**ADDIS ABABA UNIVERSITY**

**ADDIS ABABA INSTITUTE OF TECHNOLOGY**

**SCHOOL OF CHEMICAL AND BIO-ENGINEERING**


# Optimization and Characterization of Silica Synthesized from Rice husk

**By:**

**Mizer Girmay**

**A Thesis submitted to School of Chemical and Bio-engineering, Addis Ababa institute of Technology, Addis Ababa University in partial fulfillment of the requirements for the degree of Master of Science in Chemical Engineering (Process Engineering)**

**Addis Ababa, Ethiopia**

**December, 2019**

**ADDIS ABABA UNIVERSITY**

**ADDIS ABABA INSTITUTE OF TECHNOLOGY**

**SCHOOL OF CHEMICAL AND BIO-ENGINEERING**

This is to certify that the thesis prepared by *Mizer Girmay*, entitled: *Optimization and Characterization of Silica Synthesized from Rice husk* and submitted in partial fulfillment of the requirements for the degree of Master of Science in process Engineering complies with the regulations of the University and meets the accepted standards with respect to originality and quality.

Signed by the Examining Committee:

| | | |
|---|---|---|
| Dr. Hundessa D. | | |
| Advisor | Signature | Date |
| Dr. Shegaw A. | | |
| Internal Examiner | Signature | Date |
| Dr.Anuradha J. | | |
| External Examiner | Signature | Date |
| | | |
| School or Center of chair person | Signature | Date |

## Declaration

I, the undersigned, declare that this thesis is my original work and has not been presented for a degree in any other university, and that all sources of materials used for the thesis have been duly acknowledged.

Name: Mizer Girmay

Signature: _____

Date of submission: December 2019

The thesis has been submitted for examination with my approval as university advisor.

Name: Dr. Hundessa Dessalegn

Signature: _____

# Table of Contents

# List of Tables

# List of Figures

# List of Acronyms

| | |
|---|---|
| AAS | Atomic Absorption Spectrophotometer |
| ANOVA | Analysis of variance |
| BBD | Box-Behnken Design |
| FT-IR | Fourier Transform Infrared Spectroscopy |
| LOI | Loss on ignition |
| NTRHA | Non treated rice husk ash |
| PEDS | Poly Ethoxy Disiloxane |
| RH | Rice Husk |
| RHA | Rice Husk Ash |
| RHAs | Rice Husk Ash silica |
| RSM | Response surface method |
| TEOS | Tetra Ethyl Ortho Silicate |
| TMOS | Tetra Methyl Ortho Silicate |
| TRHA | Treated Rice husk ash |
| XRD | X-Ray Diffraction |
| HCl | Hydrochloric acid |
| NaOH | Sodium hydroxide |

# Abstract

Rice husks are agricultural biomass waste, which is considered as renewable resources that are produced every year in Ethiopia. Despite of its non-commercial value and causing environmental pollutions, its ash content is rich in silica ($SiO_2$) and becomes an economic potential source. This study aims at utilizing this agricultural biomass waste into valuable product, silica. Silica ($SiO_2$) was prepared by using rice husk ash (RHA) as a source of silicate ($SiO^{-2}_3$) . Then further reaction of the ash with NaOH has formed Sodium silicate ($Na_2SiO_3$) solution. Then, titration of this solution with HCl forms the precipitation of silica-gel. The effect of acid pretreatment on the removal of metallic impurities and its percentage purity as well as on the properties of RHA was examined using Atomic Absorption Spectrophotometer (AAS). The percentage purity of SiO2 in the untreated RH were found 87.1% with some metallic impurities and 97.6% purity of silica is obtained from the treated RH, which proved to be effective in removing the metallic impurities to a very lower level and enhance the purity of silica in the RHA. The experiment and statistical analysis for the production of $SiO_2$ were designed using three-level-three-factor BBD for the total run of 17 experiments at operating process conditions of acid concentration (1-2N), pyrolysis temperature (450-850°C) and Pyrolysis time (1-5h). The optimal %yield were found to be 98.971% with 98.6% purity of $SiO_2$% at conditions for 1.95N pretreatment acid concentration,658°C pyrolysis temperature, and 4.95h pyrolysis time. The effects of combustion temperature and time on % yield and the structural properties of silica in the ash were also characterized using XRD and FTIR analysis. The quality of the extracted silica were determined and characterized by its physico chemical properties. Furthermore, the silica obtained from RH was compared with the commercial silica. As a result, they perform equivalency with commercially available. Also, from optimized conditions, surface area of the synthesized silica was found 779.7$m^2$/g in amorphous form.



Keyword: Rice husk, Rice husk ash, RHAs, Sodium silicate, Silica

# Acknowledgement

I glorify the Almighty of God for giving the strength and wisdom to accomplish this thesis.

I thank my institution Adigrat University for grant and also AAiT-AAU for facilitating and core to the complement of my study.

I would like to give a great respect, heartfelt appreciation and sincere gratitude to my Thesis Supervisor Dr.Eng.Hundessa Dessalegn for his thoughtful supervision, sharing his knowledge, skill, fruit full advising, constructive criticism, and for his tireless patient guidance and understanding throughout.

I also would like to express my gratitude to the technical assistances of the chemical engineering department, and especially to Ato Hintsasilasse, for the timely assistance during my experimental work. Also, my recognition goes to Dr.Yonas and Mr.Tesfaye, Department of chemistry, Computational and Natural Science, AAU especially for their support during my experimental task. I sincerely thank Mr. Elias and Mr. Anteneh for sharing experience and knowledge, with motivation in the accomplishment of this study. Also, I am grateful to my friends who motivated me and contributed much to make this research study become successful.

Sincere, my deepest boundless praise and appreciation go to my families who have been beside me throughout with endless love, support and motivation to accomplish this study.

# 1. INTRODUCTION

## 1.1. Background

Silica ($SiO_2$) is one of the valuable inorganic multipurpose chemical compounds. It is the most abundant material on the earth's crust. It can exist in amorphous or crystalline forms. Industrially, silica particles have a number of applications including use as catalyst, synthesis of shear thickening fluid, water purification, as desiccants, in solar panels, refractory bricks manufacturing, and as silicon source (Wang,*etal.*,2017;Andreola,*etal.*,2007).

However, manufacture of pure silica is energy intensive. A variety of industrial process, involving conventional raw materials require high temperatures. Alkylorthosilicates such as polyethyldiorthosilicate(PEDS),tetraethylortothosilicate(TEOS) and tetramethyl orthosilicate (TMOS) are conventional precursors for synthesis of commercial silica (Wagh,*et al.*,1999). Another conventional silica precursor is sodium silicate which itself is manufactured by expensive process of melting quartz sand with sodium carbonate at 1300°C resulting in discharge liquid effluents and significant amount of carbon dioxide which is primary component of greenhouse gases (Zulfiqar,*etal.*,20150). Thus, efforts have been made in order to find economical way to extract silica from biomass waste materials.

Biomasses, particularly agricultural residues, are seemingly promising and sustainable source of silica and are getting great attention currently. Development of a simple low energy method to produce silica from RHA would be a feasible alternative to the current high energy method. Many methods have been developed to produce pure silica from rice husk ash in low cost. (Riveros and Garza, 1986) discussed the fact that, compared with other silica sources like sand, bentonite, and diatomaceous earth, rice husk has very small amounts of contaminants that affect performance in applications requiring high purity. (Jung, *etal,* 2013) also claims that rice husk has exclusive nanoporous silica layers, which have developed throughout years of natural evolution of the plant. Thus, producing silica from rice husk has several advantages, compared to conventional production methods. In addition to environmental and economic advantages, low-energy, simpler methods to obtain pure silica can create opportunities for the development of new industrial applications of RH.

Rice plant is one of the plants that absorbs silica from the soil and assimilates it into its structure during the growth. Rice husk is the outer covering of the grain of rice plant which is the by-product of the rice milling industries and a unique crop residue with uniform size and a high concentration of silica (Madrid,*etal.,* 2012). The high grade of silica in the husk opens a possibility for its potential.

The main components of RH are lignin, cellulose, and hemicellulose, which are generally named lignocellulose (about75-80wt%) and15to28wt% of silica (Madrid,*etal.,* 2012).Through thermal treatment (calcination), the ash obtained can be constituted with amorphous silica having potential application as legend in construction materials, catalyst support, metal adsorbent, and for extraction of silica and silica based materials. When rice husk is incinerated, it generates between 17-20% ash, made up of about 87-97% silica and other metallic oxide impurities depending on the source of the husk (Ugheoke and Mamet, 2012; Rungrodnimitchai, *etal.,* 2009).Thus, the high content of silica in RHA represents opportunities for the preparation of value-added silica materials.

End use of any material including wastes depends on its structure, properties and mainly on chemical composition. Chemical compositions of rice husk and rice husk ash vary from sample to sample. This variation may be due to differences in climatic and geographical conditions, as well as methods of treatment and combustion parameters. Thus, from the materials of varying properties, to make silica of predetermined qualities and close comprehension of the interaction of various parameters that go into the synthesis of silica is required to be investigated, in order to meet the desired product.

Applications and utilization of RH has been very limited because of their tough and abrasive nature, low nutritive value, and low bulk density (Madrid,*etal,* 2012).Therefore, RHs are often considered as a biowaste. In recent years environmental demand and sustainable development have become increasingly important. It is important to study and utilize RH biowaste, and convert into valued materials. In addition, utilization of RH biomass has no competition with food or other resources which offers an advantage over other biomasses for further development towards commercialization. Rice husk is therefore can be considered as economically potential source of silica.

## 1.2. Statement of the Problem

Rice husk is an agricultural residue that abundantly available in all over the world in large quantities as a major by-product of the rice processing industries. Sometimes rice husk is discharged and burnt in the agricultural field that can be used as a fuel for power plant. But, Rice husk is one of the richest sources of silica. This material needs to be recovered and utilize as source for industrial uses with its purity of silica.

In Ethiopia, rice husk has no commercial value except its traditional uses as a source of fuel mainly in rural areas and the most common methods of RH disposal is open field burning which could result in waste of energy, air pollution, and greenhouse gas. Sometimes it is also used as a food source but Rice husk is not recommended as cattle feed since its cellulose and other sugar contents are low (Ugheoke and Mamet,2012). Therefore, a more economically benefiting and energy efficient use for RH is needed. If utilized properly, RH could be a good candidate of feedstock for silica production because of its high silica content and large availability.

Conventionally, commercial silica is manufactured in a process which uses expensive raw materials that involves high temperatures and pressure, which is energy intensive and releases significant amount of carbon dioxide (Haus, Prinz, Priess, 2012).This makes such a process less efficient. Thus, the advancement of silica technology by recycling waste components can contribute energy savings in silica production in addition to utilizing the waste in to valuable product. But, Properties and characteristics of a material are closely related to that of the parent material and the methods and techniques of its production. This also applies to rice husk ash. Rice husk ash (RHA) is a material produced by the burning of rice husk either through open field burning or under incineration conditions in which temperature and duration is controlled. Open field burning is not encouraged because of pollution problems and it also produces poor quality rice husk ash, which has high carbon content which adversely affects the silica production and also can result in a structure of highly crystalline form that is of low reactivity (Hwang and Chandra, 2016).

Thus, the RHA with purity and in amorphous form which has the potential to be used for silica synthesis can be achieved through controlled incineration process (temperature and duration).And the major source of impurity for RH silica is the carbonaceous residue from the incomplete combustion of the organic components and

several metallic impurities present in the husk. Therefore, the treatment methods and incinerating conditions essentially control the quality of RHA, especially amorphous form, which is needed for high quality of silica extraction. In this study, laboratory studies on the chemical and thermal treatment of rice husk, in removal of metallic impurities from rice husk prior to pyrolysis stage are investigated in terms of the percentage purity of silica particles as well as their properties, aiming at studying and developing the appropriate conditions to achieve a good quality product.

The emphasis of this paper is to optimize the conditions for the preparation of good quality RHA, of which silica is then extracted, and to study its properties. Also, it overlooks the effective use of RH to valuable product, silica, and investigates the optimum factors that are used to produce good yield and quality of silica.

## 1.3. Objectives

### 1.3.1. General objectives

To optimize and characterize silica synthesized from rice husk

### 1.3.2. Specific objectives

- To prepare and characterize the rice husk ash and analyze the effects of the processing parameters on the properties of the ash
- To analyze the effect of acid treatment on percentage purity and impurity reduction prior to pyrolysis and its effect on the properties of rice husk ash.
- To synthesize silica
- To optimize and characterize the produced silica

## 1.4. Significance of the Study

This research has benefits to many stakeholders in the economy and the final goal of this research project can be considered from different perspectives. Ethiopia is an importer of silica and products based on silica compounds. The Ethiopian government spends a substantial amount of foreign currency on these silica based products. Hence by producing this product from locally available raw materials we can overcome this currency for our country.

Using this research private and public industries in Ethiopia can significantly play a role by reduce the environmental impact of the usually uncontrolled burning of the by-products by utilizing this biomass waste into a valuable production addition to reducing their foreign currencies by making their own production process.

In general, the significance of this study would

- Provide a means of potential utilization of the husk for producing value-added product
- Provide an alternative approach to synthesis silica at low cost from plant biomass waste (i.e. rice husk) which has a significant source of high purity silica, which is environmental friendly and energy efficient process
- Provide a technically and economically feasible option to produce silica, which will play a major role to substitute the imported silica that saves foreign currency and create job opportunity.
- Provide a good motivation for further research studies to conduct studies on the optimization of the process and different parameters that enhance the product.

# 2. LITERATURE REIVIEW

Silica, although having a simple formula of $SiO_2$, exists in different forms in nature. Each form of silica exhibits different physical and also chemical properties, existing in the form of gels, crystalline and amorphous forms. Silica gel is characterized by being chemically inert, high surface area (700-800$m^2$/g), and strong adsorption capacity, widely used as dehumidifying desiccant, dehydrating agent, adsorbents, fillers and catalyst carrier. It is also exist with other elements in the form of ores or minerals. Still for different applications silica is prepared by synthetic methods.

The $SiO_2$ structure is based upon a $SiO_4$ tetrahedron structure. Each silicon atom is bonded to four oxygen atoms and each oxygen atom in turn bonded to two silicon atoms(Londeree,2002).Two types of functional group: silanol groups (Si-O-H) and siloxane groups (Si-O-Si) are present on the silica surface. All the chemical processes and even the physical processes like adsorption takes place on the silanol sites, the siloxane sites on the surface being inert to most of the activities.

Silica has also been reported to be found in some dicotyledonous plankton husks or seeds like rice husk and foxtail millet. Porous amorphous silica has been found to contains isolated, germinal and vicinal as the three types of silanol bonds on its surface (Dijkstar, *etal.*,2002) Isolated silanol have been found to be the more reactive species. An increase in temperature makes the silica surface more hydrophobic. The surface hydroxyl groups condense and form siloxane bridges.

## 2.1. Sources of Silica Raw Materials

The primary source of the polymorphs of silica is quartz. Quartzite rocks are the most stable and relatively pure form that can be found in almost all mineralogical rocks. Thermal and chemical processing at higher temperature are required to make a pure or more suitable (e.g. more reactive or fine-grained) product. The secondary source of silica are, silicate esters, the best known being tetraethylortho silicate. It undergoes hydrolysis during sol-gel process however these precursors are limited to health hazard, environmental unfriendly and less cost effectiveness. Lately, biomass resources such as rice husk as a source of silica are being researched for several industrial applications.

Although synthetic silica is produced commercially, the ones produced from plant origins such as rice husks have been noted to have some significant advantages over

those from mineral and synthetic origins (Zemnukhova, *etal*, 2006). In particular, the processing steps are relatively simple, energy efficient and require no elaborate infrastructure or consumption of costly reagents as in the case of the synthetic processes and besides, it is environment friendly process. In addition, the final silica powder produced from plant sources contains a narrow range of metal oxide impurities (Zemnukhova, *etal*, 2006) which makes them remarkably desirable in applications where high purity silica at humble cost is a necessary requirement. Besides, most biomass resources are waste by-products whose disposal cause environmental nuisance. Hence, developing uses for these waste resources can also lead towards sustainable development.

Table 2-1: Silica purity from different biomass wastes

| Raw material | Purity of silica in the ash | Reference |
|---|---|---|
| Teff straw | 91.8% | Bageru,Srivastava,2017 |
| Palm | 46% | Faizul,Abdullah,2013 |
| Sugarcane | 81.6% | Ash, Alves, Vitoria etal.,2017 |
| Rice husk | 95.5% | Ghorbani etal.,2015 |

Rice Husk ash is one of the most silica rich raw materials containing high silica (after complete combustion) among the family of other agro-wastes.

## 2.2. Characteristics and availability of rice husks

Rice husk is a waste by-product of the rice milling industry. It constitutes about 20% the weight of a harvested rice paddy. The mineral ash content of rice husk ranges between 15-25% of which 87-97% is amorphous silica depending on the combustion technique and conditions employed (Shinohara and kohyama, 2004; Fang, *etal.*, 2004).

The rice plant has high amorphous silica content because it naturally absorbs silica from the soil and transports silicon in the form of soluble silicic acid, $Si(OH)_4$, to its outer surfaces. The silicic acid on reaching the outer surfaces of the rice plant becomes concentrated due to evaporation and is subsequently polymerized into silica cellulose

membrane (Bryat, *etal,* 2011). Because of this natural selectivity, the rice plant limits the uptake of heavy metallic elements that are found in large concentration in other cheap sources of silica such as quartz, bentonite and diatomaceous earth. A typical proximate analysis of rice husk is shown in below.

Table 2-2: Typical proximate analysis of rice husks by different researchers

Source (Fang et al., 2004; Mansaray and Ghaly, 2007)

| | |
|---|---|
| Moisture (%) | 6-11 |
| Ash (%) | 16 - 25 |
| Volatiles (%) | 51.10 - 65 |
| Fixed Carbon (%) | 10 - 12.7 |

## 2.3. Processing of Rice husk for Silica Production

### 2.3.1. Water washing

In order to obtain high quality amorphous silica from RH, proper pretreatment is needed. Water washing of raw RH to remove adhering soil, dust, and some metal cations was found to be one of the simplest pretreatments to obtain high quality RH silica (Wang,*etal,* 2011). Wang et al. used elemental analysis to show that the simple water rinse can effectively remove most minerals except for K and Ca in RH. Compared with raw RH, the water rinsed RH is beneficial for obtaining amorphous and high-purity silica (Wang, *etal.,* 2011; Shen, *etal.,*2011).

There are still metal impurities and carbonaceous residue remaining in the synthesized silica. In order to prepare even higher purity and more amorphous silica from RH, pretreatment of RH is needed (Wang, *etal,* 2011).

### 2.3.2. Pretreatment

Many efforts have been made to reduce metal and carbonaceous impurities to synthesize high quality RH silica. Certain minerals in RH, such as K and Ca, were found to be responsible for the residual carbon and crystallinity in the synthesized RH silica.

The RHA may contain several metallic impurities such as Fe, Mn, Na, Ca, K, that they can decrease the surface area and purity of the final silica. It has been suggested that the minerals in RH, particularly K, significantly affect the purity and amorphousness of RH

silica nanoparticles (Real, *etal.*, 1997). The negative effect of $K^+$ comes from the promotion of the melting of silica particles. The melting of silica lowers the silica surface area, and is responsible for the encapsulation of impurities, that result in crystallization of silica upon cooling (Wang,*etal*, 2011). The eutectic reaction between minerals and silica during the calcination of RH is responsible (Umeda,*etal.*, 2007). Thus, the removal of these metallic impurities can be the significant factor for preparing high-quality silica from RH.

Attempts have been made to use of microbial fermentation as a pre-treatment of rice husk in order to obtain silica (Sidheswaran and Bhat, 1996). But, the method is disadvantageous in that the time required for the fermentation process to complete is too long, making it unfeasible for practical applications.

Thus, in this study acid-pretreatment is used prior to calcination to effectively remove metal impurities and for partial hydrolyzation of the organic content from RH.

### 2.3.3. Pyrolysis of RH

This step consists thermal treatment of the rice husk to produce RHA of the desirable quality for silica extraction. The aim of this step is to increase the relative amount of silicon oxide by reduction of carbonaceous materials Present in the rice husk as well as to burn out other undesirable components present in the husk. In this step RHA silica is produced for pure silica extraction. Thus, a sufficient combustion temperature is needed to reduce or remove the organic substances in the husk.

Both pretreatment (to remove mineral impurities) and calcination condition (to remove carbonaceous materials) are critical for the synthesis of high purity silica.

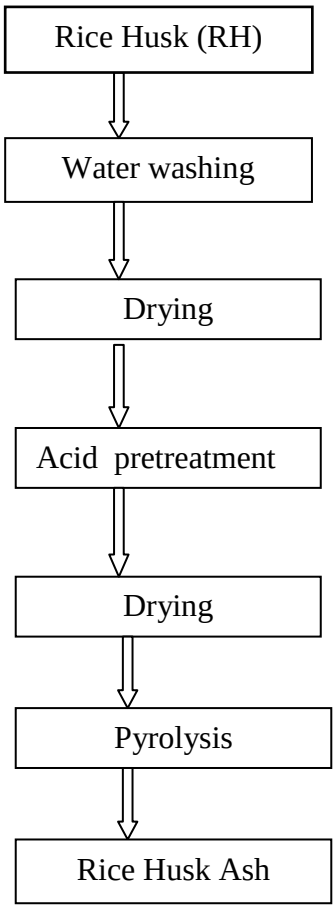


Figure 2-1: Schematic diagram of RHA preparation from RH

## 2.4. Pyrolysis conditions for the production of RHA

Two forms of silica can be formed during the combustion of rice husk process, an amorphous form, and a crystalline form. Amorphous silica of high purity, small particle size and high surface area has tremendous potentials in different chemical synthesis (Javed,*etal.,* 2009).

It is reported that burning rice husk below 700°C yielded amorphous ash and temperature greater than 800°C resulted in crystalline ash. The temperatures exceeding 700°C could also yield reactive amorphous ash, but the duration of incineration should be short (Bouzoubaa and Fournier, 2001; Bronzeoak, 2003 and Maeda *et al.,* 2001). Other investigators also concluded that the combustion environment also affects specific surface area of RHA. Therefore time and temperature must be carefully selected in the pyro processing of rice husks to ensure ash of maximum reactivity. Since then, many similar studies had been carried out, as shown in Table 2.1.

Table 2-3: Conditions of incineration for the production of RHA by different researches

| S/N | Authors | Findings | | Remarks |
|---|---|---|---|---|
| | | Temperature | Duration(time) | |
| 1979 | Mehta | > 500 °C | Prolonged periods | Amorphous silica is produced |
| | | 680 °C | Less than one minute | |
| 1984 | Khalaf&Yousif | 500 °C | 2 hr | Highly reactive RHA is produced |
| 1985 | Kapur | Above 900 °C | Not discussed | RHA cristobalite& a small amount of tridymite |
| 1986 | James & Rao | 400 °C-900 °C | 1-30 hours | Reactivity of ash depends mainly on temp. & duration has small effect. |
| 2001 | Maeda et al | Below 550 °C | Long enough to burn out fixed carbon | Quality of RHA is influenced by the incinerating temperature, and duration of incineration. |
| 2003 | Prased,Maiti, | 400-700<br>Above 900 | Not discussed<br>Not discussed | Amorphous ash<br>Crystalline silica formed |
| 2005 | Asavapisit&Ruengrit | 400-800 | One hour | 650 as optimum temp. for producing reactive RHA |
| 2008 | Nair *et al*. | 600-700 | Not discussed | Reactive amorphous silica is formed |
| 2009 | Syed,Tajwar,Javed,Zafar,Kazmi | 600-800 | Not discussed | Amorphous silica is formed |
| 2012 | Prasad, Panday | 500-600 | Not discussed | Amorphous silica |
| 2012 | Ugheoke, Mamat | Above 800 | Not discussed | Attained some degree of crystalline silica |
| 2016 | Hwang & Chandra | Temp. Exceeding 700 | Not discussed | Could also yield reactive amorphous silica but the duration of incineration should be short |

## 2.5. Properties and Characteristics of rice husk silica (RHA)

### 2.5.1. Color

One important property worthy of mentioning is the color of the silica produced at the end of each process. Color changes are associated with the completeness of combustion process as well as structural transformation of silica in the ash. When rice husk is incinerated, white rice husk ash (WRHA) and carbonized rice husk (CRH) can result depending on whether the combustion is complete or incomplete (Ugheoke, Mamet, 2012).

Ash in white color is an indication of complete oxidation of the carbon, which is also an indication of availability of large portion of amorphous silica in the ash and black coloration is due to the unburnt carbon remain within the product.(Chandrasekhar,*etal.*,2006**)** did extensive studies on the optical properties of rice husk silica processed using different pre-treatment methods and concluded that in the processes where there has been substantial leaching of the alkali metal oxides, especially the oxide of potassium, the brightness and whiteness increases. This is due to the fact that when the husk is not substantially treated, the alkali oxides enhance the surface melting of silica, thereby entrapping carbon within the silica; the more residual carbon entrapped, the darker the color of the husk is.

At high temperature, strong interaction between potassium and silica ions cause the formation of potassium poly silicate combined with carbon resulting in grey color ash (Bronzeoak, 2003). If the husk is pretreated, a major portion of its potassium will be removed due to which ash will not attain grey color. Higher temperature along with prolonged burning will result in ash with lilac pink color, representative of silica in crystalline form such as cristobalite and tridymite.

### 2.5.2. Structure

Determination of amorphous silica in RHA uses different methods and conditions of production of RHA result in silica with different quality, structure, and surface morphology. Therefore, in order to attain the desired quality of silica, it is essential to identify the most suitable production conditions. The silica in the ash undergoes structural transformations depending on the combustion conditions. The crystalline and amorphous forms of silica have different properties and it is important to produce ash with correct specifications for specific end use.

The Dictionary of Composite Materials Technology (S.M.Lee, 2010) defines amorphous silica as a naturally occurring or synthetically produced oxide of silicon characterized by the absence of a pronounced crystalline structure and whose X-ray diffraction patterns have no sharp peaks. (Pettifer et al., 1988) states that crystalline samples are characterized by well-defined bond angles which are reflected in narrow NMR resonances, whereas amorphous samples are characterized by distributions in bond angles in general leading to broad Gaussian line shapes.

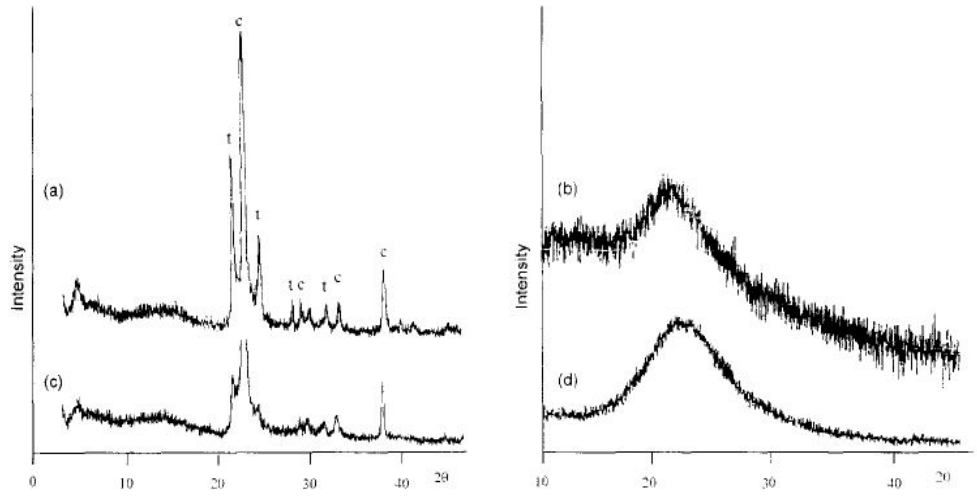



Figure 2-2: X-ray diffractograms of rice husk silica
(Hamdan,*etal.,* 1997)

Therefore, to obtain RHA of maximum reactivity (amorphousness and high porosity), time and temperature must be carefully selected in the processing of rice husks.

### 2.5.3. Surface Area

The surface area and pore volume of rice husk silica is dependent on the processing temperature, since this affects the surface melting of the silica due to the presence of alkali metal oxides. Different values of surface area and pore volume have been reported by Liou (2004); an initial increase in the surface area from 60 $m^2$/g to 80 $m^2$/g when the husk was incinerated at 350°Cand 600°C respectively. This increase was perhaps due to the burn-off of the residual carbon and the opening of new pores. Silica gel is often described as moisture absorbing. Its high specific surface area allows absorbing water readily, making it useful as a desiccant (drying agent).A typical good quality adsorbent silica gel has a surface area of 200-800 $m^2$/gm (Hafiz, Arshad, Abdul, 2009).

### 2.5.4. Morphology

It is a generally investigated from different researcher groups that silica which is formed by incinerating rice husk at controlled parameter can give in its amorphous form. It seems that particles of silica in rice husk ash are agglomerates of small nano range particles. Thus, it is very common to find aggregates of silica forming fine globules or platelets of varied sizes. Ugheoke, Mamet, 2012 found that the natural form in which it occurs in the husk is already nano silica whose size distribution is in the nano-range, which is less than 100 nm.

## 2.6. Chemical composition of rice husk ash

### 2.6.1. Loss on Ignition (LOI)

The difference in the mass of the sample before and after heating is referred as the "loss on ignition" (LOI). RHA contains some un-burnt components as well as inert components of the husks. The un-burnt component is predominantly carbon. The LOI value is the same as that of the carbon content of the ash. The percentage of carbon in RHA varies according to the production conditions (Javed,*etal,* 2009). Properly produced RHA appears to result in maximum carbon content in the range of 5-7 % (Bronzeoak, 2003).

### 2.6.2. Oxide composition

High silica content and low levels of elemental impurities are necessary pre-requisites for synthesis of high purity silica from RHA. The chemical composition of RH has been found to vary from sample to sample. Any of the differences in type of paddy, crop year, climatic and geographical conditions, soil chemistry, sample preparation, or production methods could be a reason for this variation (Rafiee, *etal,* 2012).The main oxides present in the RHA and the lost on ignition (LOI) value are summarized from literatures in the table below.

Table 2-4: Compositional analysis of rice husk ash

Source (Rhaman, Haque, Rouf, 2015)

| Constituents | Mass fraction (%) |
|---|---|
| Silica ($SiO_2$) | 80 – 90 |
| Alumina ($Al_2O_3$) | 1 – 2.5 |
| Ferric oxide ($Fe_2O_3$) | 0.42 - 0.54 |
| Calcium oxide (CaO) | 1 – 2 |
| Magnesium oxide (MgO) | 0.5 – 2.0 |
| Sodium oxide ($Na_2O$) | 0.2 – 0.5 |
| Potash | 0.58-2.5 |
| Titanium dioxide ($TiO_2$) | Nil |
| Loss on Ignition | 10 – 20 |

## 2.7. Production of Silica

### 2.7.1. Production of silica by Commercial method

The silica gel is normally prepared from commercially available sodium silicate. The sodium silicate is manufactured by smelting quartz sand with sodium carbonate at about 1500°C (Iler 1979; Brinker and Scherer 1990). The process is expensive and energy intensive due to its high temperature requirement and generates significant volumes of effluents and greenhouse gases (Haus, Prinz, Priess, 2012).On the contrary, sodium silicate can be prepared at lower temperature from the RHA, which can be considered as a cheap source for the extraction of silica. Thus, RHA can be used as an economic raw material for the production of silica.

### 2.7.2. Production of Silica from Rice Husk Ash by innovative methods

The advantage of using this proposed process is, it uses biomass waste (RH) as a raw material and its high silica content in the ash. In this process, silica is manufactured by using rice husk ash as a source of silicate or silica and this ash is then reacted with sodium hydroxide which yields the sodium silicate solution, which on further reaction with hydrochloric acid gives silica along with by-product of sodium chloride.

The basic steps in the production (extraction) of silica from RHA are;

1. Dissolution of silica in caustic soda as sodium silicate ($Na_2SiO_3$) from the RHA

$SiO_2 + 2NaOH \xrightarrow{80\text{-}90^oC} Na_2SiO_3 + H2O$ ..... (2.1)

(Ash) (Caustic Soda) (Sodium silicate)

2. Silica is precipitated from sodium silicate solution using HCl

$Na_2SiO_3 + 2HCl \xrightarrow{\text{room temp.}} SiO_2 + 2NaCl + H_2O$..... (2.2)

(Sodium Silicate) (Hydrochloric acid) (Silica) (Sodium Chloride)

3. Filtration and drying of the final product (pure silica)

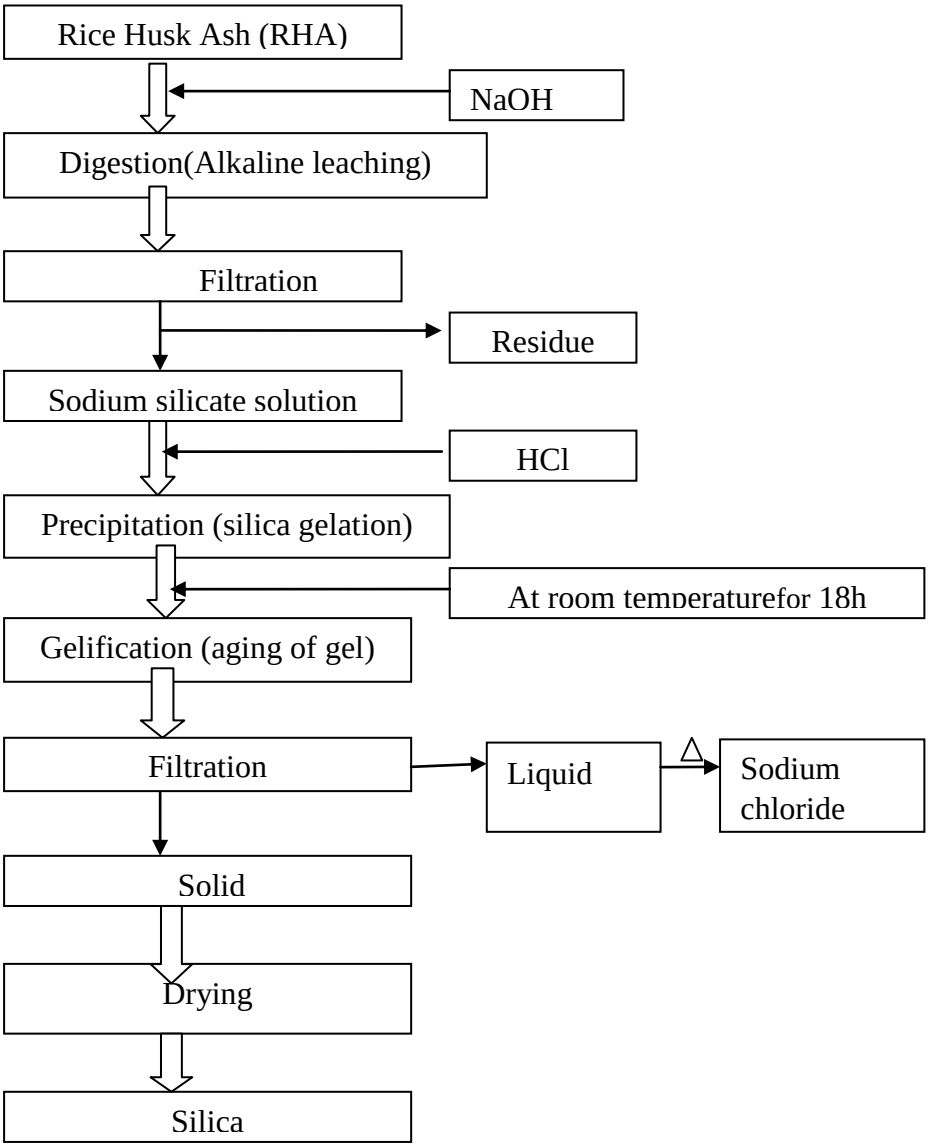



Figure 2-3: Schematic diagram of Silica synthesis from RHA

### 2.7.3. Process Description

The initial step is extraction of silica from the rice husk ash as sodium silicate solution using caustic soda. A viscous, transparent, colorless sodium silicate solution is obtained after filtration of the reacted slurry (consisting of residue digested ash, sodium silicate, water and free sodium hydroxide). In the second step, silica is precipitated from the solution of sodium silicate by drop wise addition of hydrochloric acid. The silica (wet impure silica) obtained is then filtered. Purification of this silica for removal of chloride impurities constitutes the third step of this process. For this, successive distilled water washings are given in the filter process itself. Silica after removal of chlorides (wet silica) is then dried to obtain the gel form in the final step of the process.

## 2.8. Factors affecting the quality of RHA and Silica

### 2.8.1. Effect of burning process

Rice husk ash (RHA) is a material produced by the burning of rice husk either through open field burning (uncontrolled burning) or under incineration conditions in which temperature and duration are controlled. Open field burning is not encouraged because of pollution problems and it also produces poor quality rice husk ash which can result in a structure of highly crystalline form that is of low reactivity (Hwang and Chandra, 2016). Thus, to obtain the RHA with the desire quality, the incineration conditions (temperature and time) should be controlled.

### 2.8.2. Effect of combustion temperature and time

The rice husk ash is a highly siliceous material that can be used for synthesis of pure silica if the rice husk is burnt in a specific manner. On burning rice husk, ash containing a very high percentage of crystalline silica can be formed. This crystallization is a disadvantage towards the preparation of silicon-based materials because the silica ash is rendered inactive in its crystalline form. However, if RH is burnt under controlled conditions, highly reactive amorphous silica can be produced. Therefore, Burning temperature and time are the two important factors to define whether silica remains amorphous, as in RHA, or become crystalline.

### 2.8.3. Pre-treatment Effects

The metallic ingredients have a significant effect on the quality of silica from RH, which is mainly potassium that causes surface melting and accelerates the crystallization of amorphous silica and carbon fixation in RHA. Also, a strong

interaction occurs between the metallic ions and silica which leads to a considerable decrease in the surface area. Chandrasekhar,*etal*, 2006 reported that oxides, especially $K_2O$, impart black color on the particles. Some explanations to support this phenomenon, there exists a strong interaction between oxides, especially those of potassium and sodium, contained in rice husk and the silica therein, can result in the surface melting of $SiO_2$ particles and accelerate an early crystallisation of amorphous $SiO_2$ into cristobalite, as implied by research results (Real,Alcala and craid,1996).Thus, it is necessary to use some pre-treatment methods, to reduce or remove metallic impurities in order to enhance the characteristics of the produced rice husk ash and increase the chances of obtaining silica with a good yield and purity as well as its surface area.

## 2.9. Potential and current uses of rice husk ash and amorphous silica

Two main uses have been identified, as an insulator in the steel industry and as a pozzolans in the cement industry and mainly in the production of silica.

RHA has uses of

- In the manufacture of silicon chips.
- Because of its insulating properties it has been used in the manufacturing of bricks and in insulating boards.

Silica gel (Amorphous silica) is also used for

- Silica gel is commonly used as a desiccant, due to the ability to absorb moisture from the air. It is used to dry the air in industrial compressed air systems and may also be used to keep the relative humidity (RH) inside a high frequency radio or satellite transmission system waveguide as low as possible
- Silica gel is used in chromatography as a stationary phase
- Silica has been used in the manufacture of chips, telescope glasses and optical fibers
- Microelectronic devices mainly in semiconductors because of its high mechanical resistance and high dielectric strength
- As catalyst and catalyst support
- Silica has been used in food additive as anticaking agent, defoaming agent, stabilizer, adsorbent, conditioning agent, emulsifying agent and viscosity control agent because of its hygroscopic nature
- Silica is also used in the extraction of DNA and RNA due to its ability to bind to the nucleic acids.

## 2.10. Summary of literature review (Concluding Remarks)

Studies have been explored for significant source of high purity silica and an alternative approach to synthesis of low cost silica from rice husk, a plant biomass. However, it may be concern with the production and application of RHA there are gaps in regard to the optimization conditions and its relationship with the properties of the final RHA. In these instances in producing high reactive and pure silica, process parameters or conditions need to be focused as vital. Thus, in order to get the desired quality of the product and obtain an amorphous structure, there also need to be optimization for processing conditions.

Incinerating conditions (both temperature and time) essentially control the quality of ash, which may result either in crystalline form or amorphous form. Climatic conditions and fineness, can also affect the ash properties, but not significantly. Some studies revealed that, RHA produced below 700ºC would be in amorphous form and above 800ºC would result in crystalline form. Further, most of the research attempts have concluded that lower the temperature range (400 to 800°C) longer will be the incineration time or higher the temperature range (exceeding 800ºC) shorter will be the incineration time. It can be seen from Table 2.3, conditions of incineration for the production of RHA by different research groups that, no clear fixed temperature tied with its duration has been established and there is no conclusive finding with regard to the exact temperature limit and duration of incineration that initiate the formation of silica crystals in rice husk ash or that can result on high percentage of silica. The level of impurities in rice husk was also found to affect significantly the purity of the product. However, there is no proper study on the combination effect of temperature, time, and acid pretreatment (acid concentration) on the properties, amorphousness and percentage purity of silica in the RHA and mainly the final product, silica.

Properties and characteristics of a material are closely related to that of the parent material and the methods and techniques of its production. Here, Synthesis of pure silica from RHA depends greatly on the quality of the ash (i.e. the parameters that affect the quality of RHA directly affects the yield and quality of the final product, silica). It can be seen from a review of the relevant literature that, almost all the physicochemical and purity of the products are highly influenced by combustion (incineration) conditions and the purification of alkali metals which otherwise melt during the burning process

and cause sensitivity towards the burning temperature. Thus, the reactivity and purity of silica in rice husk ash is dependent on the complex and interlinked factors of temperature, duration of incineration as well as the removal or reduction of metallic impurities (acid treatment). However, there are no exhaustive studies on the combined effect of those parameters and optimization conditions for the production of high percentage silica rice husk ash. A comprehensive study on RHA produced under various combinations of temperature and duration, in relation to their reactivity and purity has to be performed; these include characterization using various physical methods, chemical methods, and instrumental techniques. It is also relevant to establish optimum production conditions. Further, the quality of the ash has to be verified in association with the yield and purity of silica production.

# 3. MATERIALS AND METHODS

## 3.1. Materials

The major raw materials used during the experimental work were rice husk, sodium hydroxide, hydrochloric acid and ammonium hydroxide (Ammonia) solution. Rice husk was acquired from Wereta, Amhara region and all the other chemicals were analytical reagent grade and bought from different chemical stores in Addis Ababa.

## 3.2. Equipment

Reflux condenser, tubular furnace, oven, analytical balance, PH meter, sieve, crucibles, spatula, mortar pestle, stirrer, litmus paper(universal indicator), aluminum foil, different size of beakers, burette, filter paper, stirring rods, micropipettes, different size of conical, Erlenmeyer and round bottom flasks, measuring cylinder, Air permeability Blaine meter, Atomic Absorption Spectroscopy(AAS), FTIR spectroscopy and X-ray Diffractometer (XRD).

The experimental work Preparation of the raw material and its characterization such as moisture content, ash content and volatile matter was done at School of Chemical and Bio Engineering Laboratory, AAiT. Production of silica gel and analysis of the reaction mixture was also conducted at School of Chemical and Bio Engineering Laboratory. The other characterization of the ash and silica such as FTIR, XRD analysis were done at faculty of natural science department of chemistry, Arat Kilo and AAS analysis of the ash and the produced silica was done at Geological survey of Ethiopia, Geochemical laboratory.

## 3.3. Experimental frame work

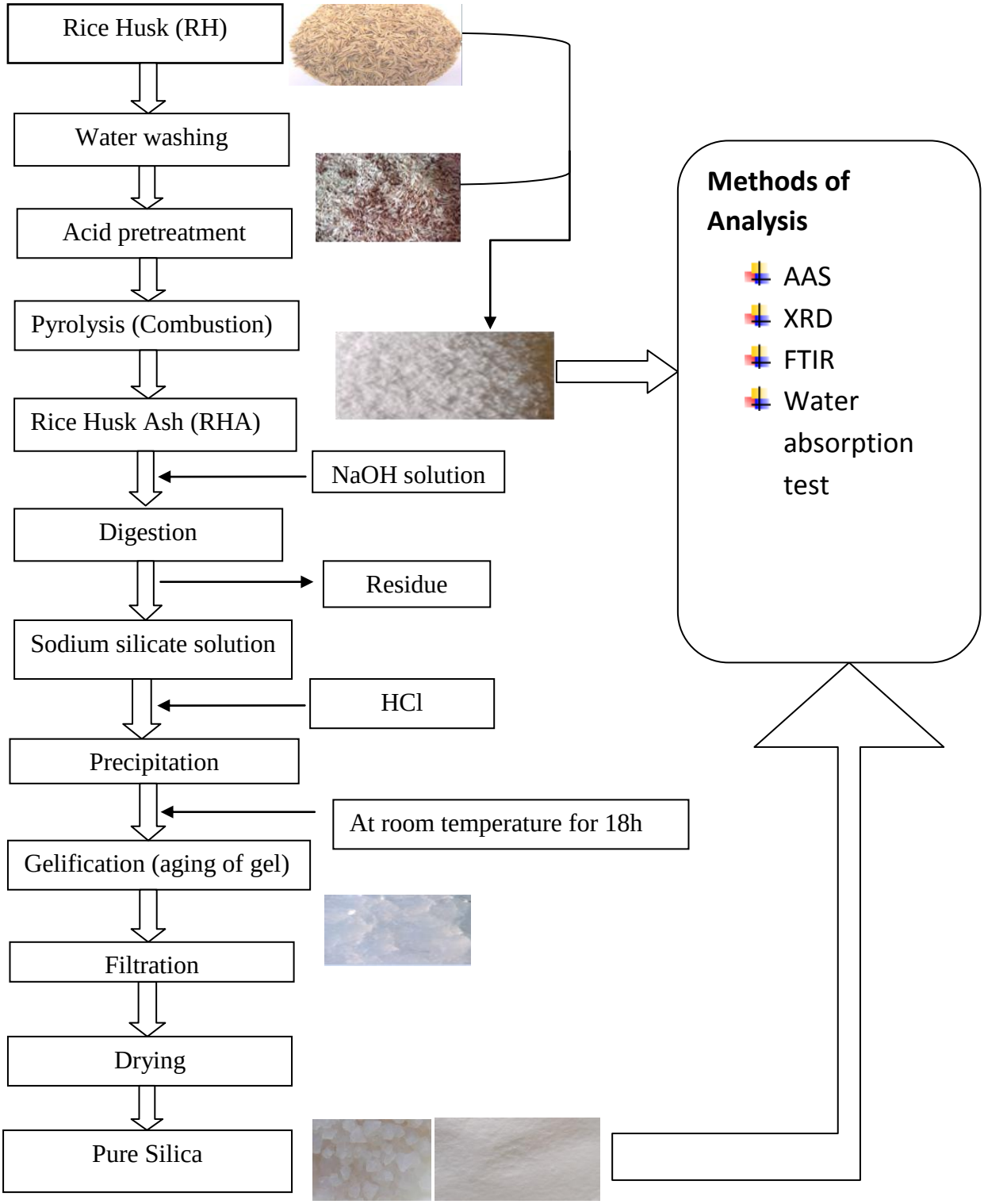



Figure 3-1: Scheme of experimental work

## 3.4. Experimental Method

### 3.4.1. Water Washing

RH was washed thoroughly with water to remove the soluble particles, dust, dirt and other sand particles present in the husk. It was then drained of any water and dried in oven at 90°C for 16 h.

### 3.4.2. Acid Pretreatment

The acid treatment was carried out with HCl solution in different concentrations with S/L (wt.) ratio of 1:10 to remove soluble elemental and metallic impurities and partial hydrolyzation of the organic content of the rice husk prior to combustion.

50g of dried WWRH and 500 ml of 1N HCl solution were mixed in a round bottom flask and heated using a reflux condenser at a temperature of 90°C for 2hr**.**The solids, after separation by settling and filtration, were washed repeatedly with distilled water, to remove the acid retained, and then dried at 90ºC for 12h. The rice husk obtained was light weight.

### 3.4.3. Rice husk Pyrolysis

RH was thermally treated to reduce the carbonaceous matter and organic substances in the husk and increase the percentage of active silica under controlled conditions. Three-parameters were applied to pyrolysis step of the experimentation. The thermal treatments for silica production and optimization were conducted in a randomized design using Design expert® 7 software. The factors for pyrolysis were incineration temperature (450 to 850 $^{o}$C), time (1 to 5 hr) and acid concentration (1 to 2N).

A considerable amount of acid washed rice husk was taken in a crucible and put in a furnace. The sample was kept in the furnace at the given temperature and time obtained from randomized design using Design expert® 7 software. The crucibles were then removed using tongs and cooled inside desiccators for 1 hr. This procedure was done for both the WWRH and ATRH to see the reduction of metallic impurities and purity of silica.

(a) (b) (c)

Figure 3-2: (a) raw rice husk, (b) Acid treated rice husk, (c) RH after combustion (RHA)

### 3.4.4. Production of Silica

Silica was produced from RHA using alkaline extraction method and sol-gel technique. This can be divided into:

**i. Digestion**

This involves the digestion of the rice husk ash with caustic with S/L (wt. %) ratio of 1:10 at specific conditions. In this process the silica in the ash gets extracted with caustic to form sodium silicate solution. After the completion of the digestion the solution is filtered to remove the non-reactive impurities and carbon residues for the residual undigested ash present in the solution and the clear filtrate was taken for precipitation.

RHA of 5.00 g were added to50ml of 2.5M NaOH and mixed thoroughly by using glass rod and then heated at 90℃ for 2hrunder vigorous stirring to dissolve silica and produce sodium silicate. Silica content of the RHA leached out to the aqueous phase in the form of soluble sodium silicate according to the following reaction.

$$SiO_2\ (Ash) + 2NaOH \longrightarrow Na_2SiO_3 + H_2O \quad \text{..... (3.1)}$$

The solution was cooled down and filtered using filter paper. The filtration process was repeated several times to obtain a clear and colorless solution. The filtrate contains the sodium silicate solution which was further used to obtain silica.

**ii. Precipitation (silica Gel preparation)**

This step involves precipitation of silica from the sodium silicate solution with acid. The silica gel is obtained by sol–gel process. The sol is prepared by a silica source solution and gelation is occurred by the addition of a catalyst.

The filtrate, a sodium silicate solution, were allowed to cool to room temperature and then slowly titrated with 1N HCl, which precipitated the dissolved silicate in the form of white gelatinous solid ($SiO_2$) with constant stirring, silica gels started to form when the PH decreased below 10, and continue by adding of HCl drop wise until the PH of the solution reaches 7, after which no further precipitate is formed.

The precipitation using HCl occurred according to the following reaction;

$$Na_2SiO_3 + 2HCl \longrightarrow SiO_2 + 2NaCl + H_2O \quad \text{..... (3.2)}$$

**iii. Aging of the gel**

The gel prepared in the above step is aged in its mother solution. When the gel is formed from the sol, it was aged for 18h at room temperature. The gels were then filtered using vacuum filter and washed repeatedly by distilled water to remove solute salts to wash off any NaCl formed due to the acid base side reaction.

**iv. Drying of the silica gel**

The solid left on the filter paper in the form of gels (silica gel) is the pure silica which was dried in an oven at 80℃ for 12h, this yields very pure silica. The solids were then ground in to powder using mortal pestle and stored in airtight plastic bag sampling bottles for further analysis and characterization. This process was followed for sodium silicate solution obtained from all the rice husk ash at various temperatures and times of pyrolysis. At final, the yield (percentage conversion) of the extracted silica was calculated using the equation given below:

$$\text{silica extraction yield}(\%) = \frac{\text{mass of produced silica}}{\text{mass of rice husk ash}} \times 100 \quad \text{..... (3.3)}$$

(a) (b) (c)

Figure 3-3: (a) Precipitated and filtered wet silica, (b) Dried silica gel, (c) Silica powder

## 3.5. Characterization Method

### 3.5.1. Characterization of rice husk

The proximate analysis of the raw rice husk (moisture content, volatile matter, fixed carbon and ash content) was determined and The measurement was done three times and the average were taken to increase the accuracy.

#### i. Moisture content

The raw water washed rice husk was put into crucible. The crucible was weighed with and without the amount of rice husk. The crucible with rice husk was dried in an oven at 105°C for 16h. The sample was removed, cool and re-weighed till constant weight is obtained. Finally, the weight was taken and compared with the initially recorded weight. The percentage weight in the husk was calculated using the formula:

$$\text{Moisture, \%} = \frac{W1-W2}{W1} * 100 \quad \text{..... (3.4)}$$

Where: W1=Weight of sample before drying (g); W2=Weight of sample after drying (g)

#### ii. Volatile matter

The muffle furnace was heated until it reaches to a temperature of 900℃andthe crucible and its cover was weighed with and without the amount of rice husk. Then, the samples were heated at 900 °C in a closed crucible for 7 minutes. The crucible were then cooled in desiccators and weighed. The weight of the sample before heating and after heating was used to determine the amount of volatile matter present in the sample. The percentage of volatile matter in the sample was calculated using the formula:

$$\text{Volatile matter, \%} = \frac{W1-W2}{W1} \quad \text{..... (3.5)}$$

Where:$W_1$=Weight of sample before heating (g); $W_2$=Weight of sample after heating (g)

#### iii. Ash Content

The muffle furnace was heated until it reaches to a temperature of 650℃. The crucible was weighed with and without the amount of rice husk. The sample was heated at 650°C in an open crucible for3 hours in a furnace. The crucible was then put in to desiccators for 1 hour to cool to room temperature and then weighed. The weight of the sample before heating and after heating was used to determine the amount of ash content present in the sample. The percentage of ash in the sample was calculated using the formula:

Ash Content, % = $\frac{W2}{W1} * 100$ ..... (3.6)

Where:W1=Weight of sample before heating (g); W2=Weight of sample after heating (ash) (g)

**iv. Fixed carbon content**

The fixed carbon content is determined by subtracting the sum of volatile matter content and ash content form 100. The value obtained is the amount of fixed carbon present in the sample expressed in percentage. The percentage of fixed carbon content in the sample was calculated using the formula:

Fixed carbon (%) = 100-(moisture% + ash% + volatile matter %) ..... (3.7)

### 3.5.2. Characterization of rice husk ash and silica

***Atomic Absorption Spectrophotometer (AAS)***

In this study atomic absorption spectrophotometer were used to characterize the chemical constituents (Major and Minor oxides) of rice husk ash as well as the extracted silica. The potential application of atomic absorption principle is to determine metallic constituents of silicate materials. $LiBO_2$ FUSION, HFattack, gravimetric, colorimetric and AAS analytical method was used in order to assess its chemical composition. The full Chemical analysis of the samples (as reported by Geological Survey of Ethiopia) is attached in the appendix section of this study.

***Fourier Transform Infrared Spectroscopy***

The FTIR spectra were recorded for qualitative characterization of surface functional groups present in RHA and the extracted silica. The infrared spectrum was recorded by passing a beam of infrared light through the sample. The FTIR spectra were recorded on spectrum 65 FT-IR (PerkinElmer) using KBr pellets. Wave number range from 4000-400 $cm^{-1}$ was used at a resolution of $4cm^{-1}$. All the spectra were recorded and processed using FTIR software.

***X-ray Diffraction (XRD)***

The phase nature of RHA and the silica extracted from the RHA was conducted using MiniFlex 300/600 +, 150at 40 kV and a current of 15 mA with Cuk*a* radiation (1.54059-1.54441). The samples were placed on a sample holder made up of silicon

wafer and the measurements were taken continuously at $2\theta$angles. The resultant intensity data was processed by using the diffraction software.

***Air Blaine permeability meter***

The surface area of silica was investigated in chemical Engineering Laboratory, Addis Ababa Institute of technology using Blaine air permeability testing apparatus shown in Appendix Fig.C11.And the procedures and measurements were done according to the laboratory manual (ASTM,C204) used to determine the specific surface area. It is measured by recording the time taken for a fixed quantity of air to flow through a compacted silica bed of specified dimensions and porosity under standard conditions. The specific surface of silica is proportional to √T where *T* is the time for a given quantity of air to flow through the compacted silica bed. The apparatus used in this research is calibrated using a standard sample (commercial silica), which of its specific surface area (SS) is 800$m^2$/g (Wikipedia, 2008).

Finally, the specific surface area of the extracted silica is calculated using the formula;

$$S = \frac{Ss\sqrt{T}}{\sqrt{Ts}} \quad \text{(ASTM, C204)} \qquad (3.8)$$

Where: S = Specific surface area of the test sample (Silica) ; Ss = Specific surface area of the standard sample used in calibration of the apparatus (commercial silica) = 800$m^2$/g ; T = measured time interval, s, of manometer drop for test sample (extracted silica), (Seconds); Ts = measured time interval, s, of manometer drop for standard sample (commercial silica) used in calibration of the apparatus (Seconds).

***Water (moisture absorption) Ability***

The moisture adsorption capacity is one of the most important properties of a silica gel as desiccant.10g of dried silica gel in a small container was placed in desiccators, the atmosphere of which was saturated with moisture by placing 100ml of water in a beaker inside. The change of weight of silica gel was recorded. This is calculated in terms of its percentage absorptive capacity using the formula:

$$\text{Moisture absorptive capacity} = \frac{\text{increase in wt.due to moist air absorbed}}{\text{wt.of sample}} \qquad (3.9)$$

## 3.6. Experimental Design for Silica Production

In this work high purity of silica was produced from the rice husk ash. Experimental data analysis was done using Design- Expert software to determine the effect of the three operating incineration process variables (temperature, time and concentration of acid pretreatment) in the properties of the ash as well as quality of the extracted silica from the RHA.

The experimental design selected for this study was response surface methodology, three-level-three-factor Box-Behnken Design (BHD) and the dependent variable used as a response parameter was the percentage yield of silica. Three-level-three-factor BHD was used in the optimization study which requires 17 experiments to be conducted. All experiments were done and the data was statistically analyzed using Design-Expert Software to obtain a suitable model equation for the percentage conversion of the extracted silica as a function of the process variables and the operating variables interaction effect was analyzed to obtain maximum percentage of silica. Table 3.1 lists the range of the three operating variables studied. The lower and higher levels are chosen from literatures (previous study) and selected by considering the operating limits of the incineration process conditions.

Table 3-1: Minimum and Maximum values of parameters

| Factors | Unit | Minimum | Maximum |
|---|---|---|---|
| Incineration temperature | °C | 450 | 850 |
| Incineration time | hr | 1 | 5 |
| Acid concentration | N | 1 | 2 |

Below in Table 3.2 the complete experimental design matrix of BBD for the factorial design was shown. The order in which the runs were made was randomized to minimize systematic errors.

Table 3-2: the complete experimental design matrix

| Run | Actual Factors | | |
|---|---|---|---|
| | Acid Conc.(%) | Temperature(℃) | Time(hr) |
| 14 | 1 | 450 | 3 |
| 1 | 2 | 450 | 3 |
| 13 | 1 | 850 | 3 |
| 10 | 2 | 850 | 3 |
| 2 | 1 | 650 | 1 |
| 11 | 2 | 650 | 1 |
| 8 | 1 | 650 | 5 |
| 7 | 2 | 650 | 5 |
| 5 | 1.5 | 450 | 1 |
| 6 | 1.5 | 850 | 1 |
| 17 | 1.5 | 450 | 5 |
| 12 | 1.5 | 850 | 5 |
| 9 | 1.5 | 650 | 3 |
| 16 | 1.5 | 650 | 3 |
| 3 | 1.5 | 650 | 3 |
| 4 | 1.5 | 650 | 3 |
| 15 | 1.5 | 650 | 3 |

# 4. RESULTS AND DISCUSSIONS

## 4.1. Characterization of rice husk

### 4.1.1. Proximate analysis of RH

The proximate analysis of the raw rice husk was shown in Figure 4-1 below. Those proximate analysis results are typically among the primary parameters used for assessing the quality of a solid material. Moisture content, ash content, volatile matter and fixed carbon content of the RH was 8.7, 29.67, 59.6 and 2.03% respectively. The rice husk has a relatively high volatile matter and ash content, and low moisture and fixed carbon content. These values are much within the range reported in the literature (Mansaray and Ghaly, 2007; Fang etal, 2004) except the high ash content and very low fixed carbon is obtained in this work which is highly effective and this favors high silica yield. Studies conducted by (Amick, 1982) concluded that high amount of ash can be produced depending on the variety, climate and geographical location of the rice husk. And this could be the reason for the variations in some of the reported values by different researchers. And also this variation can be due to the methods and techniques used in the processing, handling, and storage of the biomass.

The rice husk has a moisture content of about 8.7%, which is a well-tolerated value for production of ashes. The moisture content of rice husk substantially affects its quality during pyrolysis(combustion).An increase in moisture content of the rice husk can decrease its heating value, which in turn, reduces the conversion efficiency and performance of the system because a large amount of energy would be used for vaporization of the moisture during combustion.

The volatile matter content is also important because it characterizes the expected contamination of the product gas with condensable vapors. the volatiles burn as a gas products whereas the fixed carbon burns slowly (Mansaray and Ghaly,2007).And because of its high volatile content, RH is more readily devolatilized, thus yielding considerably less fixed carbon residue, which enhances(increases) the formation of silica in the ash and less heat is required for reactions during the pyrolysis process. Therefore the volatile content has a great influence on the combustion process.

The ash content of RH is well and very high compared to other biomass, 3-5% for wheat straw (Ghaly and Al-Taweel, 1990). Previous studies suggested that ash suitable for silica production should below in carbon but rich in ash and volatiles because the ash consists of large amount of silica with high purity under appropriate conditions. So, the high ash content would result in high percentage yield of silica. Therefore from the above results we can conclude that, the fixed carbon and ash content of the analyzed rice husk favors silica production.

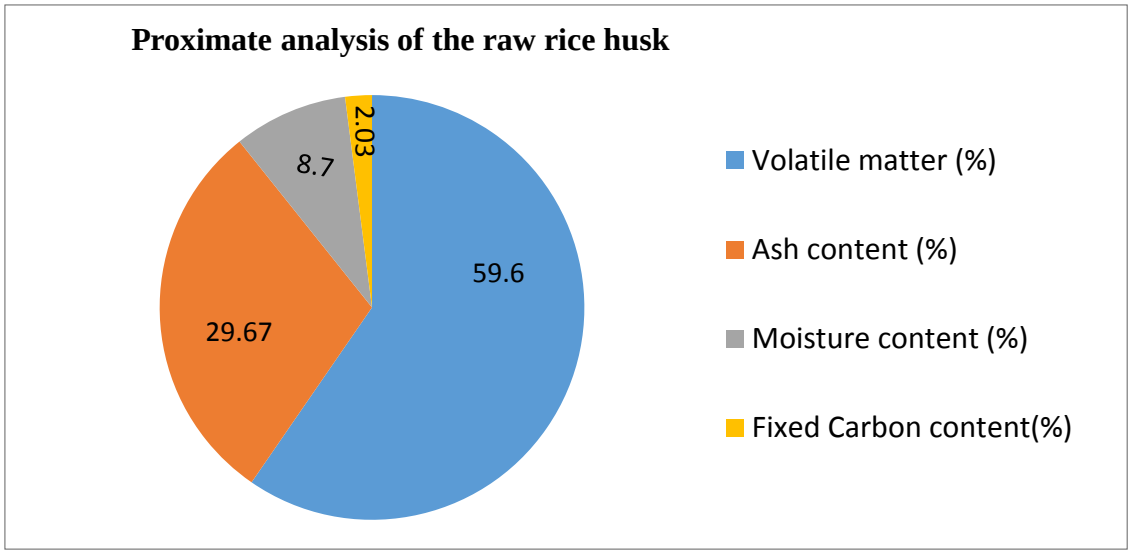



Figure 4-1: Proximate analysis of rice husk

## 4.2. Characterization of RHA

### 4.2.1. Visual Inspection of RHA after Combustion

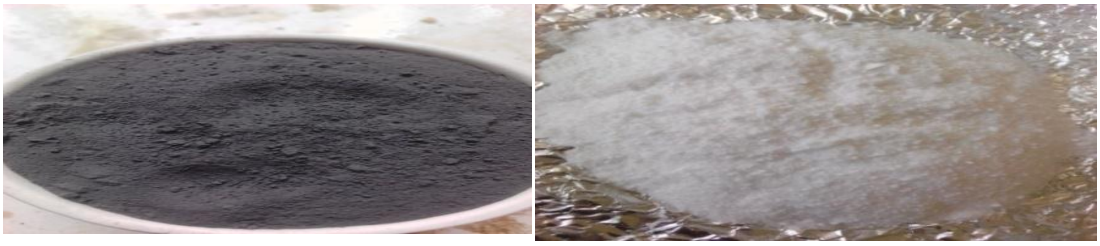
The RH powder was pyrolyzed under different conditions, including varying of pretreatment concentration of the husk before combustion, combustion temperature and time. Different color changes were observed and the results are shown in the table below (Table 4.1)

Table 4-1: Combustion temperature and time for rice husk ash (RHA)

| Run | Acid Conc.(N) | Combustion Temperature (°C) | Combustion time(h) | Observation |
|---|---|---|---|---|
| 1 | 1.5 | 450 | 1 |  |
| 2 | 1 | 450 | 3 |  |
| 3 | 2 | 450 | 3 |  |
| 4 | 1.5 | 450 | 5 |  |
| 5 | 1 | 650 | 1 |  |
| 6 | 2 | 650 | 1 |  |
| 7 | 1.5 | 650 | 3 |  |
| 8 | 1 | 650 | 5 |  |
| 9 | 2 | 650 | 5 |  |
| 10 | 1.5 | 850 | 1 |  |
| 11 | 1 | 850 | 3 |  |
| 12 | 2 | 850 | 3 |  |
| 13 | 1.5 | 850 | 5 |  |

One important property worthy of mentioning is the color of the RHA produced after incineration process. Color is one of the primary physical characteristics of RHA and its properties, and can describe the purity of silica in the ash. From the Fig below we can see the color change between the treated and non-treated rice husk ashes with our naked eyes. The physical appearance of the untreated rice husk was seen to be dark after

combustion. After pre-treatment (acid treatment on RH), the RHA was seen to be white color due to the concentration of acid added to the husk. The white color indicates that the pre-treatment has increased the purity of the rice husk ash and the black coloration is due to the unburnt carbon or surface melting of the metallic impurities remaining within the product. This is due to the fact that when the husk is not substantially treated, the alkali oxides enhance the surface melting of silica, thereby entrapping carbon within the silica; the more residual carbon entrapped, the darker the color of the husk is. The results in Fig 4.2 and Table 4.1 illustrate clearly the above interpretations. Thus, the ash property and purity of silica in the ash is highly affected by acid pretreatment, and this can be primary determined easily by the color change of the ash because the Ash obtained from acid-treated samples were completely white in colors.



(a) (b)

Figure 4-2 (a) Non Treated -RHA, (b) Treated-RHA

Incinerating Conditions, Temperature and time, are also the key factors that influence properties of the ash. During incineration under controlled conditions, thermal decomposition or organics decomposition was achieved which allows the removal of the organics from the husk and a final white ash rich in silica can be produced after complete combustion.

From the above Table 4.1, The RHA incinerated at 450 attains fully black color which indicates incomplete combustion and as the temperature increases to 650 the color changes slightly to a gray color indicates some of the organics are decomposed but some unburned carbon are still present in the husk. These impurities along with black particles are attributed to the carbon content present in the ash. On the other hand, a complete combustion (significant color change to fully white) was observed as the temperature or the time increases.

Furthermore from literatures, it was stated that color is one of the factors that affects the properties of RHA, and color changes are associated with the completeness of the combustion process (Bronze oak, 2003).Thus, Ash in white color is an indication of low carbon grade and therefore a high efficiency of decomposition or complete oxidation of the carbon is attained. In addition to temperature effect, a significant color change is observed after increasing the acid concentration, the color slightly changes and the same to the pyrolysis time, as the pyrolysis time increases the color changes from grey to complete white while even holding the acid concentration and temperature constant(E.g. from the above table, #run5 & #8, and #run6 & run9# ).

Thus, those three process parameters highly affect the properties of the ash. By acid pretreatment a final purified husk low in metallic impurities and ready for thermal treatment, and the combustion allows the efficient decomposition or removal of the organics from the husk and a final white ash rich in silica can be afterwards produced.

From the above Table 4.1 we can see that, the whiteness of the ash increases as the incineration temperature increases at the given time and acid treatment. This shows that, the un burned carbon can be removed from the ash by further heat treatment at high temperatures and time. However this usually leads to the crystallization of the amorphous silica to cristobalite and/or tridymite (Shinohara and Kohyama, 2004).Such crystallization is a disadvantage towards preparing silica based materials, because silica rendered inactive in its crystalline form (Paya,Monzoetal., 2001).The factors that affect the quality of the ash also affect the production quality of silica because properties and characteristics of a material are closely related to that of the parent material and the methods and techniques of its production. Therefore, By pretreatment methods and controlling the burning conditions (temperature and time), amorphous silica with high purity can be produced. The combustion temperature and time are the two important factors to define whether silica remains amorphous, as in RHA, or become crystalline.

Even if the color (white color) indicates the purity of silica present in the ash, it doesn't tell the structure, whether the silica in the ash is in amorphous or crystalline form. Therefore, color of the ash is not enough to characterize the quality of silica in the ash. Further investigations on the properties of the ash were conducted using XRD and FTIR in order to check the structure of silica. From the above results, RHAs that tend to have high purity (white color) were selected for further investigation to see the effect of

incinerating conditions on the structure of silica and to know at what pyrolysis temperature and time does the silica in the ash result in amorphous and crystalline form.

### 4.2.2. Chemical Composition of NTRHA and TRHA

*Characterization of Treated Rice Husk Ash (TRHA) and Alkali Metal Removal Test:*

In order to determine the acid pretreatment effect before pyrolysis process of rice husk, chemical composition of both non-treated rice husk ash (NTRHA) and treated rice husk ash (TRHA) were examined using Atomic Absorption Spectrophotometer (AAS) test. As of TRHA, the test was done for sample that undergone pretreatment in 1.5N HCl solution at 90℃ for 2 h and the NTRHA was conducted under the same conditions as the TRHA. In addition, examination of alkali metal impurities that leached out after the acid pretreatment was also examined as shown in the table below.

Table 4-2: Chemical composition of NTRHA and TRHA

| **Components** | **ATRHA** | **NTRHA** |
|---|---|---|
| $SiO_2$ (wt %) | 97.6 | 87.1 |
| $Al_2O_3$ (wt %) | <0.01 | <0.01 |
| $Fe_2O_3$ (wt %) | <0.01 | 1.32 |
| CaO (wt %) | <0.01 | <0.01 |
| MgO (wt %) | <0.01 | 0.36 |
| $Na_2O$ (wt %) | <0.01 | 0.34 |
| $K_2O$ (wt %) | <0.01 | <0.01 |
| MnO (wt %) | <0.01 | 0.08 |
| $P_2O_5$ (wt%) | 0.09 | 0.52 |
| $TiO_2$ (wt%) | <0.01 | <0.01 |
| $H_2O$ (wt %) | 1.55 | 1.44 |
| LOI (wt %) | 2.24 | 9.34 |

Table 4.2 shows the percentage chemical compositions for untreated and acid-treated RH and combustion of free carbon (unburnt carbon) present in the ash. The percentage of the $SiO_2$ in the untreated RH is 87.1% with some metallic impurities of1.32% $Al_2O_3$followed by 0.52% $P_2O_5$, 0.36% MgO and 0.34% $Na_2O$.and the acid treated RH with 97.6% purity of silica is obtained. It is interesting to note that only $P_2O_5$ was detected in the acid treated RHA, and it was also present in a trace amount (0.09%). The

Other impurities were detected below the limit of quantification <0.01% indicating a relatively significant impurities removed by acid treatment. Treatment of RH with acid proved to be effective in removing the metallic impurities to a very lower level and enhance the purity of silica in the RHA.

The percentage purity of $SiO_2$ obtained from RH treated with HCl was slightly increased as compared to the NTRHA. This result is consistent with studies by (Naser,Shafaiq etal,2015), who found that the RH treated with 0.1N HCl contains highest percentage of $SiO_2$ (91.1%) compared to the non-treated RHA(81.9%).In fact that, in this study 97.6% purity was attained which indicates slightly increasing of acid concentration increases the purity of silica. In addition, Our study shows that,HCl is better in removing metallic elements with high silica percentage purity of 97.6% compared to other acids which is conducted by Ghorbani *et al*,2015 who found pre-treating of RH using $HNO_3$founds 94.7 % and 92.89% for $H_2SO_4$.This is because chloride ion ($Cl^-$) from HCl will protonated the silicon and formed silicon chloride ($SiCl_4$) during the leaching process. $SiCl_4$ is insoluble therefore silicon was not removed during leaching process (Matori, Haslinawati, Wahabetal, 2009).

The percentage of Na in the NTRHA is 0.34 whereas in the TRHA is <0.01wt.%. This is because sodium chloride (NaCl), a soluble salt is formed. While leaching process, the $Cl^-$ will react to the metallic element to form chlorides. The metallic chloride will dissolve and remove by filtration.

Many research groups were also conducted on the percentage purity of silica in the RHA and found that the maximum range within 87-97%(Shinohara,Kohyama,2004).The measured values of rice husk ash composition in this study are very much within the ranges reported silica in the rice husk ash in a maximum percentage.

The LOI test measures the amount of unburned carbon remaining in the product. If this appears in large amount it can decrease the purity percentage of silica in the ash as shown in the above Table 4.2, the LOI decreases significantly after acid treatment from 9.34 to 2.24. (Bronzeoak, 2003) reported that, properly produced RHA appears to result in maximum carbon content in the range of 5-7%. In this study, TRHA is effectively produced even below the range with a very low amount of carbon present in the ash which tends to produce high silica yield.

### 4.2.3. Fourier Transform Infra-Red (FTIR) spectroscopy Analysis

FTIR spectroscopic tool is used to identify the key functional groups indicating structural changes in the samples. Further analysis on the presence of functional groups on the surface of the rice husk ash was analyzed using Fourier transform infrared spectroscopy.

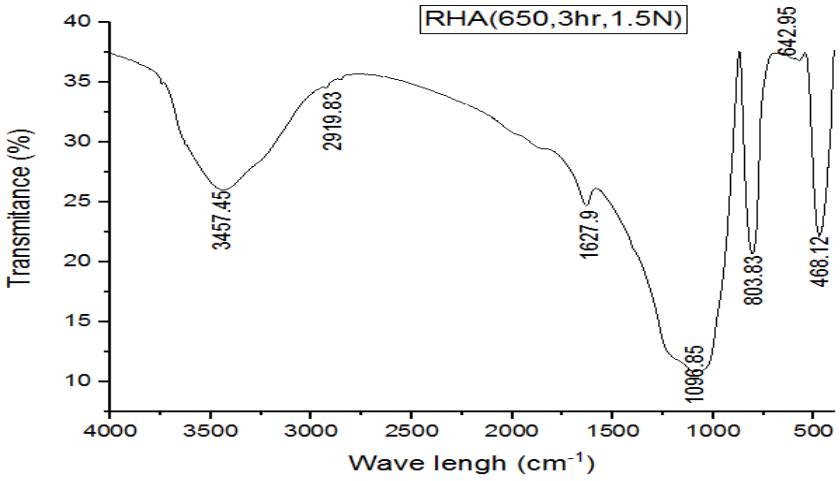



Figure 4-3: FTIR spectra of RHA incinerated at 650°C for 3hr

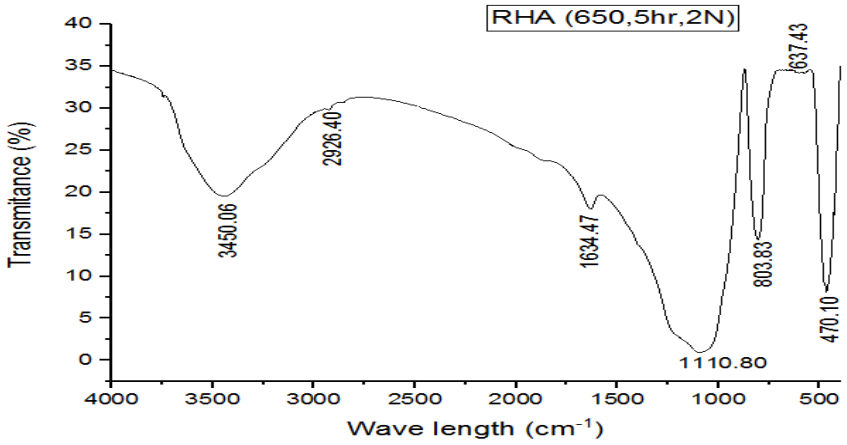



Figure 4-4: FTIR spectra of RHA incinerated at 650°C for 5hr

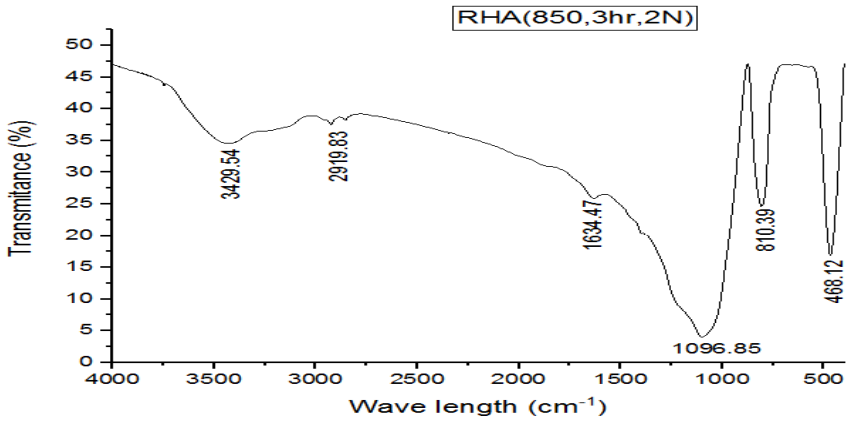



Figure 5-5: FTIR spectra of RHA incinerated at 850°C for 3hr

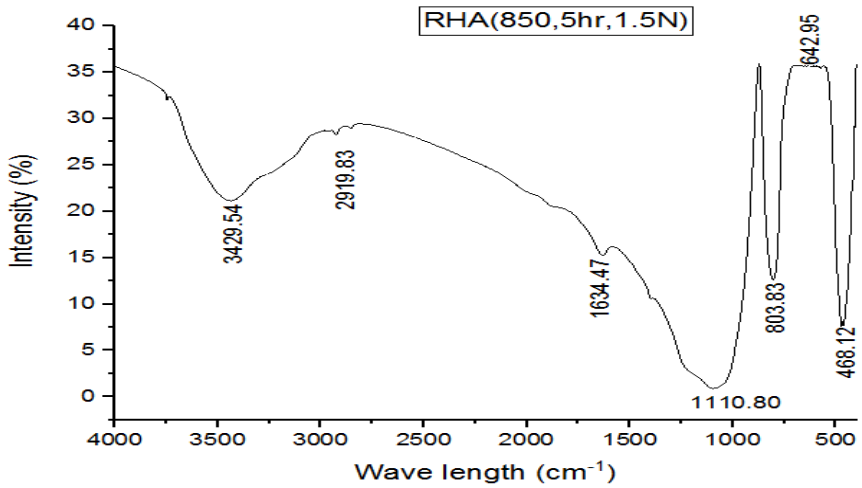



Figure 4-6: FTIR spectra of RHA incinerated at 850°C for 5hr

The above figures show that, the IR spectrum of the RHA incinerated at 650 for 3hr, 650 for 5hr, 850 for 3hr and 850 for 5hr. No significant difference was observed in the structure of the samples. All spectra contains broad absorption band which is attributable to silanol hydroxyl groups and peaks associated with the Si-O-Si stretching and bending vibration bands.

### 4.2.4 X-Ray diffraction (XRD) Analysis

Further evidence on the structure and phase change of silica in the ash were confirmed using XRD.

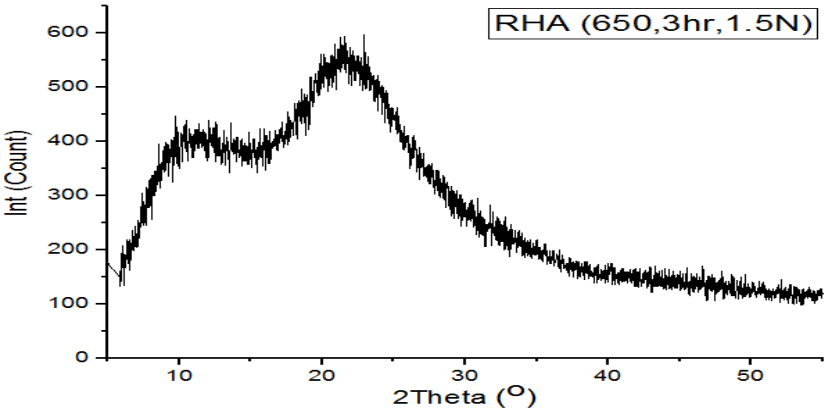



Figure 4-7: XRD pattern of RHA incinerated at 650°C for 3hr

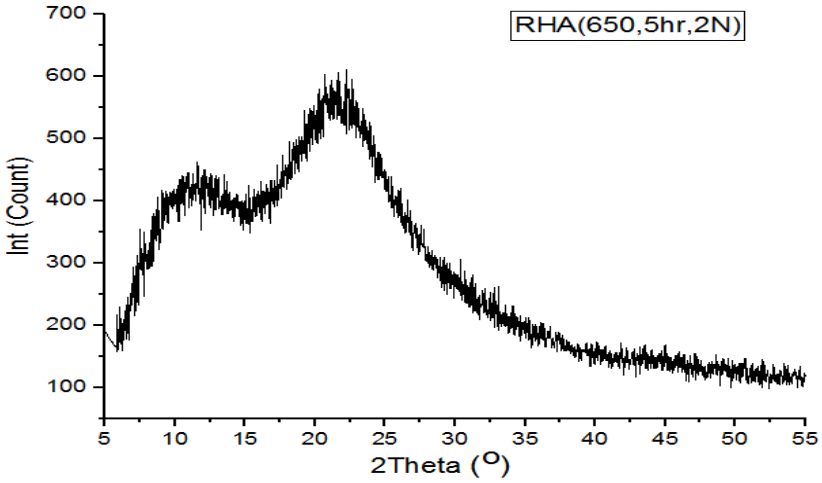



Figure 4-8: XRD pattern of RHA incinerated at 650°C for 5hr

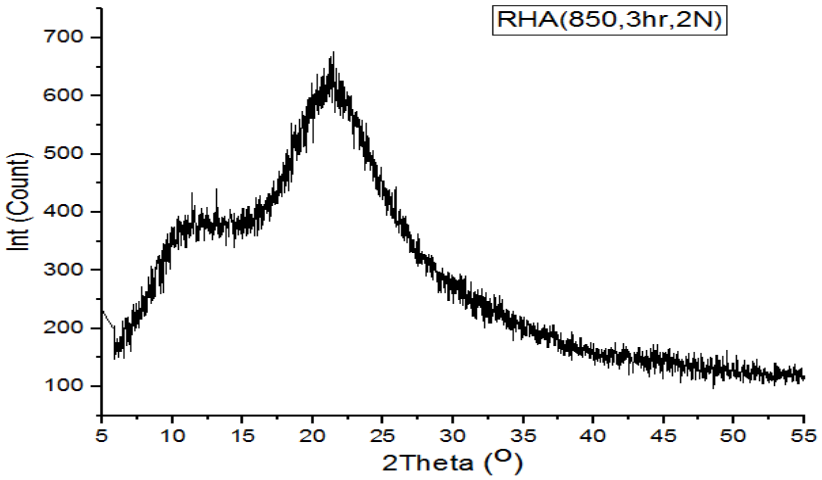



Figure 4-9: XRD pattern of RHA incinerated at 850°C for 3hr

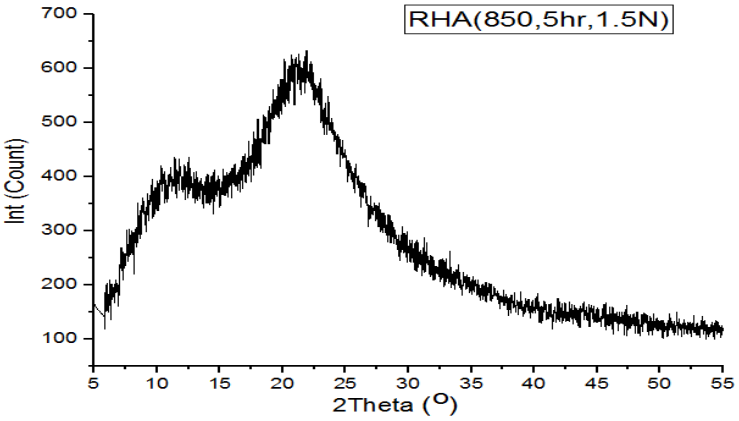



Figure 4-10: XRD pattern of RHA incinerated at 850°C for 5hr

The XRD patterns shown in Figure 4-7 and Figure 4-8 exhibit similar patterns. It shows that the silica was primarily in amorphous form as indicated by a broad peak height centered on 2θangle. The peak height indicates concentration of dominating phases, with higher concentration represented by higher peaks. Thus, typical crystal diffraction peaks (sharp) were not seen which confirms absence of any crystalline structure, and the width and weak diffraction peak around 21.75 in all patterns implied the structures of both samples were amorphous. Broad peak spanning 2θangle at 20.65, 22.35also detected, which is characteristics of amorphous structures is observed (Shelke, Bhagade, Mandavagane, 2010).

The XRD pattern of the RHAS in Figure 4-9 and Figure 4-10 shows that, slightly sharp peaks were observed at 2θ = 29.39and 38.37.this indicates that the solid is either crystalline(or) it consists of micro crystalline structure. Using Match software, the

major reflections occur at 2θ angles of 29.39° tends to tridymite phase and at 38.37 to cristoballite phase which corresponds to the crystalline form (Pijarn, Jaroenworaluck, Sunsaneeyametha, and Stevens, 2010).

It is important to prepare high purity silica with amorphous structures from rice husk by controlling the incineration conditions. Since the structure of RHA strongly depends on the burning temperature and time.

## 4.3. Statistical Analysis of the Experimental Results

### 4.3.1. Effects of experimental variables on silica production

After following a series of experimental procedures, the outcomes of those particular results are measured and analyzed using Design expert software. In this study experimental design techniques were used to determine the effects of operating parameters; pretreatment acid concentration, combustion temperature and combustion time on the efficiency of silica yield and the percentage of silica yield obtained from the experiment were used as a response parameter. All experiments were carried out in a randomized order to minimize the effect of unexpected variability in the observed response due to extraneous factors.

The experimental design selected for this study is the Box-Behnken Design (BHD).The Box-Behnken design does not have runs at the extreme combinations of all the factors, but compensates by having better prediction precision in the center of the factor space. While a run or two can be botched in these designs the accuracy of the observations in the remaining runs is critical to the dependability of the model. Using BHD, a total of 17 experiments were carried out for optimization purpose where the effect of each factor was analyzed using the experimental design techniques. The detail calculations and experimental design results are discussed in sections below and in Appendix C.

Table 4-2: Experimental values of silica yield

| Run | Pretreatment Acid con.(N) | Pyrolysis temperature(℃) | Pyrolysis Time(hr) | Yield of silica (%) |
|---|---|---|---|---|
| 1 | 1 | 450 | 3 | 63 |
| 2 | 2 | 450 | 3 | 72 |
| 3 | 1 | 850 | 3 | 97 |
| 4 | 2 | 850 | 3 | 97.4 |
| 5 | 1 | 650 | 1 | 83 |
| 6 | 2 | 650 | 1 | 88 |
| 7 | 1 | 650 | 5 | 94 |
| 8 | 2 | 650 | 5 | 96 |
| 9 | 1.5 | 450 | 1 | 56 |
| 10 | 1.5 | 850 | 1 | 96.5 |
| 11 | 1.5 | 450 | 5 | 78 |
| 12 | 1.5 | 850 | 5 | 98 |
| 13 | 1.5 | 650 | 3 | 92.5 |
| 14 | 1.5 | 650 | 3 | 91 |
| 15 | 1.5 | 650 | 3 | 93 |
| 16 | 1.5 | 650 | 3 | 91 |
| 17 | 1.5 | 650 | 3 | 92 |

Table 4-3: Design Summary of factorial designs

| Design Summary of Design expert software | |
|---|---|
| Study Type | Response Surface |
| Initial Design | BOX Behnken |
| Design Model | Quadratic |
| Experiments | 17 |
| Blocks | No Blocks |

Table 4-4: Design Expert for fitting a model to the yield response

**Response:Silicayield**

**Sequential Model Sum of Squares**

| Source | Sum of Squares | DF | Mean Square | F Value | Prob>F | |
|---|---|---|---|---|---|---|
| Mean | 1.286E+005 | 1 | 1.286E+005 | | | |
| LInear | 2056.40 | 3 | 685.47 | 18.71 | <0.0001 | |
| 2FI | 125.80 | 3 | 41.93 | 1.20 | 0.3602 | |
| Quadratic | 343.83 | 3 | 114.61 | 121.51 | <0.0001 | Suggested |
| Cubic | 3.40 | 3 | 1.13 | 1.42 | 0.3611 | Aliased |
| Residual | 3.20 | 4 | 0.80 | | | |
| Total | 1.311E+005 | 17 | 7711.84 | | | |

*"Sequential Model Sum of Squares"*: Select the highest order polynomial where the additional terms are significant and the model is not aliased.

**Lack of Fit Tests**

| Source | Sum of Square | DF | Mean Square | F Value | Prob >F | |
|---|---|---|---|---|---|---|
| Linear | 473.04 | 9 | 52.56 | 65.70 | 0.0006 | |
| 2FI | 347.23 | 6 | 57.87 | 72.34 | 0.0005 | |
| Quadratic | 3.40 | 3 | 1.13 | 1.42 | 0.3611 | Suggested |
| Cubic | 0.000 | 0 | | | | Aliased |
| Pure Error | 3.2 | 4 | 0.80 | | | |

*"Lack of Fit Tests"*: Want the selected model to have insignificant lack-of-fit.

**Model Summary Statistics**

| Source | Std. Dev. | R-Squared | Adjusted R-Squared | Predicted R-Squared | PRESS | |
|---|---|---|---|---|---|---|
| Linear | 6.05 | 0.8120 | 0.7686 | 0.6540 | 876.35 | |
| 2FI | 5.92 | 0.8616 | 0.7786 | 0.4869 | 1299.40 | |
| Quadratic | 0.97 | 0.9974 | 0.9940 | 0.9765 | 59.44 | Suggested |
| Cubic | 0.89 | 0.9987 | 0.9949 | | + | Aliased |

+ Case(s) with leverage of 1.0000: PRESS statistic not defined *"Model Summary Statistics"*: Focus on the model maximizing the "Adjusted R-Squared"and the "Predicted R-Squared". The predicted R-squared indicates the closeness of the factors for the model, it approach to 1 means good fit for the model selection, quadratic model was fit for this study.

To determine whether or not the quadratic model is significant, it was crucial to perform analysis of variance (ANOVA), table 4.5. The probability (P-values) values were used as a device to check the significance of each coefficient, which also showed the interaction strength of each parameter. The smaller the P-values are, the bigger the significance of the corresponding coefficient.

Table 4-5: ANOVA for response surface quadratic model

| Source | Sum of Squares | DF | Mean Square | F-value | P-value Prob> F | Remark |
|---|---|---|---|---|---|---|
| Model | 2526.04 | 9 | 280.67 | 297.57 | <0.0001 | |
| A | 33.62 | 1 | 33.62 | 35.64 | 0.0006 | |
| B | 1797.00 | 1 | 1797.00 | 1905.19 | <0.0001 | |
| C | 225.78 | 1 | 225.78 | 239.37 | <0.0001 | |
| $A^2$ | 2.14 | 1 | 2.14 | 2.27 | 0.1759 | |
| $B^2$ | 328.85 | 1 | 328.85 | 348.65 | <0.0001 | |
| $C^2$ | 3.70 | 1 | 3.70 | 3.92 | 0.0881 | |
| AB | 18.49 | 1 | 18.49 | 19.60 | 0.0031 | |
| AC | 2.25 | 1 | 2.25 | 2.39 | 0.1664 | |
| BC | 105.06 | 1 | 105.06 | 111.39 | <0.0001 | |
| Residual | 6.60 | 7 | 0.94 | | | |
| Lack of Fit | 3.40 | 3 | 1.13 | 1.42 | 0.3611 | not significant |
| Pure Error | 3.20 | 4 | 0.80 | | | |
| Cor Total | 2532.64 | 16 | | | | |

The Model F-value of 297.57 implies the model is significant. There is only a 0.01% chance thata "Model F-Value" this large could occur due to personal error or disturbance. Values of "Prob > F" less than 0.0500indicate model terms are significant. In this case A, B, C, AB, BC, $B^2$, $C^2$ are significant model terms. Values greater than

0.1000 indicate the model terms are not significant. This shows that the pretreatment acid concentration, pyrolysis temperature, pyrolysis time, interaction between pretreatment acid concentration and pyrolysis temperature, interaction between pyrolysis temperature and time, square of pyrolysis temperature and square of pyrolysis time affects the percentage yield of silica significantly.

The "Lack of Fit F-value" of 1.42 implies the Lack of Fit is not significant relative to the pure error. There is a 36.11% chance that a "Lack of Fit F-value" this large could occur due to noise. Non-significant lack of fit is good because we want the model to fit.

Model Adequacy Check

The model was tested for adequacy by analysis of variance. Coefficient of Variation, the standard deviation expressed as a percentage of the mean; Predicted Residual Error Sum of Squares, which is a measure of how the model fits each point in the design; the R-Squared, measure of the amount of variation around the mean explained by the model; Adj R-Squared that is a measure of the amount of variation around the mean explained by the model, Pred R-Squared, a measure of the amount of variation in new data explained by the model, and Adequate Precision, this is a signal to disturbance ratio due to random error, presented in the table 4.6, below, are used to decide whether the model can be used or not.

Table 4-6: Model adequacy measures

| | | | |
|---|---|---|---|
| Std. Dev. | 0.97 | R-Squared | 0.9974 |
| Mean | 86.96 | Adj R-Square | 0.9940 |
| C.V. | 1.12 | Pred R-Squared | 0.9765 |
| PRESS | 59.44 | Adeq Precision | 54.691 |

The value of R-squared for the developed correlation is 0.9974. It implies that 99.74% of the total variation in the percentage of conversion is attributed to the experimental variables studied. And the "Pred RSquared"of 0.9765 is in reasonable agreement with the "Adj R-Squared" of 0.9940."Adeq Precision" measures the signal to disturbance ratio due to random error. A ratio greater than 4 is desirable. Here the ratio of 54.691 indicates an adequate signal. Therefore, this model can be used to navigate the design space.

The regression coefficients and the corresponding 95% CI (Confidence Interval) High and Low are presented in table 4-7 below. If zero was in the range High and Low 95% Confidence Interval, the factors has no effect. From the 95% CI High and Low values of each model term, it could be concluded that the regression coefficients of acid concentration, temperature, time and the interaction terms of acid concentration &pyrolysis temperature and the interaction terms of pyrolysis temperature& time have highly significant effect in the production of silica.

Table 4-7: Regression coefficients and the corresponding 95% CI High and Low

| Factors | Coefficient Estimate | Standard Error | 95% CI low | 95% CI high |
|---|---|---|---|---|
| Intercept | 91.90 | 0.43 | 90.87 | 92.93 |
| A-Acid.Con | 2.05 | 0.34 | 1.24 | 2.86 |
| B-Temperature | 14.99 | 0.34 | 14.18 | 15.80 |
| C-time | 5.31 | 0.34 | 4.50 | 6.12 |
| $A^2$ | -0.71 | 0.47 | -1.83 | 0.41 |
| $B^2$ | -8.84 | 0.47 | -9.96 | -7.72 |
| $C^2$ | -0.94 | 0.47 | -2.06 | -0.18 |
| AB | -2.15 | 0.49 | -3.30 | -1.00 |
| AC | -0.75 | 0.49 | -1.90 | 0.40 |
| BC | -5.15 | 0.49 | -6.27 | -3.98 |

Development of Regression Model Equation

By designing the experimental data, the model equation (i.e. quadratic polynomial model) for silica production from rice husk that correlates the response (conversion of silica) to the process variables in terms of coded factors after excluding the insignificant terms are given below in equation (4.5).

Final Equation in Terms of Coded Factors:

$$Silicayield\ (\%) = +91.90 + 2.05 \times A + 14.99 \times B + 5.31 \times C - 0.71 \times \mathrm{A}^2 - 8.84 \times \mathrm{B}^2 - 0.94 \times \mathrm{C}^2 - 2.15 \times \mathrm{A} \times \mathrm{B} - 0.75 \times \mathrm{A} \times \mathrm{C} - 5.13 \times \mathrm{B} \times \mathrm{C} \quad \text{.....(4.5)}$$

Where; A = Acid concentration; B = temperature; C = time

The actual versus predicted values using model in the above equation (in terms of actual factors) are tabulated in table 4-8 and the detailed results are written in Appendix C.

Table 4-8: Experimental (actual) and predicted values of silica yield

| Run NO | Pretreatment Acid con.(N) | Pyrolysis temperature(℃) | Pyrolysis Time(hr) | Actual value (%) | Predicted value (%) | Residual |
|---|---|---|---|---|---|---|
| 1 | 1 | 450 | 3 | 63 | 63.16 | -0.16 |
| 2 | 2 | 450 | 3 | 72 | 71.56 | 0.44 |
| 3 | 1 | 850 | 3 | 97 | 97.44 | -0.44 |
| 4 | 2 | 850 | 3 | 97.4 | 97.24 | 0.16 |
| 5 | 1 | 650 | 1 | 83 | 82.14 | 0.86 |
| 6 | 2 | 650 | 1 | 88 | 87.74 | 0.26 |
| 7 | 1 | 650 | 5 | 94 | 94.26 | -0.26 |
| 8 | 2 | 650 | 5 | 96 | 96.86 | -0.86 |
| 9 | 1.5 | 450 | 1 | 56 | 56.70 | -0.70 |
| 10 | 1.5 | 850 | 1 | 96.5 | 96.93 | -0.43 |
| 11 | 1.5 | 450 | 5 | 78 | 77.57 | 0.43 |
| 12 | 1.5 | 850 | 5 | 98 | 97.30 | 0.70 |
| 13 | 1.5 | 650 | 3 | 92.5 | 91.90 | 0.60 |
| 14 | 1.5 | 650 | 3 | 91 | 91.90 | -0.90 |
| 15 | 1.5 | 650 | 3 | 93 | 91.90 | 1.10 |
| 16 | 1.5 | 650 | 3 | 91 | 91.90 | -0.90 |
| 17 | 1.5 | 650 | 3 | 92 | 91.90 | 0.100 |

To see how well the model satisfies the assumptions of the analysis of variance (ANOVA), the plots of residuals versus predicted (Table 4.8) were analyzed. The graph of the predicted values obtained using the developed correlation versus actual values is also shown in Figure 4-3.Normal probability plot of the raw data used to check the assumption of normality when using t-test is also plotted as shown in Fig 4.4 below. In the analysis of variance, it is usually more effective (and straight forward) to do this with the residuals. This shown below in Fig4.4 resembles a straight line. In visualizing the straight line, place more emphasis on the central values of the plot than on the extremes.

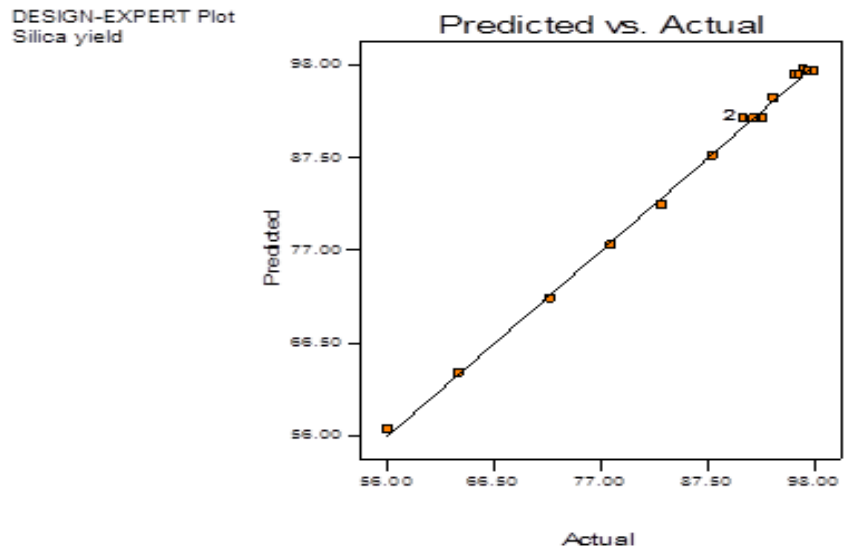



Figure 4-11: Predicted versus actual values

***Predicted versus actual values***

The graph of the predicted values obtained using the developed correlation versus actual values is shown in the above graph 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 three process variables to the percentage of conversion.

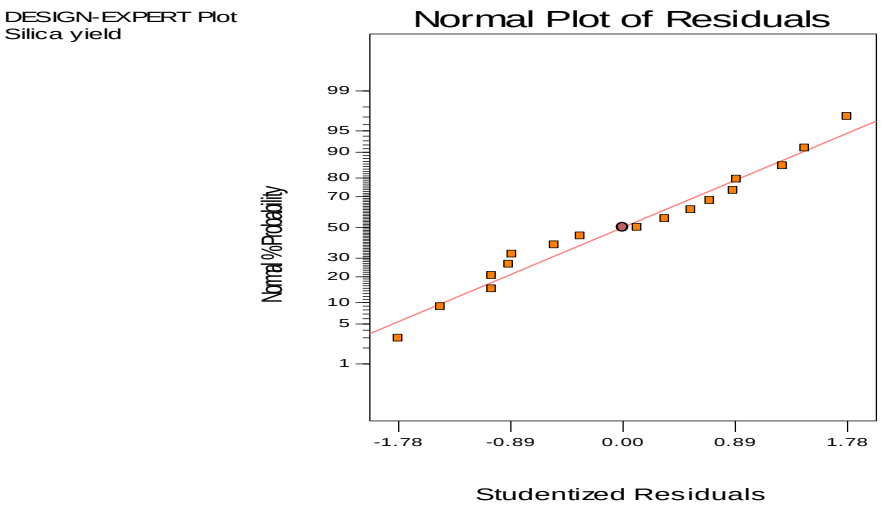



Figure 4.12 Normal probability plots of residuals

From the plot as shown above, the normal probability plot indicates the residuals following a normal distribution, in the case of this experiment the points in the plots

shows fit to a straight line in the figure i.e. the error distribution is approximately normal no Gross departure or deviations from normality occurs. This indicates the model satisfies the assumptions of ANOVA.

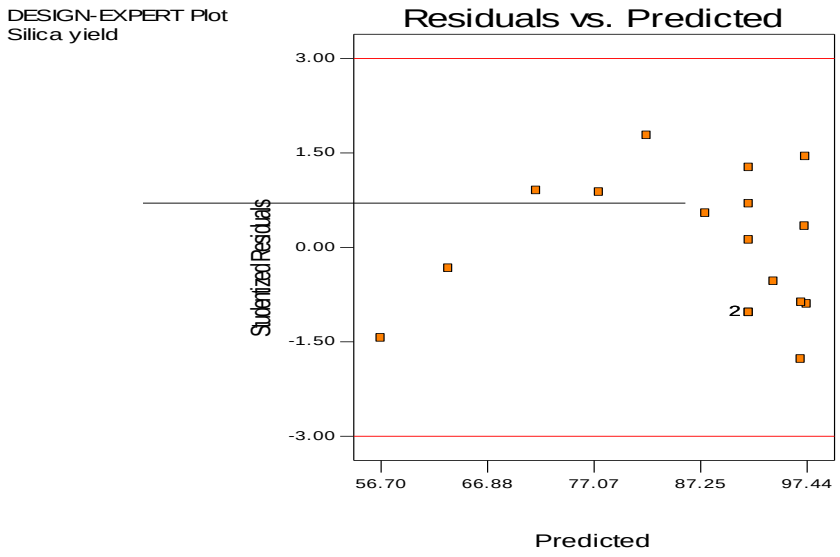



Figure 4.13 Residual versus predicted values

Examination of the residuals should be an automatic part of any analysis of variance. Through a study of residuals, many types of model inadequacies and violations of the underlying assumptions can be discovered. If the model is adequate and the assumptions are satisfied, the residuals should be structure less; that is, they should contain no obvious patterns and be unrelated to any other variable including the predicted response. The plot of the residuals versus the predicted response values (Figure 4.3), tests the assumption of constant variance. The plot shows random scatter which justifying no need for an alteration to minimize personal error.

### 4.3.2. Effect of Experimental Process Variables on Percentage yield of Silica

Based on the analysis of variance, the percentage yield of silica was significantly affected by the individual process variables and their interactions between them. both the individual process variable and their interaction effects on the percentage yield of silica is discussed in the section below.

***Effect of Individual Process Variables***

The percentage of silica yield was directly related to the process variables. They affect the yield significantly as shown in the figure below. This is due to those three

parameters are key parameters in the production of high quality of silica. As the pretreatment acid concentration removes the metallic impurities in the husk and the pyrolysis temperature and time decomposes the un-burnt component (carbon) which enhances the silica present in the husk so that the percentage yield of silica increases and also its quality after the sol-gel process.

As shown in Figure 4-8 below the percentage of conversion is significantly affected by pyrolysis temperature. It can be seen from the figure that with increasing pyrolysis temperature, the percentage of silica yield increases linearly. Such behavior could be attributed to the following reasons.

In RH, silica is predominantly in inorganic linkages, but some of the silica is also bonded covalently to the organic compounds. This portion of the silica is undissolved in alkali and can with stand very high temperatures. Once the organic part of the RH is extracted, the inorganic residue may be relative pure, forming a better source for silica. But very high pyrolysis temperature is not recommended as this can change the amorphousness of silica to crystalline form, which is not reactive.

Figure 4-9 shows that the effect of pyrolysis time on percentage of silica yield. Increasing the amount of pyrolysis time increases the percentage of silica yield significantly. Hence, as the organic compounds or the carbon present in the husk reduces the silica content increases so that the percentage of conversion increases significantly.

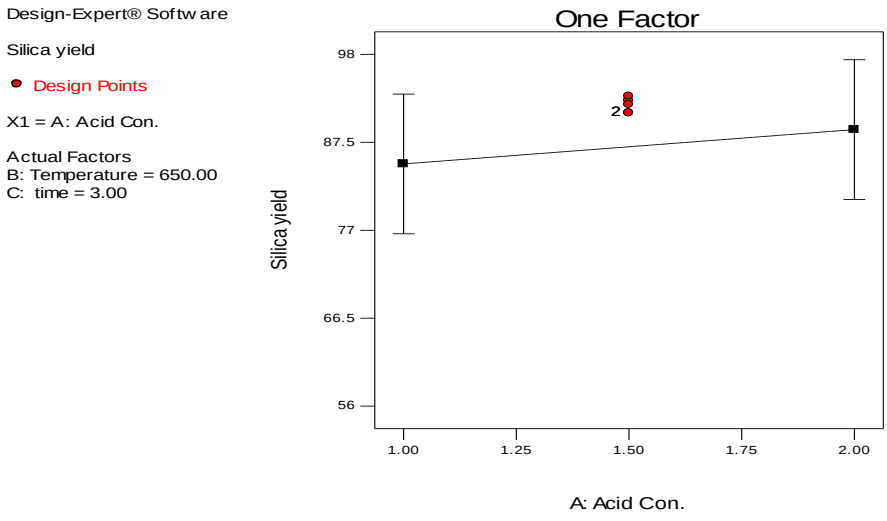



Figure 4.14 Effect of pretreatment acid concentration on percentage yield of silica

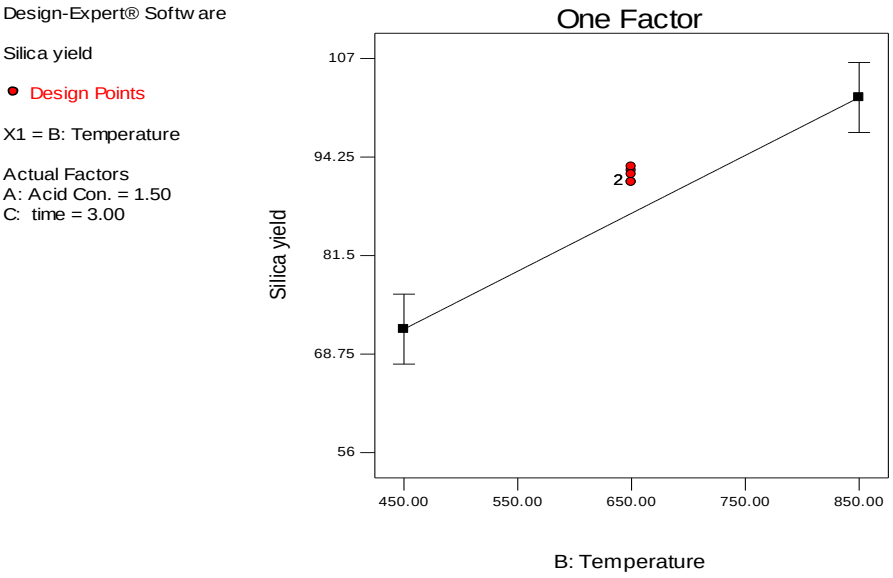



Figure 4.15 pyrolysis temperatures versus percentage yield of silica

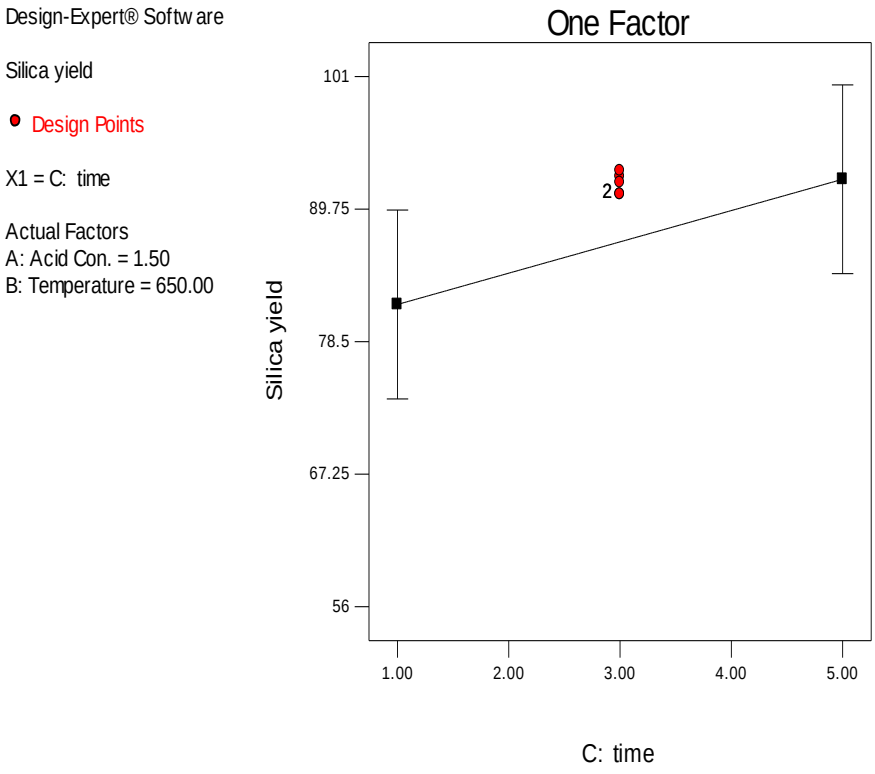



Figure 4.16 pyrolysis time versus percentage yield of silica

Pyrolysis time versus percentage yield of silica holding pretreatment acid concentration and pyrolysis temperature at center

### *Effect of Interaction between Process Variables*

The most common way to see the effects of interaction parameters on the percentage yield is in the form of a response surface plot and via response contour plot. The process variables were found to have significant interaction effects except the pretreatment acid concentration with pyrolysis time interaction. The contours and response surfaces effect are plotted in figures below as a function of the interactions of any two of the variables by holding the other value of the variable at middle.

Figure 4-19 shows the interaction of pyrolysis temperature and pyrolysis time on the percentage of conversion. A relatively higher percentage of conversion at higher temperature and time was observed. This could be due to decomposition of organic matter which lower the amount of carbon content and enhance the percentage of silica.

From Figure 4.17, the percentage of yield increased with increasing the pretreatment acid concentration up to center point and at high pyrolysis temperature. Also from Figure 4-19 the percentage of yield gets higher at optimal amount of pyrolysis temperature and higher amount of time.

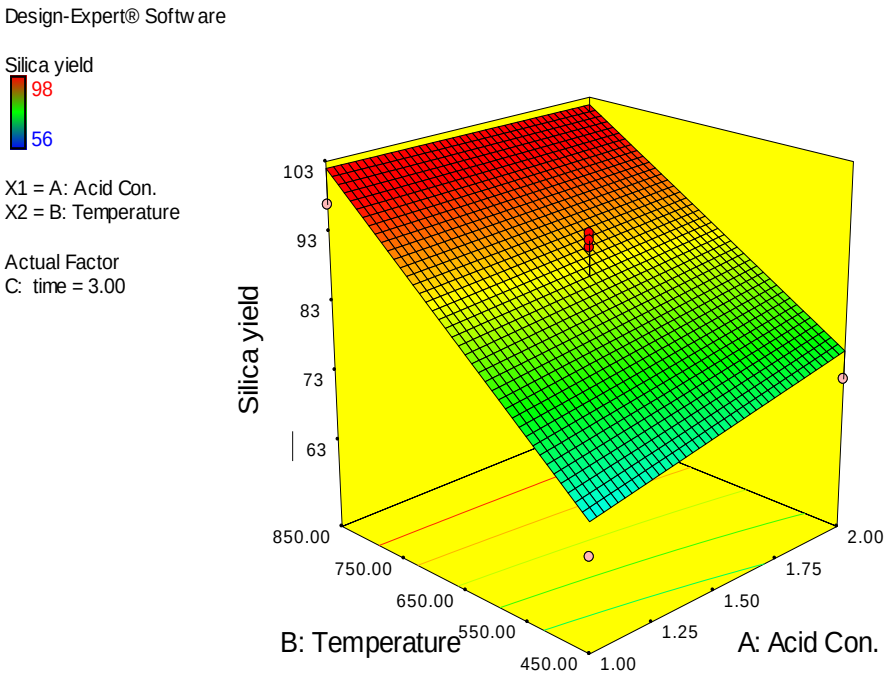



Figure 4.17 Surface plot of the interaction effect of acid concentration and pyrolysis temperature versus percentage of silica yield

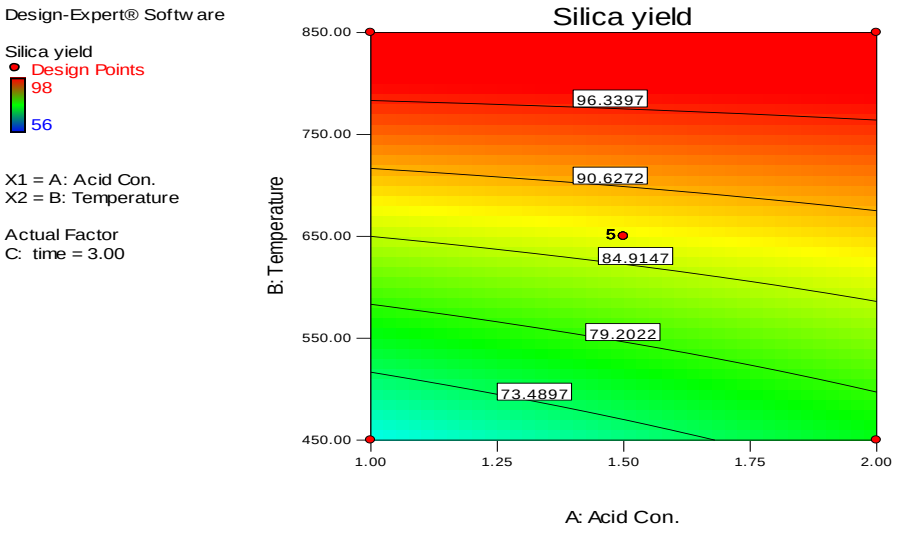



Figure 4.18 Contour plot of the interaction effect of acid concentration and pyrolysis temperature versus percentage of silica yield

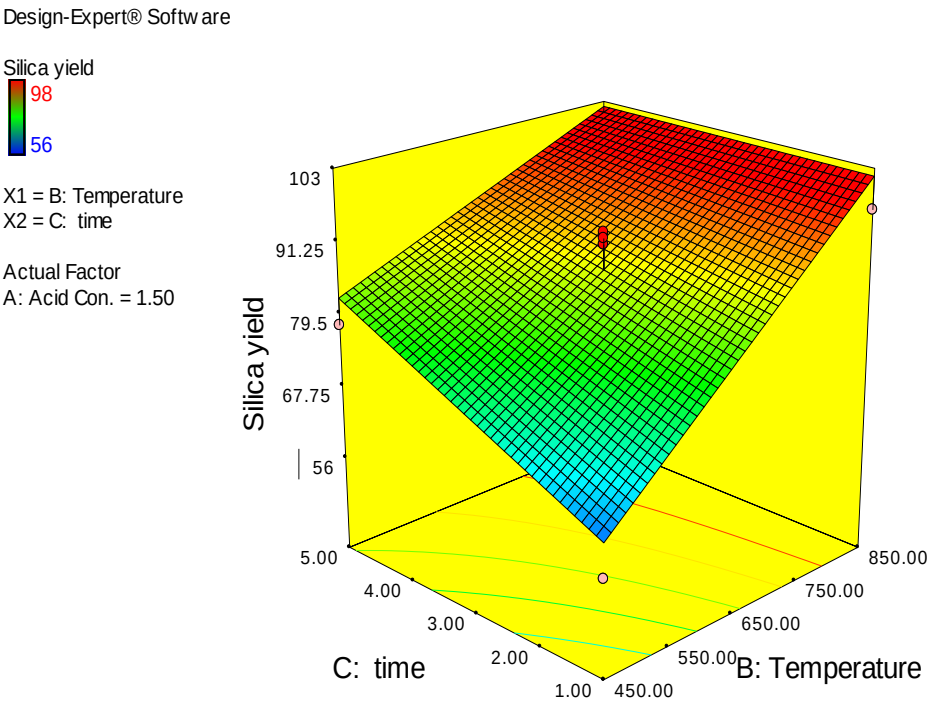



Figure 4.19 Surface plot of the interaction effect of pyrolysis temperature and pyrolysis time versus percentage of silica yield

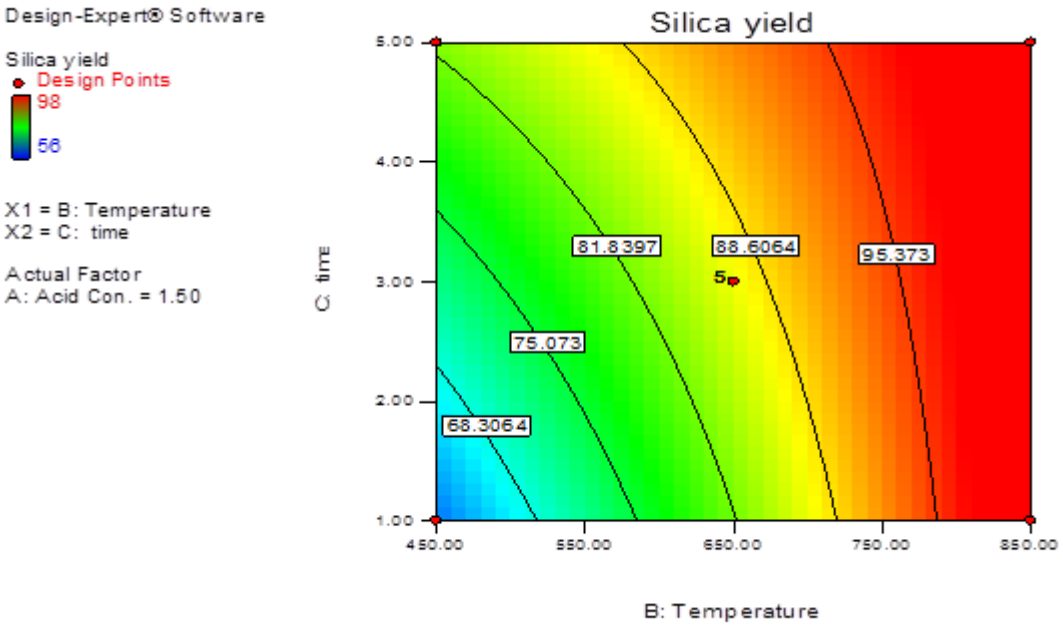



Figure 4.20 Contour plot of the interaction effect of pyrolysis temperature and pyrolysis time versus percentage of silica yield

From the three interaction effects shown in the figures and contours, at higher pyrolysis temperature and pyrolysis time, pretreatment acid concentration at the center point, always resulted in the percentage of conversion higher than when using higher range of pretreatment acid concentration and reaction temperature, pyrolysis time at the center point. This phenomenon is further supported by the fact that pyrolysis temperature and pyrolysis time are the most significant process variables that affect the percentage of yield as indicated by the highest F – value in the ANOVA as shown in Table 4-7.

The above observations can easily be explained that, at higher pyrolysis temperature and time the efficient decomposition or removal of the organics allows increasing the silica by reducing the un brunt carbon which derives the maximum yield and medium pretreatment acid concentration will ensure the removal of metallic impurities which enhance the purity of silica. Generally, detailed explanation were explained how these process parameters affect the percentage yield as well as its impurity on the previous sections (section 4.2 and 4.3)

### 4.3.2. Optimization of process variables

The results above have shown that the three process variables and the interaction among the two variables affect the percentage of conversion. Therefore, the next step is to optimize the process variables in order to obtain the highest percentage of conversion using the model regression developed. So in order to obtain the maximum percentage of conversion, the predicted combination of parameters was as follows: pretreatment acid concentration of 1.85N, pyrolysis temperature of 658, and pyrolysis time of 4.9 hr. Under these conditions, the model predicted of 98.971% with a desirability value of 1.

To validate the optimum conditions predicted by the model using desirability ramp, triplicate experiments were conducted using the optimized process conditions and mean percentage conversion value of 96.7% was obtained and the results are closely related with the data obtained from optimization analysis using desirability functions. Therefore, this study shows that rice husk can be used for synthesis of high quality of silica and optimum percentage of conversion can be obtained.

## 4.4. Characterization of silica

The key chemical parameters used to characterize the amorphous silica materials are those that potentially impact end-use performance. These include overall chemical composition and some individual components

### 4.4.1. Chemical Compositions of the extracted silica

Table 4-10 chemical composition of extracted silica

| Components | Amount (wt %) |
|---|---|
| $SiO_2$ (wt %) | 98.60 |
| $Al_2O_3$ (wt %) | <0.01 |
| $Fe_2O_3$ (wt %) | <0.01 |
| CaO (wt %) | <0.01 |
| MgO (wt %) | <0.01 |
| $Na_2O$ (wt %) | 0.08 |
| $K_2O$ (wt %) | <0.01 |
| MnO (wt %) | <0.01 |
| $P_2O_5$ (wt %) | 0.04 |
| $TiO_2$ (wt %) | <0.01 |
| $H_2O$ (wt %) | 1.25 |
| LOI (wt %) | 1.44 |

From the above table, it is cleared that experiments have been carried out successfully under lab scale to extract silica from the rice husk with high purity.

### 4.4.2. Fourier Transform Infra-Red (FTIR) spectroscopy analysis of silica

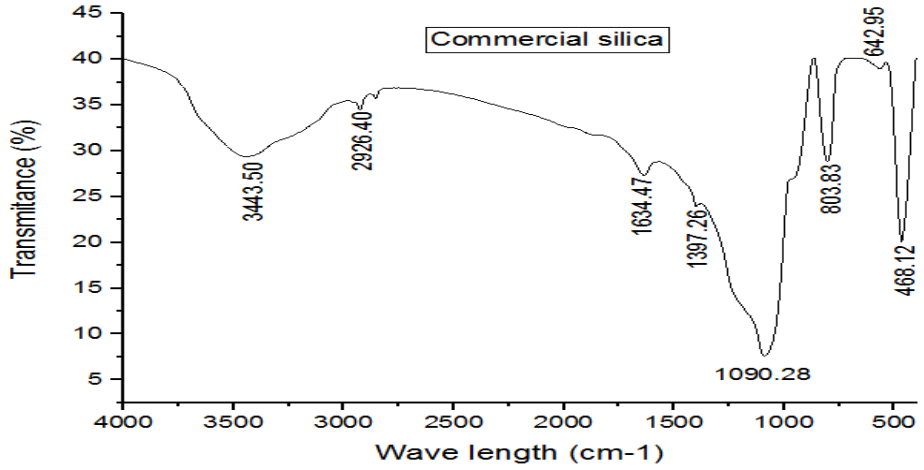



Figure 4.21 FTIR spectra of commercial silica

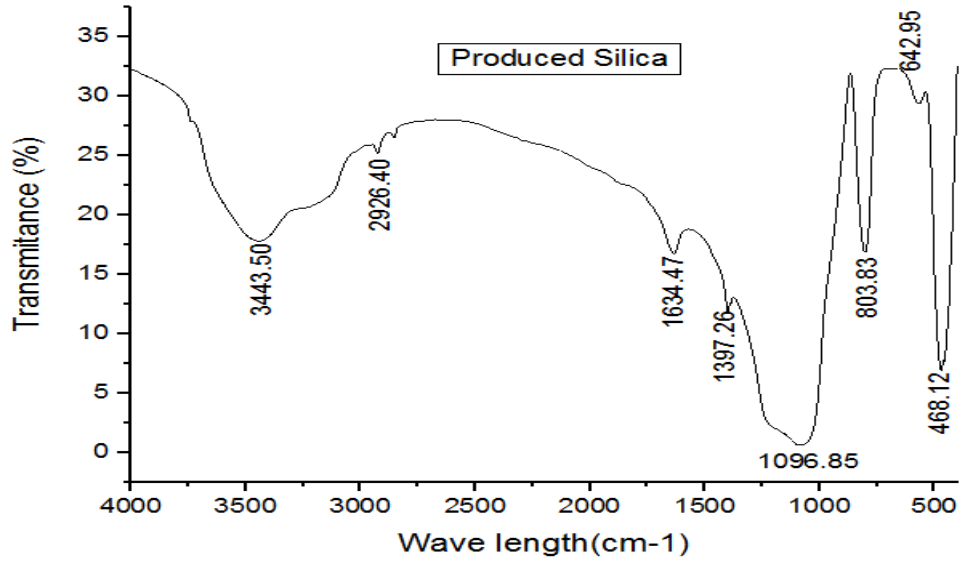



Figure 4.22 FTIR spectra of silica extracted from RHA

### 4.4.3. X-Ray diffraction (XRD) Spectrometer analysis of silica

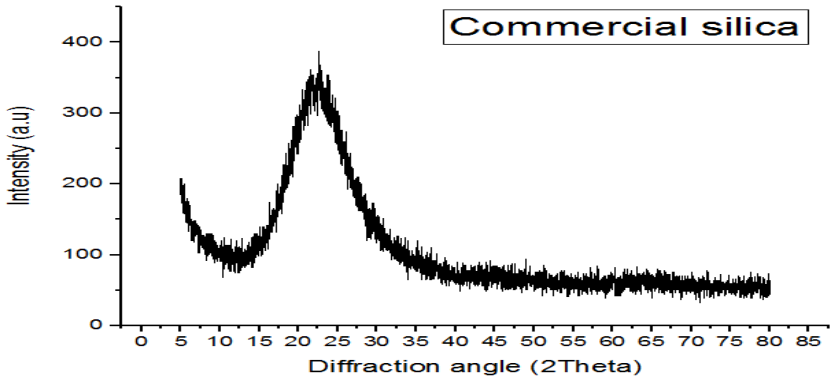



Figure 4.23 XRD pattern of commercial silica

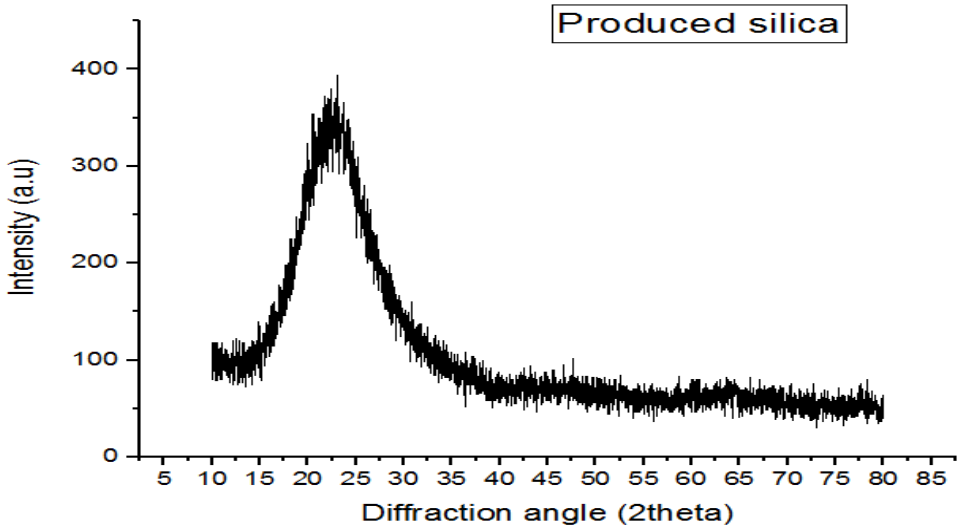



Figure 4.24 XRD pattern of silica prepared from RHA

The above figure shows the XRD pattern for the commercial and extracted silica from RHA. Sample in the range of 2θ = 10-80°. There is no peak, except the broad hump around 2θ=21.8 and 23, indicates that the rice husk silica is in amorphous phase (Yalcin, Sevinc, 2001).

It could be observed from the above figures that both of samples (commercial silica and silica prepared from RH) have similar curves. There is no significant difference in the structure when compared to the commercial silica.

### 4.4.4. Surface area analysis of extracted silica

The surface area of silica was determined by using Air permeability, Blaine meter method and it is conducted three times and the average time interval required to flow air through the samples were taken as the measured time interval of manometer drop for test sample (T) and for commercial sample (Ts). The time interval from the three tests for the commercial silica and extracted silica were therefore obtained as 60, 60, 60 (Avg. 60 sec) and 58, 57, 57 Seconds (Avg. 57.3 sec) respectively. The specific surface area of silica is then calculated as follows:

$$S = \frac{Ss\sqrt{T}}{\sqrt{Ts}} \quad \text{(ASTM, C204).....4.1}$$

Where: S = Specific surface area of the test sample (Silica); Ss = Specific surface area of the standard sample used in calibration of the apparatus(commercial silica) = 800$m^2$/g; T = measured time interval, s, of manometer drop for test sample (extracted silica) = 57.3sec; Ts = measured time interval, s, of manometer drop for standard sample used in calibration of the apparatus = 60sec; Therefore substituting the values in the above equation gives a specific surface area of 779.74$m^2$/g.

This result is consistent and in range with (Hafiz, Arshad, Abdul, 2009), who reports a typical good quality adsorbent silica gel has a surface area of 200-800 $m^2$/g. Thus, Silica gels high specific surface area allows it to absorb water readily, making it suitable as a desiccant (drying agent) in various purposes

### 4.4.5. Water absorption test

The moisture absorptive capacity of both the extracted and commercial silica was tested three times and the averages were taken. And the detail measurements are discussed in the appendix section. The results are given in Table below.

Table 4-11 Moisture absorptive capacity of extracted and commercial silica

| Sample | Moisture absorptive capacity (%) |
|---|---|
| Produced(extracted) silica | 22.13 |
| Commercial silica | 25.4 |

The moisture adsorption capacity is one of the most important properties of a desiccant. The above result shows the extracted silica adsorbed about 22.13%moisture and is comparable with the commercially available good quality of silica having moisture absorptive capacity of 25.4%. The high absorption capacity of the gel was due to its high specific surface area. The result indicates that the prepared method was efficient to produce a good specific surface area silica desiccant with good moisture absorption capacity

# 5. CONCLUSIONS AND RECOMENDATIONS

## 5.1. Conclusion

The possibility of using rice husk as a source of high silica production was verified by investigating physiochemical properties of the ash and the extracted silica, and white, pure with high specific surface area and amorphous form silica have been prepared successfully from Rice husk.

Properties and characteristics of a material are closely related to that of the parent material and the methods and techniques of its production. Also, factors affect the quality of the ash also affects the production quality of silica.

The acid pretreatment of rice husk before combustion is vital for obtaining high purity of silica from the RHA. The low impurity level of the rice husk ash showed that it is highly reached in silica. The incineration conditions (combustion temperature and time) essentially control the quality of the ash and are the important factors to define whether silica remains amorphous, as in RHA, or become crystalline. Therefore, by pretreatment methods and controlling the burning conditions (temperature and time), amorphous silica with high purity can be produced.

From the above results, we can conclude that, the major source of impurity for RH silica is the carbonaceous residue from the incomplete combustion of the organic components and several metallic impurities present in the husk. The treatment methods and incinerating conditions essentially control the quality of RHA, especially amorphous form, which is needed for high quality of silica extraction. Synthesis of silica from the treated rice husk ash was carried out and the optimum condition need to be made at very high and low combustion temperature and time have negative effect on the yield of silica and its purity.

Furthermore, the performances obtained from parameters were compared with commercial silica. As a result, they perform equivalency with commercially available. Hence, the process may be particularly relevant to our country, Ethiopia, that micro- and nano silica are imported still for different applications. Therefore, it would be economical to extract silica from the ash that may be an economic opportunity; it also takes care of ash disposal. Thus, this promotes environmental concern with the

economic values and green approaches to synthesize valuable silica material from RH biomass using energy efficient process.

## 5.2. Recommendation

This study was conducted mostly on the parent material, the material on which high quality of silica was produced. In fact that, the parameters that affect the RHA and the methods and techniques of its production, highly affects the produced silica and its properties, There are also key factors that can affect the production and properties mostly the percentage yield of silica. the parameters used during sodium silicate extraction (such as temperature and time reaction conditions, aging time and temperature, concentration of sodium silicate and gelation PH) are very important concepts not covered in this research which needs further investigations. Therefore, further studies required for improving the production of high quality and quantity rice husk silica, such as:

Further investigations will be needed to establish the useful information when considering scalability of the process and to understand the behavior and to explore the commercial application of the silica. The absorption capacity and its surface area were investigated roughly in this study which needs detail calculation on its kinetics behavior and on its pore size and other physical properties

This study may provide rice husk with another promising application Due to its high purity and contains no toxic materials. The product may be used as a precursor in preparing advanced materials and preparing high quality feedstock for different applications.

Future works need to characterize the detailed properties of the silica will eventually add value to the rice husk silica product and make it more attractive for industries that require high purity of silica at reasonable cost.

# 6. REFERENCES


A. Proctor, 1990**.** "X-ray diffraction and scanning electron microscope studies of processed rice hull silica", J. Am. Oil Chem. Soc. **,**67, 576-584.

Bageru,A.,Srivastava,V. Preparation and characterization of biosilica from teff (*eragrostis tef*) straw by thermal method http://dx.doi.org/10.1016/j.matlet.2017.06.100.

Bryant, R.; Proctor, A.; Hawkridge, M.; Jackson, A.; Yeater, K.; Counce, P.; Yan, W.; McClung, A.; Fjellstrom, R., 2011**.**Genetic variation and association mapping of silica concentration in rice hulls using a germplasm collection.Genetica**,** 139 (11-12).

C.Faizul, C.Abdullah, B.Fazlul. 2013. Review of Extraction of Silica from Agricultural Wastes using Acid Leaching Treatment 10.4028/www.scientific.net/AMR.626.997.

Chandrasekhar, S, Pramada, PN, Praveen, L, 2005, Effect of organic acid treatment on the properties of rice husk silica. J. Mater. Sci. 40, 6535.

Chandrasekhar, S, Satyanarayana, KG, Pramada, PN, Raghavan, P, Gupta, TN, 2003. Review processing, properties and applications of reactive silica from rice husk - an overview. J. Mater. Sci. 38, 3159.

Chindaprasirt, P., Kanchanda, P.,2007. Sulfate resistance of blended cements containing fly ash and rice husk ash Construction and Building Materials,21(June), 1356-1361.

D.J. Londeree, D. Wang, J. Wang, Y. Hu, 2017. Low-cost synthesis of hollow mesoporous silica spheres and its application in the removal of aromatic volatiles, Mater.Lett. doi: 10.1016/j.matlet.2017.05.016.

D. Wang, J. Wang, Y. Hu, 2017. Low-cost synthesis of hollow mesoporous silica spheres and its application in the removal of aromatic volatiles, Mater.Lett. doi:10.1016/j.matlet.2017.05.016D.

F. Andreola, L. Barbieri, F. Bondioli, A.M. Ferrari, V. Vignolese, R. Emilia, V. Amendola, 2015. "Valorization of Rice Husk Ash as Secondary Raw Material in the Ceramic Industry, Proc. 10th Int.Conf. Eur. Ceram. Soc. (ECERS).

F. Andreola, L. Barbieri, F. Bondioli, A.M. Ferrari, V. Vignolese, R. Emilia, V. Amendola, Lim, J. S.; Manan, Z. A.; Alwi, S. R. W.; Hashim, H., 2012**.** A review on utilization of biomass from rice industry as a source of renewable energy. Renewable & Sustainable Energy Reviews**,** 16 (5), 3084-3094.

Ghaly,A,E., and A.M.Al-Taweel, 1990. Physical and thermo chemical properties of cereal straws. Energy sources 12:131-145.

Hafiz.A, Arshad.S, Abdul, 2009. Synthesis of quality silica gel ; Optimization of parameters Silica Sol Silica Gel.

Haus R, Prinz S, Priess C. 2012. Assessment of High Purity Quartz Resources. In: Götze J, Möckel R, eds. Quartz: Deposits,Mineralogy and Analytics. Berlin, Heidelberg: Springer; p. 29-51.

H. Hamdan, M. N. M. Muhid, S. Endud, E. Listiorini and Z. Ramli, 1997. "Si MAS NMR, XRD and FESEM studies of rice husk silica for the synthesis of zeolites", J. Non-Cryst. Solids**,** 211, 126-131.

Hwang,C.L. and Chandra,S.2016. The Use of Rice Husk Ash in Concrete. https://3cl1105uvd.files.wordpress.com/2013/06/book-bysatish- chandra-220504.pdf (assessed 27 - 4- 2016).

H. Yousift, M.N. Al-Khalaf, Use of rice husk ash in concrete, Int. J. Cem. Comp. Light Weight Concr. 6 (4) (1984) 241–248.

Javed,S.,Tajwar,S.,Shafaq,M.etal.2009. Characterization of silica from sodium hydroxide treated rice husk.37(01),97-101.

J. Dietl, 1981. "Current Aspects in Low-cost Silicon Technology," in Proceedings Symposium on Materials and New Processing Technologies for Photovoltaics., Edited by; J.A Amick, V.K.Kapur, and J. Dietl, Pennington, NJ 10 S. Main St., Pennington 08534: The Electrochemical Society, 81-3, 48-61.

Jung DS, Ryou MH, Sung YJ, Park SB, Choi JW. 2013. Recycling rice husks for high-capacity lithium battery anodes. Proceedings of the National Academy of Sciences of the United States ofAmerica;110(30):12229-12234.

Kalapathy U, Proctor A, Shultz J. 2000. A simple method for production of pure silica from rice hull ash. Bioresource Technology;73(3):257-262.

Li, X. Zhu, 2011. Short-period synthesis of high specific surface area silica from rice husk char, Mater. Lett. 65, 1528–1530.

L. Zemnukhova, A. Egorov, G. Fedorishcheva, N. Barinov, T. Sokolânitskaya and A. Botsul, 2006. "Properties of Amorphous Silica Produced from Rice and Oat Processing Waste," Inorganic Materials, 42, 24-29.

Madrid, R.,Nogueira,C.,Margarido,F.2012. production and characterization of amorphous silica from rice husk waste,1-10.https://doi,org/ 10.1016/j.curtheres.2005.10.002

Mansaray,K.G and Ghaly,A.E, 2007. Physical and thermo chemical properties of rice husk,Energy sources,19:9, 989-1004

Matori, K. A., Haslinawati. M, Wahab. Z.,Ban, T. K., Ghani. W., 2009. Producing amorphous white silicafrom rice husk, 1(3):512-515

Ma X, Zhou B, Gao W, Qu Y, Wang L, Wang Z, et al. 2012. A recyclable method for production of pure silica from rice hull ash.Powder Technology;217:497-501.

Mehta.A.,Ugwekar.R, 2015. Extraction of Silica and other related products from Rice Husk,5(8):43-48.

M. Fang, L. Yang, G. Chen, Z. Shi, Z. Luo and K. Cen,2004. "Experimental Study on Rice Husk Combustion in a Circulating Fluidized Bed," Fuel Processing Technology, vol. 85,1273-1282.

M. Madani Hosseini, Y. Shao, J.K. Whalen, 2011. Biocement production from silicon-rich plant residues: Perspectives and future potential in Canada, Biosyst. Eng. 110 , 351–362.

M. Noushad, I. Ab Rahman, N.S. CheZulkifli, A. Husein, D. Mohamad, 2014, Low surface area nanosilica from an agricultural biomass for fabrication of dental nanocomposites, Ceram. Int. 40 4163–4171.

Nair, D.G., Fraaij, A., Klaassen, A.A.K., Kentgens, A.P.M., 2008. A structural investigation relating to the pozzolanic activity of rice husk ashes.Cem.Concr. Res. 38, 861–869.

N. Yalcin, V. Sevinc, 2001. Studies on silica obtained from rice husk,Ceramics Int. 27-219.

Patel, M.; Karera, A.; 1991.SiC whisker from rice husk: Microscopic study. Powder Metall. Int. 23 (1): 30-32.

P.B. Wagh, R. Begag, G.M. Pajonk, A.V. Rao, D. Haranath, 1999. Comparison of some physical properties of silica aerogel monoliths synthesized by different precursors, Mater. Chem. Phys. 57 214–218.

P. C. Kapur, 1985**.** "Production of reactive bio-silica from the combustion of rice husk in a tube-inbasket (TiB) burner", Powder Technol. 44, 63-67.

Pijarn, N.; Jaroenworaluck, A.; Sunsaneeyametha, W.; and Stevens, R. 2010. Synthesis and characterization of nanosized-silica gels formed under controlled conditions. Powder Technol. 203 (3): 462-468.

P.K. Mehta, 1979. Properties of blended cements made from rice husk ash.pdf, ACI Mater. J. 74, 440–442.

Prasad, C.S.; Maiti, K.N. 2003. Effect of substitution of quartz by rice husk ash and silica fume on the properties of whiteware compositions: Ceramics International, v 29, n 8, p 907-914.

Prasad,R., Panday. 2012. Rice husk ash as a renewable source for the production of value added silica gel and its application: An overview, 7(1), 1-25.

P. Sidheswaran and A. N. Bhat, 1996**.** "Recovery of amorphous silica in pure form from rice husk", Trans. Ind. Ceram. Soc.,55, 93-97.

Rafiee E, Shahebrahimi S, Feyzi M, Shaterzadeh M.2012. Optimization of synthesis and characterization of nanosilica produced from rice husk (a common waste material). International NanoLetters,2(1),29.

R. Condradt, P. Pimkhaokham and U. Leela-Adisorn.1992. “Nano-structured silica from rice husk,” Journal of Non-crystalline Solids, vol. 145, pp. 75-79.

Real, C.; Alcala, M. D.; Munoz-Paez, A.; Criado, J. M., XAFS.1997**.** analysis of the potassium-silica interaction in rice husks. Nuclear Instruments & Methods in Physics Research Section B-Beam Interactions with Materials and Atoms**,** 133 (1-4), 68-72.

Rhaman,M., Haque,M., Rouf,M.etal. 2015. Preparation and characterization of activated carbon & amorphous silica from rice husk, Bangladesh Journal of Scientific and Industrial Research,50(4),263.

Riveros H, Garza C. 1986. Rice husks as a source of high purity silica. Journal of Crystal Growth; 75(1):126-131.

R. V. Krishnarao and M. M. Godkhindi, 1992**.**"Studies on the formation of SiC whiskers from pulverized rice husk ashes", Ceram.Int**,**18, 35-42.

S. Chandrasekhar, P. N. Pramada and L. Praveen, 2005**.** "Effect of organic acid treatment on the properties of rice husk silica", J. Mater. Sci.**,** 40, 6535-6544.

S. Chandrasekhar, P. N. Pramada and J. Majeed,2006**.** "Effect of calcination temperature and heating rate on the optical properties and reactivity of rice husk ash", J. Mater. Sci.: Mater. Electron., 41, 7926-7933.

Shen, J. F.; Liu, X. Z.; Zhu, S. G.; Zhang, H. L.; Tan, J. J., 2011**.** Effects of calcination parameters on the silica phase of original and leached rice husk ash. Materials Letters**,** 65 (8), 1179-1183.

Silica–Titania. 2002. composites for water treatment, M. Eng. Thesis, University of Florida amorphous silica originated from rice husks. Materials Transactions**,** 48 (12), 3095-3100.

S. M. Lee, 2010. "Dictionary of Composite Materials Technology," Accessed online at http://composite.about.com/library/glossary/a/bldef-a329.htm.

Sun, L, Gong, K, 2001. Silicon-based materials from rice husks and their applications. Ind. Eng. Chem. Res. 40, 5861.

T.H. Liou, 2004. "Preparation and characterization of nano-structured silica from rice husk", Mater.Sci. Eng.,364, 313-323.

Thuadaij, N and Nuntiya, A. 2008.Synthesis and Characterization of Nanosilica from Rice Husk Ash Prepared by Precipitation Method.CMU.J. Nat. Sci. Special Issue on Nanotechnology, 7(1).

T. Lee, R. Othman, F.Y. Yeoh, 2013. Development of photoluminescent glass derived from rice husk, Biomass and Bioenergy. 59, 380–392.

Todkar,B., Deorukhkar,O.,Deshmukh,S.,2016. Extraction of Silica from Rice Husk.37(01),22-67.

T.W. Dijkstra, R. Duchateau, A. Rutger, van Santen, A. Meetsma, 2002. G.P.A. Yap, J. Am. Chem. Soc.124, 9856–9864.

Ugheoke,I.,Mamet,O.2012. Journal of Science and Technology A critical assessment and new research directions of rice husk,6,430-448.

U. Kalapathy, A. Proctor, J. Shultz, 2000. A simple method for production of pure silica fromrice hull ash, Bioresour.Technol.73- 257.

Umeda, J.; Kondoh, K., 2010**.**High-purification of amorphous silica originated from rice husks by combination of polysaccharide hydrolysis and metallic impurities removal. Industrial Crops and Products**,** 32 (3), 539-544.

Umeda, J.; Kondoh, K.; Michiura, Y., 2007**.**Process parameters optimization in preparing high-purity of amorphous silica.

U. Zulfiqar, T. Subhani, S. Wilayat Husain, 2015. Towards tunable size of silica particles from rice husk, J. Non.Cryst.Solids. 429, 61–69.

W.Ash,R.Alves,T.Vitoria,S.Rovani,D.Fungaro,.2017.Green Synthesis and Characterization of Bio silica Produced from Sugarcane Waste Ash doi: 10.1155/2017/6129035.

Wang, W.; Martin, J. C.; Zhang, N.; Ma, C.; Han, A.; Sun, L.2011**.**Harvesting silica nanoparticles from rice husks.Journal of Nanoparticles Research**,** 13 (12), 6981-6990.

Wu, G, Wang, J, Shen, J, Yang, T, Zhang, Q, Zhou, B, Deng, Z, Bin, F, Zhou, D, Zhang, F: 2000. Properties of sol–gel derived scratch-resistant nano-porous silica films by a mixed atmosphere treatment. J. Non-Cryst. Solids 275, 169.

Yalçin, N, Sevinç, V,2001. Studies on silica obtained from rice husk. Ceram. Int. 27, 219.

Y. Shinohara and N. Kohyama, 2004. "Quantitative Analysis of Tridymite and Cristobalite Crystallized in Rice Husk Ash by Heating," Industrial Health, 42,.277-285.

Y. Wang, A. Kalinina, T. Sun, and B. Nowack, 2016. “Probabilistic modeling of the flows and environmental risks of nano-silica,” Science of the Total Environment, vol. 545-546, pp. 67–76

# 7. APPENDICES

## Appendix A: Experimental Results

Table A-1 Moisture content of rice husk

| Run | Sample weight (g) | | | Moisture Content (%) | Average Moisture content (%) |
|---|---|---|---|---|---|
| | W1 | W2 | $\frac{W1-W2}{W1}$ | | |
| 1 | 77.6 | 70.5 | 0.09149 | 9.15 | 8.7 |
| 2 | 76.9 | 70.7 | 0.0806 | 8.06 | |
| 3 | 74.5 | 67.8 | 0.0899 | 8.99 | |

Table A-2 Volatile matter of rice husk

| Run | Sample weight (g) | | | Volatile matter (%) | Average Volatile matter (%) |
|---|---|---|---|---|---|
| | W1 | W2 | $\frac{W1-W2}{W1}$ | | |
| 1 | 1.986 | 0.811 | 0.5916 | 59.16 | 59.6 |
| 2 | 2.0295 | 0.8285 | 0.59177 | 59.1777 | |
| 3 | 1.997 | 0.789 | 0.6049 | 60.4907 | |

Table A-3 Ash content of rice husk

| Run | Sample weight (g) | | | Ash Content (%) | Average Ash content (%) |
|---|---|---|---|---|---|
| | W1 | W2 | $\frac{W2}{W1}$ | | |
| 1 | 23.1 | 6.7 | 0.29 | 29 | 29.67 |
| 2 | 23.4 | 7.2 | 0.30769 | 30.769 | |
| 3 | 57.8 | 16.9 | 0.29238 | 29.238 | |

Table A-4 Experimental (actual) and predicted values of silica yield

| Diagnostics case statistics | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Standard order | Run order | Actual value (%) | Predicted value (%) | Residual | Leverage | Student residual | Cook's distance | Outlier |
| 1 | 14 | 63 | 63.16 | -0.16 | 0.750 | -0.335 | 0.034 | -0.312 |
| 2 | 1 | 72 | 71.56 | 0.44 | 0.750 | 0.901 | 0.244 | 0.887 |
| 3 | 13 | 97 | 97.44 | -0.44 | 0.750 | -0.901 | 0.244 | -0.887 |
| 4 | 10 | 97.4 | 97.24 | 0.16 | 0.750 | 0.335 | 0.034 | 0.312 |
| 5 | 2 | 83 | 82.14 | 0.86 | 0.750 | 1.776 | 0.946 | 2.219 |
| 6 | 11 | 88 | 87.74 | 0.26 | 0.750 | 0.541 | 0.088 | 0.511 |
| 7 | 8 | 94 | 94.26 | -0.26 | 0.750 | -0.541 | 0.088 | -0.511 |
| 8 | 7 | 96 | 96.86 | -0.86 | 0.750 | -1.776 | 0.946 | -2.219 |
| 9 | 5 | 56 | 56.70 | -0.70 | 0.750 | -1.442 | 0.623 | -1.592 |
| 10 | 6 | 96.5 | 96.93 | -0.43 | 0.750 | -0.875 | 0.230 | -0.859 |
| 11 | 17 | 78 | 77.57 | 0.43 | 0.750 | 0.875 | 0.230 | 0.859 |
| 12 | 12 | 98 | 97.30 | 0.70 | 0.750 | 1.442 | 0.623 | 1.592 |
| 13 | 9 | 92.5 | 91.90 | 0.60 | 0.200 | 0.691 | 0.012 | 0.662 |
| 14 | 16 | 91 | 91.90 | -0.90 | 0.200 | -1.036 | 0.027 | -1.042 |
| 15 | 3 | 93 | 91.90 | 1.10 | 0.200 | 1.266 | 0.040 | 1.335 |
| 16 | 4 | 91 | 91.90 | -0.90 | 0.200 | -1.036 | 0.027 | -1.042 |
| 17 | 15 | 92 | 91.90 | 0.100 | 0.200 | 0.115 | 0.000 | 0.107 |

Table A-**5** Effect of process variables on the physical properties of the ash and silica

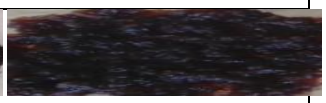
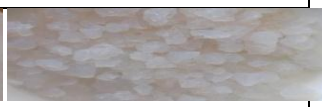
| Run | Acid Conc.(N) | Combustion temperature (°C) | Combustion time (hr) | Physical appearance of RHA | Physical appearance of silica |
|---|---|---|---|---|---|
| 1 | 1.5 | 450 | 1 |  |  |
| 2 | 1 | 450 | 3 |  |  |
| 3 | 2 | 450 | 3 |  |  |
| 4 | 1.5 | 450 | 5 |  |  |
| 5 | 1 | 650 | 1 |  |  |
| 6 | 2 | 650 | 1 |  |  |
| 7 | 1.5 | 650 | 3 |  |  |
| 8 | 1 | 650 | 5 |  |  |
| 9 | 2 | 650 | 5 |  |  |
| 10 | 1.5 | 850 | 1 |  |  |
| 11 | 1 | 850 | 3 |  |  |
| 12 | 2 | 850 | 3 |  |  |
| 13 | 1.5 | 850 | 5 |  |  |

Table A-6 Moisture absorptive capacity (%) of extracted silica

| Run | Sample weight (g) | | | $\frac{W2-W1}{W1}$ | Moisture absorptive capacity (%) | Average Moisture absorptive capacity (%) |
|---|---|---|---|---|---|---|
| | W1 | W2 | Increase in wt. due to moist air absorbed, (W2 -W1) | | | |
| 1 | 10 | 12.21 | 2.21 | 0.221 | 22.1 | 22.13% |
| 2 | 10 | 12.31 | 2.31 | 0.231 | 23.1 | |
| 3 | 10 | 2.12 | 2.12 | 0.212 | 21.2 | |

Table A-7 Moisture absorptive capacity (%) of commercial silica

| Run | Sample weight (g) | | | $\frac{W2-W1}{W1}$ | Moisture absorptive capacity (%) | Average Moisture absorptive capacity (%) |
|---|---|---|---|---|---|---|
| | W1 | W2 | Increase in wt. due to moist air absorbed, (W2 -W1) | | | |
| 1 | 10 | 12.69 | 2.69 | 0.269 | 26.9 | 25.4% |
| 2 | 10 | 12.41 | 2.41 | 0.241 | 24.1 | |
| 3 | 10 | 12.52 | 2.52 | 0.252 | 25.2 | |

## Appendix B: Calculation Part

B1: Fixed carbon content

$$FC = 100 - (MC + AC + V.M)$$

$$FC = 100 - (8.7 + 29.67 + 59.6)$$

$$= 2.03$$

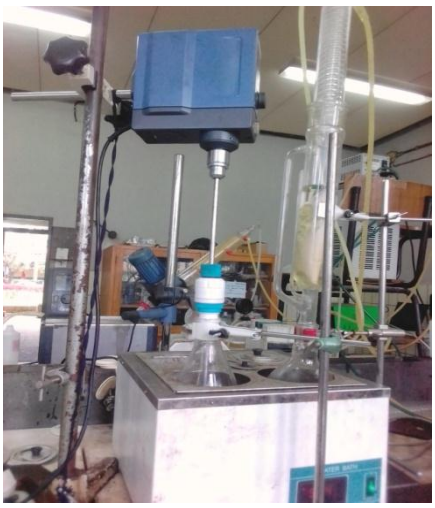
## Appendix C: Laboratory Equipment's and Samples Photo


C1: Reflux condenser for acid treatment of RH

C2: Acid Treated RH


C3: Furnace

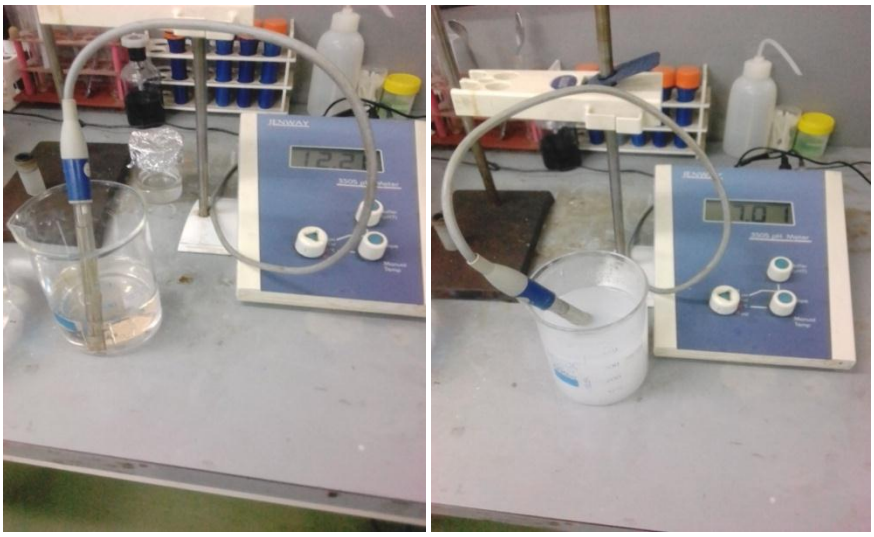
C4: RH after Combusted(RHA)



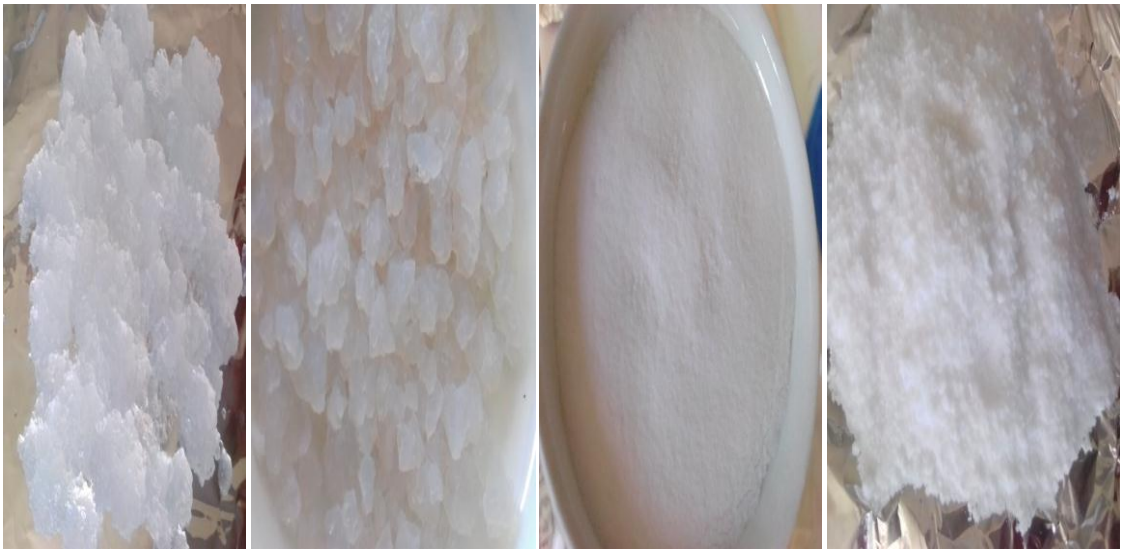
C5: Magnetic stirrer

C6: Vacuum filter

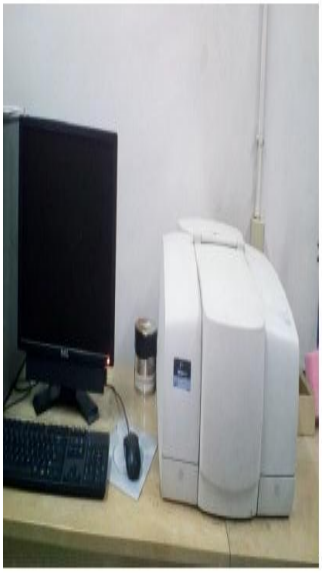
C**7:** Sodium silicate solutions



C8: sodium silicate solution before and after neutralization



C9: Silica products in gel and powder forms



C10: FT-IR instrument C11: Air permeability blaine meter C12: Moisture absorptive test

# Appendix D: Chemical analysis of RHA and Silica

Table-D1: Chemical analysis of RHA

| | GEOLOGICAL SURVEY OF ETHIOPIA | Doc.Number: GLD/F5.10.2 | Version No: 1 |
|---|---|---|---|
| | GEOCHEMICAL LABORATORY DIRECTORATE | | Page 1 of 1 |
| Document Title: | Complete Silicate Analysis Report | Effective date: | May, 2017 |

Issue Date: - 06/05/2019

Customer Name:- Mizer Girmay.

Request No: GLD/TR/275/19

Report No: GLD/TR/225/19

Sample type: - Ash.

Sample Preparation: - 200 Mesh

Date Submitted: - 17/04/2019

Number of Sample: Two (2)

Analytical Result: In percent (%) Element to be determined Major Oxides & Minor Oxides

Analytical Method: $LiBO_2$ FUSION, HF attack, GRAVIMETERIC, COLORIMETRIC and AAS

| Collector's code | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | CaO | MgO | $Na_2O$ | $K_2O$ | MnO | $P_2O_5$ | $TiO_2$ | $H_2O$ | LOI |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| ATRHA | 97.60 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | 0.09 | <0.01 | 1.55 | 2.24 |
| WWRHA | 87.10 | <0.01 | 1.32 | <0.01 | 0.36 | 0.34 | <0.01 | 0.08 | 0.52 | <0.01 | 1.44 | 9.34 |

**Note:** - This result represent only for the sample submitted to the laboratory.

| Analysts | Checked By | Approved By | Quality Control |
|---|---|---|---|
| Tihitna Beletkachew<br>Yohannes Getachew<br>Tizita Zemene<br>Yergalem Abraham<br>Bethlehem Tefera | Dessie Abebe | Gosa Haile | Negash Worku |