GENETIC ALGORITHM APPROACH FOR OPTIMISATION OF SILICA EXTRACTION FOR MICRO-CRYSTALLINE SILICON PRODUCTION

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CERTIFICATION

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ABSTRACT

Solar collectors mainly produced from poly-crystalline (P-Si) and micro-crystalline silicon (µ-Si) are in high demand in Nigeria due to persistent power challenges. The silicon are mostly imported and µ-Si is preferable due to its low cost. The µ-Si is extracted from Rice Husk (RH). However, the procedure of setting its optimal process variables (temperature, time and solvent volume) which are determinants of the reduction in cost is under reported in the literature. The aim of this study was to develop an approach for the optimisation of the extraction of µ-Si from rice husk using Genetic Algorithm (GA).

Ofada (F36) RH was collected from Erin-Oke town of Osun State in Nigeria. The RH was analysed for Volatile Matter (VM), Fixed Carbon (FC) and Ash constituents using standard method. The RH (1Kg) was run through two processes, one was treated with water to obtain Prewashed Rice Husk (PRH), while the other with 1 mole of oxalic acid in the range of 10-50 mL to obtain Leached Rice Husk (LRH). Central Composite Design (CCD) was used to determine the experimental combinations of the predictor variables: temperature (400-800ºC), time (2-6 h) and solvents (water and oxalic acid).Ten grams each of PRH and LRH were used to determine their silica yields (Y1 and Y2). Response equations were used as a fitness function for the GA optimisation. Optimal process variables levels predicted by the GA were validated by confirmatory experiments. The silica and silicon were characterised using X-Ray Diffraction and Scanning Electron Microscope. Optimal silicon was investigated using Raman spectroscopy. Data were analysed using t-test at $\alpha_{0.05}$.

The VM, FC and ash content were 70.7, 11.3 and 18.0%, respectively, while the Y1 and Y2 for the 75 experimental combinations from CCD were 86.9-92.3% and 93.2-98.0%, respectively. Second order response surface equations gave the best fit for Y1 and Y2. The optimal values of the predictor variables from the GA, namely: temperature, time and solvent volume were 648.8ºC, 6 h, 40.0 mL and 657.9ºC, 3.6 h, 40.0 mL for PRH and LRH, respectively. There were no significant differences between the values obtained from GA and those of the validation. The characterisation for both PRH and LRH showed amorphous silica, which implies that it is not hazardous to human beings. However, silica from LRH revealed porosity of large grain size due to acid leach, which makes it better for solar collectors' production than silica from PRH. The morphology of silicon produced from PRH and LRH revealed P-Si and μ-Si, respectively. Silicon yield of 2.3 g was observed in PRH and 4.2 g was observed in LRH respectively. Peak of 520.0 cm^{-1} was observed for silicon from LRH which was not significantly different from the peak for $\mu - Si$ (521 cm^{-1}).

Leached Rice Husk was best for the production of Micro-crystalline silicon, while Prewashed Rice Husk was best for Poly-crystalline silicon through Genetic Algorithm. This is an effective tool for the determination of optimal predictor variables levels for silica production.

Keywords: Rice husk, Micro-crystalline silicon, Optimisation of extraction.

Word count: 492

DEDICATION

This work is dedicated to the Almighty Father who gave me the grace and courage throughout the programme**.**

I also dedicate this work to my Late Sister, Architect. Dr. (Mrs) Abiola O. Baba, and also to my parents, Mr and Mrs, Peter Olawale, for their motivation.

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ABBREVIATIONS

PRH	Pretreated Rice Husk
LRH	Leached Rice Husk
HCl	Hydrochloric Acid
HF	Hydrofluoric Acid
µ-Si	Micro-crystalline silicon
GA	Genetic Algorithm
SEM	Scanning Electron microscope
XRD	X-Ray Diffraction
EDX	Energy Dispersive X-ray Spectroscopy
RH	Rice Husk
VM	Volatile Matter
FC	Fixed Carbon
A	Ash
µ-Si	Micro-crystalline Silicon
P-Si	Poly-crystalline Silicon

CHAPTER ONE

1.0 INTRODUCTION

1.1 Background to the Study

Silicon is a chemical element that has atomic number of 14; also the commonest element. The earth is made of more than 90% of silicon. It has grey colour with a metallic lustre, it is very strong, brittle and likely to be affected by chipping. Its melting point is 1414 ^{o}C and boiling point 3265 ^{o}C (Antonio and Steven, 2003). It is a semiconductor and the various types of silicon are crystalline and non-crystalline. The crystalline types are mono and poly crystalline while the non-crystalline are amorphous, Cadmium -Telluride (CdTe) and thin film silicon. Solar cell silicon can either be micro-crystalline (Nano-crystalline), mono-crystalline, amorphous, polycrystalline or multi-crystalline.

Silicon is a major component in making a solar cell. It is used in Phototvolatic (PV) industry in making different forms of solar panel. The main difference is in the purity. The purity is based on how perfectly arranged the silicon molecules are. The single crystal solar cells are the best with highest space efficiency of 15-20%; and lives the longest with warranty of 25years. The disadvantage is that they are expensive and if the solar panels are partially covered with shade or dirt, the entire circuit will breakdown. Poly-crystalline solar cell are simple and cost less but slightly worse than micro-crystalline and its disadvantage is low efficiency of 13-15%. Furthermore, thin film solar cells and string ribbon solar cells have efficiency of 7-13% (NERL, 2011). Micro-crystalline silicon is very useful in making micromorph (two layers with upper layer made of micro-crystalline silicon and lower layer using amorphous silicon). PV technologies are divided into three. First generation technologies are: crystalline silicon either mono or multi crystalline; second generation technologies are: Cadmium-Tellurde Indium Selenide (CIS); Copper Indium Gallium Diselenide (CIGS), Amorphous, micromorph (amorphous/ microcrystalline), and the third generation technologies which are : Organic PV and Concentrating PV(CPV) that are still subject to demonstration and has been mass produced. Solar energy has relatively low operation and up keeping costs. Nigeria is blessed with abundant solar energy with about 5250 Whm^{-2}/day as the annual average daily amount generated. The coastal area has 3500 Whm^{-2}/day while at the northern boundary it is 7000 Whm^{-2}/day. The amount of sunshine hours is about 6.5 hours all over Nigeria (Chineke and Igwiro, 2008).

Nigeria’s per capita power capacity is 28.5kW and produces 3,920 W which is inadequate for domestic consumption (Ibidapo and Ajibola, 2011). The lack of stable power supply in Nigeria has reduced the growth of the energy sector industries. Furthermore, the power sector has a significant effect on the lives of the populace and also takes central role in the economic transformation process in Nigeria. The country has been suffering from the problem of inadequate power for the past since over two decades. There is need for stable power supply in Nigeria in order to improve industrial development which would benefit the Nigerian energy and industrial sectors. There is campaign for using Renewable Energy in Nigeria today, in order to reduce the greenhouse effect and global warming. Furthermore, solar power will also enhance energy with minimum environmental effect (Nwoke *et al*., 2005).

Solar energy is regarded as the leading choice for the off-grid power generation because it can be installed in any location and can also be suitable and perfect for any power system required as long as enough PV panels are installed. It is also highly reliable based on the fact that it performs operation without faults. Generally, about 83% Nigerians are in areas without constant electricity supply (Uzorh and Nnanna, 2014). Therefore, building sustainable solar energy is highly rewarding via harnessing solar radiation using solar energy technology as a way to increase electricity supply. Moreover, poverty problem can also be solved or minimised if electricity problem is solved as more local industries will emerge and local goods will be produced and sold at lower prices. Since, there is abundant supply of sun energy in Nigeria, efforts should be intensified towards research and development geared towards solar energy conversion. Research needs to be tailored towards production of silicon which is a major component of solar panels production from available agricultural waste by converting agro residue into wealth.

Main sources of silicon raw materials are from rocks and biomass. Rice husk is an agricultural waste with high amount of silica content. Rice husk is a waste from rice producing areas in Nigeria; hence converting it into silicon production will reduce cost of waste treatment and also convert an agricultural waste into wealth. It was reported in the literature that polycrystalline silicon was produced from rice husk ash and if further purified can be useful for solar grade silicon. Temperature and time are the conditions which determine whether an amorphous or crystalline silica can be observed from calcinating rice husk. Furthermore, there is need to find the optimal conditions that will maximise the silica output generated from rice husk for large amount of silicon that will be produced.

GA is an optimisation technique which is based on survival of the fittest and is used mainly to determine the optimal process parameters. Literature is sparse on setting the optimal process variables for extracting amorphous silica from rice husk for micro-crystalline silicon production from rice husk. However, Genetic Algorithm (GA) will be used to observe the optimal conditions for the silica extraction.

This work is focused on setting the optimal process variables (temperature, time and solvent) to extract amorphous silica from rice husk for production of micro-crystalline silicon.

1.2 Statement of the Problem

Silicon which is a major component for a solar power is expensive and it is divided into crystalline and non-crystalline silicon. The crystalline is mono-crystalline and polycrystalline while the non-crystalline are: amorphous, micro-crystalline and thin film silicon. Conversion laboratory efficiency of large scale commercialisation for mono-crystalline is: 12.5-16 %, micro-crystalline is: 12-20% while it is 11-14 % for polycrystalline silicon. Though micro-crystalline silicon is expensive to produce, it is more efficient, more resistant to water droplets from thunderstorm and also diffuses sunlight better, initiating the need to find a cost effective process for its production. Problem associated with rice husk is high carbon content which produces smoke during the burning process thereby causing domestic and environmental problems. It also causes cancer via burning the husk at extremely high temperature (Haiping *et al.*, 2015). It is important to solve this problem by pretreating the husk before calcination. Rice husk contains high content of ash of about 90-98% and can be used as a primary source for silicon production.

1.3 Aim and Objectives

The aim of this project is to develop an approach for the optimisation of the extraction of micro-crystalline silicon from rice husk using Genetic Algorithm (GA).

The objectives pursued included to:

i. Determine and observe the effect of the extraction variables on the yield of silicon from rice husk;

ii. Formulate and develop models of silica yields with regard to the extraction variables (temperature, time and solvent);

iii. Define and solve the optimisation problem of micro-crystalline silicon produced from rice husk using Genetic Algorithm; and

iv. Validate the result of the optimisation.

1.4 Justification for using Rice Husk for Micro-Crystalline Silicon Production

Solar cell technology is advancing as a green and reliable source of electricity. Solar collectors mainly produced from poly-crystalline silicon (P-Si) and micro-crystalline silicon (µ-Si) are in high demand in Nigeria on account of power challenges. This shortage of supply silicon in the market is as a result of the ever increasing demand that needs to be bridged. Solar collectors are produced from poly-crystalline and micro-crystalline silicon (µ-Si) which are mostly imported. Micro-crystalline silicon is a better component for the manufacture of solar collectors.

This research will determine optimal process variables (temperature, time and solvent volume) that are determinants of the reduction in cost which is under reported in the literature.Commercial value of rice husk is due to its high silica content.

1.5 Scope and Delimitations

The scope of this research consists of the following elements:

i. This research is undertaken to develop GA theoretic approach for the optimisation of the extraction of micro-crystalline silicon.

ii. This research compares the amount of silicon yield from Prewashed Rice Husk and Leached Rice Husk processes

iii. The research considers setting optimal process variables and development of models of silica yield with regard to the extraction variables.

iv. This research validates the values of GA predicted for silica yield with those of the confirmatory experiment

1.6 Hypothesis

Based on the research the following hypotheses were tested:

H_o: The effects of the two portions of RH on silica yield are the same

H_1 Alternative: The effects of the two forms of RH on silica yield are not the same

1.7 Outline of the Succeeding Chapters

Chapter two presents the literature review, methodology used by previous researchers on the existing works on micro-crystalline silicon production. Chapter three discusses model development GA Optimisation via Matlab software and the validation of the model. In chapter four, results were presented while chapter five presents the conclusions of the study.

CHAPTER TWO

2.0 LITERATURE REVIEW

This chapter includes the review of works that have been carried out on the silica extraction, types of silicon, solar cells, micro-crystalline silicon production; Genetic Algorithm, appraisal of the existing works on the micro—crystalline silicon production and finally the concept of the proposed method to select GA approach for optimizing amorphous silica for micro-crystalline silicon was established.

2.1 History of Silicon

Silicon occur naturally and is found in dusts, sands as silica or silicates. However, about 28% by mass of earth crust composed of silicon after oxygen (O'Mara et al., 1990). Periodic Table shows it as the fourteenth element, in group IV. Its colour is dark grey. Its properties are similar to diamond. Its boiling point is 3265 ºC, Density is 2.3290 Km/m^3; and heat capacity of 22.3 J/mol K and 1414 ºC is its melting point (Bendix and Jeffery, 1991). Silicon's properties are presented in Table 2.1.

Table 2.1. Properties of Silicon

_Colour	Gray –black
Phase	solid
Hardness (Mohs)	7
Density (g/cm^3)	2.329
Melting point (K)	1683.2
Boiling point (K)	355
Heat of Atomisation (kJ/ms. K)	452
Thermal conductivity (J/ms .K)	149
Electron Configuration	[Ne] $3S^2 S^2 P^2$
Electron Affinity (KJ/ms.K)	133.6
Heat of Fusion (Kj/ms. K)	39.6
Common Oxidation Numbers	-4, +4

Source: (Antonio and Steven, 2003)

The most important component of most semiconductor devices is silicon arising from its many industrial uses. It has a metallic soft glow in its crystalline form and it is grey in colour. Moreover, silicon is prone to chipping and it’s very brittle and also very strong. However, Nitric Acid and Hydrofluoric do not affect it but it reacts with halogens and dilute alkalis (Hodson *et al.*, 2005). Though its pure form is 99.99%. Silicon is used in in glass manufacturing industries. Furthermore, also known as semiconductor material. It is a great important commodity in solar energy and in computer inventing business on account of its physical property.

According to Antonio and Steven (2003) silicon is attacked by water vapour or by oxygen transform into a surface layer of silicon-dioxide, at higher temperature. It is used as alloying element in steel, brass, aluminium and bronze. Synthetic oils, sealers and anti-foaming agents uses silicon metal in small quantity for composition of silicones (Fthenakis, 2004). Silicon chips are also used in making solar cells.

Abrasive material, in steel manufacturing industry, makes use of silicon (Cutler, 2008). It is in extreme short supply and will remain so for years to come. It is often stressed that silicon is in almost unlimited supply on the earth. However, this is just as naive as to the assertion that there is enough hydrogen in water (Sedra and Smith, 2004). Demand and capacity of silicon production in tons is shown in Figure 2.1.

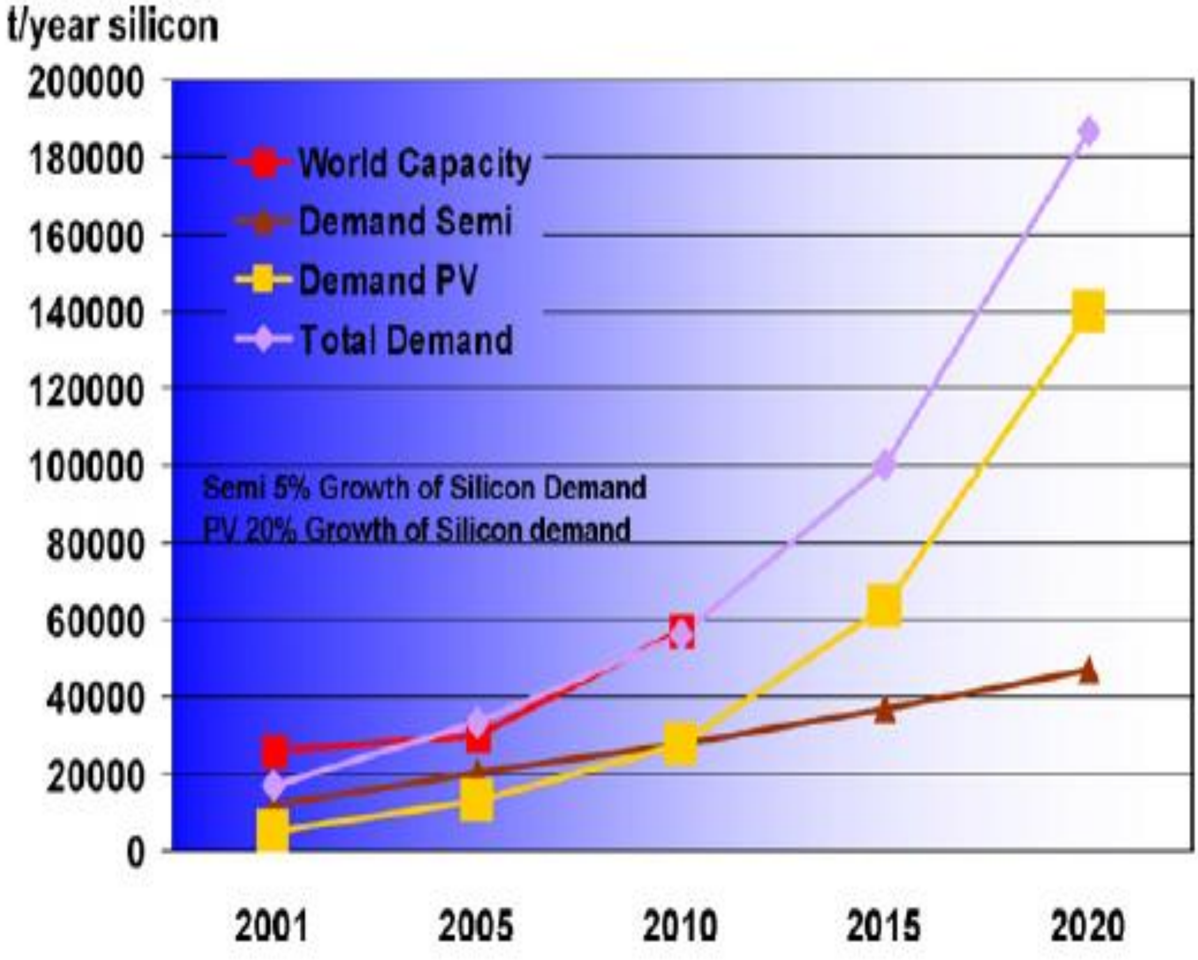


Figure 2.1. Demand and Capacity of Silicon Production (tons)

Source: (Müller *et al*., 2006)

Types of silicon:

2.1.1 Crystalline Silicon

The most suitable semi-conductor for use in P-N junction solar cells is the one whose band gap is the same amount to photon energies of about 830nm, band gap ~1.5Ev, and is nearly the centre of the solar spectrum (Chopra *et al.,* 2000). Nevertheless, no appropriate elemental semiconductor substances of this category are available. Notwithstanding, in photovoltaic cells silicon is the principal substance used in its production and is processed using various non-identical techniques based on its calculated approach. Solar cells made from crystalline silicon at times known as first generation solar cells are predominantly classified into two groups: mono-crystalline and poly-crystalline.

2.1.2 Mono-crystalline Silicon

According to Meyer *et al.,* (2004), mono-crystalline silicon is a continuous single crystal usually produced by the Czochralski crystal growth. The efficiency of mono-crystalline silicon cells is proportionately high and its electrical characteristics are fixed. A high price with the use of proportionately thick wafers of pure silicon for averagely 40% of the whole manufacturing cost is the important determinant. This acknowledged that significant manufacturing and cost curtailment industries would only likely be using less substance or finding reasonable substitute. Notwithstanding the high price, 40% of the solar cells manufactured in 2002, are sole crystal silicon and as stated in manufacture’s data of 2004, 15% is the efficiency for single crystalline silicon (Chopra, *et al.*, 2000).

2.1.3 Poly-crystalline Silicon

Poly-crystalline or multi-crystalline silicon is not a single crystal. Literature review proved that it can be manufactured using substandard silicon substance. Crystals of different measurements were produced throughout the procedure, which demonstrates faults at the border of different crystals. It is then cut into plates used in modules which reduces the efficiency of the single-crystalline cells. Green, 2004 stated that polycrystalline produced was 50% with 10-12 % efficiencies.

2.1.4 Thin Film Silicon

Amorphous silicon also known as thin film silicon can take in solar radiation better than crystalline silicon. The total efficiency of 6% is lowest. The silicon film can be used in glass or other materials, like plastics. Amorphous silicon cells constituted approximately 8% of world’s solar cell manufactured in 2002. The core problem with amorphous silicon cell is its instability (Chopra *et al.,* 2000).

2.1.5 Ribbon Silicon:

This kind of multi-crystalline silicon is produced by cutting flat thin films from molten silicon. Ribbon silicon has reduced efficiencies than poly-Si, it also saves manufacturing prices (Antonio and Steven, 2003).

Future beliefs on crystalline silicon solar cells

It was reported that crystalline silicon cell give high efficiencies with important features for industrial production in solar cells. The impacts of novel technologies such as Quantum dots (QDs) and photon management is good as research and development on crystalline silicon solar cells continues (Tatsuo, 2010).

2.2 Sources of Silicon Raw Materials

Dietl (1981) identifies two major sources of silicon raw materials. The primary source of silicon is silicon dioxide commonly known as silica. They are relatively in pure form that can be found in almost all mineralogical rocks (Hunt, 1990). Second source is in biomass such as rice husk and been researched intensively for several industrial applications (Shinoraha and Kohyama, 2004). Most biomass resources are waste by-products whose disposal causes environmental nuisance (Kingsley, 2010).

Characteristics of Amorphous Silica

Amorphous silica is synthetically produced oxide of silicon characterised by the absence of a noticeable crystalline structure whose XRD patterns have no sharp peaks. The classification of amorphous silica into gel or powder largely depends on bond between the colloidal particles. Silica gels are characterised by a coherent three dimensional network of contiguous particles whilst small granules of submicron particles that are weakly linked together is silica powder (Kingsley, 2010).

2.3 Existing Silicon Manufacturing Technologies

Currently, the most commercially established silicon synthesis methods are the carbothermic reduction of silica in submerged electric arc furnace resulting in metallurgical grade silicon (MG-Si) and the conventional Siemens or trichlorosilane process for electronic grade silicon (EG-Si). These two well- established processes produce bulk silicon material that lies on the extreme end of the purity requirements for solar grade silicon. Thus, the approaches to synthesis of solar grade silicon are currently pursued along the improvement of solar grade (Fereday, *et al.*, 1996).

2.3.1 Production of Metallurgical-Grade Silicon (MG-Si)

The submerged arc furnaces are usually used for commercial carbothermic production of silicon. The furnace consists essentially of a set of pre-baked carbon electrodes, refractory lined steel crucible and the charge mix. The charge mix typically comprises silica in the form of lumpy quartz or quartzite rocks, coke or coal, and wood chips. The coke is the reducing agent and the wood chips serve to improve charge porosity. This furnace is also useful for adjusting the raw materials as needed to correct the charge composition as well as prevent any gaseous build up in the furnace (Fereday *et al.*,1996).The overall reaction to produce silicon metal can be represented by the following equations:

$$SiO_2(S) + 2C = Si(l) + 2CO(g) \qquad 2.2$$

The process however produced gaseous silicon monoxide (SiO) and silicon carbide (SiC), Liquid silicon was produced in the inner hot zone of the furnace at temperature range of about 1900 to 2100 °C. The reactions are described by the following equations (Ceccaroli and Lohne, 2003):

$$\mathrm{SiO_2(s) + 2C = Si\ (l) + 2CO\ (g)} \qquad 2.3$$

$$2SiO_2(l) + SiC = 3SiO(g) + CO(g) \qquad 2.4$$

$$SiO(g) + SiC(s) = 2Si(l) + CO(g) \qquad 2.\ 5$$

$$SiO(g) + 2C(s) = SiO(s) + CO(g) \qquad 2.6$$

$$2SiO(g) = Si(l) + SiO_2(s) \qquad 2.7$$

2.3.2 Production of Electronic Grade Silicon (EG-Si)

Electronic grade silicon commonly known as polysilicon or semiconductor grade silicon is produced mainly by the Siemens- process. The first part of the process involves halogenation of finely ground MG-Si in a fixed or fluid bed reactor with gaseous hydrochloric acid (HCl) in the presence of copper as catalyst. Mixtures of chlorosilanes are obtained while SiH_3Cl, SiH_2C_2 are recycled and the heavier fractions are utilised through a series of fractionating columns to produce purified triclorosilane (SiHCl3). The $SiHCl_3$ is subsequently decomposed in the presence of hydrogen at temperature of 1000 -1100^{0}C over inverse U-shape hot filaments in a Siemens reactor. The overall reaction process can be represented as conceived by Goetzberger *et al.*, (2003) as:

$$Si(s) + 3HCl(g) = HSiCl_3(g) + H_2(g) \quad \text{(at } 300^0\text{C)} \qquad 2.8$$

$$2HSiCl_3 \sim (g) + H_2(g) = SiCl_4(g) + 2HCl(g) \quad \text{(at 900-1100 } ^0\text{C)} \qquad 2.9$$

Poly-silicon produced from the Siemens reactor reaches a purity in the order of 9-11N and are further processed into single crystal silicon by the Czochralski crystal growth technique. The Siemens process produces silicon of unparalleled purity. However, it is limited by the high cost of the final silicon products, low volume of production due to the relatively slow nature of the decomposition reactions, complex set up, energy intensive, and the use of high corrosive chemicals which can potentially burden the environment in terms of emissions (Goetzberger *et al.*, 2003). Presently, modifications have been made to the process to include decomposition of silanes (SiH_4) over seed silicon granules in fluid bed reactors. However, the cost reduction potential of the final silicon product by the original process and its variants still remain low.

2.4 Renewable Energy (RE) Commercialisation

Renewable energy technologies are the important donors to the world energy security. It also reduces greenhouse gases (GHGTs) effects (Renewable Energy, 2007). There are three generations of renewable energy technologies according to the International Energy Agency which are:

2.4.1 First-Generation Technologies of RE

First-generation technologies are used in later part of 19th century from industrial change. They are: hydropower, biomass combustion, geothermal power and heat.

Their later usage relies on the investigation of the rest of the probable resource and on prevailing problems pertaining in the environment.

2.4.2 Second-Generation Technologies of RE

These are solar thermal technologies; examples are wind power and photovoltaic. These are just coming into market. Trades for second-generation technologies were robust, at the same time improved over the previous years.

2.4.3 Third-Generation Technologies of RE

Third-generation technologies include biomass gasification, bio-refinery technologies, solar thermal power stations and ocean energy. Majority are on the horizon and have comparability to other renewable energy technologies (Renewable Agency, 2007). Biomass that can be used for silica extraction are Corn stalks, wheat straw and rice straw and wood waste. According to IEA (2007); renewable energy efficiency policies are complementary tools for sustainable energy which needs to be developed.

2.5 Nanotechnology Boosts Solar Cells Performance in Solar PV Cell

Nanoscale materials are substances or materials of approximately 100 nm. Nano-materials are very minute.

Nanotechnology are also used in various fields related to energy saving, energy, conversion, manufacturing equipment by reducing materials, and renewable energy devices. Renewable energy targets done legally is as suggested by the United Nations Environment Program (UNEP,2006). Inefficiencies and their expensive manufacturing cost are the two major known drawbacks in conventional solar cells. The main problem is inefficiency.

Three significant effects of Nano-structured layers in thin film solar cells are listed as follows:

i. light generated electrons and holes need to be transported in shorter path and recombination losses will be reduced. The absorber layer thickness in nano-structured solar cells can be as thin as 150 nm substitute of several micrometers in the traditional thin film solar cells

ii. Due to multiple returns of rays of light, the actual film thickness produces better effective optical path for its absorption

iii. Thirdly, varying the size of nano particles converts the energy band gap to desired form or value.

However, this research is based on investigating the optimal process parameters to optimize extraction of micro-crystalline silicon from rice husk. Micro-crystalline silicon is the most effective type of silicon for a solar collector. Ultraviolet light efficiently couple to nanoparticles produces electricity (Suresh, 2013).

The bulk materials have smaller radius than semiconductor crystals. Nevertheless, Bohr radius is larger than nanocrystals diameters. Larger nanocrystals is the red light with longer wavelengths while small nanocrystals absorb small nanocrystals with shorter wavelengths or bluer light (Sethi, *et al.*, 2011). It was reported in the literature that converting bulk silicon into separate or nano-sized particles improved solar cells. This nanoparticles depending on different sizes, exhibit emission of light.

2.5.1 Improving the Efficiency of Solar Cells by Using Semiconductor Quantum Dots (QD)

Semiconductor quantum dots (QD) increase the efficiency of solar cells. Quantum dots have also been extensively studied for PV applications had been based on Quantum Dots

It was reported that the motivations depends on: (i) QD synthesis which are used together with solution-based processes.

(ii) small nanoparticles, or quantum dots(QD) (Topinka, 2007; Gregg, 2005).

Si/Ge QD solar cells advantages are:

1) Infrared spectral region gave higher light absorption,
2) At higher temperature, photo current increases
3) Better radiation hardness compared with conventional solar cells,
4) Standard silicon solar cell (Topinka, 2007; Greg, 2008).

2.5.2 Nanotechnology: Improvement on the solar Cell

The present nanotechnology solar cells are not efficient as traditional ones. Nanoparticles are coated with Quantum dots which convert high-energy photons into multiple electrons. Furthermore, as quantum dots increases spectrum of sunlight waves by 65 per cent, conversion efficiency increases. Quantum dots is also used in the hot carrier which is another phase.

The photo conversion efficiency in nanostructured electrode and utilization of CNT network anchor light is used in harvesting semiconductor particles by assisting the electron transport to the collecting electrode surface in DSSC. This is a challenge when transporting electron across the particle network. CNTS attached in Cdse & CdTe it induces charged transfer process under visible light irradiation.

Charge injection from excited CdS into SWCNT excitation of CdS nanoparticle is observed. Enhancement in interconnectivity of titanium dioxide particles and the MWCNTs in the porous titanium dioxide film is based on circuit current density (Landi *et al.*, 2005).

Application of Nanotechnology Use in Solar Cells.

It was reported in the literature that nanotechnology aids in production of clean energy and its transmission and conversion via more efficient and precise applications. Energy output of low-cost photovoltaic (solar cells) increment is one of the most exciting possible short term applications of nanotechnology (Drexler, 1996)

The nanotechnology advantages in solar cells are listed below:

1) It also makes collection more productive and makes transmission easier. It was reported in literature that energy lost in transmission from power plant and its final destination on account to resistance in the wires is 7 and 10 percent. However, technology is currently developed on use of carbon nanotubes that 10 times more conductive than the copper wires that allow electrons to flow down wires easily as photons of light through optic cables.

2) Nanotechnology helps to change the environment via utilisation cheap solar cells (Nayfeh, 2004)

3) Nanotechnology is useful for solar cells in military. US Department of Energy concluded that nanotechnology is one of the most useful methods for getting cheap and highly efficient solar energy as reported in the literature.

A company in the USA (Konarka Technologies) uses nanotechnology to create flexible plastic solar cells which are powerful than most inflexible semiconductor cells.

However; flexible, roller-processed solar cells have the potential to turn the sun's power into convenient source of energy. The efficiency of plastic photovoltaic solar cell is not great, but covering cars with Plastic photovoltaic solar cells or making solar cell windows would generate the power and save the fuel and also help to reduce the emission of carbon gases (Sethi *et al.*, 2011).

2.5.3 Theory and Future Trends in Solar Cells

Solar cell absorbed electromagnetic radiation from the sun. Negatively charged electron from valence band is given by a photon while a positively charged vacancy, called a hole is left behind. However, it is expected that energy will be diminished as heat while electron is reduced or else the photon must have greater energy than the bandgap.

An electron is created by the photon and bandgap while hole is in excitation and are free to move in the semiconductor crystal. Energy moves to the electrical contact, and acts as charge carriers, which gives a slow and steady external current.

Light conversion process is based on the structure of the solar cell. A solar cell is composed of semiconductor material (Gregg, 2005). Not all incoming light from solar are converted into usable energy. Furthermore, sun radiation appears in different colours, however blue light is more efficient while red light is less. Electrons are excited by higher energy light but beyond bandgap, energy is lost as heat. Ultraviolet light is filtered out by the silicon in a conventional solar cells. Ultraviolet light is efficiently couple to sized nanoparticles and produces electricity (Suresh, 2013).

2.5.4 Advantages and Limitations of Solar Energy

2.5.4.1 Advantages of solar Energy

The advantages of solar energy are listed as follows:

1.Security: The US military concluded that solar power, if combined with microgrids; provides secure electricity.

2. Jobs & Economy:

Wind energy industry, coal industry and natural gas industry provided jobs due to solar energy invention. Solar power is good for creating jobs and improving the economy especially in the areas with poor electricity distribution.

3. Peak Power: Electricity demand increases daily, because it is used mainly during the time. At that time, electricity is most expensive because there are small number of suppliers available with less competition. So, the electricity generated from solar energy systems is actually much more valuable (Harin, 2007).

4. Energy Independence: Introducing solar power systems can cut down their energy dependence. PV panels for solar systems have low maintenance because they are easily installed.

2.5.4.2 Solar Energy Limitation

The limitation of solar energy is probably the cliche that “the sun doesn’t shine all the time” if not the world would certainly run on solar power (Zachary, 2014)

Furthermore; PV cells are expensive (but getting cheaper) and lastly

Solar panels functioning effectively in countries which do not have a lot of sunlight every day.

2.5.5 Types of Solar PV System

The three main classification of solar PV systems are:

i. Grid-connected (or grid-tied) and
ii. Off-Grid (or stand-alone) solar PV systems.
iii. Grid-Connected with Battery backup

I. Grid-connected solar PV systems

Majority of the solar PV systems are put on buildings.

There are two parallel power sources to a building: solar PV system and the power grid. The power supply feeds all the loads connected to the main source. The size of the solar PV system depends on amount of power supply to the grid. If there is no sunlight to produce PV electricity at night, the power grid will provide all of the building’s needs. Grid-connected solar PV system significant is to reduce the dependence on electricity.

Grid-connected systems consist of:

i. Solar panels mounted on the roof
ii. An inverter
iii. A power meter
iv. Junction box
v. power meter

iv. A disconnect switch

II. Off-grid solar PV systems

Areas without power grids makes use of off-grid solar PV systems are used in areas without power grids. These are usually installed at isolated sites. It is used in areas where it is costly to tap electricity from the power grid.

An off-grid solar PV system uses rechargeable batteries to store electricity for use where there is little or no output from the solar PV system at the night.

These systems are:

i. Solar panels

ii. A rectifier

iii. A charge controller for battery

iv. A junction box

v. Power meter

vi. A disconnect switch

vii. An inverter

III. Grid-Connected with Battery Backup: This system has a “battery bank” collect the power generated from the solar panels. Power stored in the batteries are used during power failure.

This system consists of:

i. A charge controller
ii. ii. A junction box
iii. Solar panels
iv. An inverter
v. A battery bank
vi. A power meter
vii. A disconnect switch (NABCEP, 2008).

A solar PV system is produced from either crystalline or thin film PV modules. Individual PV cells are interconnected to form a PV module. PV cells are composed of light-sensitive semiconductor electrons to generate electric current. Two broad groups of technology for PV cells are crystalline silicon and thin film. Majority of PV cells are made from crystalline silicon while thin film is increasing in popularity.

Thin film PV modules that are commonly available are: mono-crystalline silicon, CIgS thin film silicon, Poly-crystalline silicon and flexible amorphous thin film.

Crystalline Silicon and Thin Film Technologies

Silicon wafers of 150-200 microns (one-fifth of a millimetre) thick are used. 0.3 to 2micrometres thick, deposited onto glass or stainless steel substrates are used for making thin film.

Cost of raw material are lower than capital equipment and processing costs because the semiconductor layers were thin film. Conversion efficiency is the major difference in PV cell technologies apart from aesthetic difference, as summarized in Table 2.2. Crystalline silicon PV array module efficiency is halved because thin film amorphous silicon PV array requires twice its space.

Table 2.2: Conversion Efficiencies of various PV Module Technologies

Conversion Efficiency	Module Efficiency Technology
Mono-crystalline Silicon	15-21.5%
Poly-crystalline Silicon	13-16%
Copper Indium GalliumSelenide (CIGS)	10-13
CadmiumTelluride (CdTe)	9-12%
Amorphous Silicon (a-Si)	5-7%

Source: (Green, 2011)

Photovoltaic Efficiency: The Temperature Effect

According to Swapnil, *et al.,* (2013), solar cell performance decreased with increasing temperature, owning to internal carrier recombination rates, caused by increased carrier concentrations. Operating temperature is based on electrical efficiency and the power output of a PV module. Solar PV performance is based on temperature coefficient of power in hot climates. Panels are either cooled actively or passively. External source is used to run in active system while in a passive system, no power is added.

A passive system is an array of panels that are set on roof of 2 feet (61cm) to allow air to naturally flow behind the panels and remove heat, or a white–coloured roof that prevents the surface around the panels to prevent heat. An active system on the other hand; have fans to blow air over the panels from heating and causing additional heat gain. An active system is used with a solar power plant constructed in the desert uses an active system

Temperature affects the flow of electricity by changing the speed at which electrons travels. Low temperature makes PV panels are more effective.at low temperature, therefore cooling panels function for higher efficiency and produce more power.

Temperature decrease by one degree Celsius when voltage increases by 0.12V for polycrystalline PV panels; so temperature is 0.12V/C. The general equation for estimating the voltage for a material at a specific temperature is:

$$V_{oc,ambient} = TempatureCoefficientX\,(T_{STC}[^{O}C] - T_{ambient}[^{o}C] + V_{OC,rated}V] \qquad 2.10$$

where;

$V_{OC\ (\ mod)}$= Open circuit voltage at module temperature

Tambient [oC]=module temperature

VoC rated=open circuit at STC;

$T_{STC}[^{O}C]$=temperature at standard test conditions ,25^{o}C, 1000W/m^{2}solar radiance

As an example, for polycrystalline, the equation IS:

$$V_{OC,new} = 0.12[{}^{V}\!/_{C}]X\,25[^{O}C] - T_{ambient}[^{o}C] + V_{OC,rated}[V] \qquad 2.11$$

Crystalline technologies have larger negative temperature coefficient than most thin film technologies. They lose the ability to absorb as temperature rises.

According to Guda and Aliyu (2015), PV array has higher energy conversion efficiency of 13.4% during the harmattan while 12.43% during sunny season when the average seasonal temperature is 46 ^{o}C, 0.5 Volts and current is produced by most PV cells, which depends on the solar irradiance and geometry of the cell is produced by most PV cells. (Halne, 2000). PV module data sheet temperature coefficient is shown in Table 2.3.

Table 2.3. Temperature coefficient of various PV cell Technologies

Technology	Temperature Coefficient [%/°C]
Crystalline silicon	-0.4 to -0.5
CIGS	-0.32 to-0.36
CdTe	-0.25
a-Si	-0.2

Source: (NERL, 2009)

The solar module

The solar module is surrounded by protective material which is made of silicon semiconductor which are then embedded in ethylene vinyl acetate. Backing is made of polyester film. The glass cover which is a lightweight plastic covers satellite arrays, found on terrestrial arrays. Electronic parts are made of copper. The frame is either steel or aluminium which is binded by silicon (NERL, 2009).

How to Choose a Solar System

Solar electricity depends on number of batteries, capacity of the inverter and number of solar panels .The amount of sunlight absorbed is much more important than the temperature. Solar panels work well in cold climate because they don’t overheat, thus enhancing its performance, as observed in the literature. The key things that affect solar electric system are: amount of sunlight received, amount of conventional power to offset the solar system, budget, amount of space you need on the roof or in the yard where solar panels will be mounted.

Space and Orientation: Maximum space needed is 100 square feet for highly effective performance of solar system. If the roof does not face south, solar electric system can still be used.

Roof tilt: aids the path of the sun, but requirements vary with location. Proper tilt needs to be calculated based on the solar resource of the area. Solar panels are also integrated into roof shingles and tiles.

Size; If the roof is more than 15 years, it is advisable to change it before purchasing solar electric system.

Shading: Shading a panel reduces its performance as it blocks sunlight. Solar panels are shaded by structures like: trees, nearby buildings and electrical cables.

Ground-Mounted Systems: if there isn’t enough roof space, then a ground-or pole-mounted solar system, with same orientation and tilt can be used (NERL, 2009).

2.6 Solar Photovoltaic Technologies

Sunlight changes directly into electricity using photovoltaic effects. It is one of the fastest upcoming renewable energy technologies in the global electricity generation (Jingbi *et al.*, 2013). Solar PV systems are easily available to individuals, and small-enterpreneurs that wants use right their own methods for generation of electricity prices (Joachim *et al.*, 2002).

Benefits of PV technology are listed below:

PV is a renewable resource;

It can be used virtually anywhere and at any time;

PV technology has no fuel costs and relatively low operation and maintenance (O&M) costs.

2.6.1 First Generation PV Technologies: Crystalline Silicon Cells

The most commonly used material in the PV industry is crystalline silicon which is within the electronic industry which is in mass production.

Three main types of crystalline silicon cells are:

Monocrystalline;

Polycrystalline; and

EFG ribbon silicon and silicon sheet-defined film growth (EFG ribbon-sheet c-Si). (Green, 2002). However, 87% of global PV sales in 2010 was the amount generated for crystalline silicon technologies (Schott, 2011). The efficiency of crystalline silicon modules ranges from 14% to 19% as shown in Table 2.4.

Table 2.4. Comparison of different Photovoltaic Cell

Sub-Types	Mono-Crystalline	Poly-Crystalline	CdTe	CIGS	a-Si	Multi Junction
	Purity 99.99999%	Purity 99.99999 %	Low temperature Sensitivity	Captures large spectrum	Amorphous silicon	GaAs/cis a-Si/mc-Si
Description	Crystalline Silicon wafer		Semiconductor deposited on glass			
Module efficiency	High		Low			
Performance under heat	Performance degrades with higher temperatures		Up to 60% lower heat coefficient than crystalline silicon modules, making it a good choice in hot climates			
Space required per kWp	Polycrystalline :10m^2-30m^2 Depending on cell spacing Monocrystalline :>8m^2		Glass- glass laminate ~25 m^2			
Degradation	Degradation		Degradation			
Direct or diffuse light	Direct or diffuse light		Direct or diffuse light			
Amount of photovoltaic material needed	Poly silicon: 8g/W		CdTe:0.22g/W			
Efficiency Production	15-20%	13-15%	10%	12%	7%	36%
Efficiency (lab)	25%	21%	16%	20%	10%	20%
	~7M^2	~8M^2	~10M^2	~10M^2	~12M^2	~8M^2

Source: (Sethi *et al.*, 2011)

2.6.2 Second Generation PV Technologies: Thin Film Solar Cells

Thin-film solar cells has low cost for generation of electricity than crystalline Silicon solar cells. Thin-film solar cells comprised of successive thin layers of 1 to 4 µm thick, of solar cells deposited on materials such as glass, polymer, or metal. They require less semiconductor material to generate electricity in order to absorb the same amount of sunlight. Thin films can be assembled into flexible and lightweight structures, which can be easily integrated into components. The three primary types of thin-film solar cells are:

- Amorphous silicon (a-Si and a-Si/µc-Si);
- Cadmium Telluride (Cd-Te); and
- Copper-Indium-Selenide (CIS) and CopperIndium-Gallium-Diselenide (CIGS).

2.6.3 Third Generation PV Technologies

Third-generation PV technologies are still at the pre-commercial stage. The four types of third-generation PV technologies are as follows:

- Concentrating PV (CPV);
- Dye-sensitized solar cells (DSSC);
- Organic solar cells; and
- Novel and emerging solar cell concepts (Jingbi *et al.*, 2013).

2.7 Polymer Solar cell

Photovoltaic effect is the process in which polymer solar cell produces electricity. Highly purified silicon crystals are used in most commercial solar cells which is similar to the material used in the production of integrated circuits and computer chips. Interest is generated in alternative technologies based on high cost of silicon solar cells and their complex inventing process. Polymer solar cells do not have any environmental pollution though they have lightweight and are cheap. Polymer solar cells are transparent, and are used in making windows, walls, flexible electronics, etc. (Joachim *et al.*, 2002).

Polymer solar cells have stability problems (Scharber *et al*., 2006). Over 10% efficiency via a tandem structure is beneficiary to polymer solar cells. The main difference between solar cells based organic materials and conventional inorganic photovoltaic (IPV) cells is structure for excitons in molecular materials, rather than in free electrons and holes.

An exciton in an organic semiconductor is considered as a tightly coulombicly bound electron hole pair. The electrical neutrality and the strong binding energy between the hole and the electron is called the mobile excited state. However, the processes involved in the conversion of photons into electrical energy are not the same as those occurring in IPV cells (Gregg, 2005).

Basic processes in organic solar cells

Five important processes for effective organic photovoltaic cells in solar energy are:

1. Absorption of light and generation of excitons
2. Diffusion of excitons to an active interface
3. Charge separation
4. Charge transport
5. Charge collection

2.8 Assessment of Solar Radiation Patterns for Sustainable Implementation in Nigeria

Nigeria is facing power shortage. Six thousand 6,000Mega Watt generating capacity was installed by Power Holding Company of Nigeria (PHCN) now GenCOS with peak demand of 30,000MW which provided 3,000MW with loss of 30-35 % incurred during transmission (Stanley, 2008; Hall, 2006).

Summary of the Nigerian Electricity Industry Scorecard for the First-half of 2008 showed a little improvement of 5,567,706MWH and 3,761,794MWH during the first and second quarters respectively, with loss of 10-20 % whichg occurred during transmission. Also, 0.153, 0.125, 0.089, and 0.079 for 2002, 2004, 2006 and 2007 respectively were estimated as per capital energy consumed in Nigeria. These values show great differences when compared with 1.78 and 0.68 per capita for World average and Africa respectively needs urgent attention (NERC, 2008; Sambo, 2001). There is an abundant renewable energy source across Nigeria which makes sustainable energy technologies (SETs) a viable option for the country.

Solar energy is from sunlight for producing electricity using photovoltaic (PV) solar cells. Photovoltaic technology is the shortest conversion of sunlight into electricity using semi-conductor devices called solar cells, which are almost maintenance free and have a long life span. The longevity, simplicity and minimal resources used to produce electricity via PV make this a highly sustainable technology (IEA, 2011).

Solar collectors produces solar energy in form of heat while solar PV panels produces solar energy in form of electricity which are manufactured with varying electrical outputs ranging from a few watts to more than 100 watts of direct current (DC). Solar radiation data is still very rare for developing countries where there is an acute shortage of conventional source of energy. However, many attempts were made to develop models that can predict the amount of solar radiation available at a given place using small parameters (Akpabio *et al.,* 2005; RISE, 2010).

The resources available for sustainable power generation in Nigeria was explored by NERC. It was observed that average daily solar radiation vary from 7KW/m^2/day in the northern border regions to 5KW/m^2/day in the coastal regions of South, and an average daily sunshine hours is 8 hours/day in the northern border regions to 6hours/day in the coastal regions of South. It was then concluded that availability of sunshine for solar energy in Nigeria is in three classes; low, medium and high regions respectively (Iloeje, 2004, NERC, 2008).

Businesses that rely on electricity become less efficient and lose profit due to power shortage. Therefore, research effort to develop alternative sources of energy should be made better in the country for domestic power supply of electricity to a cluster of households and shops and also for urban and rural homes in Nigeria. According to NASEF (2007), solar PV panels challenge are: high initial capital investment, low public awareness, lack of suitable institutional framework, regulatory and technical standard and local manufacturing of solar system parts. Abdulsalam *et al., (*2012); considered solar radiation data as prerequisite to sustainable power supply through solar energy. It was also reported that 22.88MJ/m^2/day, 18.29MJ/m^2/day and 17.08MJ/m^2/day are annual mean of monthly global solar radiation for high, medium and low zones respectively.

Solar sunshine duration for high, medium and low zones are12.06 Hrs/day, 12.04 Hrs/day and 12.03 Hrs/day. Results showed that by tracking, solar radiation could be 100% above either in the morning or late in the evening. Tracking duration of the sunny period for a day is about 13 hours which is almost 1½ hours longer than when no tracking is used. The energy conversion efficiency of PV module used was also measured to be 10.2 % which is normal for the type of silicon cells used in the module. The efficiency depends on the manufacturing process, materials used and spectral distribution of the incident solar radiation (Gulma and Bajpai, 1983).

2.9 Why Solar Energy is one of the Key Solutions to the World Energy Demand

The sun is the most abundant energy source. Wind, fossil fuel, hydro and biomass energy have their origins in sunlight. This means all the solar energy received from the sun in one day can satisfy the whole world's demand for more than 20 years. Each year, the worldwide demand for energy is expected to keep increasing by 5 percent. Solar energy is the only source of energy to satisfy such a steadily increasing demand in our society, so it has attracted many researchers. Electricity is high grade energy that easily converted into other forms like mechanical energy or heat energy. If electricity is stable with easy transportation of its transmission, the electric power will increase its shares in demand sectors (Yinghao, 2011).

Photovoltaic's (PV): attractions:

It converts sunlight directly to electricity.
Sunlight is the most abundant renewable resource (175 PW).
Electricity is a form of energy for many uses
.it has long lifetime (>20 years) (Naresh *et al.,* 2013)

Photovoltaic's: drawbacks:

Sunlight is very spread out (<1 kW/m^2)
It is irregular
Electricity is difficult to store
Crystalline PV cells are expensive compared to other means of power generation.

2.10 History of Rice

Rice is a family of *Oryza* **s***ativa* and *Oryza glaberrima.* It is a staple food for a large part of the world's human population (Vellupillai *et al.*, 1997). Grain crops in Nigeria are shown in Plate 2.1.

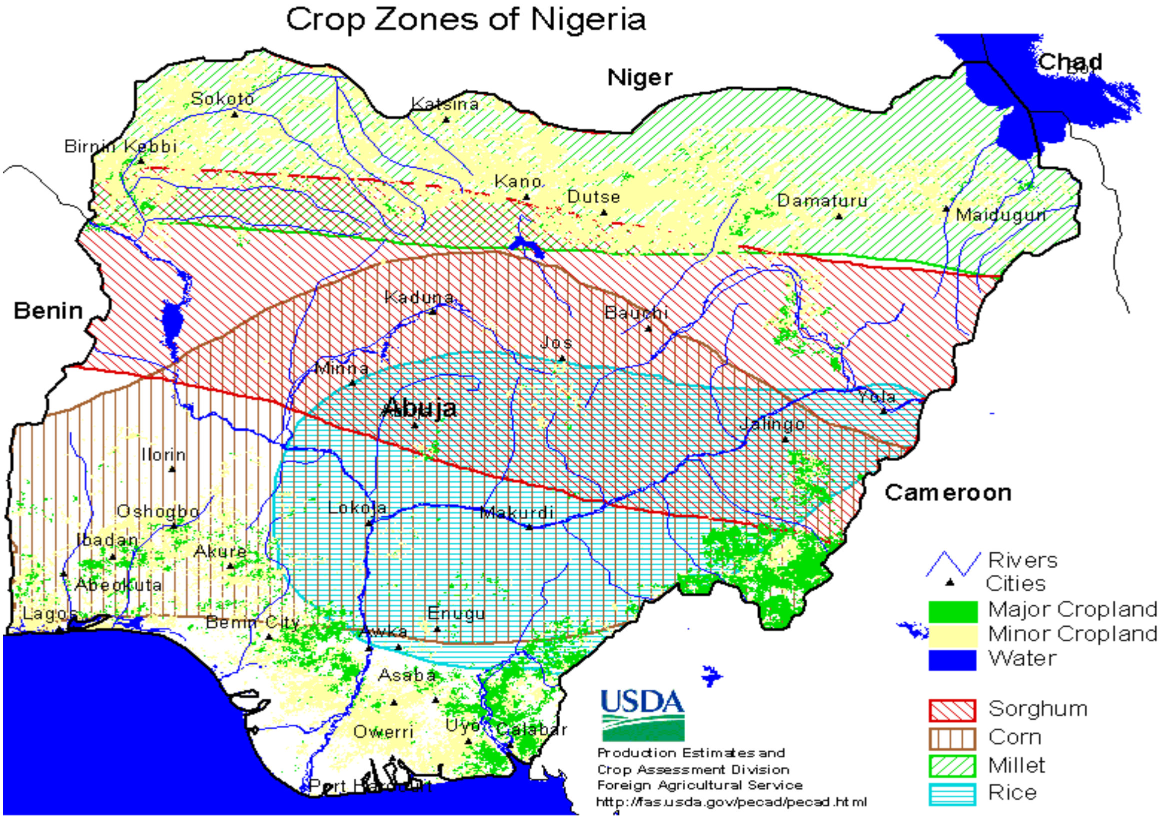


Plate 2.1. Grain Crop Zones in Nigeria

Source: (Dugje, 2000)

2.11 Rice Agronomy and their Geography

Rice production ranked 6th grade in Nigeria in relation to crops like sorghum, millet, cowpea, cassava and yam (Singh *et al.*, 1997). Rice grows in all the geographical zones. Summary of rice system is presented in Table 2.5.

Table 2.5: Summaries of Rice System

Type	**Characteristics**	**Geographical Spread**
Upland	Rainfed rice grown on free-draining fertile soil. This is also called dry upland.	Widespread, except coasts, high rain forests and Sahel.
Hydromorphic	Rainfed rice grown on soils with Shallow ground water table or an impermeable layer. This is also called wet uplands.	Widespread at the fringes of streams and intermediate zones between upland of rivers and swamps in the savannah. .
Lowland	Rainfed or irrigated rice in aquatic conditions or medium ground-water table. Water covers the soil completely at some stage during the cropping season. These are called shallow swamps.	Very widespread from high rain-forest to Sahel.
Deep Inland Water	Rainfed rice grown on soils with with deep water tables. The rice crop floats at some stage and harvesting may be done from a canoe.	Found in Sokoto-Rima basin and Chad Basin, floodplains of Niger, Benue, Kaduna, Gbako, Hadejia and Komaduga-Yobe
Mangrove Swamps	Rice grown at the coast or swamps of the high rain forest.	Coastal areas and Warri Area in Delta state.

Source: (Dugje, 2000)

2.12 Rice Husk

Rice has rice husk as its waste. In 2007, 628 million tons of paddies were obtained annually in Nigeria (Okutani, 2009). Almost 20kg of rice husk were obtained from 100kg of rice. It is a by-product from rice mill used as an energy source in many industries such as in biomass plant.

Calcinating of rice husk (hull) generates rice husk ash which is rich in silica which is economically feasible raw material for producing natural silica (Kalapathy *et al.*,2000[b]). Amount of ash in rice husk ash is between 18 and 20% (Wiki rice, 2007). The major constituent of rice husk ash is silica and Table 2.6 presents composition of rice husk ash. It economical to extract silica from the ash because of its high ash content which has wide market value and also takes care of ash disposal.

Table 2.6. Composition of Rice Husk Ash on Dry Basis

Element	Mass Fraction (%)
Silica	80-90
Alumina	1-2.5
Ferric Oxide	0.5
Titanum dioxide	Nil
Calcium Oxide	1-2
Magnesium Oxide	0.5-2.0
Sodium Oxide	0.2-0.5
Potash	0.2
Loss on Ignition	10-20

Source: (De Lima *et al.*, 2011)

Soluble silicates produced from silica are utilised in making of glass, ceramics and cement as a major component and also in pharmaceuticals, cosmetics and detergent industries as a bonding and adhesive agents (Kalapathy *et al.*, 2000[a]). Silica also has been utilized as a main forerunner for inorganic and organometallic applications in synthetic chemistry e.g. catalysts.

Existence of silica in dried amorphous form is an example of the industrial significance of rice husk (RH). RH is made up of 80% organic volatile substances while the remainder is 20% silica (James and Subbarao, 1996). Chemical structure of rice husk ash differs from rice husk to rice husk which may be as a result of geographical , climatic environments and also amount of fertiliser used (Govindarao, 1980).

2.13 Solid Waste from Combustion Process

Huge amount of solid waste in the form of ash was obtained from industrial combustion processes apart from producing air pollutants. Coal combustion in coal-usually generates residue consisting of organic matters, not completely burnt but known as coal ash. However, coal ash is divided into two parts, namely fly ash and bottom ash (Kingsley, 2010).

Furthermore, agricultural industries like palm oil processing and rice mills use their biomass solid waste as boiler fuel producing steam for electricity. Mahlia et al., (2001); stated that large amount of biomass solid waste was produced in form of fibres, shell and empty fruit bunch in oil palm processing mill.

By-products of rice milling produce large quantities of rice husk and rice straw which are in large quantities (Bronzeoak, 2003). Rice husk are used in modern rice milling as a source of fuel for electricity generation and this will also produce an additional solid waste in the form of ash. Characteristics of these ashes vary, depending on the combustion conditions.

2.13.1 Solid Waste from Rice Production

Rice husk is available in every continent apart from the Arctica and Antarctica. It is the main food and it is next to wheat in production.

Rice straw and rice husk are major by-products (waste) from rice mills as shown in Table 2.7. The ash obtained is approximately 90-96 % silica in amorphous form. Ashes from burning of rice husk is a useful by-product (Brouzeoak, 2003). Major constituent of rice husk and rice straw are hemicellulose lignin and cellulose. Rice by-products is now become an important issue.

Table 2 7. Selected Properties of Rice Straw and Rice Husk

	Rice Straw	Rice Husk
Generated Quantity	(Harvesting) 2-8tons/ha	(Paddy Milling)
Moisture content	60% (wt basis) 10-12% (dry weather)	20-22%Wt of paddy 10%
Density	75Kg/m^3 (loose straw) 100-180Kg/m^3 (packed straw)	100-150Kg/m^3 200-250Kg/m^3
Carbohydrate	Cellulose: 43%	Cellulose: 35%
Component (Average)	Hemicellulose: 25% Lignin: 12%	Hemicellulose: 25% Lignin: 20%
Calorific Value:	14-16MJ/Kg	14-16MJ/Kg
Moisture content:	14%	10%
Silica content:	83%	90-96%

Source: (Bronzeoak, 2003)

2.13.2 Rice Husk Ash (RHA)

Amount of husk produced from every 100 kg of paddy milled is 20 kg of husk. Approximately one fifth of burnt rice husk is obtained from its original amount (Amutha *et al.,* 2010). Rice husk is high in its ash content when measured with the rest of biomass fuels. Type of ash obtained is dependent on the burning technique. Structural transformations of silica in rice husk ash is dependent on time and temperature. Amorphous ash is formed from combustion temperature of 550-800 °C, while crystalline ash is formed at higher temperature. Table 2.8 shows the ash and silica content of some plants (Ranasingle, 1993).

It was observed from Table 2.8 that in rice straw contains of 15 % of ash and 82 % of silica while rice husk contains 22.15 % of ash and 93% as deduced from Table 2.8. (Mohamed and Taher, 2006).

Table 2 8: Ash and Silica Content of some Plants

S/N	Plant	Part of Plant	Ash %	Silica%
1	Sorghum	Leaf sheath epidermis	12.25	88.75
2	Wheat	Leaf sheath	10.48	90.56
3	Corn	Leaf sheath	12.15	64.32
4	Bamboo	Nodes (inner portion)	1.44	57.40
5	Bagasse	------	14.71	73.00
6	Lantana	Leaf and Stem	11.24	23.38
7	Sunflower	Leaf and Stem	11.53	25.32
8	Rice husk	-----------	22.15	93.00
9	Rice straw	------	14.65	82.00
10	Bread fruit tree	Stem	8.64	81.80

Source: (Ranasingle, 1993)

2.14 Amorphous Silica from Rice Husk

Silica extraction from rice husk can be subjected to alkaline extraction or heat treatment in various thermal treatment technologies like: inclined step-grate furnace, cyclonic furnace, muffle furnace, fixed bed, rotary kiln and tubular reactor as shown in Table 2.9.

Table 2.9. Existing Methods and Technologies of Amorphous Silica from Rice Husk

Method/Technology	**Description**	**References**
Alkaline Extraction	NaOH was mixed with RHA and boiled in an air tight Erlenmeyer flask for 1 hour with continuous stirring. The solution was then filtered and residue (carbon) was removed. The filterate formed was cooled to room temperature and titrated with acid (HCl or H_2SO_4) mixed until pH7 was achieved. The solution was left for 18 hours to form gel (silica)	Kamath and Proctor (1998), Kalapathy *et al.*, (2000b)
Electric furnace	Silica from RHA was prepared using muffle furnace and fixed bed combustor between 500-1150 ^{o}C.	Hamad and Khattab (1981
	Raw and acid leached rice husk combusted in electric furnace at temperatures of 500-750 ^{o}C. amorphous silica was obtained up to 720 ^{o}C.	Chakraverty and Kaleemullah (1991)
	Heating of rice husk 600-800^{0}C for 3hours under Helium flow	Real *et al.*,(1996)
	Rice husk was burnt in a muffle furnace at furnace at 600 ^{0} C for 4hours in static	Yalcin and Sevinc (2001)

	air and in a stainless steel tubular reactor placed in a muffle furnace at 600 ^{0}C in various flowing atmosphere (argon oxygen, air or oxygen)	
	Active silica with high specific surface area was produced after heat –treating at 700^{0}C for 6 h in air in an electric oven.	Della *et al.,* (2002)

2.15 Use of Rice Husk Ash (RHA)

1. Steel Industry: RHA is used in steel industries. This type of steel is manufactured by uninterrupted moulding method which was substituted for the older ingot method. It is considered as a perfect insulator because of its small thermal conductivity. As a result of these insulating characteristics that tundish powder emerged. The ashes are used to encase the tundish, stop quick cooling of the steel and make certain an even solidification. (Vellupillai *et al.*, 1997). Every tonne of steel manufactured uses about 0.5 to 0.7 kg of RHA (FAO, 2002).

2. Cement and Concrete: RHA is used in two different areas which are: in the production of low cost construction blocks and in the making of quality concrete.

RHA has two roles in concrete production:

a.) It is used as a component in Portland cement, lowering the price of concrete thereby reducing the price of construction blocks and;

b.) As an admixture in the making of quality concrete.

Amorphous silica produced from Rice Husk Ash is acceptable for pozzolanic task.

a. Low cost building blocks: Ordinary Portland Cement (OPC) is costly and is classically the most important and also the most costly reagent of cement; but its replacement with RHA leads to improved inexpensive and reasonable price (UNIDO, 1985).

Portland cement is highly expensive in some countries and that changing fifty (50) percent Portland cement with rice husk ash was with 25% reduction in cost (Tuts, 1994).

b. Concrete: RHA is used to increase quality of concrete (UNIDO, 2004). Although, it is difficult (and highly priced) to handle, to move and to blend, it is now the preferred choice for very good quality concrete. The American Society for Testing and Materials places Rice Husk Ash in similar category as silica fume.

3. Refractory Bricks: Refractory bricks used RHA for its production due to its insulating properties. Refractory bricks are utilized in advance furnace that are opened to severe temperature like furnaces utilized for manufacturing molten iron and in the making of cement clinker (Vellupilai, *et al.*,1997).

4. Lightweight Construction Materials: The presence of rice husk ash being utilised in making of lightweight encasing boards for insulation

5. Silicon Chips: Indian space research organisation invented technology for producing high purity precipitated silica from RHA for use in the computer industry.

6. Vulcanising Rubber: Rice husk ash proved to be better as vulcanising agent for ethylene- propylene-diene terpolymer (EPM) and is also suggested as dilute filler for EPM rubber. Type of ash used in not stated. (Siriwandena *et al*., 2001).

Other uses of RHA are:
manufacture of roof tiles;
running agent for fire extinguishing powder;
Abrasive filler for tooth paste;
beer clarifier;
Extender filler for paint; and
Production of sodium silicate films (Kalapathy et al., 2000b)

2.16 Temperature Limits of Silica Crystallisation in Rice Husk Ash

Temperature limits for crystallisation of RHA had been carried out since 1974 (Bartha and Huppertz, 1974); Haslinawati *et al.*, (2009) revealed that at 900°C and above RHA ceramic sintering showed crystal phase. Studies on temperature limit of silica crystallization are shown in Table 2.10. It was reported in the literature that no conclusive results was observed on temperature limit range from 700 to 900 ^{o}C for silica crystallization in RHA. This is due to disparity in thermal treatment methods, combustion environments or types of rice husk used.

Hamad and Khattab (1981) confirmed crystalline silica occurred at high air rates while amorphous silica was obtained at low air rates. Temperature distribution in the combustion zone is based on the thermal treatment method which affects the degree of mixing or turbulence. Cristobalite formation occurred in RHA at 800 °C in a heating period of 12-15 hours in Kapur (1985) while in Nakata *et al.*, (1989),with heating period of 1 to 5hours,cristobalite crystals was formed at 900 ^{o}C . Level of impurities in rice husk differs based on rice husk variety and source. Amorphous ash was observed from water-washed rice husk after heating for 1 hour at 900 °C (Gorthy and Pudukottah, 1999). Formation of crystals was observed in RHA after heating at 725 °C for same time according to Bartha and Huppertz (1974).

Temperature Limits on Crystallization of Rice Husk from Literatures is illustrated in Table 2.10. Moreover this work will entail the use of pre-treatment of husk (PRH and LRH) for determining the reactivity level of silica and its yield which will be compared to the reported one

Table 2 10: Temperature Limits on Crystallisation of Rice Husk from Literature

Temperature Limits ^{o}C	References	Remarks
700^{o}C	Chakraverty *et al*., (1988)	Ash obtained from raw rice husk and hydrochloric acid treated rice husk gave amorphous silica at 700 ^{o}C for1.5 hours Hence acid treatment did not affect the silica structure.
	Patel *et al*., (1987)	below 700 ^{o}C is preferred to prevent transformation to crystalline form.
	Kaupp (1984) and Sciefelbein (1989)	showed transformation RHA from amorphous state to a crystalline state at temperature beyond 700 ^{o}C.
	Conradt *et al*., (1992)	The RHA at temperature greater than or equal to 700 ^{o}C is crystalline.
	Della *et al*., (2002)	Amorphous silica powder was produced after heat-treating at 700 ^{o}C for 6 hours.
	Sumran and Kongkaichuichay (2003)	Silica from rice husk was prepared via three methods; one step combustion, fluidised bed combustion and alkaline extraction at temperature 600 ^{o}C (one step combustion) and 700 ^{o}C (fluidised bed combustion).
800 ^{O}C	Hamad and Khattab (1981)	Rice husk burnt was in a muffle furnace at 500-11500C for 1 hour. Amorphous state was observed below 600 ^{o}C while

		crystallisation of cristobalite took place at 800 ^{o}C.
	Kapur (1985)	showed transformation of silica from 600-800^{o}C and first appearance of cristobalite phase at 800 ^{o}C.
	Huang *et al*., (2001)	Amorphous silica was obtained at 700-800 ^{o}C.
900 ^{o}C	Hanafi *et al*., (1980)	Rice husk ash was fired at temperature range of 500-1400 ^{O}C for 3 hours in an showed from XRD result that at 900 ^{o}C nucleation process for the formation of the low-form cristobalite phase was pronounced.
	Nakata *et al.*, (1989)	combustion of rice husk in an electric furnace at the temperature range of 400-1500 ^{o}C showed that. Amorphous silica was observed below 500 ^{o}C while above 900 ^{o}C, was cristobalite
	Gorthy and Pukkottah (1999)	Black RHA was subjected to cacination at 400-1100 ^{o}C for 1 hour in high purity argon atmosphere and no crystalline phase formation even at 900 ^{o}C.
	Chouchan *et al*., 2000)	XRD showed highly amorphous silica at 700 ^{O}C according to XRD analysis, but at

higher temperature to 900 °C; showed crystalline silica.

Factors influencing the Ash Properties

RHA made in unconstrained environment is not likely to be required for any successful implementation. The ash determinants are: temperature and period, rate of heating, geographical location, fineness, colour and crop variety; Incinerating conditions.

Geographical Location

The physical and chemical characteristics of ash that relied on the soil chemistry, paddy variety, fertiliser implementation and climatic were reported (Chandrasekhar *et al.,* 2002). Table 2.11 showed the chemical properties of RHA in three different Countries:

Table 2.11. Comparison of Chemical Properties of RHA from different Locations

Constituents	Malaysia (wt%)	Brazil (wt.%)	India (wt.%)
Silica (SiO_2)	93.10	92.90	90.70
Alumina	0.21	0.18	0.40
Iron	0.21	0.43	0.40
Calcium	0.41	1.03	0.40
Potassium	2.31	0.72	2.20
Magnesium	1.59	0.35	0.50
Sodium	*	0.02	0.10
Sulphur	*	0.10	0.10
Loss on Ignition	2.36	*	4.80

Note:* not reported

Source: (Muthadhi *et al.,* 2007)

Incinerating Conditions

Burning rice husk at less than 700 °C yielded amorphous ash and temperature more than 800°C gave crystalline ash (Maeda *et al*., 2001).

Sen and Ghosh (1992) showed that burning at 700 °C for three minutes was enough for complete combustion of rice husk. According to Nehdi *et al.,* (2003), rice husk ash could be acquired at firing from temperature range from 750 °C to 850 °C using a torbid reactor. The introduction of a two-step kindling method whereby rice husk was preheated to a certain temperature between 300°C -350 °C and then later raised to a required temperature, greater than the flashpoint and retained for a stipulated time was reported by Sugita (1993). The technologies of ash manufacture differ from open-heap kindling to particularly outlined incinerators as well as fluidised beds. Beside the temperature range, period of kindling is also essential in managing the features of ash.

Nakata *et al*., (1989) observed that formation of critobalite was raised with the presence of potassium. The crystallization of silica in rice husk started with crytobalite then tridymite as reported in literatures (Hanafi *et al.*, 1980) while Shinohara and Kohyama (2004) concluded that crystallisation of pure silica started with tridymite followed by cristobalite. However, high concentration of potassium and presence of impurities favoured the formation of trydimite at 1200°C (Hanna *et al*., 1984).

Crystallisation of silica in ground ash was dominated by tridymite compared to unground ash, dominated by cristobalite. Hanna *et al.,* (1984). It was concluded that addition of iron in the rice husk (impregnated with ferrous sulphate solution soaking in ammonia solution) acts as an inhibitor for the formation of crystals from silica and carbon in the ash.

‘It was reported in the literatures that potassium is responsible for lowering the crystallisation temperature of silica in RHA’ hence it is expected that its removal would alter the crystal transition temperature to the range similar to pure silica. Washing the rice husk with water will remove potassium which is highly soluble in water.

Rate of Heating

An essential element in controlling the quality of Rice Husk Ash is the heating rate. Therefore, high speed combustion of rice husk lead to increased leftover carbon in the ash (Maeda *et al.,* 2001). The changing of silica from amorphous state to crystalline state is 800 °C. However, Amutha *et al.,* (2010) reported that crystalline silica is formed at temperature higher than 700 ^oC. Amorphous silica is produced if the burning duration is shortened. The changing from initial amorphous formation to crystal happens by kindling the husks at 1100°C or higher (Shinoraha and Kohyama, 2004).

Fineness

Mainly, raising the fineness of the reacting substances favoured reactivity. Likewise, reactivity of Rice Husk Ash is accredited to high content of amorphous silica and its permeable nature. Rice Husk Ash with its pervious nature has a large increased surface area whereas its normal area still stands reasonably high. Compared to silica fume with normal particle size of 0.1µm, RHA with particle size of about 45µm has three times higher surface area (Chandrasker *et al.,* 2005). Mehta (2001) offered reason to support that, as Rice Husk Ash obtains its pozzalanicity from its internal surface area, crushing of rice husk ash to a high degree of fineness is prevented. Crushing for a duration of 15 to 30 minutes led into particle size around 45µm Maeda *et al.,* (2001). Rice Husk Ash in amorphous configuration is a succulent with delicate substances. Prolonged crushing with high energy for fineness of around 45µm may not be demanded.

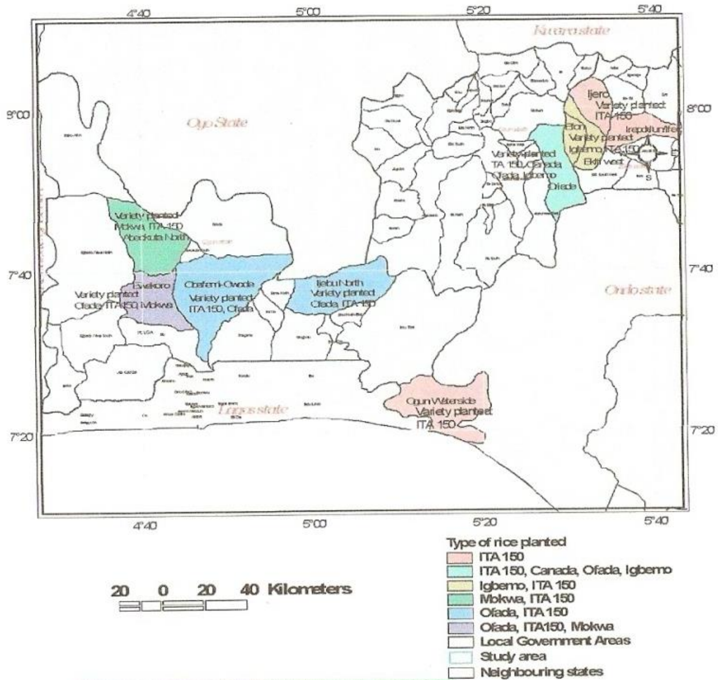
Colour

The completeness of kindling method and at the same time the configuration change of silica in the ash are linked with colour variations. Ash of white colour can be seen as an evidence of total carbon oxidation; it is also a proof of presence of huge amount of amorphous silica found in the ash. The interrelationship between potassium and silica ions lead to the emergence of potassium polysilicate combined with carbon emerging in grey colour when temperature is raised. A greater part of the potassium will be taken out and ash will not achieve grey colour whenever ash is pre-treated with acid (Chandrasekhar *et al.,* 2005). Still at high temperatures coupled with continuous firing, the outcome is ash with lilac pink colour, indicative of silica in crystalline shape, such as: cristobalite and tridymikte. The three colours distinctly stand for amorphous, transition and crystalline states of ash emergence.

2.17 Rice Process Description

Traditional rice processing in Erin-Oke Town in Nigeria entails soaking of paddy in a rectangular mould and then parboiling of paddy rice in cylindrical drums heated using fuel wood and the three-stone cooking stoves, sun drying of the parboiled rice or drying in a local fabricated dryer and then milling. The three-step process in parboiling are soaking (in a rectangular mould), steaming and drying. During parboiling process, about 30% moisture content (wet basis) is required which may be achieved when the paddy is soaked in water at room temperature for 36 to 72 hours. Moisture reduction takes place rapidly during the first stage of drying from about 18 to 38% moisture content, but is slow from 14 to 18% moisture content. The drying should be stopped at about 18% moisture content to allow the paddy temper for several hours before continuing the drying to 14% (Olaf *et al.,* 2003). Parboiling paddy provided a higher milling yield and reduced nutrient loss during milling and cooking. Cracks developed within the grain during maturity often cause breakage upon milling.

These internal cracks cannot be seen by naked eyes, it breaks the grains into smaller portions during cooking and pre-cooking washes. The raw rice husk from Erin-oke (Osun State) is usually decomposed by burning (field). Plate 2.2 shows the map of rice production clusters and the varieties of rice cultivated in Nigeria.



LGA	VARIETY PLANTED
Ijero	ITA 150
Ekiti West	Igbemo, ITA 150
Efon	Igbemo, ITA 150
Irepodun/Ifelodun	ITA 150
Oriade	ITA 150, Canada, Ofada, Igbemo
Abeokuta North	Mokwa, ITA 150
Obafemi-Owode	ITA 150
Ijebu North	Ofada, ITA 150
Ewekoro	Ofada, ITA150, Mokwa
Ogun Waterside	ITA 150

Plate 2.2. Ofada Rice Production Clusters and Various Rice Cultivating zones in Nigeria.

Source: (UNIDO, 2004)

2.18 Rainwater and Distilled Water

Rainwater harvesting is the accumulation and deposition for reuse (rainwater, 2013). The rainsaucer that is similar in shape to a big funnel is used to obtain rainwater direct from the sky rather than using the corrugated iron that cover the upper part of a house. This reduces the possibility of pollution and gives portable water for developing countries (Kim, 2013).

Distilled water is water boiled to remove dissolved minerals like iron and calcium. When the steam cools down to form condensate, this form distilled water which is more useful for research purposes where purity is essential. Components of distilled water are two parts of hydrogen to one part of oxygen.

Difference between distilled water and purified water is that: purified water has been filtered to certain specifications depending on whatever or whoever is filtering it while distilled water is what scientists use to do experiments. If distilled water is drunk, it will cause body imbalance.

Distilled water is liquid to vapour while rainwater is simply: vapour to liquid.

2.19 Genetic Algortihm

Genetic Algorithms (GA) usually check dynamic system with no previous importance or understanding regarding the system. It works rightly with chain of features being the framework set, not the framework themselves (Varsek, *et al.,* 1993). GAs are moveable from one application into another. Genetic algorithms can be used on a broad range of difficulties and search spaces. The ideas and fundamental principles are the same.

Literature on Genetic Algorithm (GA)

Forgarty (1989) studied the analysis of effect of varying mutation probability on GA. The optimum probability of mutation is between 0.0-0.3(Waghoo and Pervez, 2013).

The basic process for a genetic algorithm is outlined as follows:

(1) **Initialization**: Here an initial population is created. The population is usually randomly generated and can be any desired size from only a few individuals to thousands.

(2.) **Evolution:** every individual of the group is then assessed and at the same time fitness merit is also determined through how well it fits with the craved demands.

(3.) **Selection**: fitness is considered here via putting aside the unwanted designs and retaining the best individual in the population.

(4) **Crossover**: new individuals are brought into existence

(5) **Mutation**: Mutation naturally works by making a little difference at random to an individual’s genome.

(6) **And repeat**! : start again from step two until when an end stage is achieved. The summary is shown in Figure 2.2.

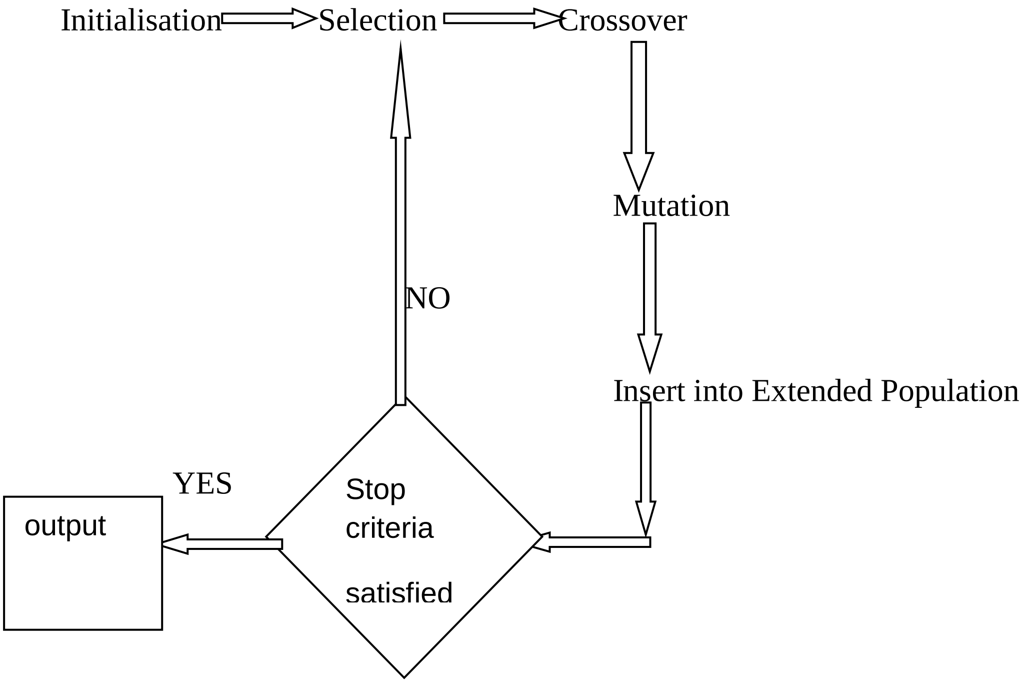


Figure 2.2. Information Flow for the GA Steps

Source: (Kulvinder and Rakesh, 2010)

The population is unsystematically put in a condition appropriate to the start of the operation. Genetic Algorithms (GAs) are adaptive heuristic search algorithm based on the evolutionary ideas of natural selection and genetics. The basic principles of GAs are designed to replicate methods important for development, explicitly for those that follow the theory by Charles Darwin on survival of the fittest; as such they constitute a brilliant undue advantage of random search within a defined search space to find solution to difficulties.

GA is one of the possible means of solving difficulties with no pre-ideal solution. It is a process of natural selection based on stochastic search algorithm modelled on what underlines a process by developing into different forms (Stuart and Peter, 2008). Its principle is based on an iterative manner by generating new populations of strings from old ones. An evaluation function associates a fitness measure to every string indicating its fitness for the problem (Goldberg, 1989).

GA is a possible means of solving difficulties with no pre- ideal solution.

Importantly, Genetic algorithms are processes of "breeding" programmes with answers to maximum usage by simulated evolution. Not only do GAs provide other process of finding solutions, but many real world problems which are not solvable by traditional methods can be solved by GAs (Soumadip *et al.*, 2010)

Multi-objective optimization problems are solved using GA Sole-aim GA can be simply adjusted to look for groups of several uninfluenced solutions. The capability of GA to concurrently explore separate areas of a solution space makes it likely to discover various set of solutions for hard problems with non-convex, discontinuos and multi-modal solution spaces. The crossover operator of GA may exploit composition of solutions with respect to various goals to form new non-controlled solutions in non-researched areas of Pareto front. Majority of the GA does not need the utilisers to make preferential selection, focused on estimate of the true pareto font.

It was observed by Jones *et al.*, (1999) that 90% of the goal techniques for optimisation focused on estimation of the true Pareto front for the underlying difficulty is based on 90% of the techniques to the various goal. Initial various-goal of GA, is known as Vector Evaluated Genetic Algorithms (VEGA), as suggested by Schaffer (1985).

Design of Experiments (DOE)

Design of Experiments is based on designing, coordinating, studying and clarifying controlled tests to find out the determinants that guide the value of a variable or group of variables (Fasanya, 2014). The statistical design include Factorial design, Central Composite Design and Box Benkhen Design.

Factorial Fractional Design: When the investigator picks n levels for each of variable number (K factors) and runs with all combinations that are adequate to exist in the design, which referred to as n^k factorial design. The number of runs required by a full n^k ! Factorial design increases geometrically as k increases.

Central Composite Design: contains an embedded factorial or fractional factorial design with center points augmented with points belonging together that permits estimation of curvature.

Box-Behnken Design: is an independent quadratic design with no embedded factorial or fractional factorial design. The treatment combinations are at the midpoints of edges of the process space and at the centre. The designs are rotatable (or near rotatable) and require three level factors. The designs have limited capability for orthogonal blocking when compared with the central composite designs. Box-Behnken designs allow minimum number of levels (Simpson *et al.*, 2004).

Response Surface Methodology Formulation

Response surface methodology (RSM) is the combination of mathematical and statistical modelling techniques for effective modelling and analysis of problems in which the response is affected by several variables with the objective of finding the correlation between the response and the variables (Box and Draper,2007). A second-degree polynomial model was suggested by Box and Wilson in their theory (Meyer and Montegomery, 1995). It was concludedd that this model is only an approximation, but it is used because the model is easy to estimate, (Box and Draper, 2007). In the general case, the response is described in equation 2.10:

$$Y_u = \beta_o + \sum_{i=1}^{s} \beta_1 X_1 + \sum_{i=1}^{s} \beta_{11} X_{11}{}^2 + \sum_{i,j=1}^{s} \beta_{i,j} X_{i,j} \;\; \beta_{i,j} X_{i.j} XX_i X_j + \varepsilon_i \ldots\ldots\ldots\ldots\ldots\ldots\ldots 2.10$$

In this study, RSM was applied for predicting the objective function for extraction of silica from rice husk. Furthermore, second order response model of the parameters was developed and formulated.

The steps in RSM are listed as follows:

- Conduct the experiment with the independent variables;
- obtain a fitted equation. Normally, regression methods are used in this step. Frequently, a linear model represents the model sufficiently well;
- move the experimental point in the direction of steepest ascent (or descent if a minimum is sought) and repeat the previous steps;
- when little improvement is obtained, the optimum is near;
- conduct a 3-level factorial experiment around this point;
- obtain a fitted quadratic equation by regression method;
- determine the optimum; and
- verify the obtained results.

RMS was applied to obtain the process variable levels and the yield of silica for the number of experimental runs generated .When RSM was used, the objective is not only to investigate the response over the space, but also to locate optimum process variables. The combination of factors (variables) which gave the optimal response was also obtained. Reaching the optimum is difficult when the response is taken into account; then a response surface model is built for each response within the ranges selected (Alvarez *et al.,* 2009).

2.20 Appraisal of the Previous Works

Sunlight is relatively abundant in Nigeria, so there is need to convert it into solar energy to solve the power challenge in the country. Literature reviews on previous work done on silica extraction from rice husk had been itemized and discussed in section 2.19 and also in Table 2.10. No report was stated on GA approach for optimising process variables (temperature, time and solvent) for amorphous silica extraction from rice husk to produce micro-crystalline silicon. Rather reports had been extensively on amorphous silica extraction from rice husk for a solar grade silicon. Reviews from literature showed that firing at 700 ^{o}C yields amorphous silica while temperature above it gives crystalline silica. It was also observed that among the amorphous silica, the level of reactivity varies based on the surface structure by SEM. Optimization of time and temperature are important for cost effectiveness. Furthermore, no report of the application of RSM to generate experimental run for the extraction of amorphous silica from husk and also to determine the yield via the interaction of the constraints. For instance, the open burning of rice husk is cancerous so there is need to burn at a specific temperature to turn attention to formation of crystalline ash. Rice husk readily available in rice cultivation areas converts and agricultural residue into a viable product for use in micro-crystalline production.

The concept of RSM was employed to develop fitness function for the GA optimisation in the Matlab software for silica formulation which constituted constraints for the maximization.

Therefore, the present approach is thus to formulate a mathematical formulation for maximizing amorphous silica from husk using RSM and then to use GA for determining the optimal process variables for micro-crystalline silica production from rice husk. Furthermore, the micro-crystalline silicon produced will be compared to standard.

CHAPTER THREE

3.0 METHODOLOGY

In this chapter, a methodology for developing GA approach for predicting the optimal variables (temperature, time and solvent) for amorphous silica extraction from rice husk for micro-crystalline silicon production is discussed. The methodology adopts a combination of mathematical and statistical modelling techniques, inferential statistical analysis, mathematical programming techniques and experimental validation procedures.

The mathematical and statistical modelling techniques adopted relevant steps in the response surface methodology (RSM) concept of Jouhaud *et al.,* (2007). The adopted methods and concept is summarised as follows:

Step 1: Experimental Design and data collection: To determine the silica yield based on interactions of the variables

Step 2: Development of response equation: which was used for the fitness function in the GA optimisation approach.

Point estimate was used for this research based on what was reported in the literature that calcination of rice husk for amorphous silica extraction is between range of 400 - 800 ^{o}C based on effect of other factors.

The following sections present the methodology in the order in which they were pursued.

3.1 Materials and Methods

The materials used for this research are:

i. water;
ii. Oxalic Acid and
iii. Rice Husk

Methodology for Amorphous Silica Extraction from Husks

Ofada (F36) Rice husk was used for this research; Control husk (Untreated):Uh0; was used for the trial experiment in order to observe the time that combustion started. The RH (1Kg) was run through two processes: one was treated with water to obtain

Prewashed Rice Husk (PRH) while the other with 1 mole of oxalic acid in the range of 10-50 m L to obtain Leached Rice Husk (LRH) were considered for firing test of this study. The proximate and ultimate analyses on raw Uh0 was performed to determine the constituents. The result of proximate constituent of Uh0 is as stated in Table 3.1.

Table 3. 1: Proximate and Ultimate Analyses of Raw Rice Husk as Collected

Proximate Analysis (% dry basis)		
S/N	Constituents	%
1	volatile Matter (VM)	70.68
2	Fixed Carbon (FC)	11.33
3	Ash	17.99
Ultimate Analysis (% dry ash-free basis)		
4	Carbon	45.20
5	Hydrogen	6.30
6	Nitrogen	1.31
7	Oxygen	47.19

Proximate analysis result obtained was compared to result observed by Mustafa and Emre (2013) with VM: 64.1, Ash: 11.1; FC: 22.4 and Moisture content: 22.4% and it was concluded that higher amount of ash was acquired from this research.

TRIAL COMBUSTION:

Uh0, PRH and LRH were subjected to calcination with temperature range of 50 -800 ^{O}C; in order to decide the temperature at which significant calcination was observed. No significant change was observed in the husks until when the temperature reached 400 ºC, and at this temperature burning started. Therefore, it was inferred that the burning commenced at 400 ºC.

The relevant temperature for the research was 400-800 ºC.

According to Olawale and Oyawale (2011; 2012), Optimal temperature of 700 ºC was observed at the temperature where maximum amount of silica and highest specific surface area were observed in the husks.

3.2 Equipment

The equipment used in extracting silica from husk for silicon production are discussed below:

Muffle Furnace: Muffle furnace with temperature ranging from 0 to 1200 ºC was used

Pot: was used as the plate to burn the rice husk.

Digital Weighing Balance: Portable weighing balance known as digital scout Proscale weighing balance made by QHAUS Print**.**

Spatula: The rice husk was gradually put inside the pot via a spatula to get the desired amount needed for the experiment;

Measuring Beakers: Used to measure Oxalic Acid

Conical Flakes: Used to mix and prepare 1 Mole of Oxalic Acid

Filter Paper: Used to filter leached rice husk.

Plate 3.1: Empty Clay Pot on a Digital Weighing Balance

3.3 Procedure for Amorphous Silica Extraction from Husks

PRH: This husk was initially prewashed with water to remove impurities that might be present in the husk. The process removed large amount of potassium, sodium, chlorine and sulphur in the husks when washed. Impurities eliminated the inherent problem on formation of low melting point compounds which interfered in the oxidation of carbon.

The husk was subjected to slow heating until it reached 700 ^{o}C and burnt for time variation of 1-6h. It was then allowed to cool inside the furnace before it was removed and then analysed for silica yield. According to Krishnarao *et al.*, (2001), burning of rice husk led to the formation of silica ash, from grey to black colour depending on inorganic impurities and unburned carbon contents. According to Della *et al*., (2002), the two major factors that determines if the silica produced from RHA is amorphous or crystalline are time and temperature. Nevertheless, according to Pudukottah and Gorthy (1999), ash from water-washed rice husk was amorphous even at 900 ^{o}C for one hour.

LRH: Here, husk was post treated for further purification. The combination of the process was based on the design desirably selected. This is the further purification of husks with Oxalic Acid. Oxalic Acid of 1mole was used for the post purification because it was reported that it removes more impurities than Acetic Acid. This type of acid can be produced locally when micro-organism is cultured on some plants. The objective is to compare the yield and type of silica via the most reactive (best) silica for optimal process of silicon production**.**

Digestion of husk in Oxalic Acid Leaching Process

10 g of the cleaned rice husk was added to Oxalic acid of 1mole of range:10-50 mL and heated for 90 minutes with constant mixing and it was then left for a period of 20 hours to cool. For this test, amount of Oxalic acid used for the leaching of the rice husk was 1 Mole. The supernatant was then drained and then cleaned properly with water for several times in order to remove the oxalic acid permanently. Muffle furnace was used to burn the rice husk into ash at 700 ^{o}C and time of 6hvariation of 1-6h. Then checked at frequent intervals and recorded.

The observation of the ashes via slow heating process and normalised cooling of the portions of husks used are as itemised in the Appendix 2.

3.4 Analytical Techniques

The ashes from the obtained rice husk are analysed via XRD to determine whether they are amorphous or crystalline. It was then washed to isolate silica (SiO_2) and to remove unwanted silicate products. HF Evaporation method was used to gravimetrically estimate SiO_2. Silica structure was determined via X-Ray Mini Diffraction, for the type of silica (phase structure) whether amorphous, crystalline, mono-crystalline or poly-crystalline and Scanning Electron Microscope (SEM) for its particle structure.

3.5 Model Development

The models were developed using a Response surface methodology (RSM). Basically, RSM relates product properties by using regression equations that describe interrelations between input parameters and product properties (Jouhaud *et al.*, 2007). The preliminary task is the identification of variables, parameters or states, inputs and outputs involved in silica extraction from rice husk.

3.5.1 Identification of the design quantities

F (36) Ofada was run through two processes. The input variables identified are the quantities of ingredients while the output variable identified as the yield after combustion of the F36. The classification of these variables is presented in Table 3.2.

Table 3.2: Classification of Set of Quantities

Type	**Description**	**Symbol**	**Units**
Inputs	**Ingredients**		
	Temperature	A	^{o}C
	Time	B	H
	Solventvolume(water/OxalicAcid)	C	mL
Output	**Silica extracted**		
	Yield	F	%

3.5.2 Experimental Design and Statistical Analysis for (F36) Rice Husk

Two portions of husks considered in this research for silicon production were: water pre-treated husk: (PRH) and Oxalic Acid pre-treated husk: (LRH). Effect of interactions of variables (temperature. time, solvent) was determined using RSM for PRH while oxalic acid was used instead of water volume for LRH. Factorial design was used to generate 75 runs. The 75 experimental runs were made via factorial design in this study in order to observe silica yield in each of the experimental combinations of the predictor variables. Statistical analyses were conducted on results from PRH and LRH. Two response equations were developed which were used as fitness function in GA optimisation tool.

3.5.3 Response Surface Methodology

RSM is a practically, economically and relatively easy method to use method for modelling processes in engineering applications.

In this study, Central Composite Design (CCD) was used to optimise the experiment. Moreover, RSM is a combination of mathematical and statistical techniques to develop the response equation. The input factors for PRH are: Temperature range of 400- 800 ^{o}C; Time variation of 2 -6 h, solvent volume (water volume) of 10-50 mL and husk of 10 g while for the LRH: Temperature range of 400-800 ^{o}C; Time variation of 2-6 h, Solvent volume (Oxalic Acid) content of 10-50 mL and husk of 10 g. Water volume was used to purify the husk in PRH while rice husk LRH was treated with Oxalic Acid for further treatment of husks i.e leaching of husks. The significance for RSM was to observe the yields of silica from the two forms of husks at different combination levels of the variables. Optimal yield from the two forms of husks was also observed based on the interaction of the variables.

This study assumed second order polynomial. Maximisation of the polynomial thus fitted was performed by numerical techniques, using the mathematical optimizer procedure of the Design Expert 6.8 that deals with constraints. The constraints are set to get the coded value of a variable between lower and upper limits for an optimum response. The response surfaces were plotted as a function of the three variable.

Justification for second order polynomial

It was used because it accommodates the interactive effects of the variables. It enables one to estimate both the individual effects and the interactive effects of the factors and thus is normally used for a reactive system like this present research.(Jouhand *et al.*, 2007, Karunakaran, 2006).

Procedure for RSM is as stated below:

i. Identification of predominant variables
ii. Development of the experimental design
iii. Developing the mathematical model
iv. Determination of constant coefficients of the developed model
v. Testing the significance of the coefficients
vi. Adequacy test of the developed model using ANOVA
vii. Analysis of the input effect on the output (response)

3.5.4 Factorial Design using Central Composite Design (CCD)

CCD was based on three variables and five levels for this research. A CCD consists of a complex 2K factorial design, where the factor levels are coded with the usual -2, -1, 0, +1, +2 value. This is called the factorial portion of the design. For this design, formulation for the experimental run are generated based on the following*:*

Replicates of factorial point =3
Replicates of axial point= 3
Centre point = 3
Total number of experimental runs =75
[Not center points=72, Center points=3]
Alpha-=2

CCD works effectively, highly recommended and is most frequently used for designs and was used for this research because of the following advantages:

i. It creates rotatability in the design. Designs with this property, exhibits circular contours.
ii. Central composite design is usually carried out in blocking style which help the experiment could not be done in one day or to be done in a batch wise.
iii. It gives sequential design which is a desirable feature.
iv. It helps to give design options

The experimental runs were based on three variables, five levels namely: X1 (Temp.) ^{o}C, X2: (Time) h, and X3: (solvent volume) mL. Variation for each variable spaced around the centre point ratios along with the equations relating to the actual and coded ratios are presented in Table 3.3 and the resulting design of the 75 experimental runs as shown in Table 3.4. However, the yield generated for amorphous silica yield is shown in Table 3.5.

Table 3.3: Range and Levels of Independent Variables selected for Amorphous Silica Extraction from PRH

Variables	(X)	(±increment)	-2	-1	0	+1	+2
Temp.(° C)	X1	100	400	500	600	700	800
Time (h)	X2	1	2	3	4	5	6
Solvent vol (mL)	X3	10	10	20	30	40	50

Where X and Xn ratios are related by the following equations:

$$X_1 = \frac{(x_1 - 600)}{100}; \quad X_2 = \frac{(x_2 - 4)}{1.0}; \quad X_3 = \frac{(x_3 - 30)}{10} \qquad (3.1)$$

Table 3.4. Central Composite Design for PRH

Std Run	Order run	Block	X1	X2	X3
1.	3	Block 1	-1.00	-1.00	-1.00
2.	57	Block 1	-1.00	-1.00	-1.00
3.	46	Block 1	-1.00	-1.00	-1.00
4.	19	Block 1	1.00	-1.00	-1.00
5.	71	Block 1	1.00	-1.00	-1.00
6.	54	Block 1	1.00	-1.00	-1.00
7.	27	Block 1	-1.00	1.00	-1.00
8.	44	Block 1	-1.00	1.00	-1.00
9.	6	Block 1	-1.00	1.00	-1.00
10.	1	Block 1	1.00	1.00	-1.00
11.	33	Block 1	1.00	1.00	-1.00
12.	38	Block 1	1.00	1.00	-1.00
13.	67	Block 1	-1.00	-1.00	1.00
14.	47	Block 1	-1.00	-1.00	1.00
15.	59	Block 1	-1.00	-1.00	1.00
16.	48	Block 1	1.00	-1.00	1.00
17.	32	Block 1	1.00	-1.00	1.00
18.	10	Block 1	1.00	-1.00	1.00
19.	15	Block 1	-1.00	1.00	1.00
20.	49	Block 1	-1.00	1.00	1.00
21.	43	Block 1	-1.00	1.00	1.00
22.	70	Block 1	1.00	1.00	1.00
23.	30	Block 1	1.00	1.00	1.00
24.	40	Block 1	1.00	1.00	1.00
25.	31	Block 1	-1.00	-1.00	-1.00
26.	11	Block 1	-1.00	-1.00	-1.00
27.	56	Block 1	-1.00	-1.00	-1.00
28.	68	Block 1	1.00	-1.00	-1.00
29.	50	Block 1	1.00	-1.00	-1.00
30.	7	Block 1	1.00	-1.00	-1.00
31.	12	Block 1	-1.00	1.00	-1.00
32.	9	Block 1	-1.00	1.00	-1.00
33.	45	Block 1	-1.00	1.00	-1.00
34.	62	Block 1	1.00	1.00	-1.00
35.	16	Block 1	1.00	1.00	-1.00
36.	41	Block 1	1.00	1.00	-1.00
37.	53	Block 1	-1.00	-1.00	1.00
38.	23	Block 1	-1.00	-1.00	1.00
39.	65	Block 1	-1.00	-1.00	1.00
40.	17	Block 1	1.00	-1.00	1.00
41.	69	Block 1	1.00	-1.00	1.00
42.	14	Block 1	1.00	-1.00	1.00
43.	13	Block 1	-1.00	1.00	1.00

44.	22	Block 1	-1.00	1.00	1.00
45.	39	Block 1	-1.00	1.00	1.00
46.	21	Block 1	1.00	1.00	1.00
47.	26	Block 1	1.00	1.00	1.00
48.	8	Block 1	1.00	1.00	1.00
49.	58	Block 1	-2.00	0.00	0.00
50.	25	Block 1	-2.00	0.00	0.00
51.	75	Block 1	-2.00	0.00	0.00
52.	55	Block 1	2.00	0.00	0.00
53.	37	Block 1	2.00	0.00	0.00
54.	60	Block 1	2.00	0.00	0.00
55.	18	Block 1	0.00	-2.00	0.00
56.	61	Block 1	0.00	-2.00	0.00
57.	63	Block 1	0.00	-2.00	0.00
58.	20	Block 1	0.00	2.00	0.00
59.	35	Block 1	0.00	2.00	0.00
60.	29	Block 1	0.00	2.00	0.00
61.	42	Block 1	0.00	0.00	-2.00
62.	36	Block 1	0.00	0.00	-2.00
63.	64	Block 1	0.00	0.00	-2.00
64.	52	Block 1	0.00	0.00	2.00
65.	28	Block 1	0.00	0.00	2.00
66.	5	Block 1	0.00	0.00	2.00
67.	24	Block 1	0.00	0.00	0.00
68.	2	Block 1	0.00	0.00	0.00
69.	51	Block 1	0.00	0.00	0.00
70.	34	Block 1	0.00	0.00	0.00
71.	73	Block 1	0.00	0.00	0.00
72.	66	Block 1	0.00	0.00	0.00
73.	4	Block 1	0.00	0.00	0.00
74.	74	Block 1	0.00	0.00	0.00
75.	72	Block 1	0.00	0.00	0.00

Table 3.5. Planning Matrix of Yield1 (Y1)

S/N	X1	X2	X3	response
1.	400	2	20	86.90
2.	400	3	20	87.32
3.	400	4	20	87.56
4.	400	5	20	87.89
5.	400	6	20	87.94
6.	500	2	20	87.96
7.	500	3	20	88.38
8.	500	4	20	88.93
9.	500	5	20	88.34
10.	500	6	20	89.52
11.	600	2	20	89.64
12.	600	3	20	89.85
13.	600	4	20	89.91
14.	600	5	20	89.94
15.	600	6	20	89.99
16.	700	2	20	90.04
17.	700	3	20	91.14
18.	700	4	20	91.32
19.	700	5	20	91.79
20.	700	6	20	91.84
21.	800	2	20	86.34
22.	800	3	20	86.71
23.	800	4	20	86.79
24.	800	5	20	86.83
25.	800	6	20	86.94
26.	400	2	30	87.03
27.	400	3	30	87.15
28.	400	4	30	87.22
29.	400	5	30	87.40
30.	400	6	30	87.47
31.	500	2	30	88.21

32.	500	3	30	88.32
33.	500	4	30	88.72
34.	500	5	30	88.76
35.	500	6	30	88.94
36.	600	2	30	89.02
37.	600	3	30	89.75
38.	600	4	30	90.41
39.	600	5	30	90.56
40.	600	6	30	90.88
41.	700	2	30	90.92
42.	700	3	30	91.05
43.	700	4	30	91.67
44.	700	5	30	92.04
45.	700	6	30	92.06
46.	800	2	30	88.43
47.	800	3	30	88.6
48.	800	4	30	88.65
49.	800	5	30	88.71
50.	800	6	30	88.93
51.	400	2	40	87.53
52.	400	3	40	87.61
53.	400	4	50	87.73
54.	400	5	40	87.81
55.	400	6	40	87.89
56.	500	2	50	88.41
57.	500	3	40	88.51
58.	500	4	40	88.83
59.	500	5	40	88.91
60.	500	6	40	88.79
61.	600	2	40	89.21
62.	600	3	40	89.82
63.	600	4	40	90.51
64.	600	5	40	90.63
65.	600	6	40	90.94

66.	700	2	40	90.99
67.	700	3	40	91.2
68.	700	4	40	91.72
69.	700	5	40	92.11
70.	700	6	40	92.31
71.	800	2	50	88.53
72.	800	3	40	88.62
73.	800	4	50	88.68
74.	800	5	40	88.81
75.	800	6	40	88.89

Response Surface Analysis and Optimization for LRH

The experimental runs were based on three variables, five levels and four factors, namely: X1(Temp.) ºC, X2 (Time) h, X3 (solvent volume: water volume / Oxalic Acid volume) mL. Variation for variable spaced around centre point ratios with the equations relating to the actual and coded ratios are presented in Table 3.6 and the resulting design of the 75 experimental runs as shown in Table 3.7.However, silica yield is shown in Table 3.8.

Table 3.6. The Range and Levels of Independent Variables Selected for the Optimisation of Amorphous Silica of LRH.

Variables	(Xn)	(±increment)	-2	-1	0	+1	+2
Temp.(° C)	X1	100	400	500	600	700	800
Time (h)	X2	1	2	3	4	5	6
Solvent (mL)	X3	10	10	20	30	40	50

Table 3.7. Central Composite Design for LRH

Std Run	Order run	Block	X1	X2	X3
1.	3	Block 1	-1.00	-1.00	-1.00
2.	57	Block 1	-1.00	-1.00	-1.00
3.	46	Block 1	-1.00	-1.00	-1.00
4.	19	Block 1	1.00	-1.00	-1.00
5.	71	Block 1	1.00	-1.00	-1.00
6.	54	Block 1	1.00	-1.00	-1.00
7.	27	Block 1	-1.00	1.00	-1.00
8.	44	Block 1	-1.00	1.00	-1.00
9.	6	Block 1	-1.00	1.00	-1.00
10.	1	Block 1	1.00	1.00	-1.00
11.	33	Block 1	1.00	1.00	-1.00
12.	38	Block 1	1.00	1.00	-1.00
13.	67	Block 1	-1.00	-1.00	1.00
14.	47	Block 1	-1.00	-1.00	1.00
15.	59	Block 1	-1.00	-1.00	1.00
16.	48	Block 1	1.00	-1.00	1.00
17.	32	Block 1	1.00	-1.00	1.00
18.	10	Block 1	1.00	-1.00	1.00
19.	15	Block 1	-1.00	1.00	1.00
20.	49	Block 1	-1.00	1.00	1.00
21.	43	Block 1	-1.00	1.00	1.00
22.	70	Block 1	1.00	1.00	1.00
23.	30	Block 1	1.00	1.00	1.00
24.	40	Block 1	1.00	1.00	1.00
25.	31	Block 1	-1.00	-1.00	-1.00
26.	11	Block 1	-1.00	-1.00	-1.00
27.	56	Block 1	-1.00	-1.00	-1.00
28.	68	Block 1	1.00	-1.00	-1.00
29.	50	Block 1	1.00	-1.00	-1.00
30.	7	Block 1	1.00	-1.00	-1.00
31.	12	Block 1	-1.00	1.00	-1.00
32.	9	Block 1	-1.00	1.00	-1.00
33.	45	Block 1	-1.00	1.00	-1.00
34.	62	Block 1	1.00	1.00	-1.00
35.	16	Block 1	1.00	1.00	-1.00
36.	41	Block 1	1.00	1.00	-1.00
37.	53	Block 1	-1.00	-1.00	1.00
38.	23	Block 1	-1.00	-1.00	1.00
39.	65	Block 1	-1.00	-1.00	1.00
40.	17	Block 1	1.00	-1.00	1.00
41.	69	Block 1	1.00	-1.00	1.00
42.	14	Block 1	1.00	-1.00	1.00
43.	13	Block 1	-1.00	1.00	1.00
44.	22	Block 1	-1.00	1.00	1.00

45.	39	Block 1	-1.00	1.00	1.00
46.	21	Block 1	1.00	1.00	1.00
47.	26	Block 1	1.00	1.00	1.00
48.	8	Block 1	1.00	1.00	1.00
49.	58	Block 1	-2.00	0.00	0.00
50.	25	Block 1	-2.00	0.00	0.00
51.	75	Block 1	-2.00	0.00	0.00
52.	55	Block 1	2.00	0.00	0.00
53.	37	Block 1	2.00	0.00	0.00
54.	60	Block 1	2.00	0.00	0.00
55.	18	Block 1	0.00	-2.00	0.00
56.	61	Block 1	0.00	-2.00	0.00
57.	63	Block 1	0.00	-2.00	0.00
58.	20	Block 1	0.00	2.00	0.00
59.	35	Block 1	0.00	2.00	0.00
60.	29	Block 1	0.00	2.00	0.00
61.	42	Block 1	0.00	0.00	-2.00
62.	36	Block 1	0.00	0.00	-2.00
63.	64	Block 1	0.00	0.00	-2.00
64.	52	Block 1	0.00	0.00	2.00
65.	28	Block 1	0.00	0.00	2.00
66.	5	Block 1	0.00	0.00	2.00
67.	24	Block 1	0.00	0.00	0.00
68.	2	Block 1	0.00	0.00	0.00
69.	51	Block 1	0.00	0.00	0.00
70.	34	Block 1	0.00	0.00	0.00
71.	73	Block 1	0.00	0.00	0.00
72.	66	Block 1	0.00	0.00	0.00
73.	4	Block 1	0.00	0.00	0.00
74.	74	Block 1	0.00	0.00	0.00
75.	72	Block 1	0.00	0.00	0.00

Table 3.8. Planning matrix of Yield 2

S/N.	X1	X2	X3	Response
1.	400	2	20	93.22
2.	400	3	20	93.62
3.	400	4	20	94.46
4.	400	5	20	94.46
5.	400	6	20	94.89
6.	500	2	20	95.4
7.	500	3	20	96.40
8.	500	4	20	96.32
9.	500	5	20	95.82
10.	500	6	20	95.39
11.	600	2	20	96.1
12	600	3	20	96.19
13.	600	4	20	96.12
14.	600	5	20	96.08
15.	600	6	20	96.03
16	700	2	20	97.32
17.	700	3	20	97.44
18.	.700	4	20	97.24
19.	700	5	20	97.12
20.	700	6	20	97.01
21.	800	2	20	95.51
22.	800	3	20	95.61
23.	800	4	20	95.39
24.	800	5	20	95.32
25.	800	6	20	95.29
26.	400	2	30	94.01
27.	400	3	30	94.21
28.	400	4	30	94.17
29.	400	5	30	94.10
30.	400	6	30	94.04
31.	500	2	30	95.68

32.	500	3	30	96.41
33.	500	4	30	96.25
34.	500	5	30	96.20
35.	500	6	30	96.15
36.	600	2	30	96.23
37.	600	3	30	96.71
38.	600	4	30	96.62
39.	600	5	30	96.49
40.	600	6	30	96.36
41.	700	2	30	97.56
42.	700	3	30	97.65
43.	700	4	30	97.40
44.	700	5	30	97.25
45.	700	6	30	97.04
46.	800	2	30	95.54
47.	800	3	30	95.69
48.	800	4	30	95.61
49.	800	5	30	95.39
50.	800	6	30	95.23
51.	400	2	40	94.43
52.	400	3	40	94.75
53.	400	4	50	94.65
54.	400	5	40	94.51
55.	400	6	40	94.47
56.	500	2	50	95.7
57.	500	3	40	96.72
58.	500	4	40	96.66
59.	500	5	40	96.49
60.	500	6	40	96.33
61.	600	2	40	96.81
62.	600	3	40	96.98
63.	600	4	40	96.73
64.	600	5	40	96.42
65.	600	6	40	96.39

66.	700	2	40	97.72
67.	700	3	40	97.98
68.	700	4	40	97.34
69.	700	5	40	97.29
70.	700	6	40	97.24
71.	800	2	50	96.61
72.	800	3	40	96.75
73.	800	4	50	96.55
74.	800	5	40	96.41
75.	800	6	40	96.35

3.5.5 Model Assumptions

The assumptions for the model developed are:

I. The same quantity of husks

II. The quantity of ash produced was based on temperature and time of calcination.

III. Amorphous silica was produced from the two husks.

3.5.6 Response Equation for Silica Extracted to be generated

The resulting yield for each F36 were generated. A central composite rotatable design was adopted (Cocharan and Cox, 1957). In this design, experiments were randomized in order to maximise the effects of unexplained variability in any responses due to extraneous factors. In order to analyze the experimental design by response surface methodology, it was assumed that there existed n mathematical functions, $f_h(h=1,2,....,n),$ for each response variable, Y_h in term of m independent variable $X_i\,(i=1,2,....,m)$.

$$Y_h = f_h(X_1, X_2, ..., X_m). \qquad (3.2)$$

In this experiment, n = 4 and m = 1. In order to approximate this function, a second order polynomial equation was assumed.

$$Y_h = b_{h_o} + \sum_{i=1}^{m} b_{h_i} X_i + \sum_{i=1}^{m} b_{h_{ii}} X^2{}_i + \sum_{i \neq j=1}^{m} b_{h_{ij}} X_i X_j \qquad (3.3)$$

Where b_{h_o} is the value of fitted response at the centre point of the design, i.e. (0,0), and b_{h_i}, $b_{h_{ii}}$ and b_{ij} are linear, quadratic and cross product regression term respectively.

3.5.7 Optimisation Model

An optimisation problem was formulated to maximise amorphous silica from two forms of husks for micro-crystalline silicon production subject to constraints (temperature, time and solvent volume) as given below:

Maximise $Q = f(X_1, X_2, X_3)$

Subject to $q_i = f(X_i) \leq b_i, i = 1$ (3.4)

Problem formulation for PRH

The objective is to maximise amorphous silica

$$\begin{aligned} &PRH = f(temp, time, .solventvolume) \\ &Max.PRH \\ &s.t: \\ &400 \leq A \leq 800 \\ &2 \leq B \leq 6 \\ &10 \leq C \leq 50 \end{aligned} \tag{3.5}$$

Where A= Temperature variation,

B= Time Variation,

C= water volume for the purification

Problem formulation for LRH

Objective is to maximise amorphous silica from husk type 2

$$\begin{aligned}
&LRH = f(Temp., Time, solventvolume) \\
&Max.LRH \\
&s.t: \\
&400 \le A \le 800 \\
&2 \le B \le 6 \\
&10 \le C \le 50
\end{aligned} \tag{3.6}$$

Where: A =Temperature variation,

B= Time Variation

C= Solvent volume: Amount of Oxalic Acid for the pretreatment**.**

3.6 GA Optimisation

GA is based on getting the best solution in the regions of space containing high proposition of good solution; and the best of the regions is identified by robust sampling of the solution space. The main attractions to GA are: the computational efficiency and simplicity of operation.

Mathematical model developed for each of the 2 forms of RH (F36) were the objective functions. It was optimised by using a Genetic Algorithmic to obtain the optimal variables for the highest yield in the optimal process.GA was considered to optimise the process variables of the best fitness via survival of the fittest.

Genetic Algorithm techniques in MATLAB for optimization are in 2 ways. These are:
i. Using the Genetic Algorithm Function ‘ga’ at the command line.
ii. Using the Genetic Algorithm Tool, a graphical interface to the genetic algorithm.
This research considered the Genetic Algorithm Tool
The genetic algorithm tool is a graphical user interface that enables the use of genetic algorithm without working at the command line.
The three main stages in GA are: Reproduction, Cross-over and Mutation.

3.6.1 Basic Steps in GA Optim Tool

The basic steps in GA Optim Tool in Matlab software are:
Open the GA Tool window
Select solver; GA Solver
Enter the mathematical representation developed in a saved M. file and then input in the *‘fitness function ’*
Enter the number of variables and the bounds. Note that you must enter the bound via[]
Enter the GA parameters
Click the start button
Algorithm ends, when the best fitness is observed
The Genetic algorithm uses the following five conditions to determine when to stop: i. Maximum Number of Generation. ii. Maximum Time Limit. iii. Maximum Fitness limit. iv. Stall Generations. v. Stall Time Limit. The Algorithm stops as soon as any one of these five conditions are met. The block representation of GA is shown in Fig.3.1

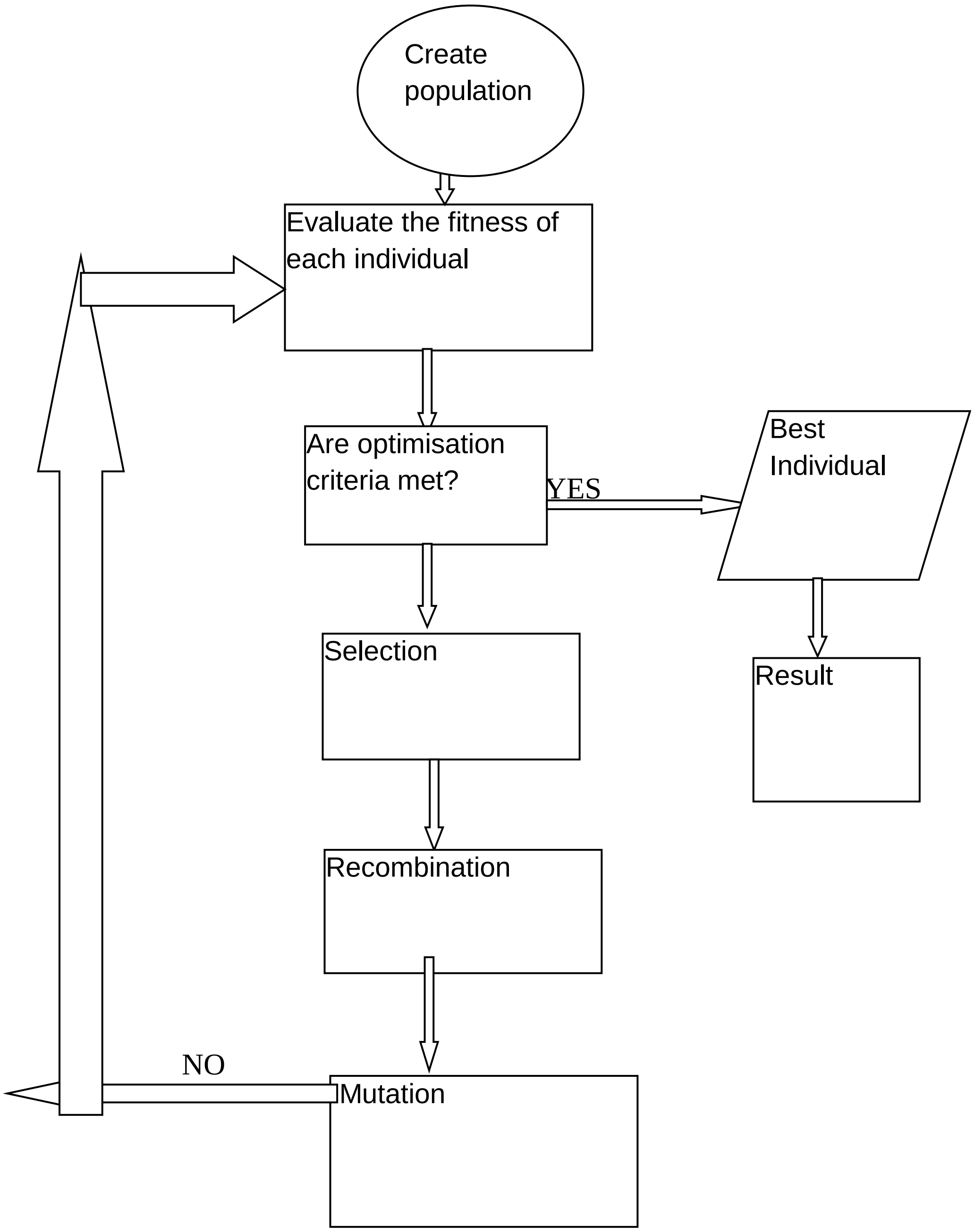


Figure 3.1. Block representation of Genetic Algorithm Model

3.6.2 Steps for optimising process variables via GA

The steps for optimising process variables are iterated below:

i. create M.file of the function (this is the response generated in the RSM) to be the optimised function.

ii The number of variables must be determined also before running the GA solver in the optimization tool page in the matlab software

iii. The created M.file of the functions to be optimised will be used as the fitness function that serves as the object function.

{Note for the fitness function: open the m.file then click on ‘open m.file when debugging .then click on Run configuration for the created m.file. therafter. Write the created m.file as the finess function.

iv. Then enter the necessary inputs such as the fitness function using: @ before the filename of the M.File created for a specific function. The default conditions or parameters used as population size, selection, mutation, crossover, hybrid function and stopping criteria. The parameters can be altered as to satisfy whatever the user desire for the optimization of the function.

v. After setting all the necessary inputs in the GA Tool, and the optimisation will start by clicking the start button in the Run solver. To show the plots of the function:
click on any of the plot to sign in the tool section such as: best fitness to show the generated values.

Click History in the new window output function. And any option chosen for the level will be displayed.

The command window will then show the iteration number.

As GA is terminated, the results are generated.

3.6.3 GA optim tool as generated in the Matlab Software

The mathematical representation was developed in the GA.

Model was written using statistical toolbox.

Two responses were generated for each yield of PRH & LRH respectively. To develop the mathematical equation; columns were represented as: C2: Temp; C3: Time; C4: Solvent volume (Water volume /Oxalic Acid volume); C5: Oxalic Acid: C7; Yield 1 and C8: Yield 2.

The model developed was saved in a new created M.file and the function to be optimised was used as the fitness function that served as the objective function.

Number of variables: For this research three variables: temperature, time and solvent (water content/ Oxalic Acid content) were used. (F36) Husk was not considered as the fourth variable because its interaction effect was zero.

Since variables are three, the model development were used in the GA optimization tool.

Then the solver used was: ga Genetic Algorithm.

The objective function in the GA was minimised but when maximised: it was negative.

The objective function was written as:

@olamide for PRH and @olamide1 for LRH (for fitness function to be recognized it has to have: ‘@” before it {so that it can be recognized by the software}.These are the responses generated in the RSM which was saved in the m.file.

Bounds for the variables are:

Lower: [400 2 10]   Upper: [800 6 50]

Population type; Double vector

Population size used: 100

Since 75 experimental runs were generated; then 100 was chosen as population. It was observed from literature that the population should be higher for good parent interaction. An interaction of parent generation used was from P1 to P100.

Reproduction: here genes are formed.

Reproduction: determines how the genetic algorithm creates children at each new generation. Elite count specified the individuals that are guaranteed to survive to the next generation. Set Elite count a positive integer less than or equal to Population size for this research it was set as default.

Crossover fraction: it specifies the fraction of the next generation that crossover produces. Mutation produces the remaining individuals in the next generation. Set Crossover fraction to be a fraction between 0 and 1, either by entering the fraction in the text box, or by moving the slider.
Crossover used was 0.8

Mutation: This is one of the last GA operations; it is the occasional random alteration for values of string positions. In binary strings, this simply means changing 1 to 0, or vice versa. Mutation function makes small random changes in the individuals of the population, which provide genetic diversity and enables the genetic algorithm to search a broader space.
Mutation used was 0.2
Scaling function used was Rank

Selection Function: Tournament.
Trial and error was done for selection function and the best optimal was observed in tournament

Stopping criteria: This determines what causes the algorithm to stop. Generations specify the maximum number of iterations the genetic algorithm performs.

Time limit specifies the maximum time in seconds the genetic algorithm runs before stopping.

Fitness limit: If the best fitness value is less than or equal to the value of Fitness limit, the algorithm stops.

Stall generations: If the weighted average change in the fitness function value over Stall generations is less than Function tolerance, the algorithm stops.

Default was used as the stopping number (100) for the GA parameter in the GA optim Tool in the Matlab software.

Stopping Generation Number means that before the iteration reached 100, an optimal result ought to be observed; if not then the generation number can be increased.

The defaults used in the GA parameters as itemized in the GAoptim Tool are: Scaling function, mutation, hybrid and the stopping criteria.

After the necessary inputs in the GA Tool, the optimisation and the start button are clicked.

When the optimal solution was reached at the specific iteration of nth the running stopped and the results were generated with the best fitness. Moreover, optimal parameters were then observed.

3.7 Validation Procedure

Model validation was done for the generated variables.

Deviation of GA predicted via the optimal process parameters observed was tested with experimental run for PRH and LRH respectively.

3.8 Procedure for Silicon Production

Ashes from PRH and LRH were respectively subjected to metallothermic reduction production for silicon production. Flow diagram for silicon production is shown in Figure 3.2.

3.8.1 Metallothermic Reduction Process

The best SS and SM of amorphous silica from PRH and LRH were subjected to metallothermic reduction process for the produced silicon. The magnesium turning (99% purity) was ground via agate mortar. Plate 3.2 shows agate mortar with magnesium turnings. Specific amount of silica was mixed with 5% excess of Magnesium turning so that the excess magnesium vapourised. The mixture was then pyrolyzed in a muffle furnace at 650˚C for one hour, then cooled to room temperature before it was removed from the furnace.

3.8.2 Leaching of Reduction Products

Preheated acid was introduced into the reduction product contained in a closed Teflon beaker. Leaching was done twice, first was to selectively leach out magnesium by-products and other impurities via HCl and Acetic Acid in ratio 4:1, volume of 15ml. The final leaching was HF and Acetic Acid in ratio of 1:9 of 15ml. The Acetic acid was initially used and later followed by the HF acid. Leaching was carried out at 700 ºC for 1h. The leaching procedure was adapted from Amick et al., (1980) and Hunt et al. (1984) to remove Mg, MgO and unreacted SiO_2. The silicon obtained was then examined again with SEM, XRD and Raman Spectra which was compared with the standard silicon.

Justification for Magnesium: the use of magnesium turnings resulted in reduced number of unwanted by-products phases

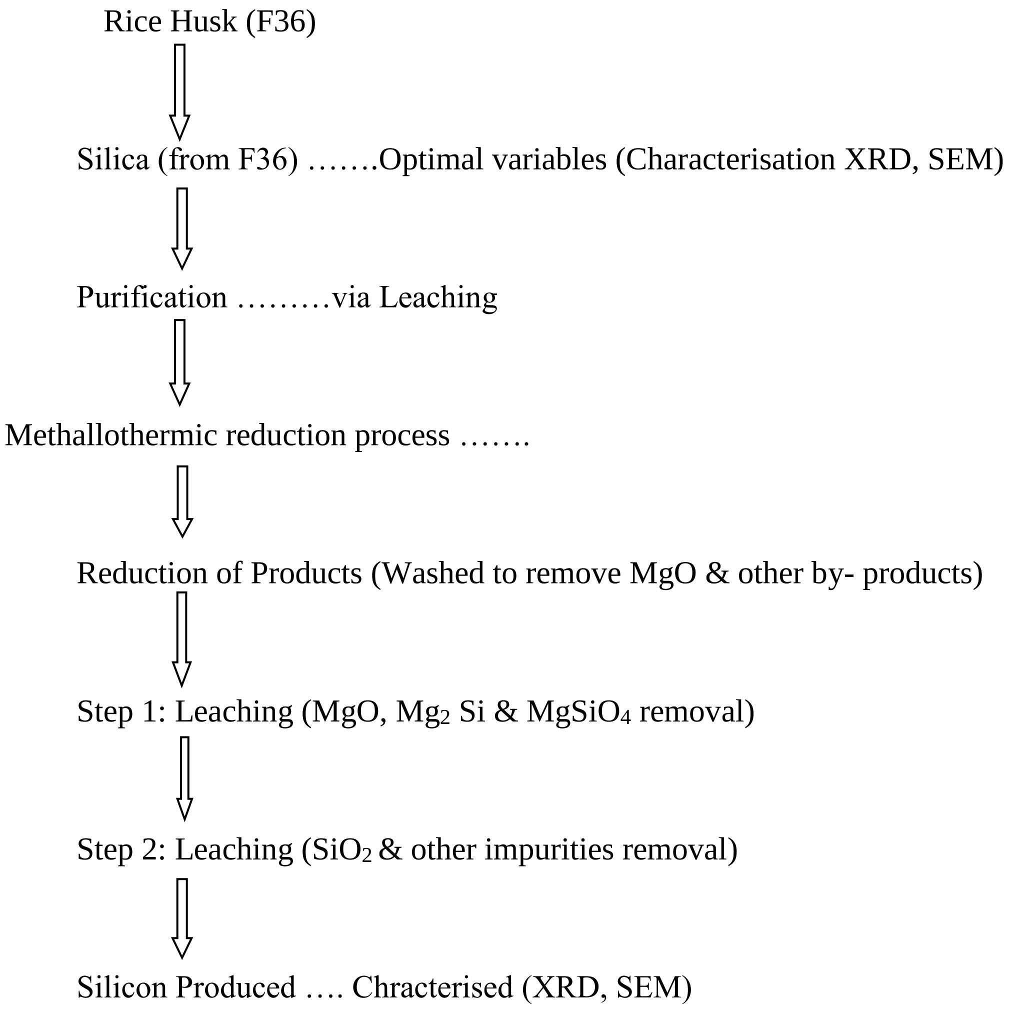


Figure 3.2. Flow Diagram of the Experiment for silicon Production

Plate 3. 2: Agate Mortar with Magnesium turnings

3.9 Validation of Silicon Produced

Silicon produced from most reactive amorphous silica from PRH and LRH via metallothermic reduction process were analysed to determine its type using XRD. The preferred silicon was re-analysed again with Raman Spectroscopy to further determine the silicon type. This operation was carried out to compare the silicon produced with the standard.

3.10 Statistical Inference on Micro-crystalline Silicon

Statistical inference on micro-crystalline silicon produced was done using t-test analysis for comparison of the silicon produced from rice husk in this research with:

I. Silicon produced from rice straw (Guzman *et al.,* 2015);

II. Silicon produced from growth of carbon nanotubes by the HF-CVD method using simple route (Bakr *et al.,* 2014); and

III. Standard silicon wafer (EDX, 2015).

CHAPTER FOUR

4.0 RESULTS AND DISCUSSION

This chapter presents the results on the ANOVA in RSM both for PRH and LRH. Furthermore; GA optimisation, results on the validation of the silica extraction from F36 and result on confirmatory experiment of the Genetic Algorithm optimal process variables predicted were discussed.

4.1 Response with ANOVA in RSM for PRH and LRH

Table 4.1 described the results of test of significance for every regression coefficient. The coefficients of each factor as well as the coefficients of determination obtained for each model is also presented Considering the test for comparing the variance estimated with all the terms with the residual variance (Large F-Value) and low for the low terms (P-values), all the model terms are significant and have very strong effect on F 36 with $P<0.05$.

The coefficients of determination for multivariate linear regression (R^2) for PRH and LRH are: 70.98% and 86.18%. It means that in PRH only 30.02% of the total variations were not explained by the model. Furthermore, in LRH only 19.32% of the total variations were not explained by the model. The results indicated that the fitted quadratic models accounted for more than 70% of the variance in the experimental data. Based on t- statistics, the regression coefficients that 95% are not significant are discarded while those that are significant were selected for the models of silica yield.

The regression equation 4.1 generated by type 1 (PRH) with the interactions between Temperature, Time and solvent is:

$$90.62+0.78X_1+0.40X_1X_3 \qquad 4.1$$

The response generated in equation 4.2 from RSM for LRH is stated in Terms of Coded Factors as:

$$96.93+0.87X_1+0.29X_3-1.76X_1^2 \qquad 4.2$$

As shown in the equations 4.1 & 4.2; the terms of the models were significant. These models showed that the composition ratio and actual composition all have effect on the yield.

The goodness of fit of the model was checked by the coefficient of determination of the multivariate linear regression (R^2). A good fit should have R^2 to be at least 0.8 (Guan and Yao, 2008). In this case; R^2 in LRH was 0.8616 (86.16%) for silica yield attributed to the independent factors while it is 0.7098 (70.98%) in PRH.

These fitted models were tested for adequacy and consistency using Analysis of Variance (ANOVA) and the values of various computations are as presented in Table 4.2. The results from the ANOVA revealed that the F-Values for PRH and LRH are 17.73 and 44.53 respectively. These are significant at the 95% level. However, for PRH with F-Value of 17.73 and P-Value of 0.0001 is significant while in LRH with higher F-Value of 44.53 and P-Value of 0.0001 showed that LRH is more significant on account ofAdj.R^2 OF 84.27%. The results of the second order response surface model fitting in the form of ANOVA are presented in Table 4.2. The model F-Value (terms used to estimate effects) in LRH of 44.53 with P-Value of 0.0001 implied a high significant and better regression model.

The value of the adjusted determination coefficient (Adj R^2) is 0.8427 (84.27%) in LRH while it is 0.6696 (66.96%) in PRH. The Adj. R^2 in LRH was also high supporting a high significance of the model (Khuri and Cornell,1987) and all P-Values less than 0.05; implying that the model proved suitable for the adequate representation of the actual relationship among the selected factors . Hence the model could be used in theoretical prediction of the silica yield from RH.

Justification for using Adjusted R^2 and R^2

R^2 is used when dealing with one variable but for multiple variables, Adj.R^2 is reported because it takes into consideration the interaction of the variables i.e multiple variables.

.

Table 4.1 Estimated coefficients of the response models for the silica yield.

Response	Model Terms	Coefficients	Standard Error of coefficients	SS of Squares	T-value	P-value	R^2
PRH	Interc	90.62	0.25	-	-		
	ept	0.78	0.15	22.96	27.89	0.0001*	
	x_1	0.46	0.15	8.09	9.83	0.0026	
	x_2	0.30	0.13	4.61	5.60	0.8886	
	x_3	0.029	0.21	0.016	0.020	0.0327	70.98
	x_1x_2	0.40	0.18	3.92	4.76	0.0001*	%
	x_1x_3			90.73	110.20	0.6602	
	x_1^2			0.23	0.27	6	
	x_2^2			0.33	0.40	0.5310	
	x_3^2						
LRH	Interc	96.93	0.12	-	-		
	ept	0.78	0.071	28.34	150.89	0.0001*	
	x_1	-0.40	0.071	0.061	0.32	0.5713	
	x_2	0.29	0.061	4.22	22.48	0.0001*	
	x_3	-0.24	0.10	1.10	5.85	0.0184	
	x_1x_2	0.11	0.087	0.32	1.70	0.1969	86.16
	x_1x_3	-0.094	0.087	0.22	1.18	0.2822	%
	x_2x_3	-1.76	0.12	40.80	217.21	0.0001*	
	x_1^2	-0.25	0.12	0.85	4.54	0.0369	
	x_2^2	0.12	0.11	0.24	1.30	0.2585	
	x_3^2						
Significant at $p<0.05$							

Table 4.2: Analysis of variance for fitted models for specific impulse

(F36)	Source of variation	Sum of Squares	d.f	Mean Squares	F-values	p-value (prob>F)	Adjusted R^2
PRH	Model	130.89	9	14.54	17.73	0.0001*	0.6696
	Residual	53.51	65	0.82			
	Total	184.41	74				
LRH	Model	76.16	9	8.46	44.53	0.0001*	0.8427
	Residual	12.21	65	0.19			
	Total	88.36	74				

4.2 Model Developed via GA Optimisation

The model studied the effects of the numerical parameters developed for the GA in terms of the best fitness value.

4.2.1 Mathematical Model Developed for PRH and LRH

The mathematical models developed for each of the two forms of husks are represented as objective function:

Mathematical model for PRH:

```
function y=Ah1(x)

y= -(63.17975238+ 0.07886828571*x(:,1)+0.8359619048*x(:,2)+ 0.047*x(:,3)-
0.00006572857143*x(:,1).^2-0.03276190476*x(:,2).^2-
0.0014*x(:,3).^0.0005053333333*x(:,1).*x(:,2+0.0001208*x(:,1).*x(:,3)-
0.01286*x(:,2).*x(:,3)+0.0000193*x(:,1).*x(:,2).*x(:,3)); end.
```

<u>The clean model is:</u>

```
y= -(63.17975238+ 0.07886828571*x(:,1)+0.0001208*x(:,1).*x(:,3)
```

Mathematical model for LRH is:

```
function y=Ah2(x)
y = -(74.54362857 + 0.06161109524*x(:,1) + 1.540780952*x(:,2) + 0.01432*x(:,3) -
0.00004407619048*x(:,1).^2 -0.06371428571*x(:,2).^2 + 0.00121*x(:,3).^2 -
0.001517*x(:,1).*x(:,2) -0.0000651*x(:,1).*x(:,3) -0.02294*x(:,2).*x(:,3) +
0.0000304*x(:,1).*x(:,2).*x(:,3));  end.
```

<u>The clean Model:</u>

```
y = -(74.54362857 + 0.06161109524*x(:,1)  -0.00004407619048*x(:,1).^2
```

4.2.2 GA Programme Developed for the Husks

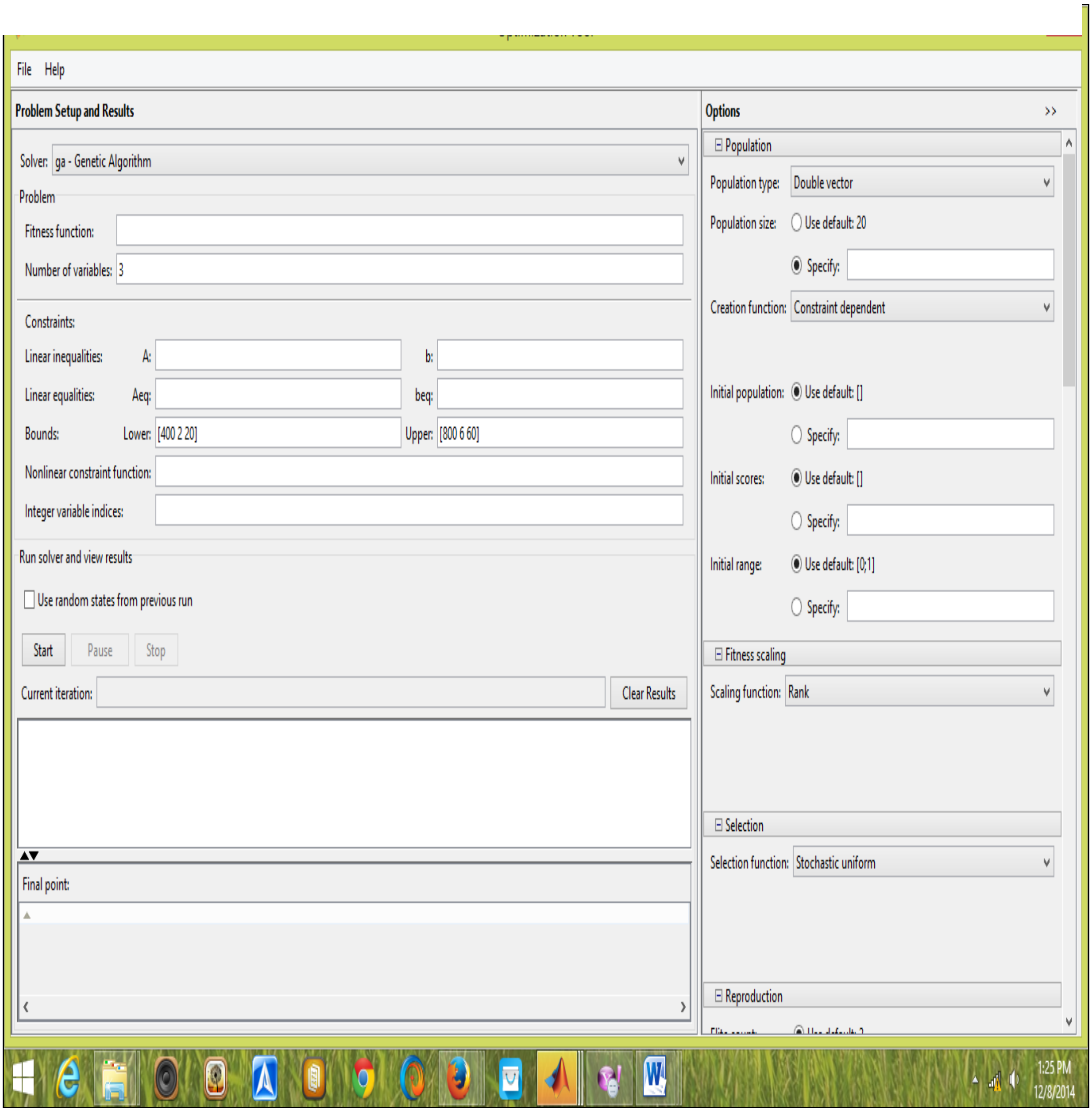
The GA Programme developed for PRH is as stated below:

```
function state = olamideplot(options, state, flag)
% GAPLOTCHANGE Plots the change in the best score from the
% previous generation.
%
persistent last_best % Best score in the previous generation
if(strcmp(flag,'init')) % Set up the plot
set(gca,'xlim',[1,options.Generations],'Yscale','log');
hold on;
xlabel Generation
title('Change in Best Fitness Value')
end
best = min(state.Score); % Best score in the current generation
if.Generation == 0 % Set last_best to best.
last_best = best;
else
change = last_best - best; % Change in best score
last_best=best;
plot(state.Generation, change, '.r');
title(['Change in Best Fitness Value' state])
end.
```

GA Programme developed for LRH is as stated below:

```
function state = olamideplot(options, state, flag)
% GAPLOTCHANGE Plots the change in the best score from the
% previous generation.
%
persistent last_best % Best score in the previous generation
if(strcmp(flag,'init')) % Set up the plot
set(gca,'xlim',[1,options.Generations],'Yscale','log');
hold on;
xlabel Generation
title('Change in Best Fitness Value')
end
best = min(state.Score); % Best score in the current generation
if state.Generation == 0 % Set last_best to best.
last_best = best;
else
change = last_best - best; % Change in best score
last_best=best;
plot(state.Generation, change, '.r');
title(['Change in Best Fitness Value'])
end.
```

The GA Optimisation tool in Matlab software is shown in Fig 4.1. The parameters under considerations were initial population, population size, crossover, probability and mutation probability



Solver: ga - Genetic Algorithm

Number of variables: 3

Bounds: Lower: [400 2 20] Upper: [800 6 60]

Population type: Double vector

Population size: ○ Use default: 20

● Specify:

Creation function: Constraint dependent

Initial population: ● Use default: []

○ Specify:

Initial scores: ● Use default: []

○ Specify:

Initial range: ● Use default: [0;1]

○ Specify:

Scaling function: Rank

Selection function: Stochastic uniform

1:25 PM
12/8/2014

Figure 4. 1. Block Chart for optim in Matlab software

4.2.3 GA Tool Box Generated

The GA toolbox generated via Matlab software for numerical parameters with maximum number of iterations, initial population, stopping criteria, crossover probability, mutation fraction and fitness function is stated below:

Solver: ga –Genetic Algorithm
Fitness function: @olamide1
Number of variables: 3
Bounds: Lower: [400 2 20]   nUpper: [800 6 50]
Population:
Population type: Double vector
Population size: 100
Creation function:
Initial population: default

Scaling function: Rank
Selection function: Tournament
Tournament size: use default: 2

Reproduction:
Cross over fraction: 0.8
Mutation
Mutation function: intermediate
Ratio: 1.0
Migration
    Fraction: 0.2
Pareto front population fraction: 0.5
Hybrid function: None
Stopping Criteria
Generation: 100
Stall generation: 100

4.3 GA Optimal Variables

The GA Optimisation run stopped at 51st iteration for each of the two forms of husks. The result is as shown in Table 4.3:

Table 4.3. GA Optimisation Variables for PRH

Temp(^{o}C)	Time(h)	WaterVolume (cL)	Stopping criteria
648.8	6	40	100
648.8	6	40	100
648.8	6	40	100
650.0	5.9	44.02	100

Objective value = 91.2718. Optimisation terminated at 51st iteration.

The best and mean fitness is shown in Figure 4.2

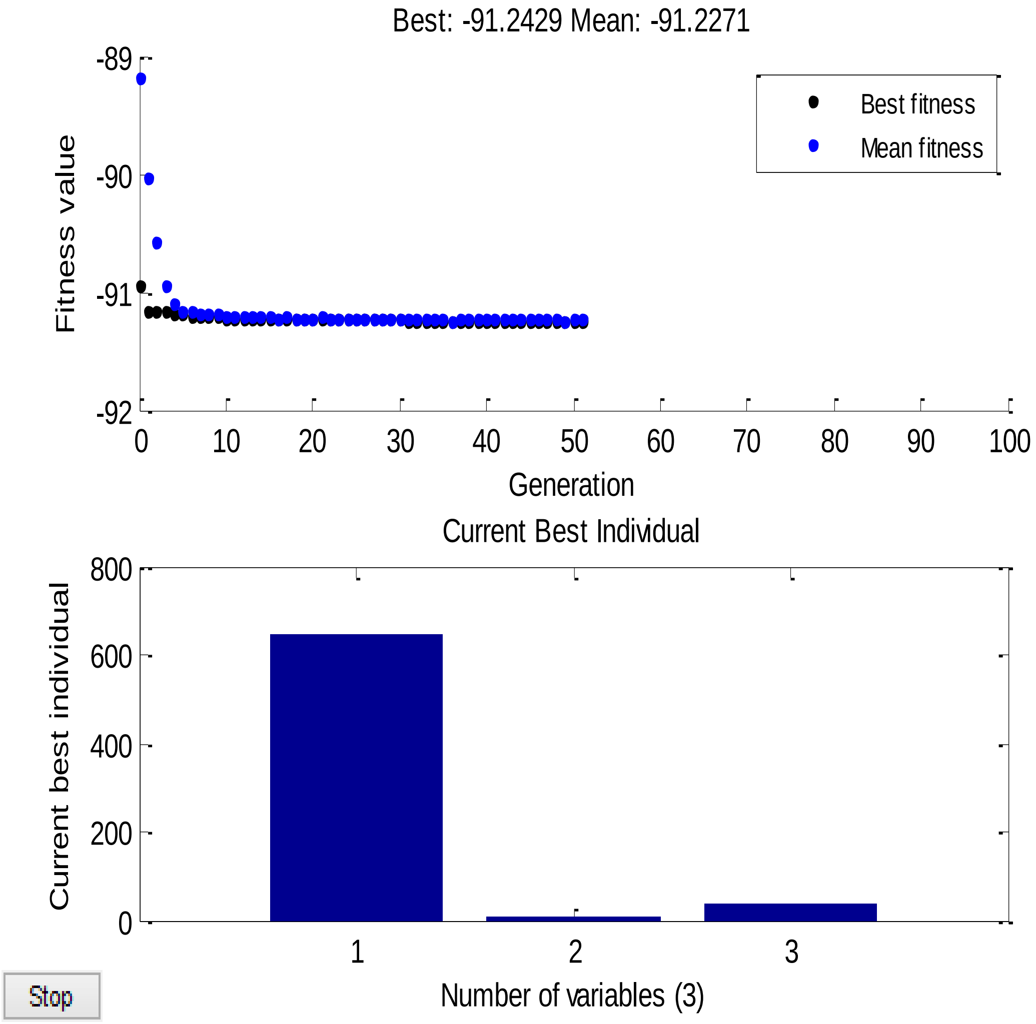


Figure 4.2. Best Fitness for PRH

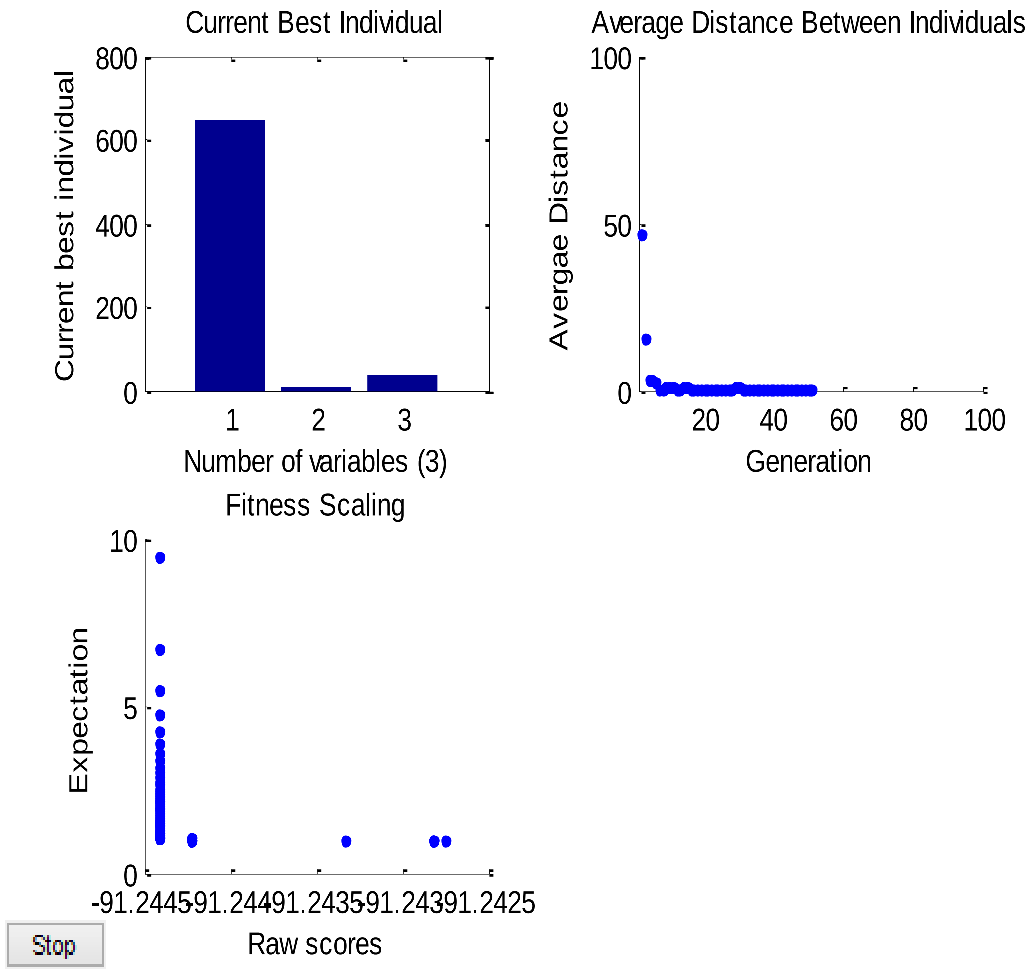
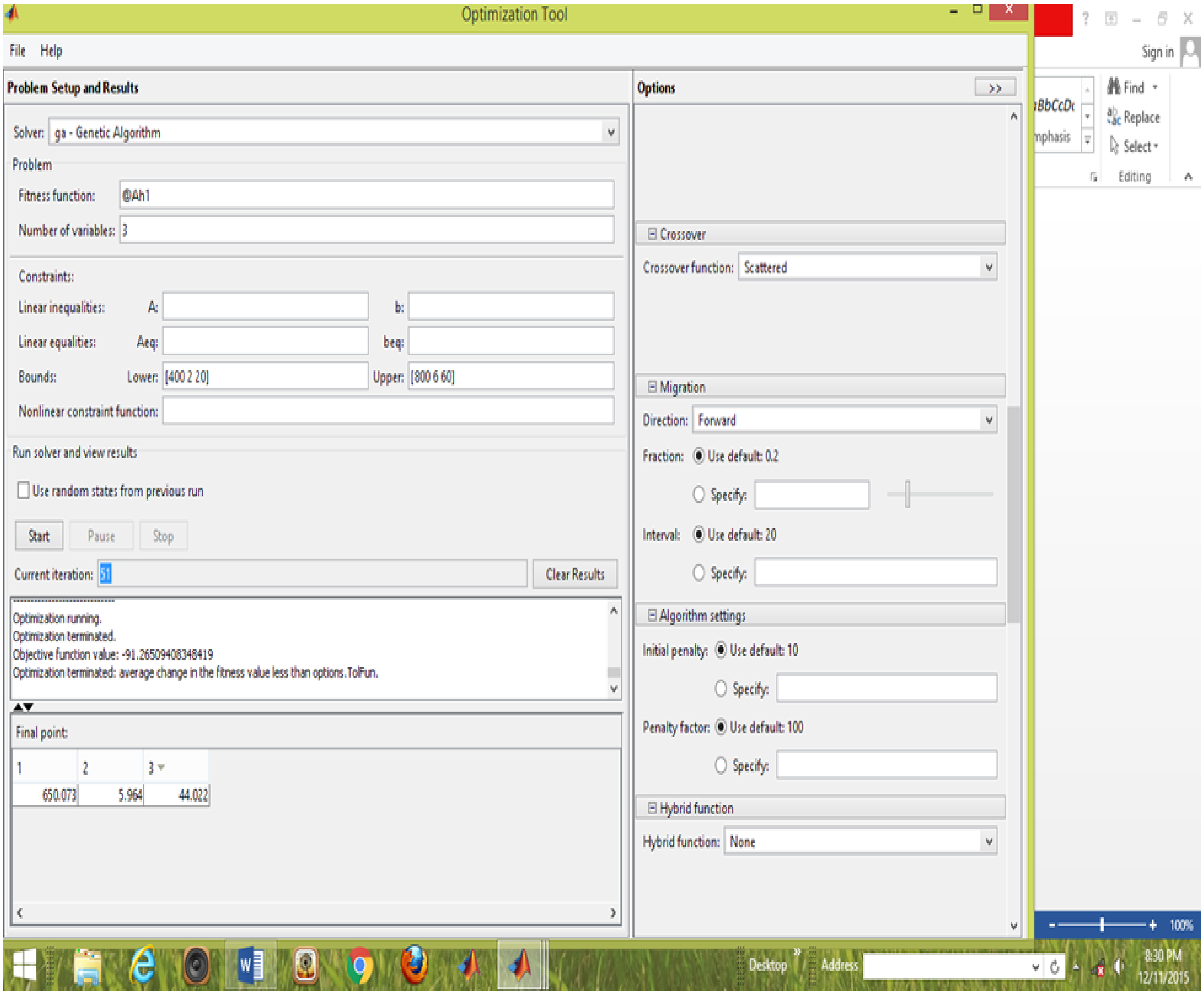


Figure 4.3. Expectation and Best Individual for PRH

The GA optimisation tool as generated for PRH is shown in Figure 4.4.The parameters under considerations are best fitness and variables with their upper and lower bounds.



Solver: ga - Genetic Algorithm

Problem

Fitness function: @Ah1

Number of variables: 3

Constraints:

Bounds: Lower: [400 2 20] Upper: [800 6 60]

Run solver and view results

☐ Use random states from previous run

Current iteration: 51

```
Optimization running.
Optimization terminated.
Objective function value: -91.26509408348419
Optimization terminated: average change in the fitness value less than options.TolFun.
```

Final point:

1	2	3
650.073	5.964	44.022

Crossover

Crossover function: Scattered

Migration

Direction: Forward

Fraction: ● Use default: 0.2 ○ Specify:

Interval: ● Use default: 20 ○ Specify:

Algorithm settings

Initial penalty: ● Use default: 10 ○ Specify:

Penalty factor: ● Use default: 100 ○ Specify:

Hybrid function

Hybrid function: None

Figure 4.4. Block diagram for GA in PRH

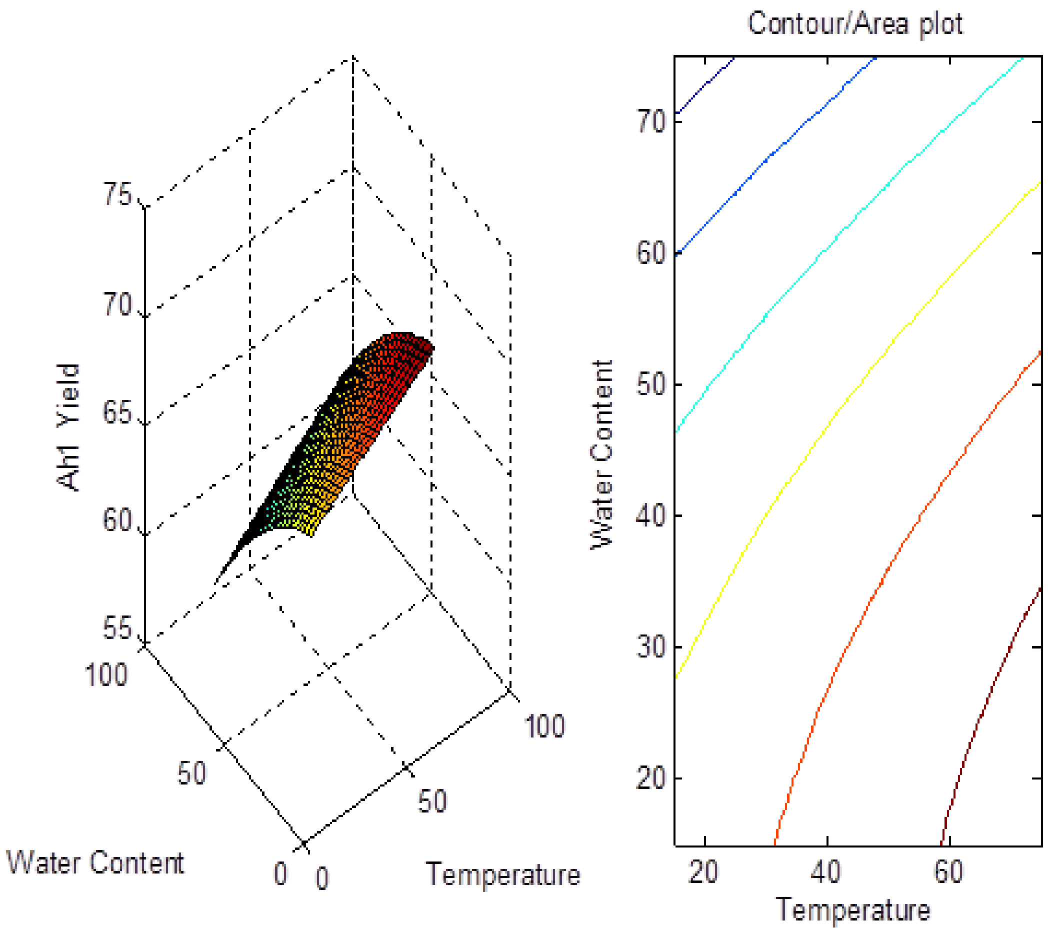


Figure 4.5. Surface Plot for PRH

The contour plot for PRH showed that each factor has their individual effects and interactive effects in the quadratic model which helps to estimate the individual effects on the interaction between the water content/volume and temperature.

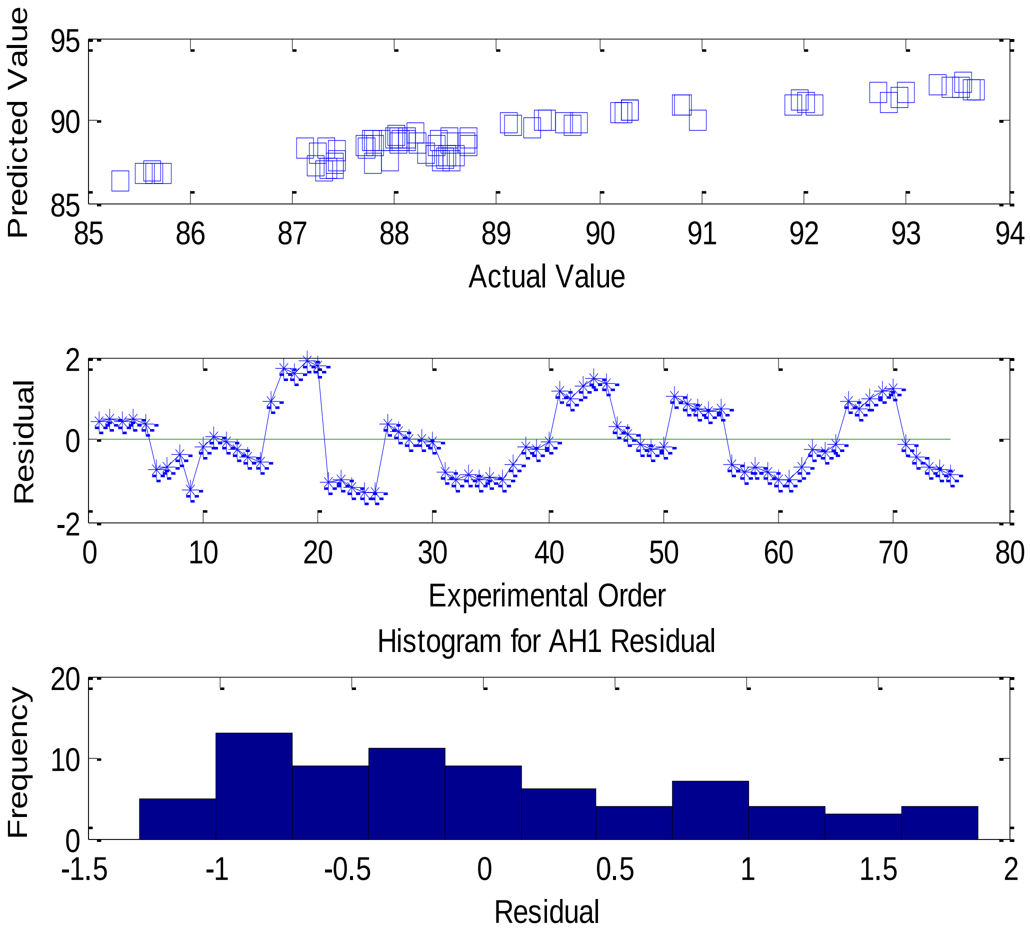


Figure 4.6. Residuals for PRH

The error generated was from +2 to -2, so the optimal fitness was 91.247±2

Table 4.4. Optimal Variables Generated For LRH

Temp (^oC)	Time (h)	Oxalic Acid content (cL)	Stopping criteria
667	3h 33min	39.9	100
657.9	3h 34min	40	100
657.9	3h 34min	40	100
657.9	3h 34min	40	100
667.9	3h 40min	39.9	100

Objective value=97.5048. Optimisation terminated at 51st iteration.

The best and mean fitness is shown in Figure 4.7

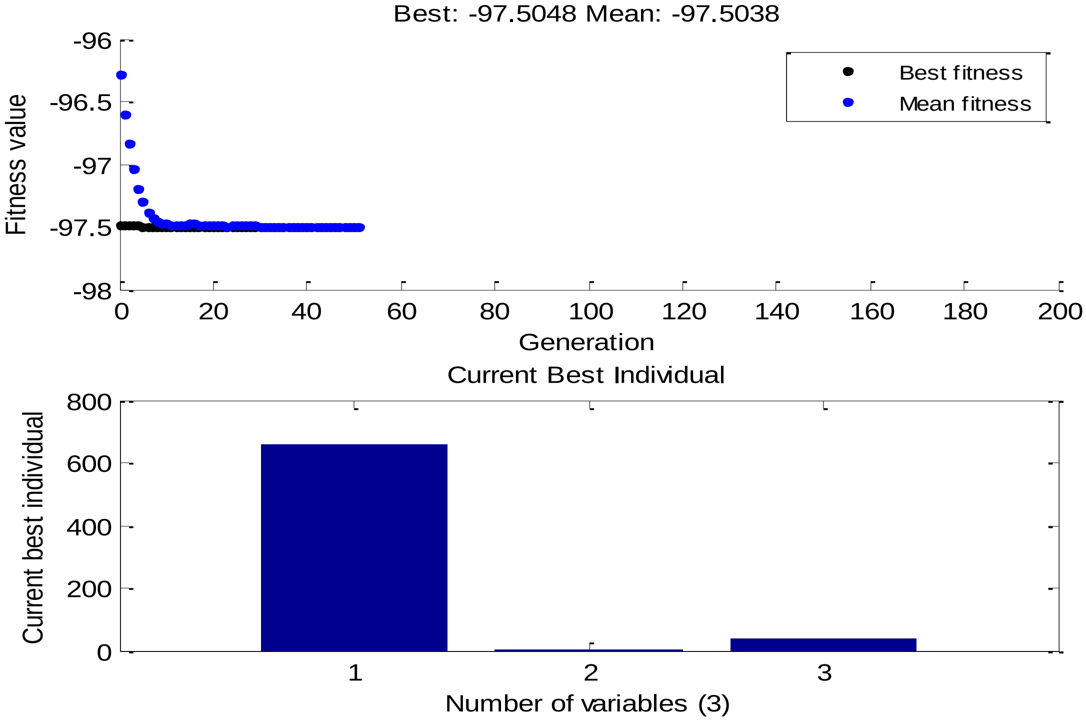


Figure 4.7. Best fitness and Mean for LRH

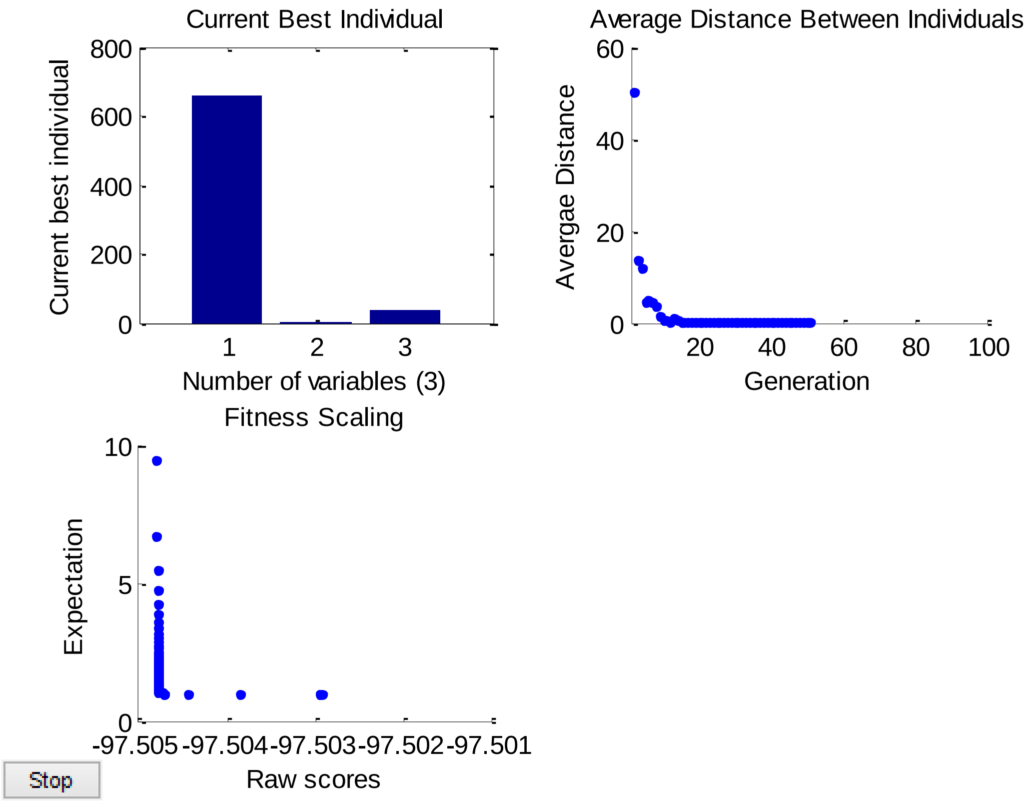
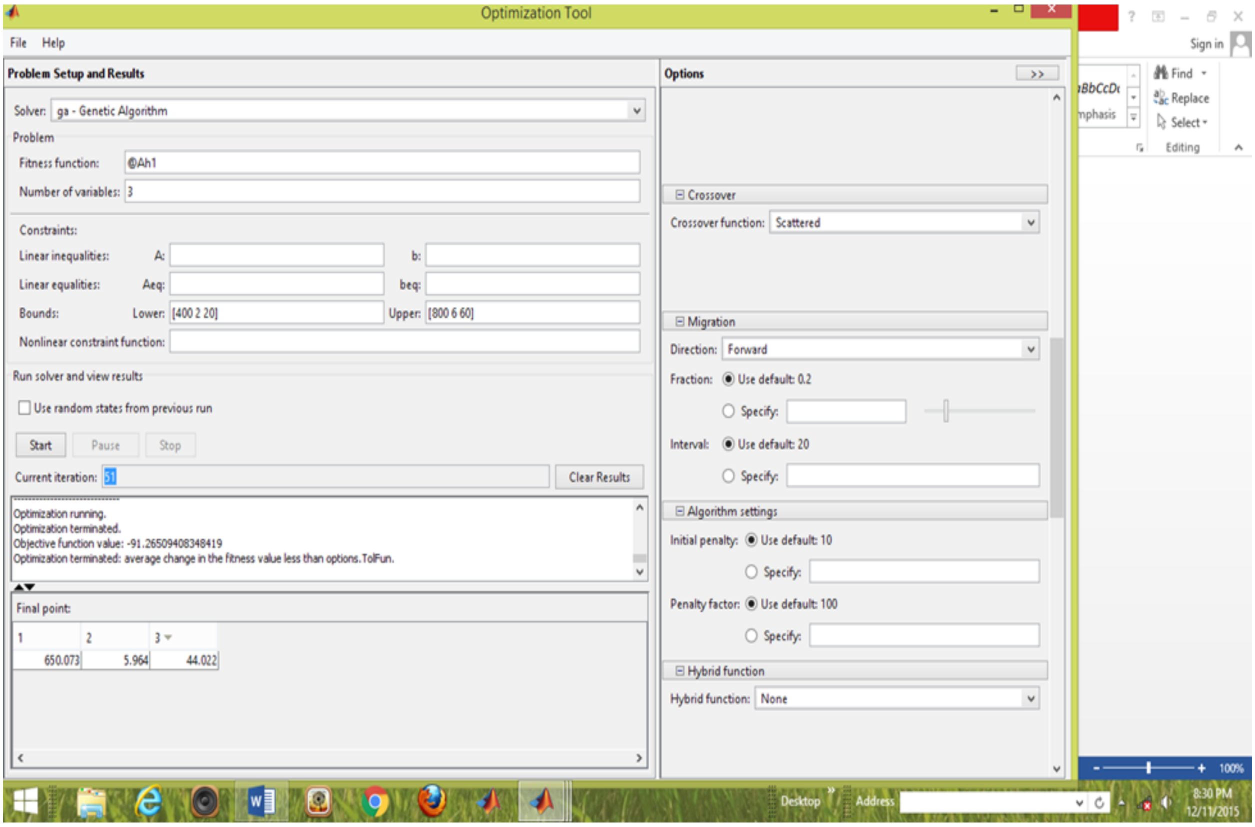


Figure 4.8. Current Best Individual and Expectation for LRH

The GA optimisation tool as generated for LRH is shown in Figure 4.9.The parameters under consideration are best fitness and variables with their upper and lower bounds.



Solver: ga - Genetic Algorithm

Problem

Fitness function: @Ah1

Number of variables: 3

Constraints:

Linear inequalities: A: b:

Linear equalities: Aeq: beq:

Bounds: Lower: [400 2 20] Upper: [800 6 60]

Nonlinear constraint function:

Run solver and view results

☐ Use random states from previous run

Current iteration: 51

```
Optimization running.
Optimization terminated.
Objective function value: -91.26509408348419
Optimization terminated: average change in the fitness value less than options.TolFun.
```

Final point:

1	2	3
650.073	5.964	44.022

Crossover

Crossover function: Scattered

Migration

Direction: Forward

Fraction: ● Use default: 0.2 ○ Specify:

Interval: ● Use default: 20 ○ Specify:

Algorithm settings

Initial penalty: ● Use default: 10 ○ Specify:

Penalty factor: ● Use default: 100 ○ Specify:

Hybrid function

Hybrid function: None

Figure 4.9. Block diagram for GA in LRH

The best fitness was denoted as: @olamide 1.Surface plot is shown in Figure 4.10.

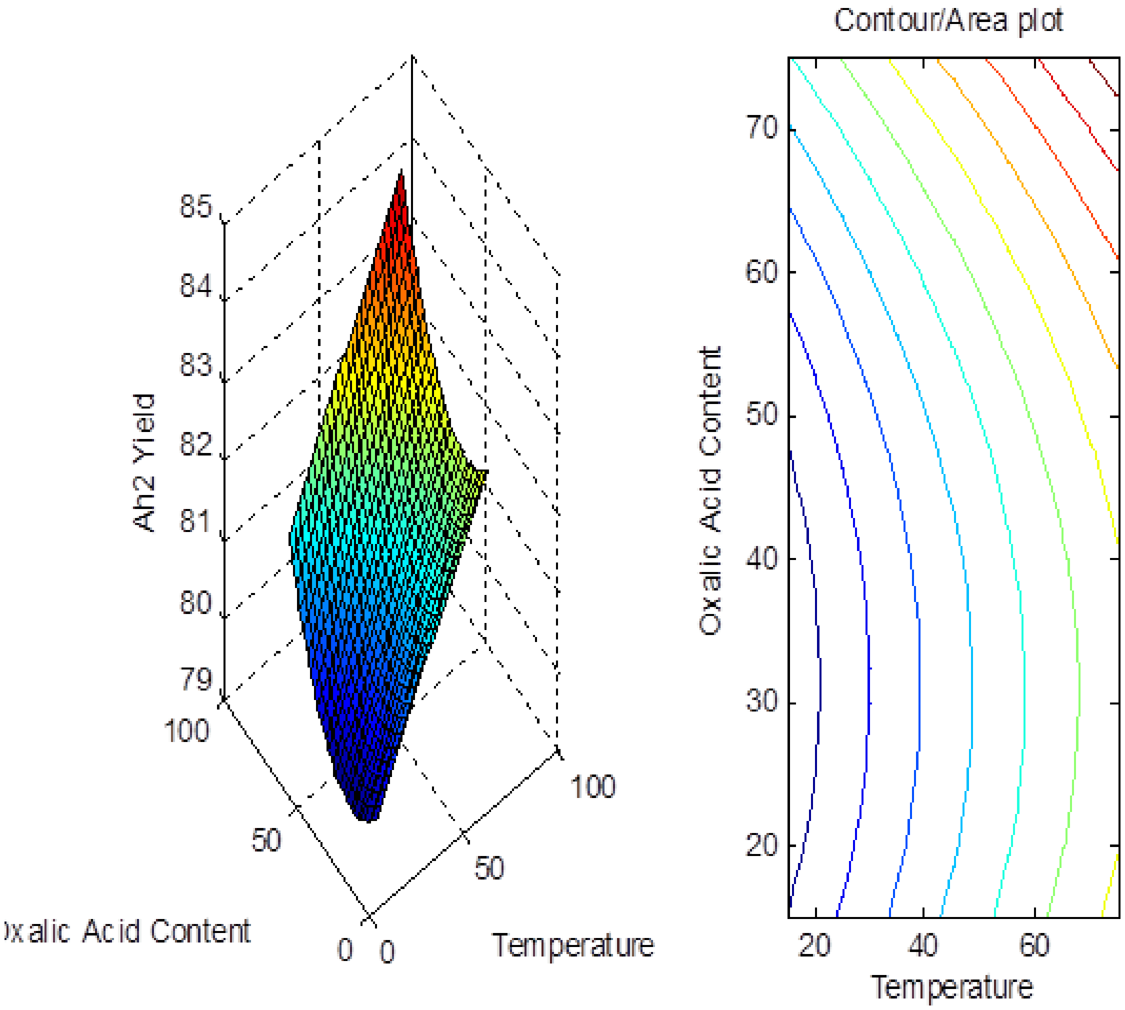
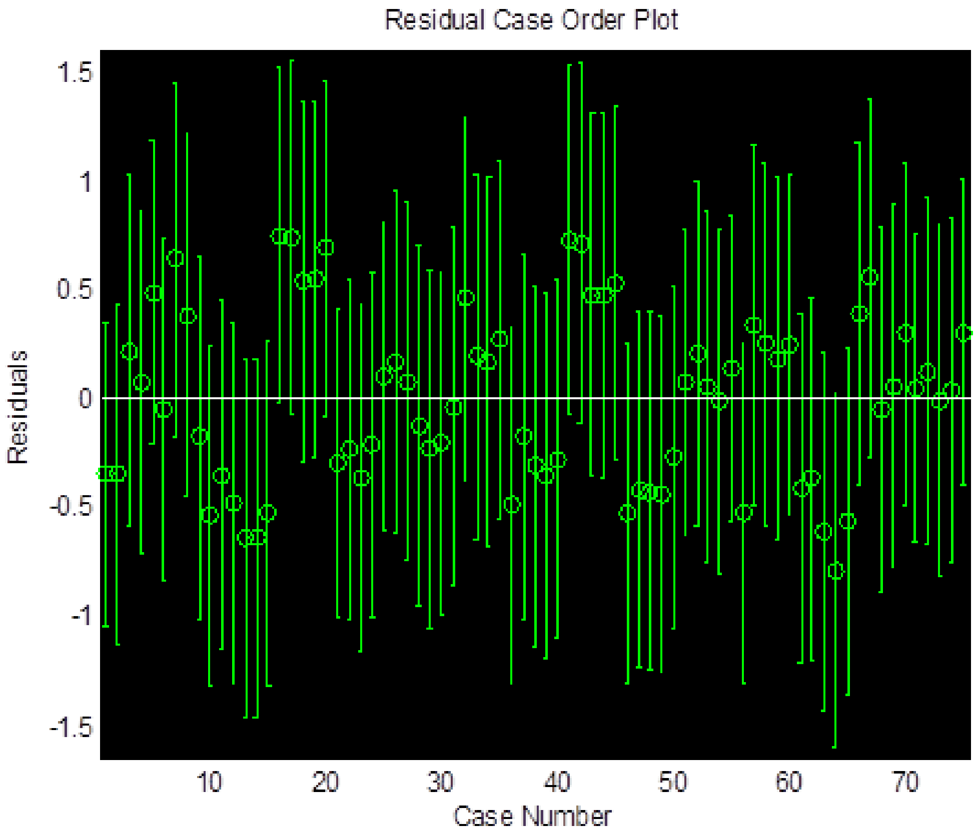


Figure 4.10. Surface Plot for LRH

The contour plot for LRH showed that each factor has individual effects and interactive effects in the quadratic model which helps to estimate the individual effects on the interaction between the Oxalic Acid content/volume and temperature.



The residual error as predicted by GA for LRH was between -1.5 and +1.5

Figure 4.11. Residuals for LRH

Discussion of ANOVA in GA optimisation

The goodness of fit was checked by the coefficient of determination (R^2). In this study, R^2 of 71.12% can be attributed to the independent variables and only 28.88% for PRH; while in LRH R^2 of 85.67% was observed. The Root Mean Square error obtained was 0.3057.

4.4 Optimisation and Validation of Silica Formulation

The GA optimal parameters were validated for each of the two forms of husks. The optimum variables obtained were Temperature: 648.8 ^{o}C, Time: 6h, Water volume 40 mL for PRH while Temperature: 657.9 ^{o}C, Time: 3h 34min, Oxalic Acid volume: 40 mL for LRH. 10g of husk was used for the pre-treatment of the husks. Best fitness of PRH is 91.2±2 while it is 97.5 ±2 for LRH respectively. The results of these two conditions were validated experimentally. The % of ash observed for the two forms of husks are as stated below:

Husk Amount of Husk used=10g

Amount of Ash % of Ash

PRH: 1.76g (17.6%) of ash was obtained while in

LRH: 2.01g of ash.

Discussion on Yield

The silica obtained via oxalic acid treated husk (LRH) at 3h 18min which was the most reactive amorphous silica was 97.88%. However, this is of higher yield than 97% that was reported by Shinohara and Kohinohara (2004) and also higher than amount reported by Mishra *et al.*, (1985) who reported that rice husk ash contained 92-97% of silica. Furthermore, 93% of silica was obtained from PRH.

4.5 Observations on ashes at temperature ranges of 400-800^{0}C for the husks

Experimental verification from laboratory revealed that the optimal temperature for amorphous silica via highest yield and highest Specific Surface Area was 700 ^{o}C. This study now subjected husks to calcination at optimal temperature of time variation of 1-6 h to determine the effect of time on the type of ash, colour of ash and yield of silica.

Central Composite Design (CCD) was used to determine experimental combinations of the predictor variables. Seventy-five experimental combinations from CCD was observed was from the numeric optimisation in 6.8.Design Expert Software.

Calcination of the identified rice husk process parameters showed that dull white and completely white ashes were obtained at 3h and 6h respectively. According to Olawale and Oyawale (2011), the Burning Temperature Dependence of Rice Husk Ash for Optimal Silica Production was 700 ^{o}C. Moreover, according to Olawale *et al.*, 2012, it was observed that pre-treatment of rice husk with oxalic acid gave a highly reactive amorphous silica. Nevertheless, significant effects of calcinations time are at: 1h, 3h and 6h respectively. However, Nayak and Bera (2009) stated that: when rice husk is calcined at 6h, complete combustion takes place.

Digestion of Ashes

100ml of fairly concentrated HCl was added to each of the samples and was leached for 2h to remove most of the soluble impurities present in it. It was allowed to cool at room temperature and then washed with distilled water several times. The ashes were re-calcined for one hour for further removal of impurities still present from the amorphous silica produced. The silica obtained were analysed again with XRD and SEM to determine the best SS and the best SM of amorphous silica.

The colour of the ashes obtained at each hour differs and the objective is to produce completely white ashes so the effect on time variation as observed is as stated in Table 4.5.

Table 4.5. Results observed during calcination of 1-6h

Time (h)	Observation
1	100% black char was observed
2	Significant change from greyish of 25% to 75% dull white
3	Completely dull white colour was observed
4	50% dull white and 50% white colour
5	80% white and 20% dull white
6	100% white colour

4.6 Characterisation of the Prepared Silica via HF Evaporation Method

Silica prepared from PRH and LRH correlated with the yield reported in the literature. HF evaporation method was used for extracting the silica. Amorphous structure, high specific surface area, large pore volume and high reactivity were very important for determining highly reactive silica. The X-Ray middle Diffraction of the ash samples was done for both PRH and LRH to determine the most reactive amorphous silica from the two forms of husks. The structure and morphology of amorphous silica for this research was done via Scanning Electron Microscope (SEM).'Since, Nuclear Magnetic Resonance (^{Si}NMR) for determining the reactivity of silica was not available', the reactivity was analysed and determined via surface morphology with SEM. Silica obtained was analysed again using SEM. Silica at 3h 34min from LRH was observed to be better than silica from PRH at 6h.The morphology powder of the silica from LRH revealed a broad peak of amorphous silica at 2 theta=22 degree. Plate 4.1shows Surface Morphology (SM) of silica obtained.

Plate 4.1. SS of PRH at 6h

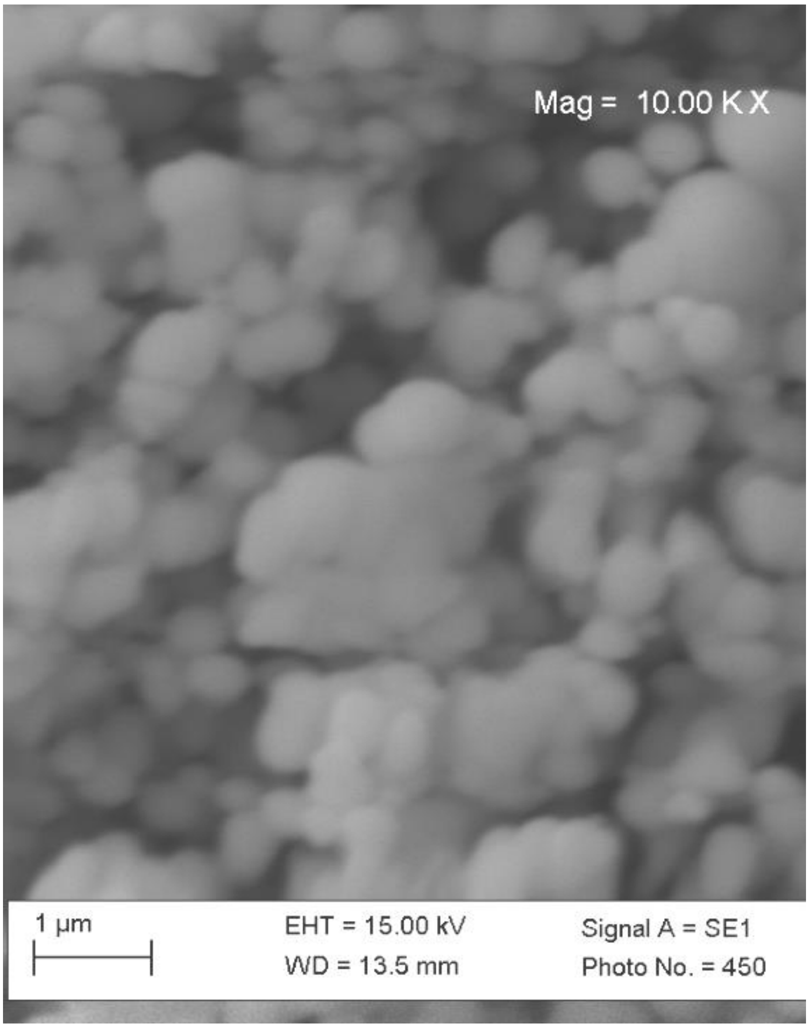


Plate 4.2. SM of Silica from LRH

The SM result in Plate 4.2 showed better microstructure morphological silica at LRH due to its acid leach which was spherical (colloidal) morphology and its XRD patterns is as shown in Plate 4.3.

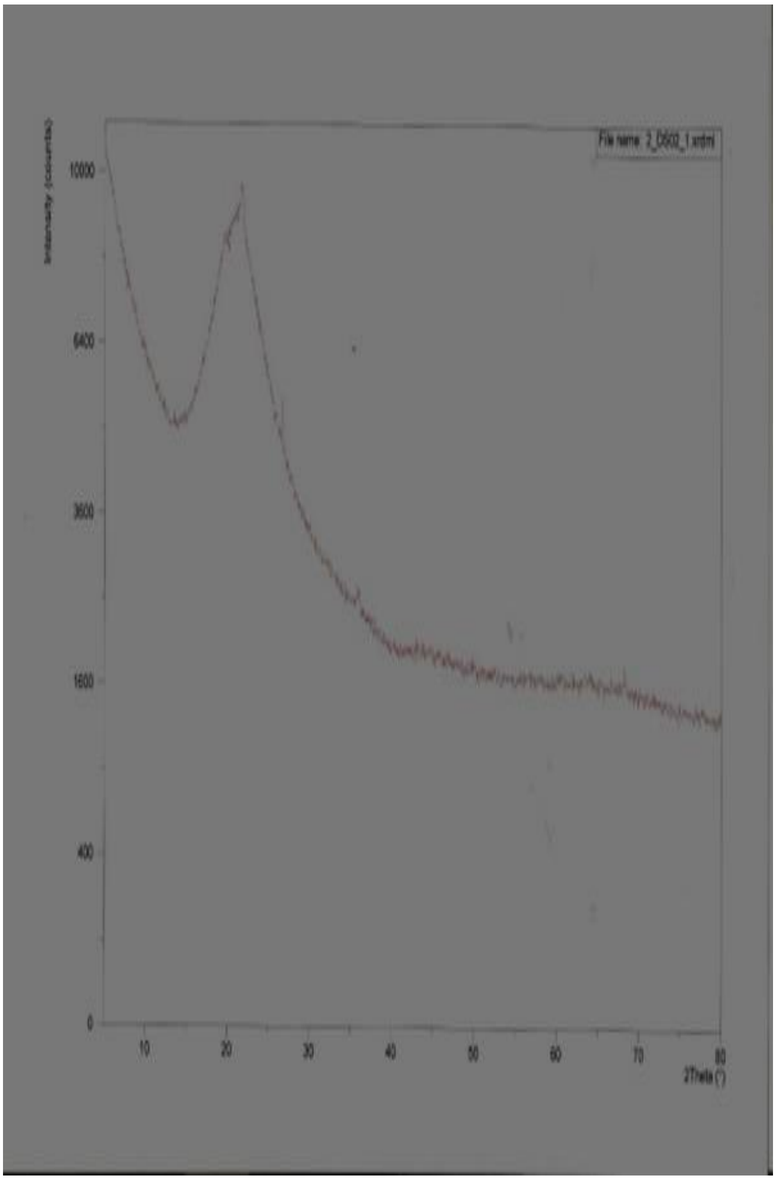


Plate 4.3. XRD of SS for LRH

This plate indicates the formation of amorphous silica from LRH

4.7 The statistical inference of PRH and LRH

Statistical Inference via t-test paired two samples for means for the two portions of husks (PRH and LRH) used was statistically analysed as:

General test statistics assumptions are:

First: Samples should be independent

Secondly: Variance of the two populations from which the samples are drawn should be homogenous.

Result for t- test paired two sample means for PRH and LRH is as shown in Table 4.6. However, it was observed that since df is more than 120 then '∞'was used. The statistical inference via Hypothesis 'Hi' showed that the effects of the two portions of husks of RH on silica yield were not the same.

Table 4.6. T-test for PRH and LRH

	n	mean	Variance	t-stat	p-value (two tailed)
PRH	74	89.1426	2.4919	62.938	5.17588E-66
LRH	74	96.000	1.19410		
Total	148				

Since t –stat> 2.5 then it is highly significant

Critical value of t at 148@ p=0.05 is 1.645.

4.8 Micro-Crystalline Silicon Produced

4.8.1 Silicon Produced via Metallothermal Reduction Process

The silicon powder produced was greyish-black in colour as shown in Plate 4.4. It was compacted with KBr and pelletised as shown in Plate 4.5. XRD of the produced silicon observed is in Plate.4.6.The SM of silicon produced is shown in Plate 4.7 and the EDX is shown in Figure4.1. Table 4.6 shows the Energy dispersive Spectrometry (EDX) of silicon produced. However, yield of silicon from the 2 portions of (F36) husk were summarized as:

Amount of silica in PRH= 1.76g while in LRH: amount of silica =2.01g

Amount of silica used for silicon production were: 5.28g in form 1: F36 (PRH) while in form type 2: F36 (LRH) was 6.03g

Amount of Si yield PRH=2.3g (23%) LRH=4.2g (42%)

Amount of Mg turnings (5 %) excess= 2.05g

Plate 4.4. Silicon Powder

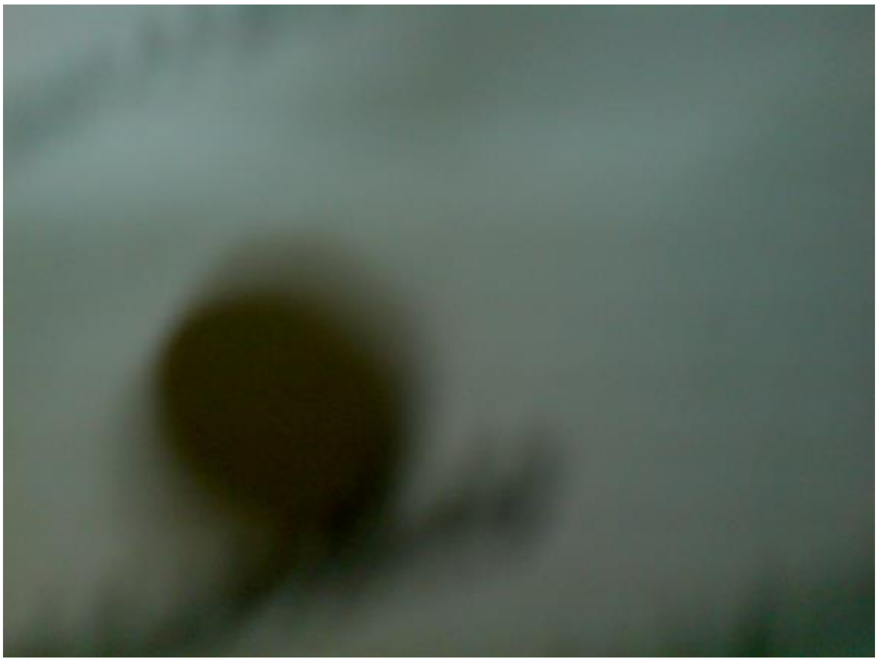


Plate 4.5: Silicon Compact

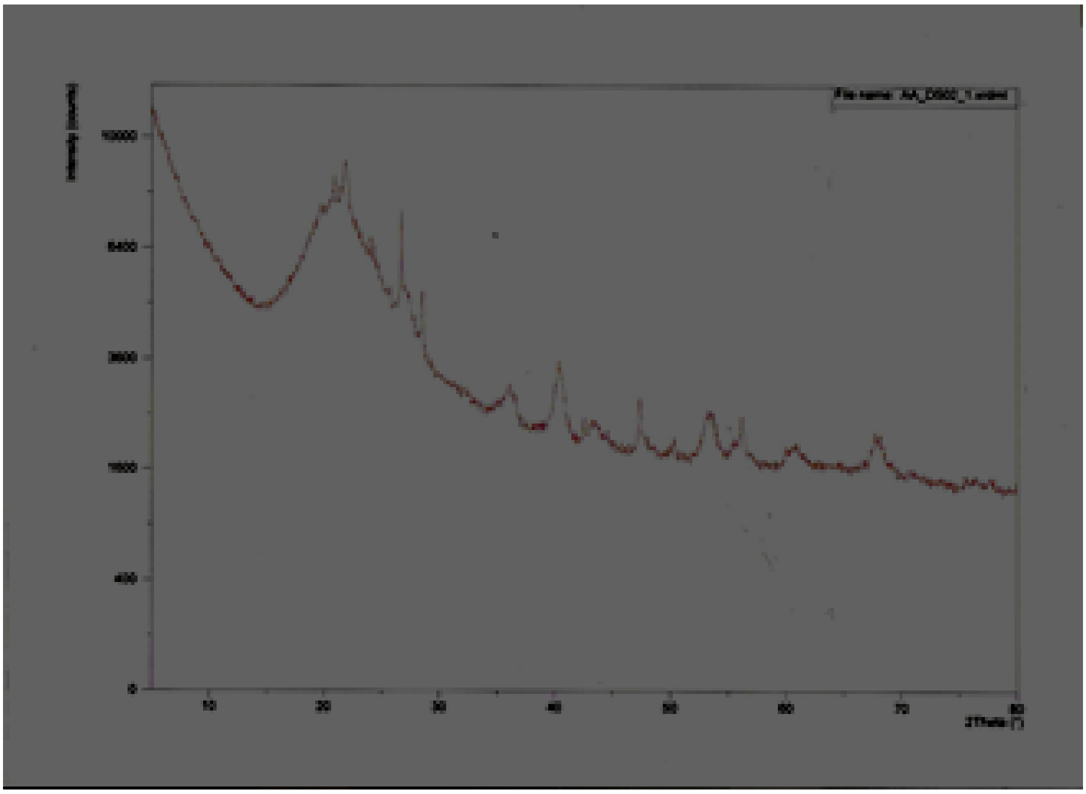


Plate 4.6. SS of Silicon Produced

(SS patterns showed micro-crystalline silicon)

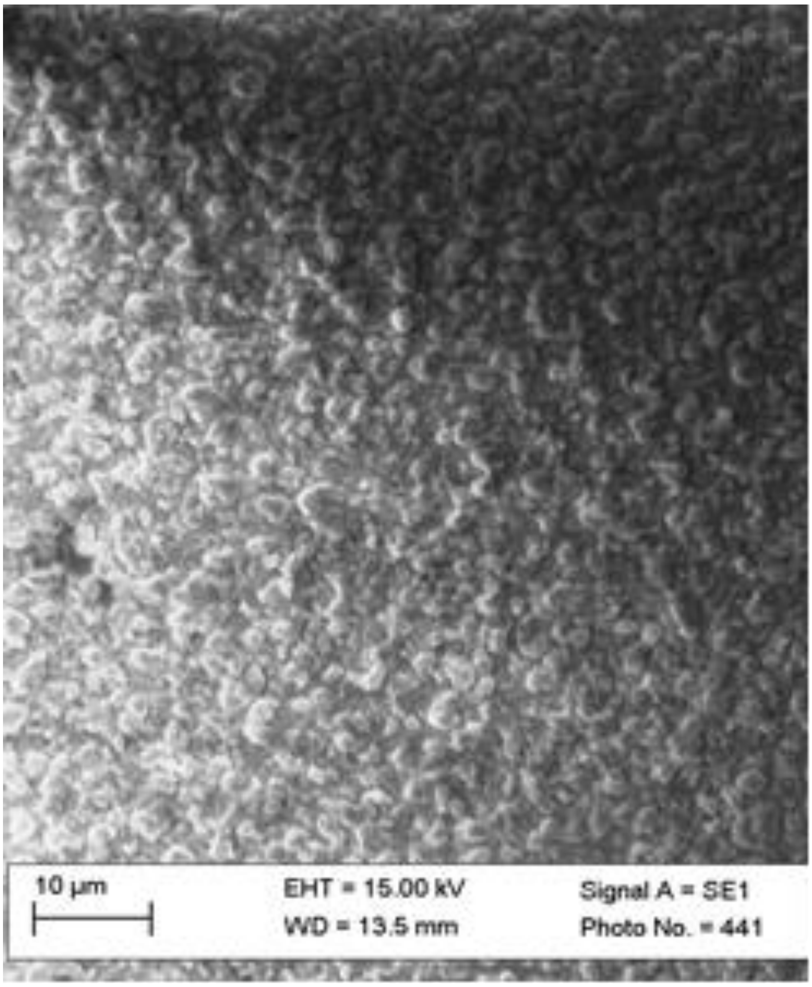


Plate 4.7. SM of Silicon Produced

This revealed porosity of large grain size on the account of acid leach observed owing to the etching of the acid used.

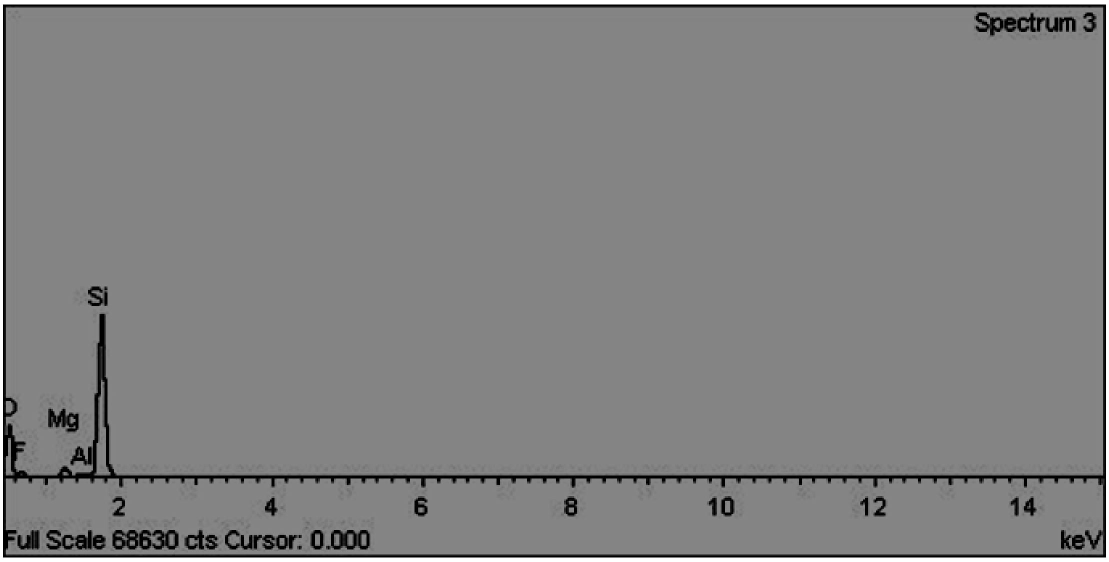


Figure 4.12. EDX of Micro-crystalline silicon Produced

Table 4.7: Elemental Analysis of Micro-crystalline Silicon Produced

Element	**Atomic Weight %**	App.Conc.	Intensity Conc	**Weight%**	Weight sigma %
C K	49. 48	0.4320	39.93	0.36	51.05
O K	58.77	0.5721	17.81	0.32	9.73
F K	2.82	0.1940	5.06	0.23	4.09
Mg K	2.42	0.7794	1.00	0.03	0.63
Al K	0.29	0.8663	0.11	0.02	0.07
Si K	47.63	0.9327	35.52	0.14	34.37
Cu K	0.65	0.7604	0.26	0.07	0.06
Total			100		100

4.8.2 Validation Result of the Micro-crystalline Silicon Produced

The Silicon produced from PRH at 6h and LRH at 3h 34min. were subjected to validation via Raman Spectra. Raman spectra analysis gives an indication of the different phase materials ranging from the amorphous, amorphous-to-Nano-crystalline transition and the full crystalline phase materials. The silicon produced from 5.28g of silica from PRH was poly-crystalline silicon of 2.3 g yield while from 6.03 g of silica from LRH, Micro-crystalline silicon of 4.2 g of higher yield with cost effectiveness and Energy savings was observed in LRH. The yield of silicon from LRH is higher than amounts reported by Banerjee *et al.*, (1982), where 188g of silica produced 60g of silicon. So yield: 0.319g of silicon.

The Raman Spectra analysis was done for the prepared silicon since it is an ideal method for the chracterisation of the crystalline or amorphous fraction of thin film solar cells.

Raman spectrum of the prepared micro-crystalline silicon was observed at wavelength of 520cm^{-1} for the narrow line while its tail was around 515cm^{-1} which are attributed to the result reported in the literature that revealed it as micro-crystalline silicon. Furthermore; the result is not significantly different from the peak of micro-crystalline silicon standard of 521cm^{-1}. The Raman spectra result of the micro-crystalline silicon is shown in Figure 4.13.

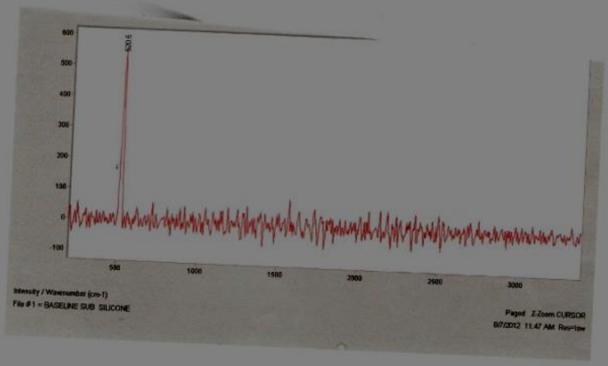


Figure 4.13.Raman Spectra of Micro- Crystalline Silicon produced

4.9 Deviation of Optimal Parameters of the GA

According to Ruben and Pradhan (2012), Validation of the GA predicted results was done in order to conform the GA predicted results as acceptable for practical use. Percentage of prediction via absolute standard error showed variation with the actual experimental results for both PRH and LRH respectively .The percentage of prediction error is calculated as

The Deviation of the GA was calculated as:

$$\frac{Experimental - GApredicted}{Experimental} X100\%$$

$$PRH = \frac{93 - 91.2}{93} X100 = 0.018\%$$

$$=1.8\%$$

$$LRH = \frac{98.55 - 97.5}{98.55} X100$$

=0.011=1.1%

Percentage prediction for PRH and LRH are: 1.8% and 1.1% respectively. Thus, the results showed that GA is valid.

4.10 Statistical Validation of the Produced Micro-crystalline Silicon

The micro-crystalline silicon (µ-Si) produced from LRH was statistically compared with Silicon produced from rice straw (Guzman *et al.,* 2015); Silicon produced from Carbon Nanotube and silicon wafer. The EDX result of silicon from LRH was statistically compared with:

EDX of rice straw,

EDX of Carbon Nanotube,

EDX of wafer silicon via

2 paired T-test was done and the summary is given in Table 4.8.

Discussion: Not significant in Table 4.8 showed that there was no perfect interactions between the variables of µ-Si (from rice husk) with µ -Si from carbon Nanotube and µ-Si with silicon wafer based on the variables of the compositions.

Table 4.8: Summary of t-test Comparison of Micro-crystalline silicon (μ-Si) % with % of Silicon from rice straw, Carbon naonotube and silicon wafer

Source of comparison	t-Stat	p(T<t)	t-critical	Remark
%(μ-Si with Si from rice straw)	-4.3611	0.0033	2.3646	sig.
%(μ-Si with Si from carbon Nanotube)	- 0.9213	0.5260	12.7062	Not sig.
%(μ-Si with silicon wafer)	1.7670	0.1205	2.3646	Not sig.

Since t stat < t critical then not significant.
No significant difference at $\alpha=0.05$

.

4.11 Investigation of the Micro-crystalline silicon (µ-Si) produced.

The properties of silicon element were used to investigate if the product from PRH and LRH were silicon or not. The properties used were the colour, phase and density.

I. Silicon Element: Colour is Grey black

Silicon from PRH and LRH: Grey-black colour

II. Type of silicon produced:

In PRH: P-Si (produced) while in LRH**:** µ-Si was produced

III. Density (g/cm^3) silicon: element: 2.33 g/cm^3

PRH: 2.27 g/cm^3 LRH: 2.27 g/cm^3

However, density is 2.3g/cm^3 in 1.decimal place

Boiling point of the silicon produced could not be determined in the laboratory because boiling point of silicon is high (3265 ^{o}C).

The density determination can be achieved using PYCNOMETER method, Displacement method and Buoyancy method. The displacement method is another way in which Archimedes' Principle can be used in determining the density of bodies and liquids.

However, PYCNOMETER method and Displacement method were used in this research.

Mass of the product =0.5g

Vol of cylinder + liquid=149.9cm^3

Vol of cylinder + liquid + sample= 150.12cm^3

$$Density \rho = \frac{mass}{volume} = \frac{0.5}{(150.12 - 149.9)} = \frac{0.5}{0.22} = 2.27 g/cm^3$$

CHAPTER FIVE

5.0 SUMMARY, CONCLUSION AND RECOMMENDATIONS

5.1 Summary

Leached Rice Husk was best for the production of Micro-crystalline silicon while Prewashed Rice Husk was best for Poly-crystalline silicon through Genetic Algorithm. This is an effective tool for the determination of optimal predictor variables levels for silica production. Amorphous silica was successfully extracted from rice husk ash and their physio-physical properties showed that silica from Leached Rice Husk revealed porosity resulting from grain size due to the leach and this made it a better silica for production of solar collectors.

Genetic Algorithm showed that optimal process variables for Prewashed Rice Husk are: temperature: 648.8 ^{o}C, Time: 6 h and Solvent volume (water volume): 40 mL While for Leached Rice Husk was temperature: 657.9 ^{o}C, Time: 3h 34 min (3.6h) and solvent volume (Oxalic Acid volume): 40 mL.

The optimsation result was investigated and it showed no significant difference between the values of Genetic Algorithm and those of the confirmatory experiment. This confirmed that the models were dependable.

Genetic Algorithm Approach

Factorial design in RSM was used to observe silica yield based on the interactions of the variables. The responses generated were used as the fitness function in the GA optimistion tool; variables bound were inputted. Population size of 100, Population type: Double, Mutation fraction: 0.2, crossover: 0.8; Scaling function: Rank: and Selection Function: Tournament were used to determine the optimal process levels.

Optimal process variables via GA for PRH was: Temp: 648.8 ^{o}C, Time: 6 h, Water content: 40cL. Moreover for LRH, optimal process parameters was Optimal Temperature: 657.9 ^{o}C, Time: 3 h 34 min (3.6h); Oxalic Acid content: 40 mL. Best fitness of 91.2 was observed in PRH but it was 97.5for LRH. However 10g of husk was used for each treatment.

5.2 Conclusions

Based on the results, we conclude as follows;

i. Yields of silicon extracted from rice husk were determined and observed.
ii. Models were formulated and developed for silica extracted.
iii. Optimisation problem of micro-crystalline silicon produced from rice husk using Genetic Algorithm was defined and solved.
iv. GA models developed were validated. It was established that there was no significant difference between the values of Genetic Algorithm and those of the confirmatory experiment.

5.3 Recommendations

The following are areas recommended for further studies

i. Rice husk form another region in Nigeria can be used to compare the results of the silica yield with the results both observed in this study and with the results reported in the literature.
ii. Another bio-waste with ash as a constituent can be used to determine the yield and type of silica extraction.

5.4 Contribution to Knowledge

Genetic Algorithm has demonstrated a novel approach for setting the optimal process variables for the extraction of silica and micro-crystalline silicon production.

This work has demonstrated the conversion of a waste (Rice Husk) into a useful product.

Better method has been achieved to safely dispose of the poisonous waste that constituted great health hazard for citizen.

APPENDICES

APPENDIX 1

Table A1.1: Chemical Constituents of Raw Rice Husk Ash Analysis at 400-800 °C

Temp. °C	SiO_2 %	Fe_2o_3 %	Zn (mg/kg)	Mn (mg/kg)	CaO (mg/kg)	MgO %	Na_2O %	K_2O %	LOI %	SSA (mm^2/g)
400	81.25	0.37	46	587	407.4	0.26	0.88	0.88	0.75	100
500	81.06	0.4	140	340	606.2	0.28	0.9	0.9	0.1	25
600	82.51	0.46	102	440	392	0.24	0.86	0.89	0.5	75
700	82.97	0.41	280	380	684.6	0.32	0.88	1.01	1	125
800	81.88	0.39	85	334	427	0.16	0.81	0.92	0.33	50

Table A1.2. Chemical Constituents of Prewashed Rice Husk Ash via Atomic Absorption Spectrophotometer Analysis at 400-800 °C.

Temp. °C	SiO_2 %	Fe_2O_3 %	Zn (mg/kg)	Mn (mg/kg)	CaO (mg/kg)	MgO %	Na_2O %	K_2O %	LOI %	SSA (mm^2/g)
400	82.94	0.35	25	325	364	0.11	0.77	0.77	1.08	133.3
500	81.38	0.34	150	466	393.4	0.2	0.9	0.9	0.25	58.3
600	82.76	0.35	34	316	358.9	0.26	0.81	0.81	0.75	108.3
700	83.42	0.29	92	433	407.4	0.17	0.86	0.86	1.25	158.3
800	81.66	0.3	66	283	404.6	0.42	0.63	0.62	0.5	75

Table A1.3. Chemical Constituents of Raw Rice Husk Ash Analysis at 400-800 °C

Temp. °C	SiO2 %	Fe2o3 %	Zn (mg/kg)	Mn (mg/kg)	CaO (mg/kg)	MgO %	Na2O %	K2O %	LOI %	SSA (mm^2/g)
400	42	157	203	0.18	1.3	0.51	1.71	150	0.22	42
500	220	268	184.8	0.18	1.98	0.47	0.67	75	0.31	220
600	62	177	291.2	0.26	1.01	0.27	1.33	125	0.21	62
700	46	215	396.2	0.11	1.14	0.28	2.33	216.6	0.23	46
800	60	201	376.0	0.29	1.12	0.31	0.92	100	0.2	60

Where LOI-Loss on Ignition,

SSA-Specific Surface Area

APPENDIX 2

Characterisation of Raw Rice Husk Ash, Prewashed Rice Husk Ash and Leached Rice Husk Ash

The chemical constituents of rice husk ash at temperature ranges from 50 – 800 °C was determined using Atomic Absorption Spectrophotometer (AAS).

The chemical constituents of rice husk ash calcined at 50 – 800 °C was determined using standard wet chemical methods to observe the Optimal Silica, optimal specific surface area and its characterisation temperature. Tables A1-A3 showed the % of some of the chemical constituents of rice husk ash with silica as major element (~93.7%). Moreover, Mishra *et al.,* (1985) also support the result and concluded in his research that rice husk contained 92-97% of silica. HF evaporation method was used to gravimetrically estimate silica amount; while Na_2O and K_2O were estimated by flame photometer, UV-Visible Spectrophotometer by calorimetric for Fe_2O_3 and other trace elements by atomic absorption spectrometer.

The specific surface area was measured by BET nitrogen adsorption method and also according to ASTM D626 (1997). Highest specific surface area of $125 m^2/g$ at 700 °C was observed while there was decrease to $50 m^2/g$ at 750 °C for the first method (Raw rice husk ash). Moreover, highest specific surface area of $158.3 m^2/g$ was at 700 °C, while there was decrease $75 m^2/g$ at 750 °C for the second method (Prewashed rice husk ash). Lastly, the specific surface area at 700 °C was $216.6 m^2/g$ while it was $100 m^2/g$ at 750 °C (Leached rice husk ash).

Calcination Time of 6 Minutes from 400 – 800 °C for the Raw Rice Husk (Uh0), PRH and LRH

Rice husk ash contained high % of K_2O, Fe_2O_3, Na_2O and Zn as the major impurities. High percentage of K_2O acted as the activator during the combustion. Potassium (K) present in the rice husk caused surface melting and accelerated crystallization of amorphous silica to form cristobalite ass reported by Hanafi *et al.*, (1980).

Krishnarao and Godkhind (1992) reported the presence of carbon irrespective of temperature. K_2O dissociated on heating at ~620K to form elemental potassium and caused surface melting. The carbon got entrapped and lost direct contact with air which prevented its oxidation on further heating.

Dissolution of potassium oxide at 347 ^oC formed elemental potassium that caused surface melting and also accelerated the crystallisation amorphous silica to form cristobalite was reported by Krishnarao *et al.,* (2001). Furthermore, washing effectively reduced the potassium content in the rice husk thereby the ash gave a lighter shade in prewashed and leached rice husk ash. Highest specific surface area and highest silica were produced at 700 ^oC. According to Mansaray and Ghaly, (1988a) sodium and potassium reacted with silica in the ash to form eutectic mixtures with low melting points. According to Armesto *et al.*, (2002), melting point of eutectic mixtures might be as low as 600-700 ^oC at high concentration of sodium or potassium.

Table 4.4, based on amount of silica at 700 ^oC was agreed with Mishra *et al.*, (1985) result that approximately 92 - 97% silica is in rice husk. It was also stated that oxalic acid reduced amount of Fe_2O_3 and K_2O drastically in the ash. Lime reactivity (CaO): Increase in temperature increased the amount of lime reactivity and was optimal at 700 ^oC but decreased at 750 ^oC as reported in the literature. It was reported that crystallization of silica was prevented by controlling the temperature, time, burning and rate of heating (Chandraskhar *et al.,* 2002). The lime reactivity was calculated from the difference in Calcium concentration before and after treatment with the ash. CaO is higher in Leached rice husk ash. Comparing the SSA (Specific Surface Area) results with Mehta 1995, which had SSA from 50 to 100(m^2/g) at 500 – 700 ^oC, MEANS that the results obtained from raw rice husk ash correlated which was from 25 - 125 (m^2/g). The three parameters that usually affected SSA were the particle size, Calcination temperature and Calcination time. According to Chandrasker *et al.*, (2005) the reactivity of silica was directly related to the amorphous nature and surface area.

LOI (%) is usually ≤ 6. Chemical composition of pozzolanic material limits as recommended in the Brazilian Standard NBR 13956 (ABNT, 1997) did not reach the minimum amount of silica. The experimental results with the limits suggested by the International Standards ASTM C-618 (2003) for calcined natural pozzolans and coal fly ash (Di Campos *et al.*, 2008) is ideal for the residual material under evaluation.

Loss of ignition of rice husk ash according to Dafico (2001) and Ismail and Waliuddin (1996) are 11.8% and 8.9%, whereas from the results at optimal temperature of 700 ^oC for Raw Rice Husk Ash was 1.00, Prewashed Rice Husk Ash was1.25 and for Leached Rice Husk Ash was 2.33. The dark colour of the ashes indicated carbon because at the optimal temperature for the Leached Rice Husk Ash; minute black particles was visualized. That showed that the time was short and there was incomplete combustion.

Oxalic acid was highly effective in reducing the Fe_2O_3 present in the ash. XRD result at 3h showed that oxalic acid treated rice husk ash (LRHA) produced amorphous silica of good quality as observed from analysis.

However, highest specific surface area of 16.82mm^2/g was the highest amount at 3h and SEM result presented appropriated morphological characteristics of the best silica (Olawale *et al.,* 2012). By chemical analysis, it showed that impurities in the rice husk were substantially removed by acid treatment. When rice husk was subjected to acid treatment, most of the potassium was removed. Oxalic acid for the leaching process for the rice husk in the calcination methods reacted with oxygen to produce water and carbon dioxide. It also reduced the concentration of impure elements in the silica.

APPENDIX 3

Table A3.1. Predicted Yield and Error in GA for PRH

S/N	Yield 1	Predicted Yield	Error
1	86.90	87.3120952380952	-0.474217765356918
2	87.32	87.7848761904761	-0.532382261195738
3	87.56	87.9631809523809	-0.460462485588095
4	87.89	88.3870095238095	-0.565490412799549
5	87.94	88.3163619047619	-0.427975784355137
6	87.96	87.2431047619047	0.815024145174289
7	88.38	87.7278190476190	0.737928210433342
8	88.93	88.5380571428572	0.440731875793153
9	88.34	87.1338190476191	1.36538482270878
10	89.52	89.3351047619048	0.206540703859737
11	89.64	89.7286857142857	-0.0989354242365842
12	89.85	89.8053333333333	0.0497124837692979
13	89.91	89.6475047619048	0.291953328990369
14	89.94	89.4952000000000	0.494551923504559
15	89.99	89.4484190476190	0.601823483032508
16	90.04	90.9688380952381	-1.03158384633284
17	91.14	92.8374190476191	-1.86243037921774
18	91.32	92.9315238095238	-1.76469974761699
19	91.79	93.6711523809524	-2.04940884731714
20	91.84	93.6363047619048	-1.95590675294508
21	86.34	85.3235619047619	1.17725051567995

22	86.71	85.7440761904762	1.11397048728384
23	86.79	85.6501142857143	1.31338370121641
24	86.83	85.5416761904762	1.48373120986276
25	86.94	85.6387619047619	1.49670818407881
26	87.03	87.4216952380952	-0.450069215322544
27	87.15	87.3458761904762	-0.224757533535479
28	87.22	87.2355809523809	-0.0178639674168124
29	87.40	87.4108095238096	-0.0123678762122901
30	87.47	87.4315619047619	0.0439443183240860
31	88.21	87.4333047619047	0.880507015185661
32	88.32	87.3301190476190	1.12078912180817
33	88.72	87.8724571428571	0.955300785778708
34	88.76	87.7603190476191	1.12627416897356
35	88.94	87.9937047619048	1.06397035990019
36	89.02	88.0194857142857	1.12392078826590
37	89.75	89.1489333333333	0.669712163416932
38	90.41	90.2039047619047	0.227956241671561
39	90.56	90.3044000000000	0.282243816254418
40	90.88	90.8104190476191	0.0765635479543858
41	90.92	92.1002380952381	-1.29810613202606
42	91.05	92.0223190476190	-1.06789571402420
43	91.67	92.9899238095238	-1.43986452440691
44	92.04	93.5230523809524	-1.61131288673664
45	92.06	93.4217047619048	-1.47914920910795
46	88.43	88.7155619047619	-0.322924239242232
47	88.6	88.7102761904762	-0.124465226271121
48	88.65	88.5305142857143	0.134783659656742

49	88.71	88.4362761904762	0.308560263244055
50	88.93	88.7275619047619	0.227637574764527
51	87.53	88.5512952380953	-1.16679451398979
52	87.61	88.4468761904762	-0.955229072567275
53	87.73	88.4879809523810	-0.863992878583125
54	87.81	88.5146095238096	-0.802425149538267
55	87.89	88.6067619047619	-0.815521566460278
56	88.41	87.8035047619048	0.686002983933095
57	88.51	87.7124190476190	0.901119593696722
58	88.83	88.1268571428572	0.791560122867090
59	88.91	88.1268190476191	0.880869364954387
60	88.79	87.7923047619048	1.12365721150492
61	89.21	88.2102857142857	1.12063029448975
62	89.82	89.1125333333333	0.787649372819755
63	90.51	90.2403047619048	0.297972862772317
64	90.63	90.2936000000000	0.371179521129882
65	90.94	90.7924190476191	0.162283871102869
65	90.99	91.8916380952381	-0.990919985974360
66	91.2	91.9672190476190	-0.841248955722597
67	91.72	92.7283238095238	-1.09934998857807
68	92.11	93.2949523809524	-1.28645356742198
69	92.31	93.5471047619048	-1.34016332131381
70	88.53	88.4075619047619	0.138301248433455
71	88.62	88.2164761904762	0.455341694339673
72	88.68	88.0309142857143	0.731941491075492
73	88.81	88.0508761904762	0.854772896660077
74	88.89	88.0363619047619	0.960330853007244

75	86.90	87.3120952380952	-0.47421776535691

Table 3.2A. Predicted Yield and Error in GA for LRH

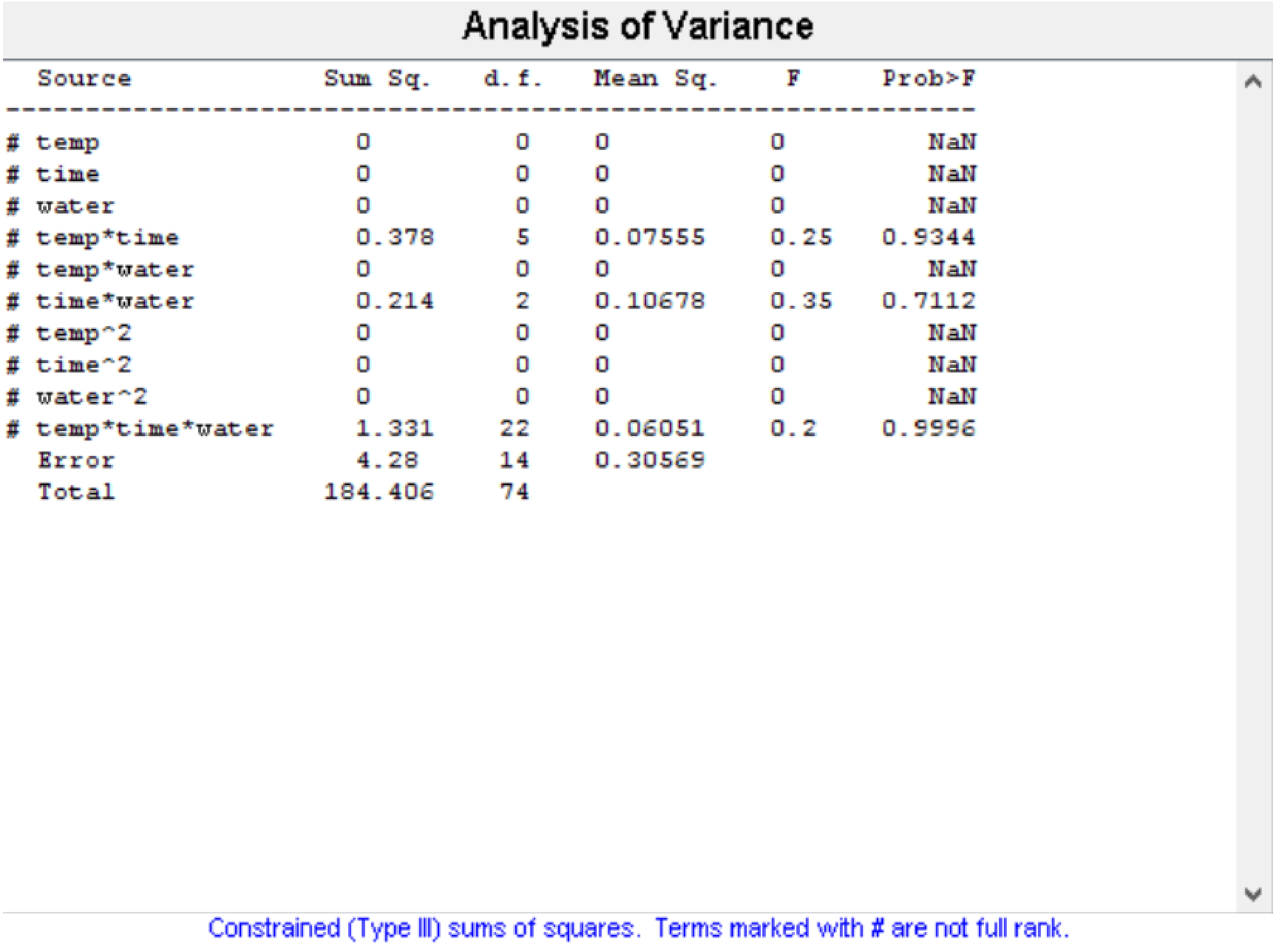
S/N	YIELD 2	PREDICTED YIELD	ERROR
1	93.22	86.4879047619048	-0.474217765356918
2	93.62	86.8551238095239	-0.532382261195738
3	94.46	87.1568190476191	-0.460462485588095
4	94.46	87.3929904761905	-0.565490412799549
5	94.89	87.5636380952381	-0.427975784355137
6	95.4	88.6768952380953	0.815024145174289
7	96.40	89.0321809523810	0.737928210433342
8	96.32	89.3219428571429	0.440731875793153
9	95.82	89.5461809523809	1.36538482270878
10	95.39	89.7048952380952	0.206540703859737
11	96.1	89.5513142857143	-0.0989354242365842
12	96.19	89.8946666666667	0.0497124837692979
13	96.12	90.1724952380952	0.291953328990369
14	96.08	90.3848000000000	0.494551923504559
15	96.03	90.5315809523810	0.601823483032508
16	97.32	89.1111619047619	-1.03158384633284
17	97.44	89.4425809523810	-1.86243037921774
18	97.24	89.7084761904762	-1.76469974761699
19	97.12	89.9088476190476	-2.04940884731714
20	97.01	90.0436952380952	-1.95590675294508
21	95.51	87.3564380952381	1.17725051567995
22	95.61	87.6759238095238	1.11397048728384
23	95.39	87.9298857142857	1.31338370121641

24	95.32	88.1183238095238	1.48373120986276
25	95.29	88.2412380952381	1.49670818407881
26	94.01	86.6383047619048	-0.450069215322544
27	94.21	86.9541238095238	-0.224757533535479
28	94.17	87.2044190476191	-0.0178639674168124
29	94.10	87.3891904761905	-0.0123678762122901
30	94.04	87.5084380952381	0.0439443183240860
31	95.68	88.9866952380953	0.880507015185661
32	96.41	89.3098809523810	1.12078912180817
33	96.25	89.5675428571429	0.955300785778708
34	96.20	89.7596809523809	1.12627416897356
35	96.15	89.8862952380952	1.06397035990019
36	96.23	90.0205142857143	1.12392078826590
37	96.71	90.3510666666667	0.669712163416932
38	96.62	90.6160952380953	0.227956241671561
39	96.49	90.8156000000000	0.282243816254418
40	96.36	90.9495809523809	0.0765635479543858
41	97.56	89.7397619047619	-1.29810613202606
42	97.65	90.0776809523810	-1.06789571402420
43	97.40	90.3500761904762	-1.43986452440691
44	97.25	90.5569476190476	-1.61131288673664
45	97.04	90.6982952380952	-1.47914920910795
46	95.54	88.1444380952381	-0.322924239242232
47	95.69	88.4897238095238	-0.124465226271121
48	95.61	88.7694857142857	0.134783659656742
49	95.39	88.9837238095238	0.308560263244055
50	95.23	89.1324380952381	0.227637574764527

51	94.43	86.5087047619047	-1.16679451398979
52	94.75	86.7731238095238	-0.955229072567275
53	94.65	86.9720190476190	-0.863992878583125
54	94.51	87.1053904761905	-0.802425149538267
55	94.47	87.1732380952381	-0.815521566460278
56	95.7	89.0164952380953	0.686002983933095
57	96.72	89.3075809523810	0.901119593696722
58	96.66	89.5331428571428	0.791560122867090
59	96.49	89.6931809523809	0.880869364954387
60	96.33	89.7876952380952	1.12365721150492
61	96.81	90.2097142857143	1.12063029448975
62	96.98	90.5274666666667	0.787649372819755
63	96.73	90.7796952380952	0.297972862772317
64	96.42	90.9664000000000	0.371179521129882
65	96.39	91.0875809523810	0.162283871102869
66	97.72	90.0883619047619	-0.990919985974360
67	97.98	90.4327809523810	-0.841248955722597
68	97.34	90.7116761904762	-1.09934998857807
69	97.29	90.9250476190476	-1.28645356742198
70	97.24	91.0728952380952	-1.34016332131381
71	96.61	88.6524380952381	0.138301248433455
72	96.75	89.0235238095238	0.455341694339673
73	96.55	89.3290857142858	0.731941491075492
74	96.41	89.5691238095238	0.854772896660077
75	96.35	89.7436380952381	0.960330853007244

APPENDIX 4

Table A4.1 ANOVA for PRH



Analysis of Variance

```
  Source              Sum Sq.   d.f.   Mean Sq.     F     Prob>F
-------------------------------------------------------------------
# temp                    0        0    0            0        NaN
# time                    0        0    0            0        NaN
# water                   0        0    0            0        NaN
# temp*time               0.378    5    0.07555      0.25  0.9344
# temp*water              0        0    0            0        NaN
# time*water              0.214    2    0.10678      0.35  0.7112
# temp^2                  0        0    0            0        NaN
# time^2                  0        0    0            0        NaN
# water^2                 0        0    0            0        NaN
# temp*time*water         1.331   22    0.06051      0.2   0.9996
  Error                   4.28    14    0.30569
  Total                 184.406   74
```

Constrained (Type III) sums of squares. Terms marked with # are not full rank.

Table A4.2. Significant effects noted during calcination

Significant effects noted during calcaintion at: 1h, 3h and 6h are stated below:

Effect of Calcination Time on Rice Husk at 1 hour

S/N	***Temp (^{O}C)***	***Type of rice husk***	***Observation***
1	648.8	Prewashed rice husk	Grey ash with about 12% char
2	657.9	Leached rice husk	Grey, off-white and black char of equal quantities was visualized.

Effect of Calcination Time on Rice Husk at 3 h. 34 min

S/N	***Temp (^{O}C)***	***Type of rice husk***	***Observation***
1	648.8	Prewashed rice husk	90% Dull white ash
2	657.9	Leached rice husk	94% Dull white ash

Effect of Calcination Time on Rice Husk at 6 hour

S/N	***Temp (^{O}C)***	***Type of rice husk***	***Observation***
1	648.8	Prewashed rice husk	White Ash
2	657.9	Leached rice husk	White Ash

APPENDIX 5

A5.1. Results on Silica Extracted from Husks (PRH and LRH)

Samples	Time	Mass before Leaching (g)	Mass after Leaching(g)	Mass after Re-calcination(g)	Silicon Yield (g)
S1 (PRH)	3h 34 min	11.0634	7.44	7.26	2.32
S2 (PRH)	6h	14.227	10.47	10.32	3.29
S3(LRH)	3h 34 min	17.034	13.37	13.10	4.17
S4 (LRH)	6h	14.227	10.47	10.33	3.295

Where S1 Represents silica from water Pre-treated Husk (PRH) at 6h

S3 Represents silica from Oxalic Acid Pre-treated Husk (LRH) at 3h 34 min

S3 Represents silica from PRH at 6h

S4 Represents silica from LRH at 6h

So; S3 was for Ah1 and S2 for LRH

Re-calcination was done to further isolate the silica from each husk

APPENDIX 6

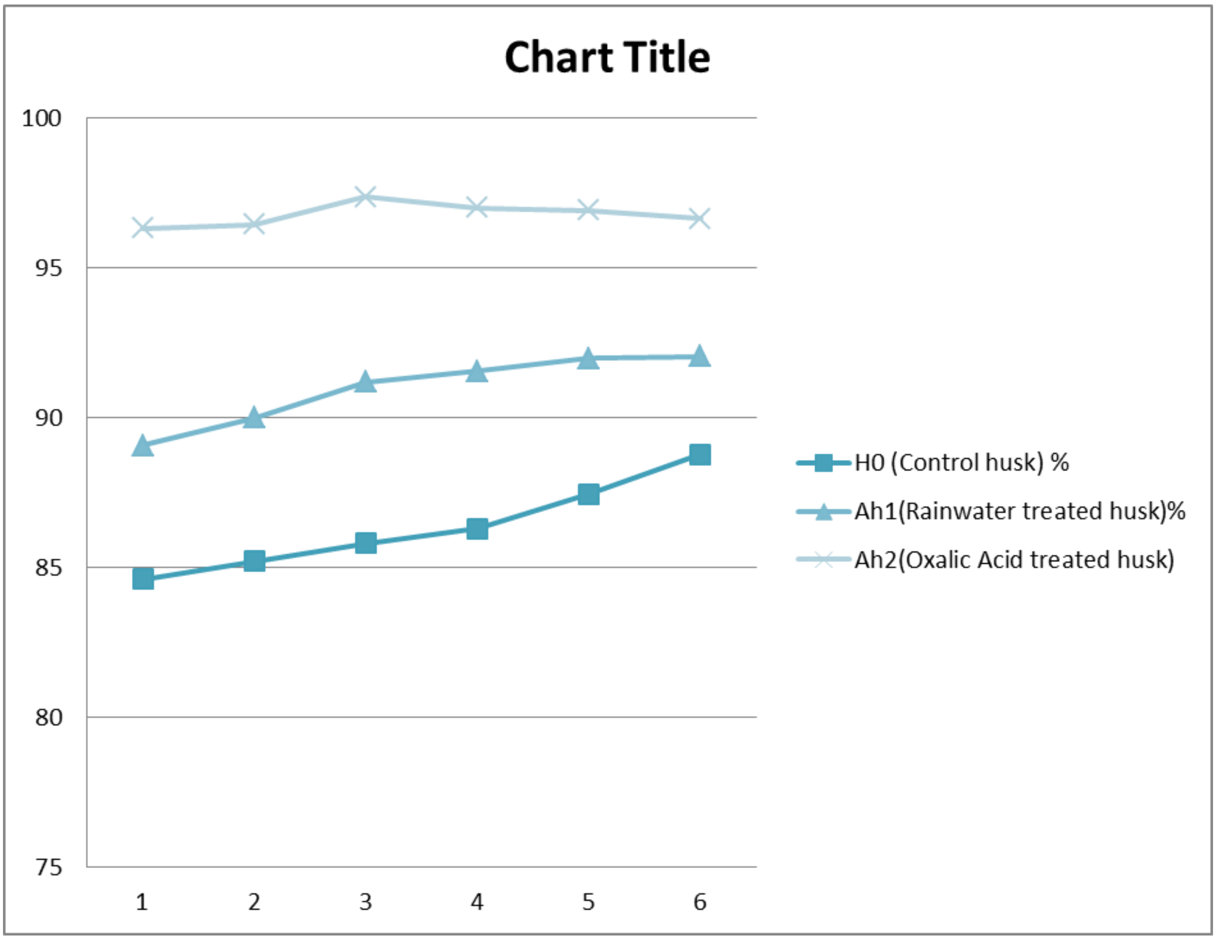
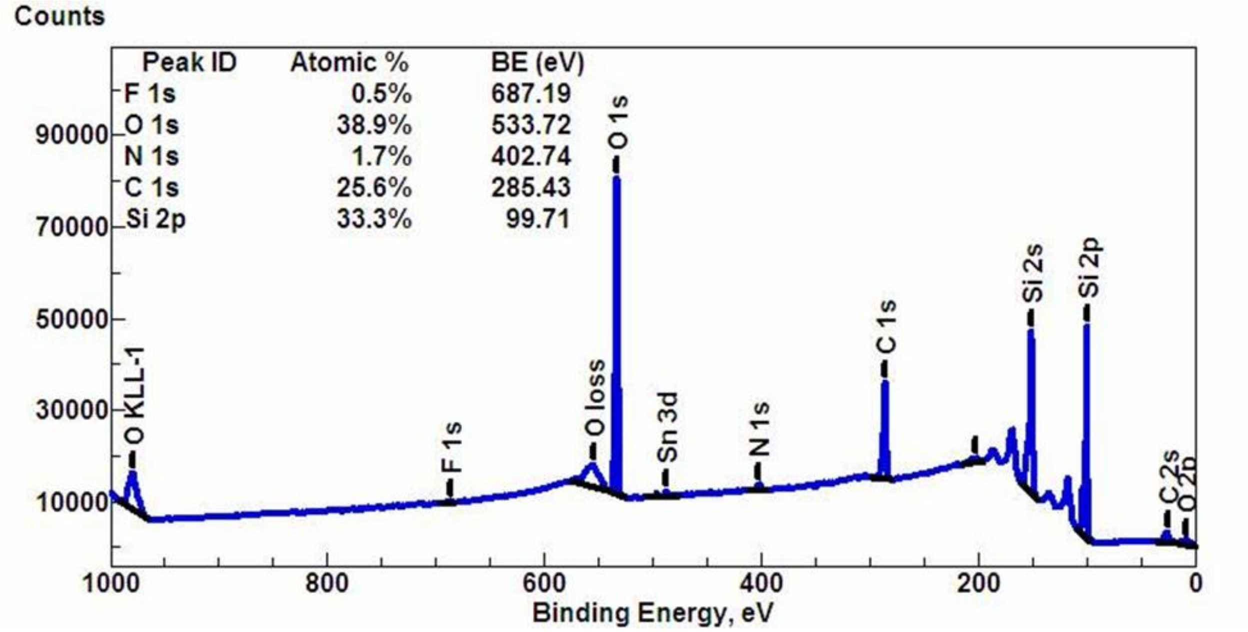


Figure A6.1: Graph of Yield Vs. Time Range: of 1-6h



Peak ID	Atomic %	BE (eV)
F 1s	0.5%	687.19
O 1s	38.9%	533.72
N 1s	1.7%	402.74
C 1s	25.6%	285.43
Si 2p	33.3%	99.71

Figure A6.2. EDX spectrum of silicon wafer, showing all elements present

It shows all the elements present on the sample surface with their binding energies and their atomic percentages.

APPENDIX 7

Table A7.1. Elemental Analysis via EDX of: µ-Si from RH, Silicon from rice straw, silicon from carbon nanotube and silicon from silicon wafer**.**

ELEMENT	**Atomic Weight.%**			
	Experiment (µ-Si)	Rice straw (Guzmen *et al.*,2015)	Carbon nanotube (Bakr *et al.*,2014)	Silicon wafer (EDX, 2015)
CK	51.05	0	87.05	2
SiK	34.37	47.13	12.05	33.3
OK	9.73	52.87	0	38.9
FK	4.09	0	0	0.5
MgK	0.63	0	0	-
AlK	0.07	0	0	-
CuK	0.06	0	0	-
N	-	-	-	-
TOTAL	100	100	100	100

Table A7.2. EDX Elemental Analysis Standard for Nano-crystalline (N-Type Silicon)

Element	Weight %	Atomic Wt. %
CK	5.21	10.87
OK	15.24	23.85
SiK	69.63	62.08
PK	1.77	1.43
InL	6.48	1.41
SnL	1.67	0.35

APPENDIX 8

Table A8.1. T-test for Two Samples Assuming Unequal Variance

Comparing EDX µ-Si with Rice straw t-Test: Two-Sample Assuming Unequal Variances

	Variable 1	Variable 2
Mean	14.28571429	50
Variance	411.7723952	16.4738
Observations	7	2
Hypothesized Mean Difference	0	
Df	7	
t Stat	-4.361192401	
P(T<=t) one-tail	0.001654686	
t Critical one-tail	1.894578604	
P(T<=t) two-tail	0.003309373	
t Critical two-tail	2.364624251	

Table A8.2. t-Test: Two-Sample Assuming Unequal Variances comparing EDX µ-Si with Silicon Wafer

	Variable1	Variable 2
Mean	14.28571429	29.45
Variance	411.7723952	29.645
Observations	7	2
Hypothesized Mean Difference	0	
Df	7	
t Stat	-1.767030522	
P(T<=t) one-tail	0.060279093	
t Critical one-tail	1.894578604	
P(T<=t) two-tail	0.120558186	
t Critical two-tail	2.364624251	

Table A8.3. Comparing EDX µ-Si with Carbon Nano-silicon

t-Test: Two-Sample Assuming Unequal Variances

	Variable 1	Variable 2
Mean	14.28571429	49.55
Variance	411.7723952	2812.5
Observations	7	2
Hypothesized Mean Difference	0	
Df	1	
t Stat	-0.921308797	
P(T<=t) one-tail	0.263029762	
t Critical one-tail	6.313751514	
P(T<=t) two-tail	0.526059524	
t Critical two-tail	12.70620473	

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