rice Husk	20	8.154	11.243	14.768	14.985	13.324
		8.056	10.857	12.543	12.663	
		8.597	10.034	13.457	13.213	
	40	6.453	11.685	14.824	14.992	13.667
		6.569	10.231	11.341	13.443	
		6.790	9.980	10.335	11.664	
	60	6.453	9.663	10.437	13.443	12.848
		6.645	8.436	9.543	11.673	
		6.907	8.243	10.654	13.430	
200	20	5.621	7.745	8.365	10.663	12.745
		5.890	7.324	9.540	12.354	
		5.987	6.340	7.845	13.231	
	40	5.673	6.103	8.940	10.467	9.764
		5.371	6.054	7.662	9.822	
		4.221	5.923	6.961	8.521	
	60	5.661	5.543	6.773	8.413	9.653
		3.561	5.321	7.745	9.661	
		4.341	5.026	8.431	10.642	
250	20	3.098	4.685	6.430	7.312	8.982
		3.442	4.765	7.459	9.311	
		3.145	4.932	5.320	8.125	
	40	3.445	5.954	6.442	7.327	7.213
		3.125	4.723	5.329	8.940	
		3.654	4.236	5.015	6.241	
	60	2.442	4.056	6.160	6.216	6.472
		1.213	4.190	7.231	6.743	
		3.532	4.214	6.931	6.832	

Appendix B: Laboratory Equipment's and Photography



B.1: Horizontal tubular furnace (Torrifar)



B.2: FT-IR instrument



B.3: Elemental analysis instrument



B.4: TGA instrument



B.5: Chemical treated and torrefied rice husk sample



B.6: Dry and torrefied rice husk sample



B.7: Equilibrium Moisture content analyzer



B.8: Hydrophobicity using water emersion test