JIMMA UNIVERSITY

JIMMA INSTITUTE OF TECHNOLOGY

FACULTY OF CIVIL AND ENVIRONMENTAL ENGINEERING

ENVIRONMENTAL ENGINEERING

POSTGRADUATE PROGRAM

PRODUCTION OF HYDROGEN FROM CORN-COB BY USING PHOTO-ELECTROCHEMICAL PROCESS

BY: - CHERINET DAWIT

A Thesis Submitted to School of Graduate Studies of Jimma University, Jimma Institute of Technology, Faculty of Civil and Environmental Engineering in Partial Fulfillment of the Requirements for the Degree of Masters Science in Environmental Engineering.

November, 2021

Jimma, Ethiopia

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Advisors

Main advisor: P. Asaithambi (PhD, Assistant prof.)

Co advisor: Kidist Jemal (Msc)

DECLARATION

I Cherinet Dawit, hereby declare that this research entitled "Production of hydrogen from corn-cob by using photo-electrochemical process" for the MSc degree at the Jimma University is my original work and has not been submitted as a requirement for the award of any degree in Jimma University or elsewhere.

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Signature ____________________ Date ___________________

This thesis has been submitted for examination with our approval as university advisor and program chairperson.

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Co – Advisor: Kidist Jemal (Msc)

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APPROVAL SHEET

As a thesis advisor, we hereby approved that we have read and evaluated this thesis prepared, under our guidance, by Cherinet Dawit Bosha entitled "Production of hydrogen from corn-cob by using photo-electrochemical process". We recommend that it can be submitted as fulfilling thesis requirement

P. Asaithambi (PhD, Assistant prof.) ___________________ ________________

Main Advisor Signature Date

Kidist Jemal (Msc) ________________ _______________

Co- advisor Signature Date

As a member of board examiner of MSc. thesis final defense examination, we certify that we have read, evaluate thesis prepared by Cherinet Dawit Bosha and examined the candidate. We recommend that, the thesis could be accepted as fulfilling the thesis requirements for the degree of masters of Science in Environmental Engineering.

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External Examiner Signature Date

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Internal Examiner Signature Date

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Chair holder Signature Date

ABSTRACT

The need to energy may be even now expanding because of generally speaking development in the planet populace and in addition the developing interest for change previously, expectation for everyday life. The globe is confronting extreme contamination issues from those by-products of fossil fuel uses. In this study hydrogen was produced in simple methodology by using environmentally available materials such as water, light and biomass which was collected from Jimma zone Asendabo. The physical properties of collected biomass was analyzed, the effect of operating parameters on hydrogen production was investigated and optimization of operating parameters was occurred with Response Surface Methodology by Design Expert Version11. The sample was collected from the study area and it was minimized into small size to dry simply and to crush it with pestle. The crushed sample was sieved with sieve size of 2mm. The sieved sample was used to characterize the corn cob and also used as electrolyte in the process. The experiment run had occurred in a dish that connected with stainless steel both at cathode and anode. Light was applied on the solution by immersing electric bulb to speed up the breakdown of water molecules into hydrogen and oxygen. The experiment was run by varying time in the interval of 1hr-4hr, pH in the interval of 5-9, temperature in the interval of 20^0C*-*35^0C *and biomass concentration in-between 5g/l and 10g/l. The physical characteristics of corn cob was analyzed and it fulfills the required standard and the effect of operating parameters were optimized through Response surface methodology of Design Expert Version11. When time increases the production rate decrease, and the production rate increase with pH approaches to 7. When biomass concentration and temperature rate increase the production rate also increase. So, the optimum hydrogen* ***(59.7922%)*** *was located at time, pH, biomass concentration and temperature of* ***1hr****,* ***6.8662****,* ***10g/l*** *and* $\mathbf{35^0C}$ *respectively. Further researches have to be carried out to increase the yield of* H_2 *gas from other types of biomass, which are pollutant in the environment but they are the sources of energy.*

Key words*: - Corn-cob, Hydrogen gas, Physical properties, Response surface methodology, photo-electrochemical,*

ACKNOWLEDGMENTS

First of all, I would like to thank the Almighty of God for His assistance; not only in my study but also throughout my entire life. I wish to express my profound gratitude and indebtedness to my advisors ***P. Asaithambi (PhD. Assistant Professor) and Kidist Jemal (Msc),*** for introducing the present topic and for their inspiring guidance, constructive criticism and valuable suggestions throughout the work of this study.

Next, my thanks goes to ***Seifu Kebede (Msc),*** Environmental Engineering Chair holder, for technical and scientifically assistance in my education and thesis work.

And my best friend ***Tademe Tegegn (Dr),*** I do not forgot for your psychological threat and moral strength in my life and during my work. My sincere thanks to all my friends and seniors who have patiently extended all sorts of help for accomplishing this study.

Finally, it was impossible to complete this study without the understanding of my family, especially my brother ***Mr. Amazon yoseph.***

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ACRONYMS

ANOVA	Analysis Of variances
BEVs	Battery Electric Vehicles
CC	Corn Cob
CCD	Central Composite Design
CSA	Central Statistical Agency
DAFCs	Direct Alcohol Fuel Cells
DC	Direct Current
DME	Di Methyl Ether
EPA	Environmental Protection Agency
FAO	Food and Agricultural Organization
FC	Fixed Carbon
IEA	International Energy Agency
IPCC	Intergovernmental Panel on Climate Change
MC	Moisture Content
MDCs	Microbial Desalination Cells
MECs	Microbial Electrolysis Cells
MFCs	Microbial Fuel Cells
NTCOs	Non-Transparent Conductive Oxides
PE	Photo Electrolyte
PEC	Photo Electrochemical Cell
PFC	Photo catalytic Fuel Cell
PHEVs	Plug-in Hybrid Electric Vehicles
PWS	Photo catalytic Water Splitting
RSM	Response Surface Methodology
SNNPR	South Nation Nationality and Peoples Region
STH	Solar-to-Hydrogen
TCOs	Transparent Conductive Oxides
USA	United States of America
UV	Ultra Violate

CHAPTER ONE

INTRODUCTION

1.1 Background of study

The globe is confronting a quickly expanding request for maintainable energy (Ibrahim, Kamarudin and Minggu, 2014). Recently, the Intergovernmental Panel on Climate Change (IPCC) has concluded that the fossil fuel and deforestation are the main cause for expanded CO_2 in the atmosphere (Ganesh, 2016). More industrialization bring not just brought technology, but also they were cutting edge life, as well as the environmental contamination. Furthermore discharges starting with factories, vehicles, and more industrial plants (Ganesh, 2016). The exploratory group keeping need broadly acknowledged the certainty that the expanding carbon dioxide level because of the utilization from claiming fossil assets impacting those greenhouse gas and global warming. Therefore, distinctive routines on outfit those energy from renewable assets need aid being developed, yet the look to dependable vitality wellsprings may be still once.

The worldwide environmental will be debilitated toward anthropogenic changes, also oil supplies are limited (Ibrahim, Kamarudin and Minggu, 2014). The interest to vitality may be even now expanding because of generally speaking development in the planet populace and in addition the developing interest for change previously, expectation for everyday life particularly in developing countries; this need committed those advancement of productive and more economical vitality framework and basic for manageable socioeconomic advancement (Staffell *et al.*, 2019).

On late A long time there bring been escalated consideration exertions to those advancement about novel innovations for the creation of hydrogen from renewable resources, primarily water and biomass (Daskalaki and Kondarides, 2009). Renewable vitality for example, bio hydrogen, bio methane or biofuel have been utilization to displace the petroleum-based vitality will look those expanding request of vitality. This will be a direct result these sorts of vitality were recouping or process starting with boundless assets including wastes. Bioenergy is embedded in complex ways in global biomass systems for food, and fodder production and for forest products as well as in wastes and residue management. Perhaps most importantly, bioenergy plays an intimate and critical role in the daily livelihoods of billions of people in developing countries. Expanding bioenergy production significantly will require sophisticated land and water use management; global feedstock productivity increases for food, fodder, forest products and energy. Substantial conversion technology improvements; and a refined understanding of the complex social, energy and environmental interactions associated with bioenergy production and use (Haron *et al.*, 2018).

Biomass is second to hydropower as a leader in renewable energy production. Biomass has an existing capacity of over 7,000 MW. Biomass as a fuel consists of organic matter such as industrial waste, agricultural waste, wood, and bark (Boutin, Ferrer and Lã, 2002).

Biomass comprises for every last one of plants developing on the world surface. It is acquired starting with those photosynthesis about CO_2, H_2O and daylight prompting those preparation from claiming molecules, cellulose, Lignocellulose and lignin hosting those same arrangement similarly as $C_6H_9O_4$. It can then be possible to regain stored energy in the combustible form by more or less effective transformation on the energetic and economic platform. This may be carried through combustion, methanation, alcoholic maturation and thermochemical transformations.

Biomass is attracting an incredible arrangement about consideration about renewable vitality wellspring of the late globe to decrease carbon dioxide (CO_2) emanation. Biomass has been utilized by human cultures for millennia and was a dominant source of energy long before the discovery of fossil fuels. It is only in recent years that biomass is being re-integrated into supplying energy at a major scale. Biomass based global annual electricity production has risen from 227 TWh in 2004 to 646 TWh in 2016 (Boutin, Ferrer and Lã, 2002).

Biomass may be a renewable resource, and the vitality inferred from biomass viewed as concerning illustration renewable energy (Ibrahim, Kamarudin and Minggu, 2014). Those vitality of the bio waste in the nature's domain need arrived at 130 Exajule for every year (EJy-1), comparing with one third of the worldwide vitality interest about 450 EJy-1(Kaneko *et al.*, 2009).

Corn cob (CC) is one of possible agrarian biomass with energy source that can be utilized for energy creation to lessen current energy source and ozone harming substance issue. It has various great sides over other biomass including its thick and special nature just as its high energy content and its low nitrogen and sulfur concentration (Anukam *et al.*, 2017). It is a farming waste that is created from maize and remains part of the ear on which the pieces develop. In the vast majority of world nations, corn cob which is the focal piece of maize is either tossed out as waste or consumed, an application with low added esteem, causing natural concern. The unloading and consuming of CC on the ranches results air contamination and different consequences for the climate. So it is a thrilling exploration region to utilize corn cob as electrolysis to get finished results with added values worldwide at exceptionally low cost. Corn cob contains hemicellulose, lignin and others in the surmised level of 73, 16 and 11 separately (Kumar, Negi and Upadhyaya, 2010). In Ethiopia, corn is a vital nourishment for some individuals and it stays the most basic agricultural collect for in excess of 70 million residence families all throughout the planet (Anukam *et al.*, 2017).

Thus enthusiasm toward extracting hydrogen from water is energized toward the compelling reason with find a renewable, manageable and naturally safe elective vitality source (Jeffery *et al.*, 2010). Hydrogen is presently utilized within industry to an amount about purposes, principally to refineries and compound plants for those handling of a mixture about chemicals (Strataki *et al.*, 2007). The enthusiasm toward hydrogen need significantly expanded in late a considerable length of time in the possibility of its use as a fuel (Strataki *et al.*, 2007). In this respect, hydrogen will be a high-energy-yield non-polluting fuel, especially at utilized within fuel cells (Strataki *et al.*, 2007). Those enthusiasm toward extracting hydrogen from water will be fuelled eventually perusing those have will find a renewable, manageable and naturally protected elective vitality source (Jeffery *et al.*, 2010). Hydrogen will be viewed as a feasible choice on today's fossil fuel based vitality particularly the point when it is processed from water also just light concerning illustration those vitality enter.

Hydrogen production from photo catalytic water splitting (without biomass) is achievable, but at a very low quantum yield (~ 1.8%) due to a thermodynamic barrier and multi-electron transfer process, while quantum yield of photo biorefinary for H_2 production is achievable above 70% (Bowker, 2012). Thermochemical strategies to those processing about hydrogen starting with light powered vitality includes: immediate thermalizes from claiming water, thermochemical cycles and cracking, reforming and gasification from claiming hydrocarbons. These forms utilization focused sunlight based radiation likewise high engineering high temperature wellspring with do those endothermic response (Tryk, Fujishima and Honda, 2000). Diverse gadgets need aid used to compass high sun oriented focus ratios: explanatory disks, tower frameworks and sun based furnaces. Those splitting of hydrocarbons comprises in the acknowledgment of the co-synthesis from claiming hydrogen and black carbon.

Photo electrochemical cell (PEC) water part need the possibility will a chance to be an efficient and expense successful path to prepare hydrogen the place the (photo electrolyte) PE for PEC framework absorb daylight also part water straightforwardly under hydrogen and oxygen (Jeffery *et al.*, 2010). The principle partake energizes PEC water part even now concern must expansion the efficiency and soundness for photoactive materials. Semiconductor materials were used to gather light vitality and process hydrogen also oxygen utilizing electrolysis. This also underpinned via those biodiversity biological community furthermore arranged similarly as long expression. Obstructions to specialized foul victory found in the semiconductor materials used to catch light energy, the photochemical device, those mix of the gadget under an operating system, and the improvement of the stockpiling necessary to adjust to the diurnal light cycle. Provided for these barriers, this might make the highest-risk approach at present in the system (Chen *et al.*, 2010).

Guidelines and regulations committed with authorize the mixing for fossil full with biofuels. Those directive 2003/30/EC that need been authorized toward European union on 2003 need quickly build the handling of biodiesel from 200kt done 2003 will more than 2Mt on 2012 and shoot once more in the same amount for 2Mt in the sequential quite a while (Haron *et al.*, 2018). The International Energy Agency (IEA) additionally predicted by those quite a while 2050, biofuels will totally trade the utilization from claiming mixed fills similarly as transportation fuel (Haron *et al.*, 2018).

This study need carried out to prepare hydrogen from corncob by utilizing photo electrochemical procedure.

1.2 Statement of problem

The current worldwide vitality interest will be mostly subject to stores for fossil fuels, which need aid depleting, and the globe is confronting extreme contamination issues from those by-products of fossil fuels uses. As the interest about vitality ceaselessly expands fossil asset must make discovered should keep fossil hotspot exhaustion and diminishing again constantly on natural effects.

In the previous years, those innovative work diversions guided towards renewable vitality advances similar to the anaerobic absorption about natural biomass also waste. Hydrogen is high energy-yield non-polluting fuel, especially at utilized within power module. However, very nearly 90% for hydrogen is at present prepared starting with fossil fuel, mostly by steam reforming for characteristic gas also petroleum. An additional approaches about transforming hydrogen will be toward those electrolysis from claiming water. Power necessary with electrolysis is inferred from the electric force grid and the predominant sources for grid electricity, burning for fossil fuels, generates the emanation for example, nitrogen oxide and particulate matter, and in addition carbon dioxide.

Biofuel, which are, generated starting with preliminary sustenance assets for example, such that starch, sugar, vegetable and creature fats might expand those worldwide nourishment unreliability. In the universe that again particular case billion don't need enough on eat. At present biofuel gotten eventually perusing two diverse routes bio-chemical and thermo-chemical methodologies. However, every of the routes need its identity or detriment.

Bio-chemical transformation transform obliges basic pre-treatment procedure should change the structure of biomass to cellulose derivation and hemicellulose for enzymatic hydrolysis. This methodology alongside high cosset of proteins expands the entirety transform expense. Those real worry to thermo-chemical transformation methodology will be the cosset from claiming substantial measure about biomass, which will be collected, transported also conveyed at the plant entryway.

The photo reactant decay of water through powder semiconductors, for furthermore without stored metals or oxides, need those disservice about generating H_2 furthermore O_2, at neighboring sites. In this way that the yield reduced toward a reactant recombination furthermore regardless obliges detachment of the exploding mixture.

In this study, photo electrochemical methodology was used to handle hydrogen from corncob. Photo electrochemical methodology need possibility on part water under hydrogen and oxygen. For addition, it will be expense successful while light may be specifically connected on the result.

1.3 Objectives

1.3.1 General objective

The general objective of this investigation is to produce hydrogen from corncob by utilizing photo electrochemical process.

1.3.2 Specific objectives

1. To analyze the physical properties of corn cobs.
2. To investigate the effect of operating parameters on hydrogen production.
3. To optimize operating parameters by using RSM.

1.4 Research question

1 What are physical properties of corncob that can I analyze?

2 What is the effect of operating parameters on the hydrogen production?

3 At what time, pH, biomass concentration and temperature can I get optimum hydrogen gas?

1.5 Significance of study

The vast majority for vitality sources bring an effect on the earth. Worries around those nursery impact and worldwide warming, air pollution, and vitality security have prompted expanding interest and more improvement on renewable vitality wellsprings for example, such that bio-fuel, solar, wind, geothermal, and hydrogen. This examine will research vitality era starting with renewable assets (biomass) as opposed fossil fuels because of constrained future accessibility from claiming petroleum and expanded natural effects.

The clean air demonstration from the Environmental Protection Agency (EPA) inferred that poisonous discharges starting with biofuel will be less the discharges starting with fossil fuel, and the carbon monoxide emanations is likewise less emanation starting with fossil fuel. Processing for hydrogen toward photo reactant debasement of biomass in photo electrochemical methodology may be an engaging research for twofold natural profits. Waste material might a chance to be expended and light is changed over under handy type from claiming vitality.

1.6 Scope of the study

This study focused on the generation of hydrogen from agricultural waste (biomass). In addition, the analysis of hydrogen gas production from biomass by using photo electrochemical reaction will conduct in Jimma University, jimma institute of technology environmental engineering laboratory.

1.7 Limitation of the study

The limitation of this study was difficult to collect the hydrogen gas produced from corn cobs using a plastic bag and to measure it. Due, to gases are fluid, compressible and often invisible they are difficult to collect and measure. In this study I collect the result by using plastic bag and the result was measured by manually by estimating it out of 100%. Due, to lack of gas chromatography instruments and lack of skilled man powers to characterize the hydrogen gas produced using gas chromatography, I used lighter to cheek the result was either hydrogen or not.

CHAPTER TWO

LITERATURE REVIEW

2.1 Sources of Energy

Again the most recent 200 years, people have turned into an ever increasing amount subject to vitality that they scrape out of the ground. In the 1700's, Just about everyone our vitality went starting with wind, water, firewood, or muscle power(Rossetti, 2012). Recently, the worldwide vitality prerequisite will be mostly met by fossil fuels which would the essential vitality source, and the wellsprings incorporate petroleum, coal, bitumen, characteristic gas furthermore tar sand. Presently hydrogen preparation through propelled innovations utilizing fossils will be understood, 95% specifically by steam reforming about natural gas (48%) (Koumi and Njomo, 2012). Hydrogen generation from different fossil assets hydrocarbon 30% also coal 18% will be principally got by the methodology for partial oxidation (Koumi and Njomo, 2012). The most recent propelled transform for hydrogen generation is perusing the electrolysis for immaculate basic water similarly as a capacity of the crude material, which permits solution for 4% of the world's interest (Antoniadou and Lianos, 2009).

This plan of action from claiming fossil assets which is not main crude material to hydrogen as well as a vitality hotspot to the techniques posed two real issues namely: the exhaustion about assets and the increment of the focuses from claiming carbon dioxide also methane; principle greenhouse gasses in the atmosphere, as they contributes individually 63% and 19% of the crest (Staffell *et al.*, 2019). Likewise an illustration, the normal for main carbon dioxide emitted of the climate with admiration to the measure from claiming methane gas constantly expended likewise investigated by the procedure about steam reforming stands 9 kg/kg for hydrogen(Koumi and Njomo, 2012). The shortage of fossil assets and the ensuing emanation from claiming CO_2 also CH_4 under nature's domain drive us will modify intends for this vitality blended up in place should fulfill both those necessities of the nearby populace and the commercial enterprises (Directorate and Agency, 2004).

Direct alcohol fuel cell (DAFCs), which proselytes concoction vitality for different fluid hydroxyl subsidiaries for hydrocarbons under electrical vitality have been rising concerning illustration new era for conservative control wellsprings to compact electronic based gadget and electric-powered vehicles (Su *et al.*, 2009). Around every last bit alcohols the electro oxidation for methanol and ethanol need been intensively investigated. However, those high instability about ethanol and separate poisonous quality of methanol might reasons not kidding useful issue in useful application (Su *et al.*, 2009).

MFCs bring been intensively examined starting with the viewpoints about configuration/operation, microbiology electrochemistry and requisition (Borole and Mielenz, 2011). For addition, MFCs would modified to need extra works for example, such that hydrogen creation or desalination, and the modified gadgets incorporate microbial electrolysis cells (MECs) and microbial desalination cells (MDCs) (Xiao and He, 2014). The possibility requisitions about MFCs incorporate wastewater treatment, remote force wellspring for sensors, preparation for worth-included exacerbates through electrochemical or electro manufactured courses also an exploration stage for seeing essential microbial breath (Speltini *et al.*, 2014).

Methanol, a standout amongst the items of CO_2 transformation courses might make straightforwardly utilized set up about gas and diesel easily in the available existing vitality circulation base without whatever significant changes, hence, there might not be any separate monetary outcomes same time transforming from fossil fuel vitality reliance to non-fossil fuel, renewable alternately sun powered vitality reliance (Mohammadi *et al.*, 2011). Methanol not best camwood be utilized similarly as a regulate fuel as well as might make changed over under results for high calorific value, such as, dimethyl ether (DME), furthermore different hydrocarbons. Methanol will be a green fuel and need practically a large portion of the vitality thickness in examination with basically utilized gas fuel. In present, the most part of the business methanol may be generated from syngas, that is a mixture about H_2, carbon monoxide (CO) and CO_2 ahead exceedingly optimized $Cu/ZnO/Al_2O_3$ impetus toward temperatures dependent upon 300°C and pressured dependent upon 100bar, ahead extensive scale mechanical plants in the request about a few million tonsil for every year (Ganesh, 2016).

Due to the profuse from claiming hydrogen as vitality bearer later on in the usage of irregular vitality sources, the most recent couple a long time need seen escalated consideration scrutinize on water separation for enlightened semi- conductors (Nowski *et al.*, 1981).

The national energy policy of Ethiopia aims to generate more power exclusively from renewable energy resources. By 2030, the current 97.6% renewable energy resources will reach 99.3%. By 2025, Ethiopia aims to access universal electricity following the National Electrification Program (NEP). To provide the ever-increasing demand for electricity, and to deal with the uncertainty in climate change, complementary energy storage and conversion technologies must be established by integrating them with renewable energy resources to alleviate the risk of overreliance on and variability of hydropower. Potential complementary energy conversion and storage technologies include different membrane technologies such as fuel cell, microbial fuel cell (MFC), salinity gradient power (SGP), hydrogen technologies, and batteries.

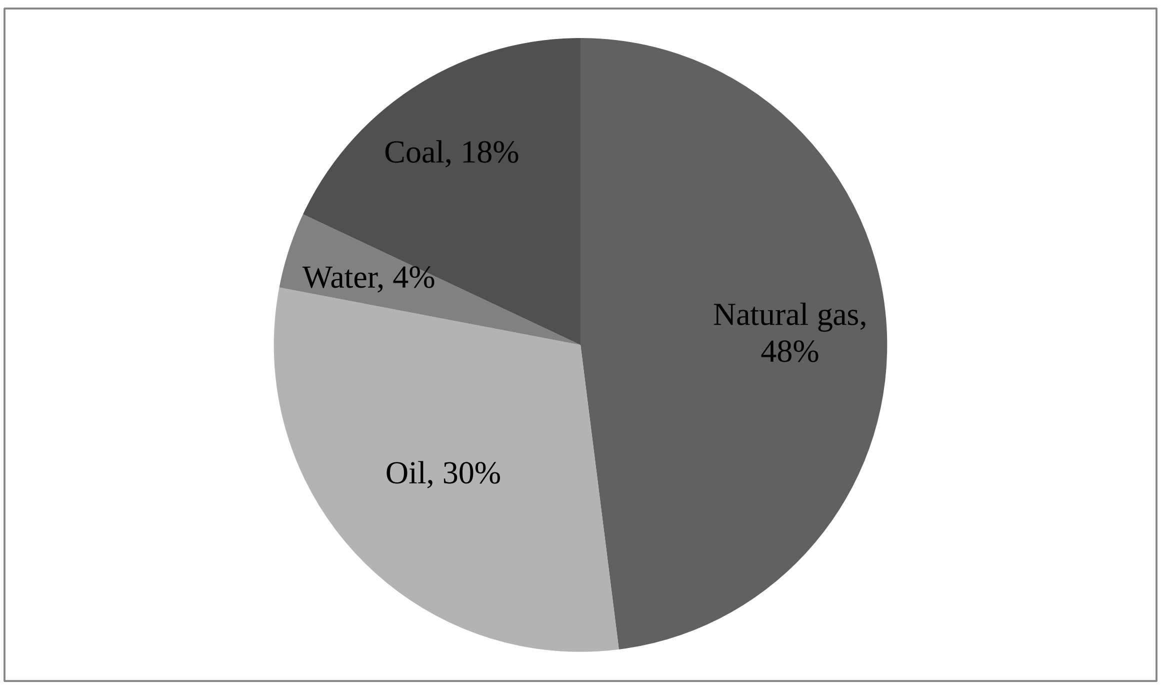

Figure 2.1 Distribution of the modes of hydrogen production (Koumi and Njomo, 2012)

2.2 Hydrogen fuel

Nowadays, issues inferred from environmental change desperately require us to find new plan fossil fuels. Around candidates, hydrogen (H_2) offers a significant number points of interest that might diminish those reliance with respect to fossil fuels, including carbonfree, abundant for nature, Furthermore secondary vitality thickness contrasted with gas (Rossetti, 2012). Therefore, concerning illustration suggested by John Bockrisin1975 (Fuels, 1973), H_2 is a possible vitality framework on fossil fuel, which incorporates those fields for production, purification, transportation, storage, application, and businesses. However, it is noted that H_2 is primarily transformed starting with fossil wellsprings by reforming courses bringing about an impostor of carbon dioxide emanation.

Currently, a few methodologies bring been recommended to prepare H_2 specifically by means of exceptionally efficient, ecologically friendly, technologically reliable, and moderately minimal effort methods. Inside this framework, photo catalysis might achieve numerous benefits from manageable development, budgetary and natural viewpoints.

2.3 Hydrogen production

The plan of action for expendable fossils sources for hydrogen creation contributes significantly of the increment in the nursery impact. This may be the thing that might have been taken forethought of actually also financially (harnessing CO_2 alternately Eco tax), fit about modifying those thresholds about elective aggressive monetary results especially renewable vitality (Dunn, 2020).

Acknowledgment about hydrogen economy obliges the processing of hydrogen for monetary furthermore reasonable way. It is the large portion perfect to prepare hydrogen vitality starting with the greater part abundant vitality sourball accessible ahead earth (which is the sun) and the large portion abundant common asset once earth (which is water). The empowering innovation to this methodology is the photo catalytic water splitting (PWS) (Mahajan, Mohapatra and Misra, 2008). The advancement of the techniques about hydrogen processing dependent upon renewable vitality wellsprings takes put to the extent that could be allowed without discharging the greenhouse gas. These systems representable elective approaches to hydrogen handling through fossils combustibles (Ji *et al.*, 2007).

2.4 Hydrogen production methods

Hydrogen produced from natural gas accounts for approximately 80% of the total hydrogen production while production from fossil fuels accounts for over 90% of the commercial hydrogen production. These industrials processes are energy intensive as they operate at very high temperatures and pressures. Other methods to produce hydrogen include the following (Archer and Steinberger-wilckens, 2018).

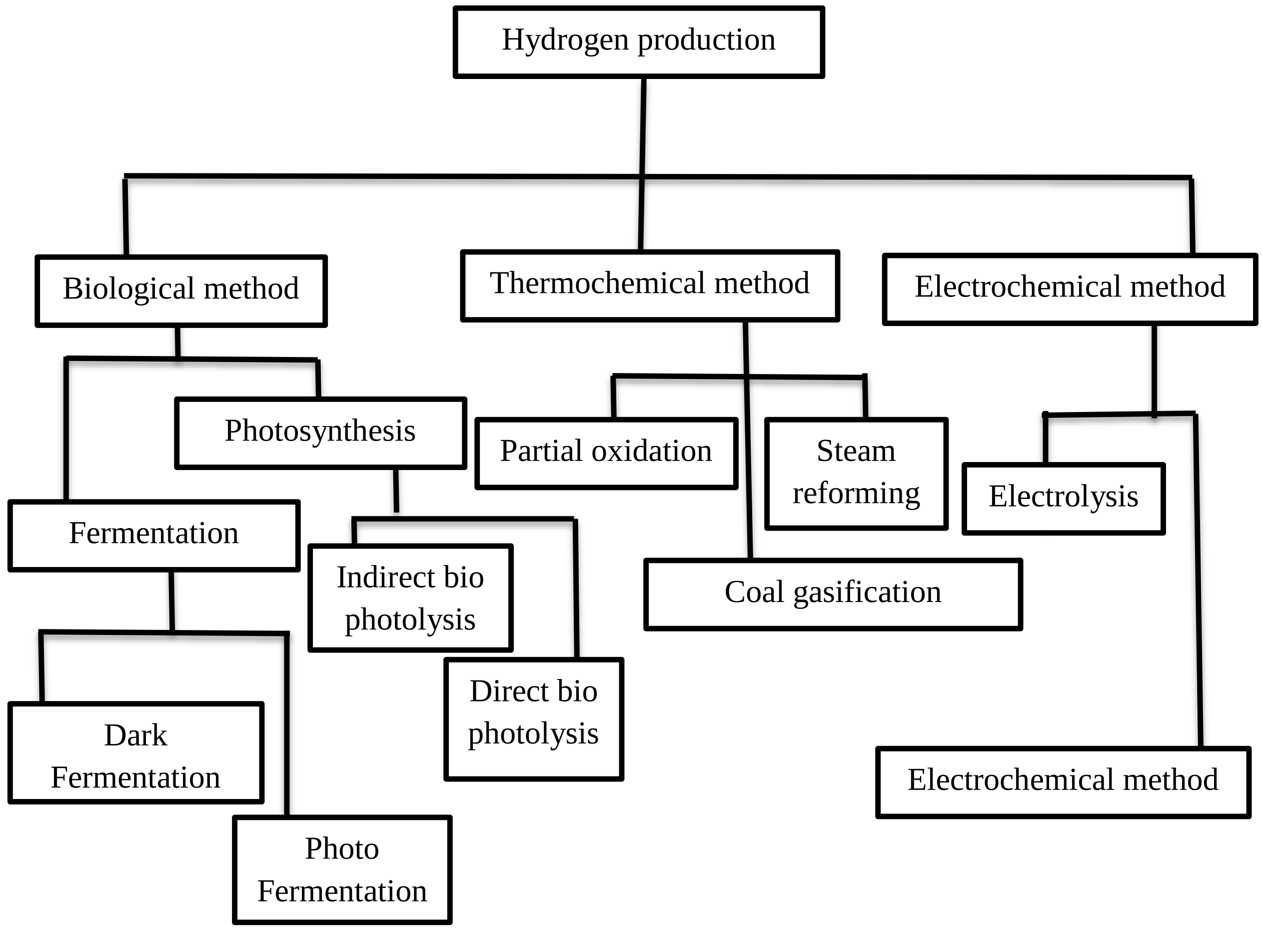

Figure 2.2 Techniques of hydrogen production from renewable energies (Archer and Steinberger-wilckens, 2018)

2.4.1 Biological methods

The procedures from claiming living H_2 generation utilizing light oriented vitality camwood make comprehensively classified under taking after unique methodologies that incorporates immediate bio photolysis, backhanded bio photolysis and photo fermentation. And living H_2 creation without light is dark fermentation (Mohammadi *et al.*, 2011).

2.4.1.1 Direct bio photolysis

The action of light on a biological system that results in the dissociation of a substrate, usually water, to produce hydrogen is referred to as bio photolysis.

$$2H_2O + 2A \longrightarrow 2AH_2 + O_2 \quad (1)$$

Where, A is an electron acceptor. For the purpose of employing these photosynthetic electrons for the reduction of protons to hydrogen by the action of a bacterial hydrogenates, the acceptor must have an oxidation-reduction potential near the potential of the hydrogen electrode and in its reduced state serve as a substrate for the hydrogenates. In this reaction oxygen produced by the photosynthesis strongly inhibits the hydrogen production (Mohammadi *et al.*, 2011).

2.4.1.2 Indirect bio-photolysis

The most credible processes for future applied research and development are those which couple separate stages of micro algal photosynthesis and fermentations (`indirect bio photolysis'). These involve fixation of CO_2 into storage carbohydrates (e.g. starch in green algae, glycogen in cyanobacteria) followed by their conversion to H_2 by the reversible hydrogenates, both in dark and possibly light-driven anaerobic metabolic processes. In indirect bio photolysis, the problem of sensitivity of the H_2 evolving process to O_2 is usually circumvented by separating O_2 and H_2. In a typical indirect bio photolysis hydrogen is produced as follows (Mohammadi *et al.*, 2011):

$$12H_2O + 6CO_2 \longrightarrow C_6H_{12}O_6 + 6O_2 \quad (2)$$

$$C_6H_{12}O_6 + 12H_2O \longrightarrow 12H_2 + 6CO_2 \quad (3)$$

2.4.1.3 Photo fermentation

This is another light-dependent method in which 90 % of product gas is hydrogen and the process releases no hydrogen sulphide or carbon monoxide. Here, photo heterotrophs (eg, purple bacteria) convert organic acids in the presence of sunlight into H_2, CO_2 and carbon compounds. The main enzymes utilized by these bacteria are nitrogenizes that require nitrogen-scarce conditions for hydrogen production. Disadvantages of this process include the use of costly bio-reactors, dependence on ATP-consuming nitrogenizes and lack of efficiency of light-harvesting antennae.

These photo-heterotrophic bacteria have been found suitable to convert light energy into H_2 using organic wastes as substrate in batch processes, continuous cultures or immobilized whole cell system using different solid matrices like agar gel and polyurethane foam. The overall reaction of hydrogen production is as follows (Mohammadi *et al.*, 2011):

$$C_6H_{12}O_6 + 6H_2O \longrightarrow 12H_2 + 6CO_2 \quad (4)$$

2.4.1.4 Dark fermentation

Dark fermentation is the main light-independent process for bio hydrogen production. In this method, anaerobic bacteria consume sugars to produce H_2, CO_2, and organic acids. It is considered the most favorable process since hydrogen is produced at a higher rate and at low cost. The process can be carried out in simple reactors, requires no light energy and can be used on a wide range of substrates at non-aseptic conditions. Dark fermentative H_2 production is preferred for bio-fuel production. The maximum possible H_2 yield per mole of glucose is 4 mole corresponding to only 33% of the substrate conversion. However, in practice, attaining this theoretical maximum yield is not possible.

$$C6H_{12}O_6 + 2H_2O \longrightarrow 2CH_3COOH + 4H_2 + 2CO_2 \quad (5)$$

Those correlation from claiming imperative living H_2 preparation techniques may be summarized in table underneath. Starting with an engineering perspective, they the sum conceivably offer those points of interest of more level cosset impetuses (microbial cells) and less energy escalated consideration reactor operation (mesospheric) over those introduce mechanical methodology for making hydrogen. However, a few biological and engineering tests must be succeed in the recent past this guaranteeing engineering gets to be a useful truth. Foremost, the cell division digestion system and fundamental natural chemistry that backing this methodology must be well caught on essential research on the system about H_2 generation by S-deprivation stays should make completed. Different obstructions should microbial based, vast scale processing from claiming H_2 incorporate (a) inalienable properties of the microbes that preclude coherence and efficiency from claiming H_2 production; (b) underlying confinements about photosynthetic efficiency; and (c) constraints of the hydrogenizes reactant capacity (Ghimire *et al.*, 2015).

Table 2.1 Comparison of important biological H_2 production processes (Koumi and Njomo, 2012)

Process	General reaction	Advantages	Disadvantages
Direct bio photolysis	$2H_2O$ +light $\rightarrow$ $2H_2 + O_2$	Can produce H_2 directly from water and sunlight Solar conversion energy increased by ten folds as compared to trees, crops	High intensity of light is required. Hydrogenizes is highly sensitive to even moderately low concentration of O_2 Lower photochemical efficiency
Indirect bio photolysis	(a)$6H_2O+6CO_2$+light$\rightarrow$ $C_6H_{12}O_6+6O_2$ (b)$C_6H_{12}O_6+2H_2O \rightarrow$ $4H_2+2CH_3COOH+2CO_2$ (c)$2CH_3COOH+4H_2O+$ +light $\rightarrow 8H_2+4CO_2$ Overall reaction $12H_2O$ + light $\rightarrow 12H_2+6O_2$	Cyanobacteria can produce H_2 from water Has the ability to fix N_2 from atmosphere	Uptake hydrogenizes enzymes are to be removed to stop degradation of H_2. About 30% of O_2 present in gas mixture
Photo fermentation	$CH_3COOH+2H_2O$+light $\rightarrow 4H_2+2CO_2$	A wide spectral light energy can be used by these bacteria Can use different organic wastes High substrate conversion efficiencies Degrade a wide range of substrates	Production rate of H_2 is slow O_2 has an inhibitory effect on nitrogenize Light conversion efficiency is very low, only 1–5%. Pre-treatment may be needed due to either the toxic nature of the substrate, Large reactor surface area, requirement and Expensive equipment.

2.4.2 Thermochemical methods

2.4.2.1 Partial oxidation

Partial oxidation of hydrocarbons involves the heating of the hydrocarbon in a low oxygen environment to create a hydrogen rich gas.

2.4.2.2 Steam reforming of natural gas

Steam reforming is right now a standout amongst those practically spread and in those same time minimum unreasonable forms of hydrogen production, through which more than 90 % of the hydrogen utilized may be handled. Its playing point hails from the high effectiveness for its operation and low operational handling expenses. The large portion habitually utilized crude materials are characteristic gas and lighter hydrocarbons. The process requires an external source of heat, which is added into the process by the direct combustion of part of the natural gas. Methodology need two phases. In the main stage, hydrocarbon crude material may be nourished under steam (500–900°C, 0.3–2.5 MPa) in a tube reactor loaded for an impetus on the groundwork of nickel oxide (or Ni + MgO, Pt, Rh). The reactant methodology obliges a desulfurized starting crude material (Demirbas, 2004).

During its reaction, syngas (H_2 + CO) is produced along with a lower proportion of CO_2 (reactions (6, 7). In the second stage, the cooled gas is led into the converters, where carbon monoxide is converted by means of steam into carbon dioxide (Eq 6).

$$CH_4 + H_2O\,(g) \longrightarrow CO + 3H_2 \text{ endothermic} \quad (6)$$

$$CH_4 + 2H_2O\,(g) \longrightarrow CO_2 + 4H_2 \text{ endothermic} \quad (7)$$

$$CO + H_2O\,(g) \longrightarrow CO_2 + H_2 \text{ exothermic} \quad (8)$$

$$CO_2 + H_2 \longrightarrow CO + H_2O \text{ exothermic} \quad (9)$$

The nascent carbonic gas is removed by a reversible exothermic reaction (9) usually implemented in two stages. In the first, so-called high temperature stage, the temperature of the products is raised to almost 500°C, which has the result of lowering the balanced yield of CO_2 and H_2. The products are then cooled to approximately 360°C and are led to the low-temperature converter filled with a highly active copper catalyst (the second stage), where the concentration of CO is lowered to 0.2– 0.3 vol. % at low temperatures of 180–230°C (Holladay *et al.*, 2009).

2.4.2.3 Coal gasification

Coal gasification is the heating and pressurizing of coal and water to create hydrogen and carbon monoxide according to the equation (equation 10).

$$C + H_2O \longrightarrow CO + H_2 \qquad (10)$$

2.4.3 Electrochemical methods

2.4.3.1 Electrolysis

In the case of water electrolysis, the reaction is mediated in a strong ionic solution in order to split water into hydrogen and oxygen gases. Electrolysis may be a methodology over which an immediate current passim through two electrodes over the water result brings about the splitting of the concoction bond of water under hydrogen and oxygen over (Equ.11).

$$2H_2O \longrightarrow 2H_2 + O_2 \qquad (11)$$

The hydrogen action H^+ reacts at the cathode, resulting in the creation of hydrogen, which is collected and later stored. H^+ created at the negative electrode (anode), and oxygen is created at the positive electrode (cathode). This method produces extremely pure H_2 a by using large amount of electricity is used (Koumi and Njomo, 2012).

2.4.3.2 Photo electrolysis

Hydrogen production, exhibiting guaranteeing effectiveness and costs, in spite of the fact that it may be at present in the stage from claiming test advancement. Currently, it may be the minimum exorbitant and a large portion successful system for hydrogen processing from renewable assets like light. Many current methods for producing large amounts of hydrogen for industrial uses utilize fossil fuels as their source of energy (Koumi and Njomo, 2012).

2.5 Electrochemical processes

Separated starting with gas reformation, those electrolysis for water is formed functional technique done commercial enterprises to the handling for hydrogen. Water electrolysis may be an electrochemical procedure permitting the decay of water under its constituent components from claiming hydrogen and oxygen much appreciated should electrical energy, as stated by those two synthetic responses independently occurring toward the anode and the cathode:

At the anode:

$$H_2O + \text{electricity} \longrightarrow 2H^+ + (1/2)O_2 + 2e^- \qquad (12)$$

At the cathode:

$$2H^+ + 2e^- \longrightarrow H_2 \qquad (13)$$

The general electrolysis reaction is

$$H_2O + \text{electricity} \longrightarrow H_2 + (1/2)O_2 \qquad (14)$$

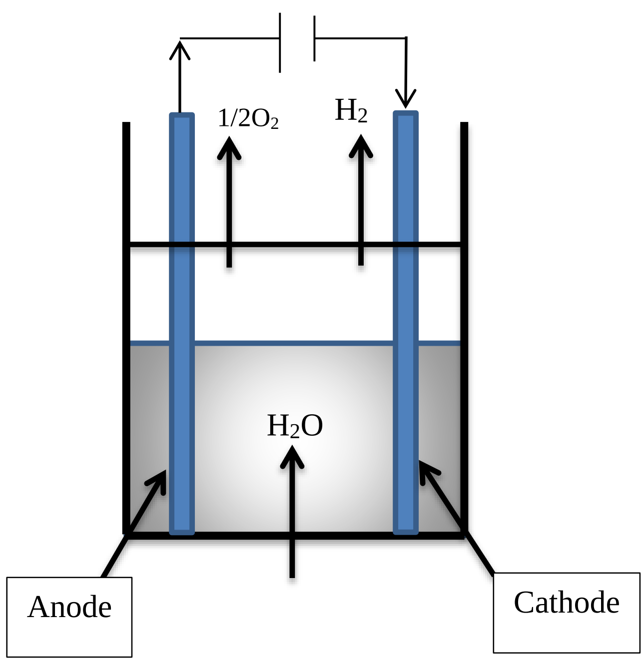

Figure 2.3 Alkaline water electrolysis process (Koumi and Njomo, 2012)

2.6 Photochemical processes

A photo catalyst absorbs UV and/or visible (Vis) light irradiation from sunlight or an illuminated light source. The electrons in the valence band of the photo catalyst are excited to the conduction band, while the holes are left in the valence band. This, therefore, creates the negative-electron (e^-) and positive-hole (h^+) pairs. Photochemical methods utilize sun oriented light to prepare those hydrolysis for water. These days two methods would know: those photo biological and the photo electrochemical (Koumi and Njomo, 2012).

2.6.1 Bio-production of hydrogen from photosynthetic microorganisms

Photo biological forms are in view of the ability for some organisms, for example, such that green algae, cyanobacteria, and photosynthetic bacteria, to go about as living impetuses in the creation for hydrogen from water and different enzymes, for example, hydrogenizes and nitrogenize. Differing qualities over microbial physiology and digestion system implies that there would varieties about separate routes done which microorganisms could transform H_2, each person for appearing advantages, and in addition problematic issues. Those H_2 digestion system of green algae growth might have been first uncovered in the promptly. The green algae growth (under anaerobic conditions) might possibly use H_2 as an electron giver in the CO_2-fixation transform or develop H_2 done both dim and the light. Despite those physiological significance of H_2 digestion system in green algae growth may be at present is concerned about fundamental research, those transform from claiming photo hydrogen creation eventually perusing green algae growth is about enthusiasm since it generates H_2 gas starting with those the greater part abundant resources, light and water. Cysts favor may be those practically advantageous species in light it need those most astounding development rate about (50 t VS/ha yr) Furthermore camwood make reaped a number times for every year. Every one microbial conversions might make conveyed out during encompassing conditions, Nonetheless easier rate from claiming H_2 processing and low yield need aid those fundamental drawbacks (Hallenbeck and Benemann, 2002).

2.6.2 Photo-electrolysis of water process

Plants catch the vitality from daylight furthermore consequently develop. Throughout this process, they transform oxygen eventually perusing oxidizing water and lessening carbon dioxide. To other words, those oxidation from claiming water and the diminishment about CO_2 would attained with light oriented vitality. Toward Similarity with characteristic photosynthesis, we started to examine the photo electrolysis about water utilizing light vitality. Photo-electrolysis for water may be those separation of a semiconducting photo catalyzer by an electric current through lighting. The thermodynamic cycles constitute a system for hydrogen creation without those intercession from claiming carbonized fossils by method for depletion and powerless to the generation for expansive add up for CO_2 answerable for the nursery impact. Those decay transform of water comprises about a warm decay or thermo electrochemical decay from claiming water with those supply (hence stocking) from claiming sun oriented vitality much appreciated to the progression about responses whose whole will be equal to (Jeffery *et al.*, 2010):

$$H_2O \xrightarrow[\text{Light}]{} H_2 + 1/2O \quad \Delta H=284 \text{ kJ/mole} \tag{15}$$

Photo electrochemical forms would even now under the stage of examination. Their usage may be normal just in the long term.

2.7 Biomass as electrolyte

Converting biomass starting with municipal, Agricola and animals clinched alongside with biofuel and electrical force need significant natural furthermore financial preferences. Those transformation about biomass under useful vitality obliges exquisite outlines and further examination. Thus, biomass will be a guaranteeing renewable vitality wellspring because of its low creation cosset furthermore basic manufacturing forms. Biofuel (hydrogen and methanol) starting with biomass will make conceivable on be utilized for transportation for near-zero air pollution, includes efficient employments about territory furthermore real commitment to decrease reliance around unstable sourball from claiming petroleum.

Presently, the solar-to-hydrogen (STH) vitality transformation efficiency is very much low, the principle motivations concerning illustration following: 1) fast photo-generated electron/hole pair's recombination, 2) fast-backward reaction, 3) unfavorable thermodynamic possibility to water splitting, 4) insufficient collecting unmistakable photons starting with sun oriented light, and 5) unsteadiness against photo-corrosion. Because of those tests stay over accomplishing general water part to H_2 generation to refined water, the opposite methodology may be to consolidate light-induced part about water and photo catalytic oxidation of biomass-derived natural substrates under an absolute process, calling as photo reactant reforming (photo-reforming).

Biomass oxidation takes place under vigorous state. Hence, biomass-derived natural substances concerning illustration electron donors (sacrificial reagents or gap scavengers, indicated here similarly as $C_xH_yO_z$) might create CO_2 and H_2O by reacting irreversibly for the gaps possibly straight forwardly alternately in a roundabout way through the framing for hydroxyl radicals ($^{\bullet}OH$).

$$C_xH_yO_z + (2x\text{-}z)H_2O \longrightarrow xCO_2 + (2x\text{-}z + y/2)H_2 \qquad (16)$$

The remaining electrons could simultaneously reduce protons to H_2 molecules, accompanied by the H_2 evolution. As expected, the photo catalytic H_2 production by overall water splitting and photo-reforming of biomass-derived organic substances have opened a new era in the field of solar energy conversion to H_2. Leading progress has been made on design photo catalysts, optimization of reaction conditions (including light irradiation, type of sacrificial reagents). Dependent upon those later research works, a present viewpoint to photo catalysis towards H_2 creation may be reviewed furthermore highlighted (Ibrahim, Kamarudin and Minggu, 2014).

2.7.1 Biomass availability

2.7.1.1 Overview of maize production in the world

Among the top 10 producers of maize worldwide, there is a large variation in production yield between the different areas: while yield is approximately 10.7 tons/hectare/year in the USA, yield is only 2.75 and 3.30 tons/hectare/year in India and Mexico respectively. Let, see in table below the overview of top 10 worldwide countries as their production yield per hectare according to Food and Agricultural Organization 2016 report.

Table 2.2 Production yield per hectare for top 10 producers worldwide (FAO, 2016).

No	Country	Million tons	Production unit per hectare (ton/hec/year)
1	USA	361	10.7
2	China	216	6
3	Brazil	60	5.2
4	Argentina	33	6.6
5	Ukraine	28	6.2
6	India	23	2.7
7	Mexico	23	3.3
8	Indonesia	19	4.9
9	South Africa	14.9	4.5
10	Romania	11.9	4.8

2.7.1.2 Overview of maize production in Africa

The situation is even more dramatic in Africa: while the yield was still reasonable in countries like Egypt (7.73 tons/hectare/year), South Africa (4.54 tons/hectare/ year) and Ethiopia (3.42 tons/hectare/year) the majority of countries have yields of less than 2 tons/hectare/year (35 of the 51 African countries producing maize) and even less than 1 ton/ hectare/year (15/51 African countries, such as Zimbabwe, South Sudan and Gambia) in 2014 Table below.

Table 2.3 Maize production yield per hectare in 2014 in top ten African countries (FAO, 2016).

No	Country	Million tons	Production unit per hectare (tons/hectare/year)
1	South Africa	14.9	4.5
2	Nigeria	10.8	1.8
3	Ethiopia	7.2	3.4
4	Tanzania	6.7	1.6
5	Egypt	5.8	7.7
6	Malawi	3.9	2.3
7	Kenya	3.5	1.7
8	Zimbabwe	3.3	2.8
9	Uganda	2.8	2.5
10	Ghana	1.7	1.7

2.7.1.3 Overview of maize production in Ethiopia

Maize handling extended quickly and changed preparation frameworks over Africa similarly as a mainstream and generally grew nourishment crop since its presentation of the landmass around 1500A. D. Maize landed for Ethiopia marginally after around the late seventeenth century, and might have been principally developed as a subsistence crop in the mid altitudes (1500– 2000m over ocean level) over southern, south-central, and southwestern parts of the organizations in the nation. Those handling framework in the 1960s furthermore for the to start with quarter about 1970s might have been genuinely subsistence, those yields scarcely surpassing 1 metric ton (1MT/ha). The rate of development to territory declined taking after those great dry season of 1974, and same time there might have been development in the 1980s, those Normal twelve-month yield might have been unstable and infrequently surpassed 1.5MT/ha. Maize preparation Furthermore its status done figuring out sustenance security in the nation gained a real center in the mid-1980s, especially spurred by the 1984 obliterating dry season and the starvation that took after. Those totally versatility of the crop and the possibility to prepare additional calories and nourishment for every territory from claiming area grew over every last bit real oats developed in Ethiopia were essential factors for recognizing maize likewise and only those national sustenance security strategy, including its incorporation under the government-led escalated consideration Agricola development system (Abate *et al.*, 2015).

Table 2.4 Percent maize area covered by organic fertilizers in selected regions of Ethiopia (2003-12). Source: CSA (www.csa.gov.et)

No	Region	Year									
		2003	2004	2005	2006	2007	2008	2009	2010	2011	2012
1	Tigray	74	-	65	59	66	60	56	55	46	48
2	Amhara	37	31	32	29	32	27	24	28	25	20
3	Oromia	24	19	22	23	25	17	21	23	19	19
4	Benshangul	26	24	28	26	27	25	24	20	20	18
5	SNNPR	18	13	13	13	16	14	9	11	11	8

Corn cobs are desirable as a sustainable feedstock because they represent about 12 percent of corn Stover remaining on the field, their removal has negligible impact on soil carbon and they have limited nutrient value to the soil (Abate *et al.*, 2015).

CHAPTER THREE

MATERIALS AND METHODOLOGY

3.1 Sampling area

The study was carried out in the Oromia regional state, Jimma zone, located at about 346 km south waste of Addis Abeba. This zone lies between latitude 7°15'N and 8°45'S and longitudes 36°00'E and 37°40'E. The elevation of the zone ranges from 880 to 3360 m.a.s.l. The area experiences an annual average rain fall of 100 mm for 8 to 10 months. The main rain season extends from May to September and the small rain season takes place from February to April. The temperature of the area varies between 8 to 28°C with an annual average of 20°C. It has sub-humid, warm to hot climate the sample was collected from Asendabo, which is one of the major corn production area of Jimma zone.

3.2 Materials and Equipment used

Corn cobs, were collected from agricultural land from local area of asendabo town, bag was used to collect and transport samples to the laboratory. Pestle used to reduce the size of the sample, 2mm size mesh sieve was used to separate sieved corn cobs, digital Balances (model-Sartorius with 0.01mg sensitivity, and model EP214C) was used to weigh samples, pH-Meter. The crucible, and oven were used to characterize the biomass. Thermometer was used to measure the sample temperature.

3.3 Characterization of corncob

Experiments were conducted to determine the moisture content, fixed carbon content, ash content, and volatile matter content of air-dried corn cob samples ground to particle size below 2.0 mm.

3.3.1 Proximate analysis

The proximate analysis gives moisture content (MC), volatile matter content, the fixed carbon content, the ash content (the inorganic residue remaining after combustion of the sample).

3.3.1.1 Moisture Content

Samples were weighed in clean preheated moisture crucible of known weight by using sensitive balance. The sample and crucible were kept in an oven 105℃ for an hour. The crucible was covered and transferred to desiccators, and weighed after reaching room temperature. The crucible was heated in the oven for another two hours and was reweighed. This was repeated until constant weight was obtained. The loss of weight was calculated as percent of weight and expressed as moisture content.

$$\text{Moisture content}(\%) = \left(\frac{(\text{Initial Mass} - \text{Moisture Mass})}{\text{Initial Mass}}\right) * 100 \quad (17)$$

3.3.1.2 Volatile Matter Content

A crucible was weighed empty, and then samples were put in it. The sample and the crucible were placed in furnace for 30 min at 600 °C. The crucible was removed from furnace and placed in a desiccators to cool, then was reweighed. The process was repeated until constant weight was obtained.

$$\text{Volatile matter content}(\%) = \left(\frac{(\text{Moisture Mass} - \text{Volatile Mass}}{\text{Initial Mass}}\right) * 100 \quad (18)$$

3.3.1.3 Ash Content

A crucible was weighed empty, and then samples were put in it. The sample and the crucible were placed in a furnace for 2 hours at 550℃. The crucible was removed from furnace and placed in a desiccators to cool, then was reweighed.

$$\text{Ash content}(\%) = \left(\frac{(\text{Moisture Mass} - \text{Ash Mass})}{\text{Initial Mass}}\right) * 100 \quad (19)$$

3.3.1.4 Fixed Carbon Content

This is the residue left after the moisture, volatile and ash is given up. It is deduced by subtracting from 100, the percentage of moisture, volatile matter, and ash content. The fixed carbon content (FC) is given as

$$\text{FC}(\%) = 100 - (\%\ \text{moisture} + \%\ \text{volatile matter} + \%\ \text{ash}) \quad (20)$$

3.4 Components of PEC cells

Those principle segments of a PEC cells are the anode electrode (photo anode), cathode and the result. Anode cathode typically named concerning illustration photo anode carries those photo electro impetus. At those photo impetus will be semiconductor just about the selective case, the photo anode transform electron and oxidation response happen. In this consider it might have been utilized knob eventually perusing straight forwardly immersing under readied result. The point when high temperature connected of the result those temperature of the result expansion speedup the redox response. Those cathode electrode carries the electro catalyst, which encourage exchange of electrons from those cathode of the fluid period. Decrease response happens during those (dark) cathode. Next, electrolyte work is with expanded conductivity and regulating those pH (Davis *et al.*, 2021). In this study the components of PEC cells used are shown in the figure below. The electrode used in both direction was stainless steel. The selection was because of its high corrosion resistance when compared with other available electrodes. Light was applied directly into the solution by immersing the electric bulb on the solution. And also the power was connected from DC power supply.

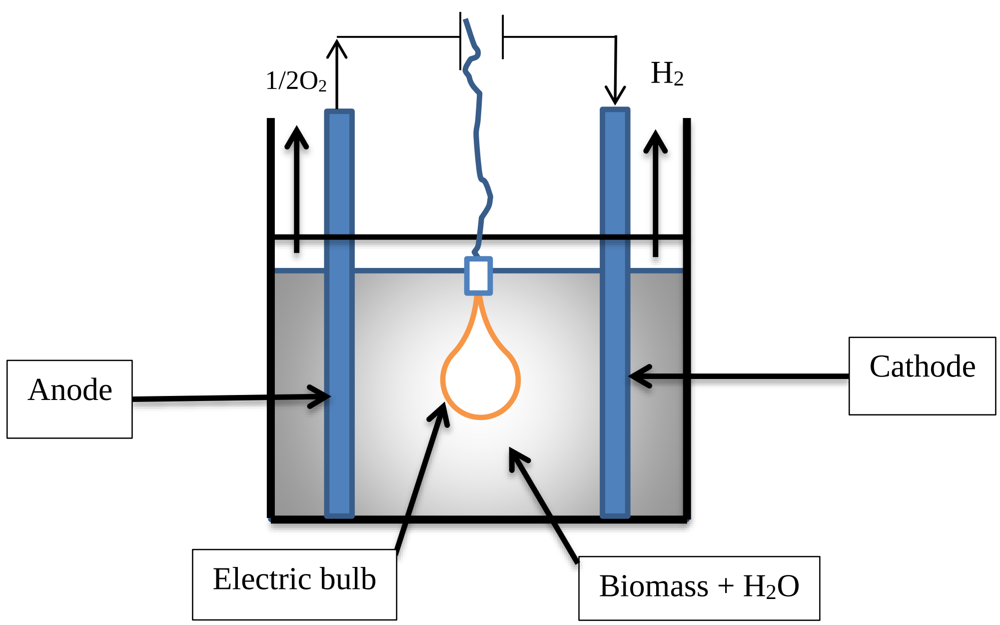

Figure 3.1 PEC Cell expiration

As the figure above shows the electrodes were connected with the sample holding dish by manually. The cracks during the linkage were closed safely to protect the infiltration of the solution. Thus, oxygen was produced on the anode ray and hydrogen was produced at cathode. Manually prepared experimental setup was shown in the figure below.

a) Solution holding dish with stainless steel electrode

b) Dish cover connected with lamp

c) Overall experimental setup

Figure 3.2 Experimental setup

3.4.1 Electrodes

Titania is the vast majority regularly utilized material for constructing those photo anode on it may be stable clinched alongside mossy cup oak compound situations and not difficult with integrate and might make saved concerning illustration a dainty mesoporous film utilizing soft-chemistry strategies. Unfortunately, titania need the hindrance from claiming just absorbing ultra-violate radiation, which accounts to best little and only those sun based radiation in the surface of the world (Lianos, 2011). The process needs a material with a good current connection (conductivity) and good resistance to corrosion. In this study Stainless steel is used as anode and light is applied directly by submersing lamp on the solution. Due to its highest corrosion resistance stainless steel was selected than other metal electrodes. This good properties of corrosion resistance of stainless steel is that they form a very thin, invisible surface film in oxidizing environments. Stainless steel also used at cathode ray.

3.4.2 Biomass electrolyte

In the photo impetus reaction, any natural substance could be utilized to photo corruption. The procedure is understood under encompassing states without selectivity for admiration to the fuel, for example, photodegradable natural substances. In the PEC, not constantly on natural substances yield those same vitality yield as far as those creation of electricity, atomic hydrogen alternately whatever viable biofuel. Bio-related compounds, for example, such that methanol, ethanol and glycerol, were utilized as an immediate fuel in the PEC because of their secondary yield and the promptly receptive data concerning their properties accounted for by an expansive amount for investigations. To addition, they need aid promptly accessible reactants as a result they would biomass items (Lianos, 2011). To improve those rate for hydrogen preparation starting with biomass in the PEC process, hydrogen will be handled during the cathode, same time biomass will be oxidized in the anode. Those oxidation of the biomass item happens in a more negative electrochemical possibility over the preparation about sub-atomic oxygen.

3.5 Experimental procedures

3.5.1 Sample Preparation

4 kg of corn cobs has been collected in bag from local available agricultural lands of asendabo, Jimma zone and has been taken to Jimma University, jimma institute of technology environmental engineering laboratory. Then the corn cobs has been crushed to fine size. A pestle used to reduce the corn cobs into small sizes of particle. These particles were sieved to 2mm in diameter by mesh sieve.

a) Collected sample

b) Minimizing the size with pestle

c) Minimizing the size with 2mm sized sieve

Figure 3.3 Sample preparation

As the sample collected, minimize it to available size, to crush it with pestle. To do this I used knife and hammer as alternative material. Then it was placed on the sun to dry it to remove the moisture. After it was dried pestle used to minimize the size to sieve. Finally 2mm sized sieve was used to get final needed corn cob size. The minimized corn cob was used to characterize the physical properties of corn cob and it was also used as electrolyte on the experiment.

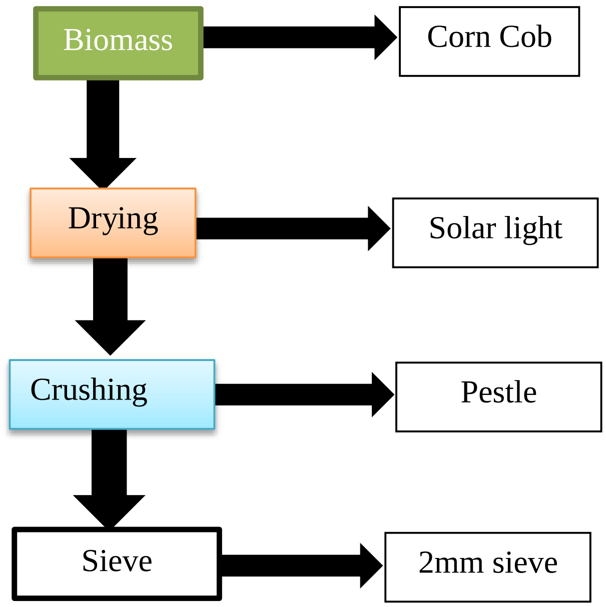

Figure 3.4 Process involved in sample preparation

3.5.2 Electrolysis process

After sieving the sample the solution of biomass with water is prepared from 2litters of pure water and at different level of operating parameters. Then stir with stirrer to mix the solution. Then after a direct current (DC) was applied to maintain the electricity balance and electrons flow from the negative terminal of the DC source to the cathode at which the electrons were consumed by hydrogen ions (protons) to form hydrogen. Biomass was oxidized in anode, hydroxide ions (anions) transfer through the biomass to anode, at which the hydroxide ions give away electrons and these electrons return to the positive terminal of the DC source. When light immersed into the solution the solution temperature increased this result expansion speedup the redox response.

a) Setup prepared to run

b) Running experimental setup

Figure 3.5 Laboratory procedure of hydrogen production

3.6 Collection of hydrogen gas

As gases are fluid, compressible and often invisible they are difficult to collect and measure. In this study 1 liter plastic bag was used to collect the sample and measurement is by estimating the amount of gas on the plastic out of 100% manually as shown in the figure below.

a) One liter plastic bag

b) Plastic bags connected with gas tubes

c) Running experiment after an hour

d) Separate the plastic from the gas tube safely when the required time riche

f) Incarcerate the tip of plastic with strap

Figure 3.6 Collection and measuring of hydrogen gas

3.7 Design of experiment

Response surface methodology contains a group of strategies for investigating for ideal working conditions through test techniques (Lenth, 2012). In Response Surface Methodology (RSM), the information about the relation between independent variables and dependent variable should be obtained in an empirical way (Sarabia and Ortiz, 2009). Four test factors, which are time, pH, biomass concentration and temperature were picked to expand the yield of hydrogen. Any polynomial model is multilinear in the coefficients. Arrangement of N experimental runs is an 'experimental design', ξ_N, and it is annotated by a matrix whose rows are the vectors X_1, X_2... X_N. In an experimental design, some experiments may be 'replicates', that is, they have been carried out under the same conditions X. When fitting with least square, a common matrix notation becomes (Sarabia and Ortiz, 2009):

$$\xi_N = \begin{bmatrix} X_{11} & X_{12} \cdots & X_{1K} \\ \vdots & \ddots & \vdots \\ X_{N1} & X_{N2} \cdots & X_{NK} \end{bmatrix} \quad (21)$$

The elements in the main diagonal of the dispersion matrix do not depend on the experimental response; consequently, it is possible to use them to compare the two designs. However, they depend on the length of the interval where each variable varies, the reason why they are standardized to obtain the so-called variance inflation factors (VIF) as

$$f(bi) = c_{ij} \sum_i (X_{ij} - x_j)^2 \quad (22)$$

Where: *f(bi)* Variance inflation factor

c_{ij} Coefficient estimate

X_{ij} Each factores from i to j run.

x_j Mean

VIF always greater than or equal to one. If VIF are greater than 3 the uncertainty in the estimated coefficient makes the model useless even if the fitting is statistically significant.

The central composite design sampling method is widely used in response surface applications. By choosing corner, pivotal, and center point, it is an ideal answer for fitting a second-order response surface model. The CCD technique additionally keeps up with the rotatability of the variety, which is useful in keeping up with the exactness of model fitting (Sarabia and Ortiz, 2009). Thus, central composite design method was selected on this study.

CHAPTER FOUR

RESULTS AND DISCUSSION

In this section the study discussed the proximity properties of corn cob, the effect of time, pH, biomass concentration and temperature on the production rate of hydrogen in the process, and optimization of operating parameters by using Response Surface Methodology.

4.1 Characterization of corncob

4.1.1 Proximate analysis

Moisture content, volatile content, ash content, and fixed carbon content of corn cob was 8.72, 80.72, 2.96, and 7.60 respectively (Anukam *et al.*, 2017). However in this study the results are not exactly in accordance with this report. The difference in these value might be happened due to a number of reasons such as the sources of corn cobs species varieties used and handling conditions. Moisture content is a measure of the amount of water present in the corn cob. As the moisture content increases in the sample of corn cob, it affects the product quality, and needs more heat for vaporization of moisture. Moisture content beyond 20% would create difficulties, however this value (9.2%) moisture content is desirable for the process to take place.

The corn cob used in this study was characterized by relatively high volatile matter content (79.4%). The volatile matter contents in corn cobs are usually high due to the organic nature of corn cobs, which indicates the corn cobs potential to create huge amounts of inorganic vapors when used as feedstock. The higher the volatile content of the biomass, the better rate because of the biomass yield up on carbonization.

Biomass ash content greater than 6% is not desirable for gasification because of the formation of agglomeration, fouling, and slagging, which leads to process efficiency reduction. However in this study the ash content (2.4%) is less than 6% which indicates the corn cob is desirable for gasification. Since the ash content was small the amount of sludge also produced and the production rate of hydrogen was increase.

Fixed carbon content of corn cob indicates the amounts of carbon present after volatile matters are driven off. In this study the fixed carbon content of corn cob was 9% which is enough. The volatile and fixed carbon contents of biomass are related to the yields and composition of solid, liquid, and gaseous products.

Table 4.1 The results of proximate analysis of the corn cob sample

No	Physical composition	Weight before dry (g)	Weight after dry (g)	Weight percentage (%wt. dry basis)
1	Moisture	10	9.08	9.2
2	Volatile matter content	10	2.06	79.4
3	Ash	10	9.76	2.4
4	Fixed carbon content			9

4.2 Effects of operating parameters on hydrogen yields

In order to manipulate the final gas composition, so as to enhance the production of H_2, a large number of operating variables, dependent upon the reactor configuration and biomass, must be considered (Florin and Harris, 2007). In this study, the hydrogen gas production yields from corn cob as a substrate at different time, pH, temperature and biomass concentration was investigated and their results were shown in Table 4.2 below. The effect of each parameters on hydrogen production rate studied and discussed in the section below.

The optimum pH for organic food waste varies from 4.5 to 7, for lignocellulose waste it varies from 5-7, whereas a neutral pH is optimal for animal manure (Anukam *et al.*, 2017). In this study maximum 60% of H_2 gas yield was observed at a time for first 1hr, pH of 7, and temperature of 35^0C and biomass concentration of 10g/l. H_2 yield inversely proportional with time which indicates the better hydrogen production when the time decrease and increase in the neutral solution with maximum biomass concentration and temperature.

The resulting data were analyzed using Design expert® 11 software to determine the effects of operating parameters in the hydrogen yield. The dependent variable used as a response parameter was hydrogen yield and the independent variables are time, pH, biomass concentration and temperature.

Table 4.2 The results of hydrogen yield at variable operating parameters

Std	Run	Factor 1	Factor 2	Factor 3	Factor 4	Response 1
		A:Time (hr)	B:pH	C:Biomass concentration (g/l)	D:Temperature (^{0}C)	H_2 (%)
1	15	1	5	5	20	37
2	18	4	5	5	20	30
3	5	1	9	5	20	36
4	24	4	9	5	20	30
5	1	1	5	10	20	40
6	3	4	5	10	20	35
7	13	1	9	10	20	45
8	25	4	9	10	20	30
9	29	1	5	5	35	40
10	12	4	5	5	35	35
11	11	1	9	5	35	40
12	28	4	9	5	35	35
13	8	1	5	10	35	50
14	30	4	5	10	35	45
15	22	1	9	10	35	45
16	16	4	9	10	35	40
17	**4**	**1**	**7**	**10**	**35**	**60**
18	6	4	7	7.5	27.5	50
19	21	2.5	5	7.5	27.5	42
20	23	2.5	9	7.5	27.5	40
21	26	2.5	7	5	27.5	50
22	27	2.5	7	10	27.5	55
23	19	2.5	7	7.5	20	45
24	9	2.5	7	7.5	35	55
25	17	2.5	7	7.5	27.5	55
26	20	2.5	7	7.5	27.5	55
27	2	2.5	7	7.5	27.5	55
28	14	2.5	7	7.5	27.5	55
29	7	2.5	7	7.5	27.5	55
30	10	2.5	7	7.5	27.5	50

4.2.1 The effect of time on hydrogen production

The longest time of the electrolysis process of seawater results a trend in declining the electric current through the electrode. And further it will results decreased in volume and rate production of hydrogen (Agustiningsih, no date). The decreasing of electric current through the equipment of electrolysis process may be assumed due to corrosion effect of electrodes (Agustiningsih, 2011). As the figure 4.1 below shows the production rate of hydrogen is slightly decreasing with time increase. This was assumed because of the corrosion effect of stainless-steel. When the time increase from one to four without the increment of other operating parameters the production rate is decreased from 50% to 42% percent. This indicates time and the production rate is inversely proportional. So, to increase the amount of hydrogen the time must be decreased.

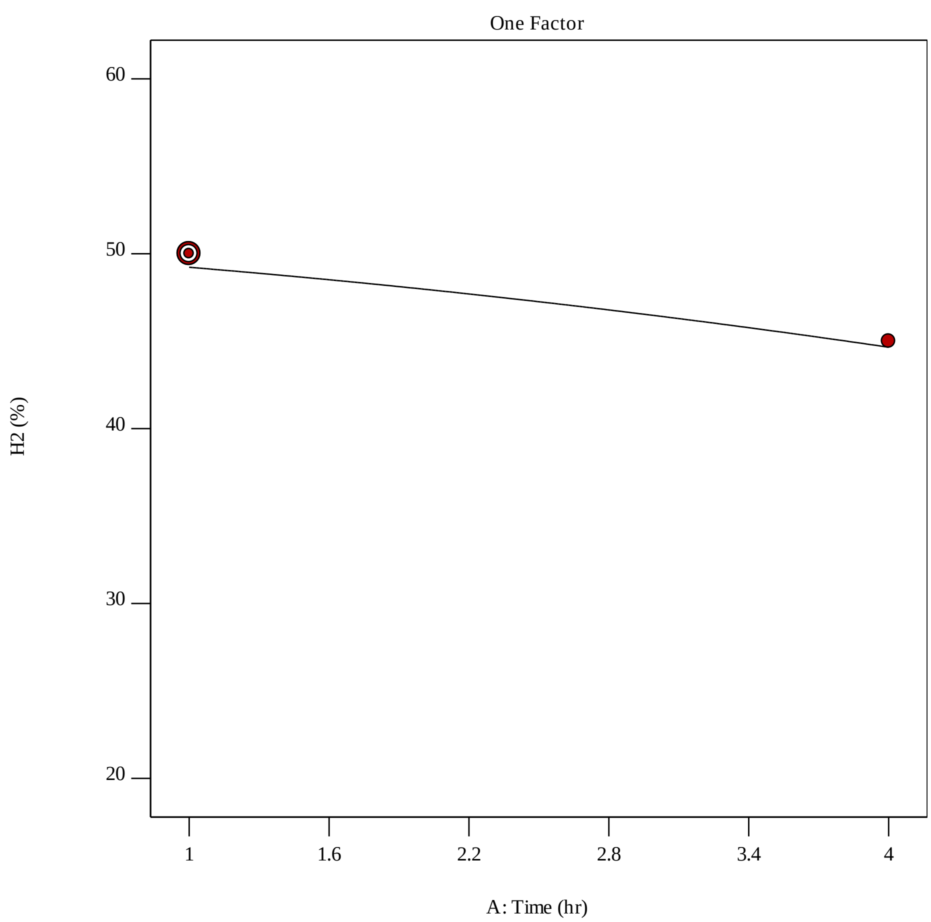

Figure 4.1The effect of time

4.2.2 The effect of pH on hydrogen production

The acidity or alkalinity of the sample may affect the response of a process in different ways. This is due to the interplay of several physicochemical phenomena influenced by pH. For pH range of 5.5 –5.7 and range of 3– 4 was analyzed. Based on the evaluation of maximum hydrogen production rate, the optimum operational pH range was about 5.5 – 5.7 (Khanal *et al.*, 2004). The neutral solution have been proven advantageous in several studies on the photo reforming of biomass-derived substrates, for the use of cellulose or lignocellulose feedstock's (Puga, 2016). Occasionally, (pH ≈ 6) has been claimed as the optimum situation for enhanced adsorption, and thus, increased H_2 evolution rates (Puga, 2016). In this study the figure 4.2 below there is a curved graph. This is due to the acidity, alkalinity and neutrality of the sample solution. Which is the due to the effect of pH. When the solution pH increase without the increment of other operating parameters the graph is slightly increasing from 5 to 7 and slightly decreasing from 7 to 9. At pH 7 the highest hydrogen was produced. Thus, at neutral solution the production rate increase.

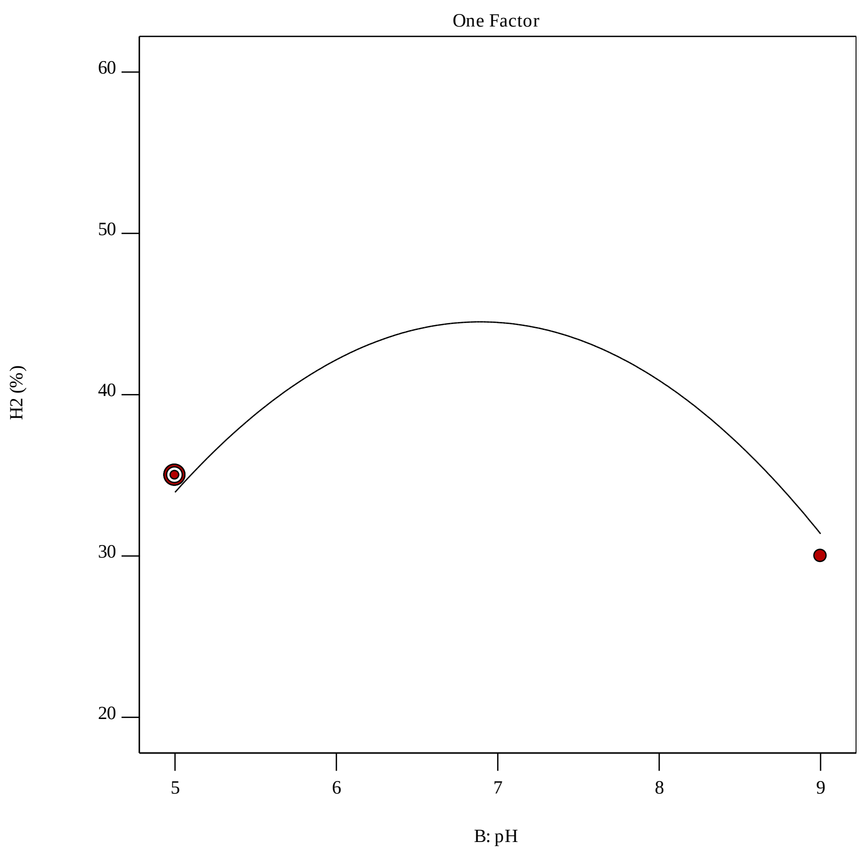

Figure 4.2 The effect of pH

4.2.3 The effect of biomass concentration on hydrogen production

Hydrogen production from photo catalytic water splitting (without biomass) is achievable, but at a very low quantum yield (~ 1.8%) due to a thermodynamic barrier and multi-electron transfer process, while quantum yield of photo biorefinary for H_2 production is achievable above 70% (Bowker, 2012). The figure 4.3 below shows the relationship between biomass concentration and the production rate of hydrogen. It shows the production rate of hydrogen increased with the concentration of biomass increase. This is because of biomass by its nature converted into liquid and gaseous biofuel through thermochemical process (Ibrahim, Kamarudin and Minggu, 2014). Thus, hydrogen production rate is directly proportional with biomass concentration on the sample solution. The biomass I used hereby was corn cob which have the better hydrolysis feedstock to maximize the production rate of hydrogen gas.

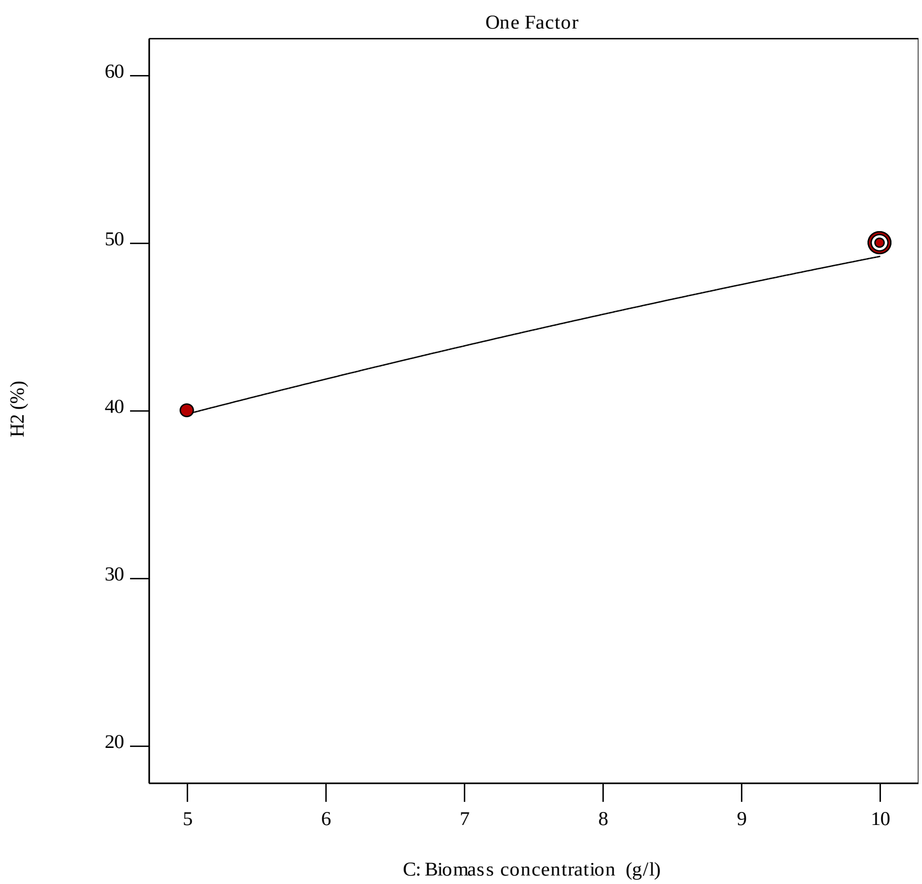

Figure 4.3 The effect of biomass concentration

4.2.4 The effect of temperature on hydrogen production

Temperature is also one of the influential parameter on the production of hydrogen from biomass. As the figure 4.4 below shows the production rate of hydrogen on y-axis increase with the increase of temperature on x-axis. When a moderate to high temperature ramp rate is used, a complex series of competing chemical reactions results in the conversion of biomass to a mixture of combustible gases including hydrogen (H_2) (Florin and Harris, 2007). H_2 production rates could be incremented by almost 50% when temperature going from 40^{o}C to 60°C (Puga, 2016). Thus, temperature and hydrogen production rate are directly proportional to each other. This is because of when temperature increase the molecule of water break down and it is changed into gas. In case of this the hydrogen gas production was maximized.

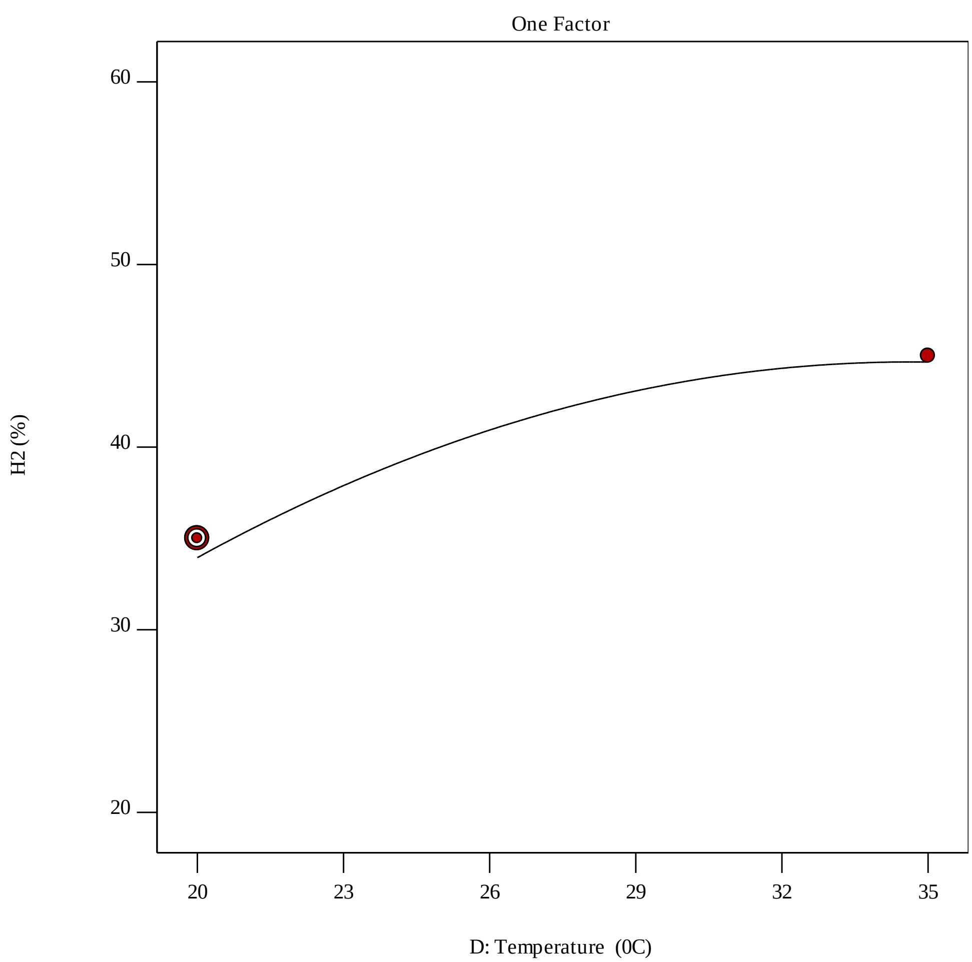

Figure 4.4 The effect of temperature

4.3 Optimization of operating parameters

The optimization of operating parameters is done by Response Surface Methodology, Design Experts version 11.1.2.0 application.

4.3.1 Build information

In this study the study type of response surface and the design type of central composite with the quadratic design model. And also there were 30 runs for three factors that depends on the number of factors and the number of blocks. In the case of CCD, the design should be divided always maintaining the axial part in a unique block (Sarabia and Ortiz, 2009). Since, the design have unique blocks central composite design method was used.

Table 4.3 Build information

File Version	11.1.2.0		
Study Type	Response Surface	**Subtype**	Randomized
Design Type	Central Composite	**Runs**	30
Design Model	Quadratic	**Blocks**	No Blocks
Build Time (ms)	8.00		

- **Factors**

There were four independent variables which are time, pH, biomass concentration and temperature with minimum value of 1hr, 5, 5g/l and 20^0C respectively and maximum of 4hr, 9, 10g/l and 35^0C respectively that were listed blow on table 4.4.

Table 4.4 Factors

Factor	Name	Unit	Type	Minimum	Maximum	Std. Dev.
A	Time	hr	Numeric	1.0000	4.00	1.18
B	pH		Numeric	5.00	9.00	1.58
C	Biomass concentration	g/l	Numeric	5.00	10.00	1.97
D	Temperature	^{0}C	Numeric	20.00	35.00	5.91

- **Responses**

There was one response that is hydrogen to be analyzed. The predicted value is in between 35% and 60%.

Table 4.5 Responses

Response	Name	Units	Observations	Analysis	Minimum	Maximum	Mean	SD	Model
R1	H_2	%	30	Polynomial	35	60	47.27	7.32	Quadratic

4.3.2 Model terms

Power calculations are performed using response type "Continuous" and parameters.

Standard errors should be similar to each other in a balanced design. Lower standard errors are better.

The ideal VIF value is 1.0. VIFs above 10 are cause for concern. VIFs above 100 are cause for alarm, indicating coefficients are poorly estimated due to multicollinearity.

Ideal R_i^2 is 0.0. High R_i^2 means terms are correlated with each other, possibly leading to poor models. The values of standard error, VIF and R^2 were shown on the table 4.6 below.

Table 4.6 Model term

Term	Standard Error*	VIF	R_i^2
A	0.2357	1	0.0000
B	0.2357	1	0.0000
C	0.2357	1	0.0000
D	0.2357	1	0.0000
AB	0.2500	1	0.0000
AC	0.2500	1	0.0000
AD	0.2500	1	0.0000
BC	0.2500	1	0.0000
BD	0.2500	1	0.0000
CD	0.2500	1	0.0000
A^2	0.6213	2.77895	0.6402
B^2	0.6213	2.77895	0.6402
C^2	0.6213	2.77895	0.6402
D^2	0.6213	2.77895	0.6402

4.3.3 Model summary statistics

In model summary focus on the model maximizing the Adjusted R^2 and the Predicted R^2, when I camper the Adjusted R^2 and the Predicted R^2 of other models displayed from design expert software with quadratic model, the value of quadratic model was maximum thus, the quadratic model is suggested because it fulfills the requirement**.**

Table 4.7 Model summary statistics

Source	Std. Dev.	R^2	Adjusted R^2	Predicted R^2	Remark
Linear	8.03	0.2462	0.1256	-0.0528	
2FI	9.10	0.2646	-0.1225	-1.5979	
Quadratic	**2.12**	**0.9685**	**0.9391**	**0.8375**	**Suggested**
Cubic	2.23	0.9837	0.9325	-0.2463	Aliased

4.3.4 Actual versus predicted value

The values in the report table 4.8 below are used to produce the normal probability graph that shows the accuracy of the predicted value. The graph was shown on the figure 4.5 below.

- **Run Order**: The randomized order for the experiments.
- **Actual Value**: The measured response data for this particular run.
- **Predicted Value**: The value predicted from the model, generated using the prediction equation, and includes block and center-point corrections, when they are part of the design.

Table 4.8 Actual versus predicted value

Run Order	Actual Value (%)	Predicted Value (%)
1	40	41.77
2	55	53.49
3	35	33.95
4	55	56.4
5	36	37.55
6	50	49.95
7	55	53.49
8	50	49.23
9	55	55.84
10	50	53.49
11	40	39.51
12	35	37.01
13	45	41.45
14	55	53.49
15	37	35.62
16	40	39.84
17	60	59.79
18	30	29.55
19	45	47.51
20	55	53.49
21	42	42.4
22	45	46.66
23	40	40.95
24	30	29.23
25	30	31.38
26	50	50.29
27	55	56.06
28	35	34.44
29	40	39.83
30	45	44.66

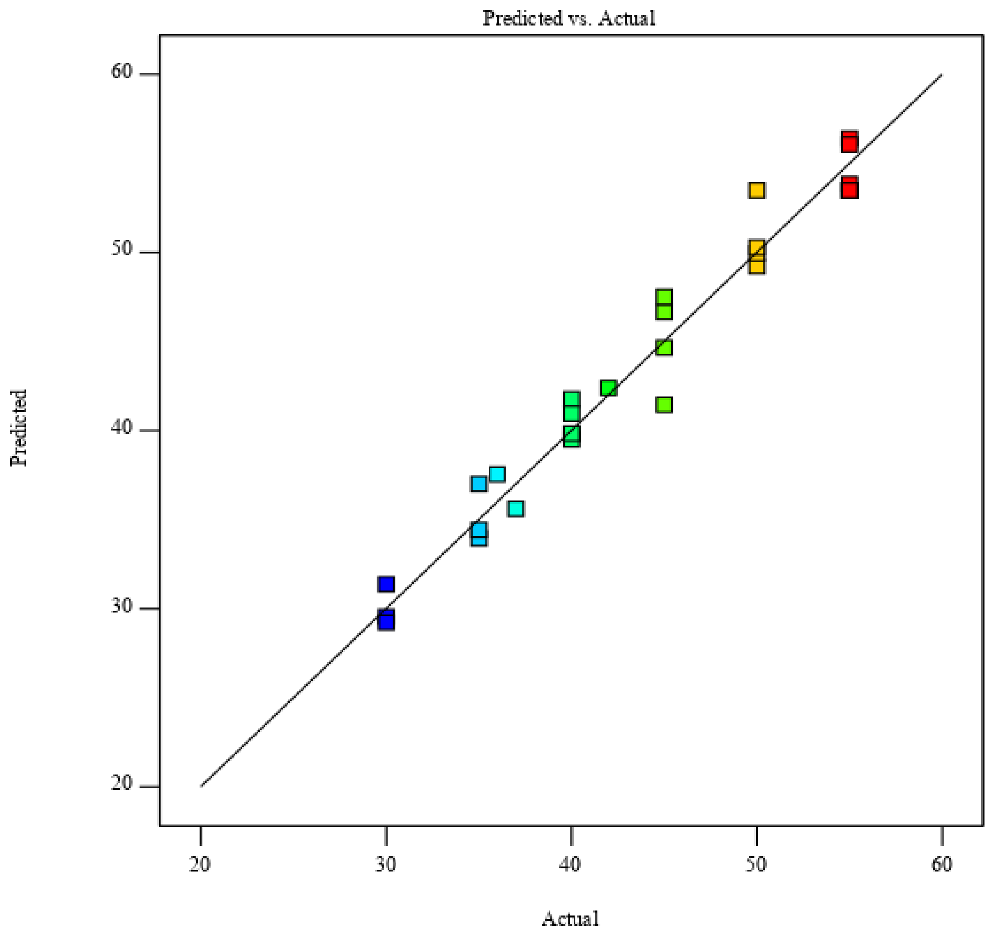

Figure 4.5 Normal probability plot

On the figure above 4.5 there are points below the diagonal line and above the diagonal line. Additionally there are points nearby the diagonal line from both sides. The points below the diagonal line are points below the predicted value and above the diagonal lines are above the predicted value. More of the points are nearby the diagonal line and on the diagonal line this shows that the prediction was more accurate.

4.3.5 Fit statistics

In the fitting statistics the coefficient of correlation R^2 approaches to unity; this indicates a close correlation between the experimental and the predicted values (Seikh *et al.*, 2019). Thus, on the table 4.9 below the R^2 value is 0.9685 which approaches to unity. So, there is a close correlation between the experimental and predicted value.

The Predicted R^2 of 0.8375 is in reasonable agreement with the Adjusted R^2 of 0.9391; i.e. the difference is less than 0.2.

Adeq Precision measures the signal to noise ratio. A ratio greater than 4 is desirable. In this study ratio of 18.127 indicates an adequate signal. This model can be used to navigate the design space. The table 4.9 below shows the fitting statistics and their value.

Table 4.9 Fit statistics

Statistics	Values
Std. Dev.	2.12
Mean	44.33
C.V. %	4.78
R^2	0.9685
Adjusted R^2	0.9391
Predicted R^2	0.8375
Adeq Precision	18.1269

4.3.6 Sequential model sum of squares [Type I]

In the sequential model sum of squares select the highest order polynomial where the additional terms are significant and the model is not aliased. In sum of squares the quadratic versus two factor interaction (2FI) was suggested because of its probability (p-value) less than 0.005 and both the models were not aliased which are quadratic and two factor interaction. Table 4.10 below shows the suggested sequential model sum of square.

Table 4.10 Sum of squares (type I)

Source	Sum of Squares	df	Mean Square	F-value	p-value	Remark
Mean vs Total	58963.33	1	58963.33			
Linear vs Mean	527.00	4	131.75	2.04	0.1192	
2FI vs Linear	39.38	6	6.56	0.0792	0.9976	
Quadratic vs 2FI	**1506.89**	**4**	**376.72**	**83.84**	**< 0.0001**	**Suggested**
Cubic vs Quadratic	32.50	8	4.06	0.8149	0.6131	Aliased
Residual	34.90	7	4.99			
Total	61104.00	30	2036.80			

4.3.7 ANOVA for the quadratic model

ANOVA for the production of hydrogen from corn cob was obtained from Design-Expert version 11.Factor coding is coded. Sum of squares is Type III – Partial.

The Model F-value of 32.96 implies the model is significant. There is only a 0.01% chance that an F-value this large could occur due to noise.

P-values less than 0.0500 indicate model terms are significant. In this case A, C, D, B^2, and D^2 are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve the model.

The Lack of Fit F-value of 1.12 implies the Lack of Fit is not significant relative to the pure error. There is a 48.00% chance that a Lack of Fit F-value this large could occur due to noise. Non-significant lack of fit is good.

Table 4.11 ANOVA for quadratic model

Source	Sum of Squares	df	Mean Square	F-value	p-value	Remark
Model	2073.27	14	148.09	32.96	< 0.0001	Significant
A-Time	186.89	1	186.89	41.59	< 0.0001	Significant
B-pH	9.39	1	9.39	2.09	0.1689	
C-Biomass concentration	150.22	1	150.22	33.43	< 0.0001	Significant
D-Temperature	180.50	1	180.50	40.17	< 0.0001	Significant
AB	5.06	1	5.06	1.13	0.3053	
AC	3.06	1	3.06	0.6816	0.4220	
AD	10.56	1	10.56	2.35	0.1460	
BC	5.06	1	5.06	1.13	0.3053	
BD	5.06	1	5.06	1.13	0.3053	
CD	10.56	1	10.56	2.35	0.1460	
A^2	0.2584	1	0.2584	0.0575	0.8137	
B^2	361.72	1	361.72	80.51	< 0.0001	Significant
C^2	0.2584	1	0.2584	0.0575	0.8137	
D^2	20.54	1	20.54	4.57	0.0494	Significant
Residual	67.40	15	4.49			
Lack of Fit	46.56	10	4.66	1.12	0.4800	not significant
Pure Error	20.83	5	4.17			
Cor Total	2140.67	29				

4.3.7.1 Coefficients in terms of coded factors

The coefficient estimate represents the expected change in response per unit change in factor value when all remaining factors are held constant. The intercept in an orthogonal design is the overall average response of all the runs. The coefficients are adjustments around that average based on the factor settings. When the factors are orthogonal the VIFs are 1; VIFs greater than 1 indicate multi-colinearity, the higher the VIF the more severe the correlation of factors. As a rough rule, VIFs less than 10 are tolerable. Table 4.12 below shows the coefficient estimate terms of coded factors.

Table 4.12 Coefficient in terms of coded factors

Factor	Coefficient Estimate	Df	Standard Error	95% CI Low	95% CI High	VIF
Intercept	53.49	1	0.6584	52.09	54.89	
A-Time	-3.22	1	0.4996	-4.29	-2.16	1.0000
B-pH	-0.7222	1	0.4996	-1.79	0.3427	1.0000
C-Biomass concentration	2.89	1	0.4996	1.82	3.95	1.0000
D-Temperature	3.17	1	0.4996	2.10	4.23	1.0000
AB	-0.5625	1	0.5299	-1.69	0.5670	1.0000
AC	-0.4375	1	0.5299	-1.57	0.6920	1.0000
AD	0.8125	1	0.5299	-0.3170	1.94	1.0000
BC	-0.5625	1	0.5299	-1.69	0.5670	1.0000
BD	-0.5625	1	0.5299	-1.69	0.5670	1.0000
CD	0.8125	1	0.5299	-0.3170	1.94	1.0000
A^2	-0.3158	1	1.32	-3.12	2.49	2.78
B^2	-11.82	1	1.32	-14.62	-9.01	2.78
C^2	-0.3158	1	1.32	-3.12	2.49	2.78
D^2	-2.82	1	1.32	-5.62	-0.0089	2.78

4.3.7.2 Final equation in terms of coded factors

The equation in terms of coded factors can be used to make predictions about the response for given levels of each factor. By default, the high levels of the factors are coded as +1 and the low levels are coded as -1. The coded equation is useful for identifying the relative impact of the factors by comparing the factor coefficients. The relationship between the factors and the response measures are modeled by quadratic regression. The regression equations formed by performing a backward elimination process. This procedure automatically reduces the terms that are not significant (Seikh *et al.*, 2019). However, the production of hydrogen depends on significant terms only.

$$H_2 = +53.49 - 3.22A + 2.89C + 3.17D - 11.82B^2 - 2.82D^2 \quad (23)$$

4.3.8 3D Expression of operating parameters on hydrogen production

Surface plots are diagrams of three-dimensional data. Rather than showing the individual data points, surface plots show a functional relationship between a designated dependent variable (Y), and two independent variables (X and Z). The plot is a companion plot to the contour plot (Statistical, Ncss and Reserved, no date). These plots are useful in regression equation analysis for viewing the relationship among a dependent and two independent variables (Statistical, Ncss and Reserved, no date). The 3D surface graphs have a curvilinear profile corresponding to the quadratic model fitted. This means all plot of interactions for surface roughness have a significant effect (Seikh *et al.*, 2019). In this study also most of the graph shows the curvilinear graph this shows that most of the terms are significant.

On the figure 4.6 below the interaction effect of time and pH on hydrogen production was studied when time decreases from 4hr to 1hr and pH increases from 5 to 7 the color of the surface plot slightly changed from green to yellowish and then after to red color. Since green color indicates the lowest production rate and red color indicates highest one so the production rate of hydrogen was increased. Additional, when time decrease from 4hr to 1hr and pH increase from 7 to 9 the color of surface plot slightly changed from red to yellowish and then after to green color this indicates that the production rate was decreased.

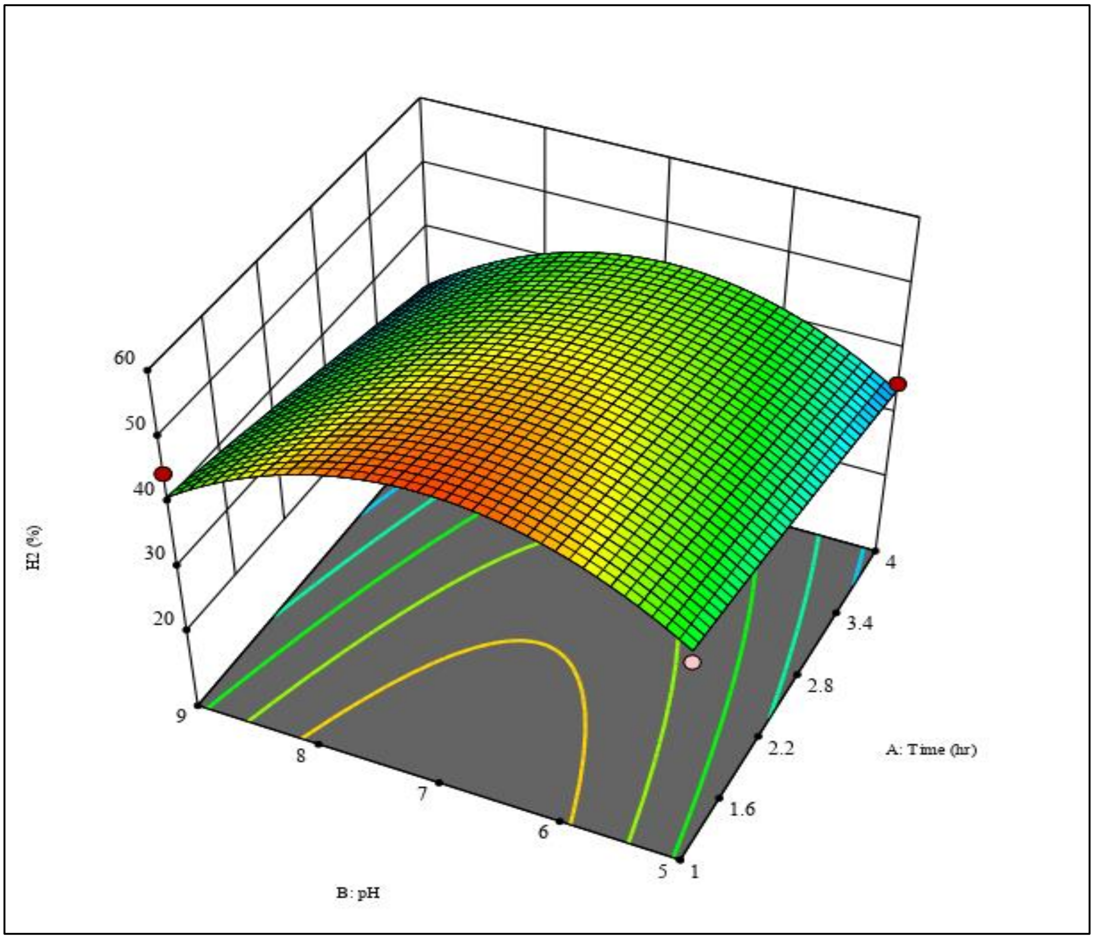

Figure 4.6 Effect of time versus pH

On the figure 4.7 below the interaction effect of time and biomass concentration on hydrogen production was studied. When time decrease from 4hr to 1hr and biomass concentration increase from 5g/l to 10g/l the color of surface plot changed from bluish to green color. Since, the blue color indicates lowest level of production and the green color indicates highest production rate than blue color so the production rate of hydrogen was increased by decreasing time and by increasing the biomass concentration and the reverse is also true.

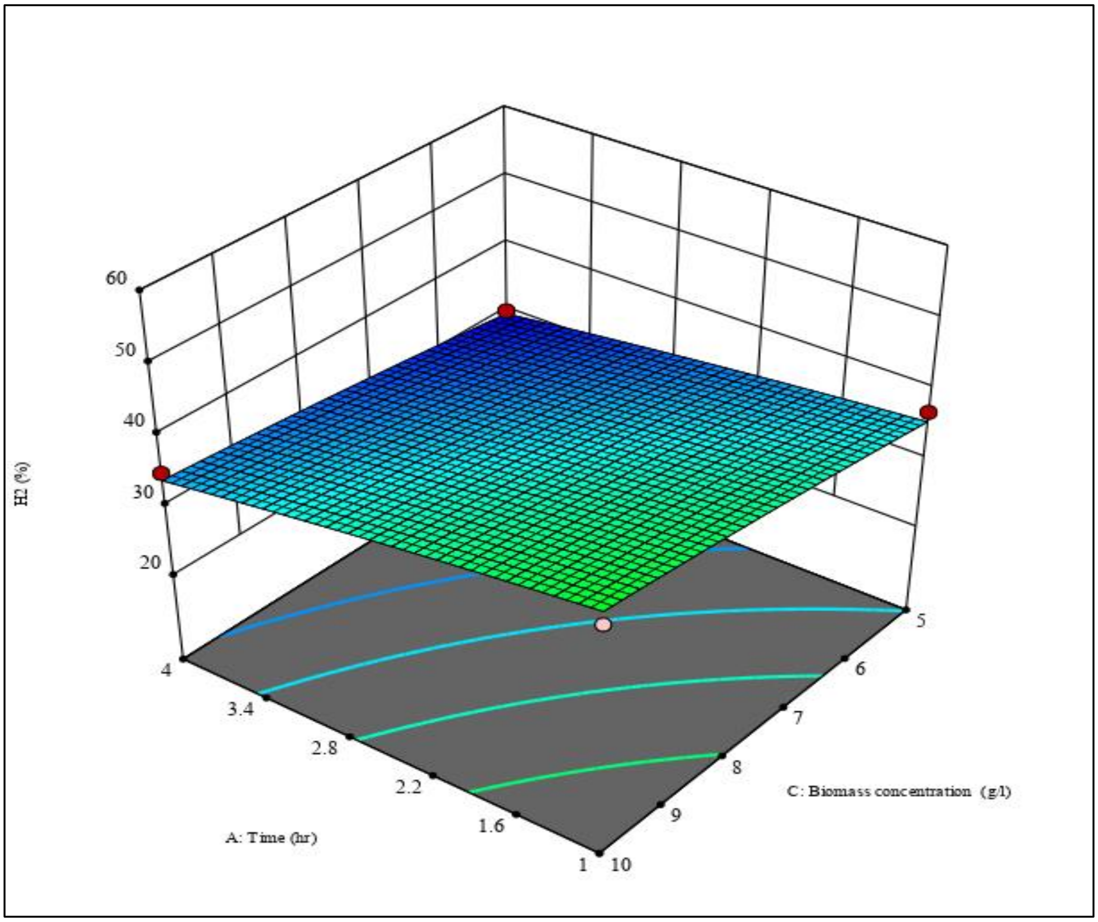

Figure 4.7 Time versus Biomass concentration

The figure 4.8 below shows the interaction effect of temperature and time on the production rate of hydrogen. When temperature increases from 20^0C to 35^0C and time decreased from 4hr to 1hr the color of the surface plot slightly changed from bluish to greenish then after to yellowish color. Since, the bluish color indicates the lowest and yellowish indicates the highest one. The production rate of hydrogen increased when temperature increased and time decreased and the reverse is also true.

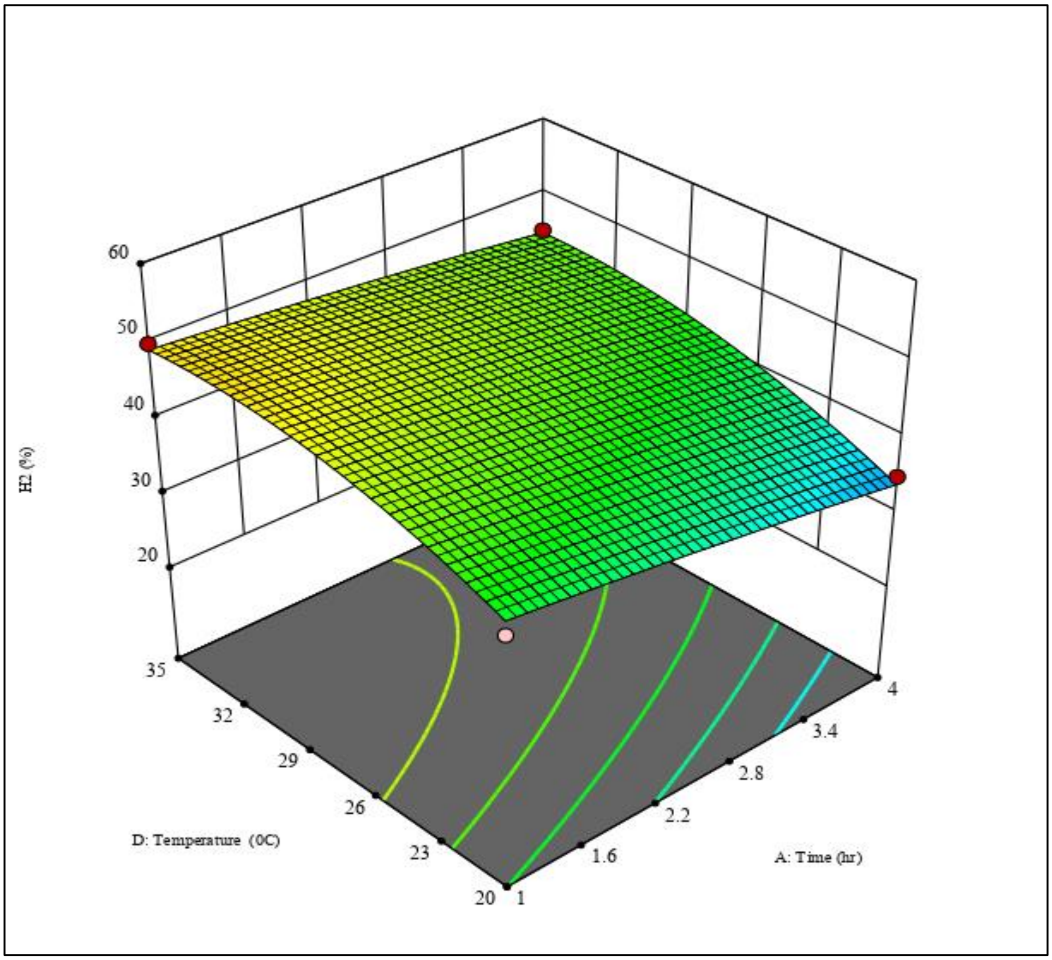

Figure 4.8 Temperature versus Time

On the figure 4.9 below the interaction effect of pH and biomass concentration on the production rate of hydrogen. When, the biomass concentration increased from 5g/l to 10g/l and pH increased from 5 to 7 the color of the surface plot slightly changed from blue to bluish and then after to the green color. Additionally, when pH increased from 7 to 9 the reverse color change happen. As I discussed before the blue color indicates the lowest level of production rate and the green color indicates the highest level. So the production rate increased at pH level of 7 and biomass concentration increased.

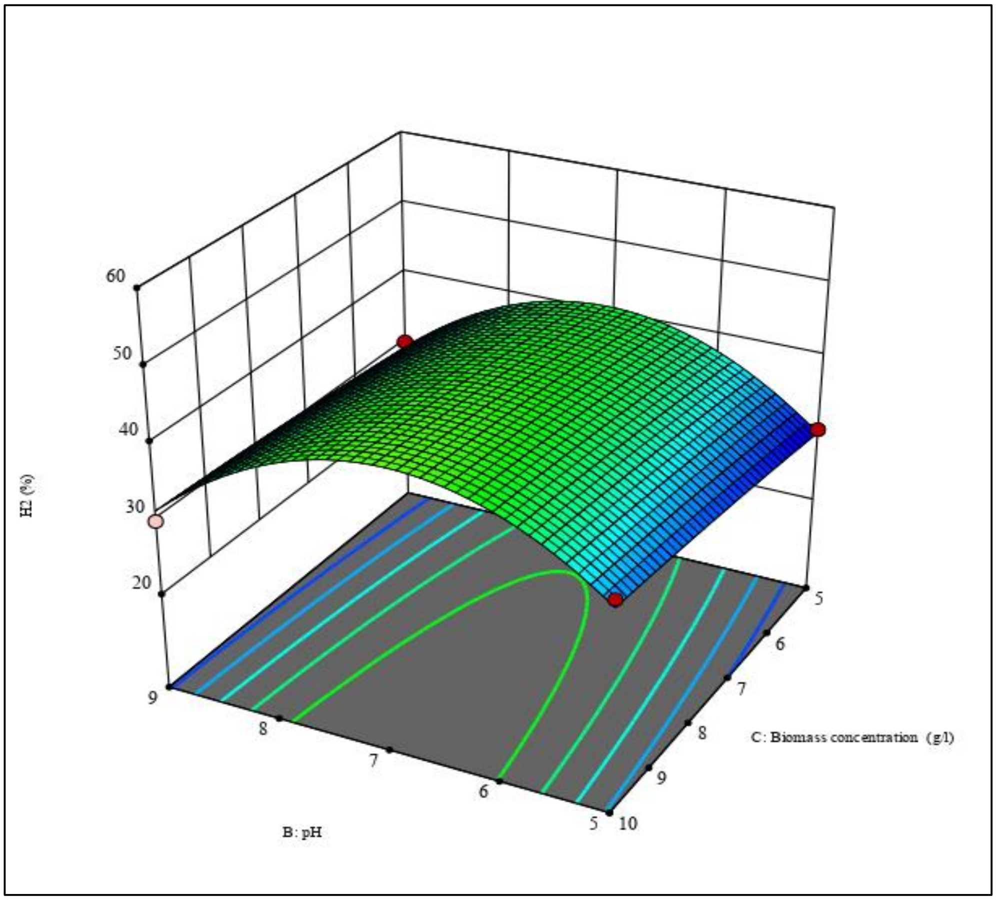

Figure 4.9 Biomass concentration versus pH

Figure 4.10 below shows the interaction effect of pH and temperature on the hydrogen production rate. When pH increased from 5 to 7 and temperature increased from 20^0C to 35^0C the color of surface plot slightly changed from green to yellow and then after to red color. As I discussed before the green color indicates the lowest one and the red indicates the highest. Thus, the production rate increased when pH increased from 5 to 7 and temperature increase. On the other side, when temperature increased from 20^0C to 35^0C and pH increased from 7 to 9 the color of surface plot changed from red to yellow then after to green. This indicates the production rate decreased when pH increased from 7 to 9 and temperature increased. At the neutral solution when temperature increased there was maximum production rate.

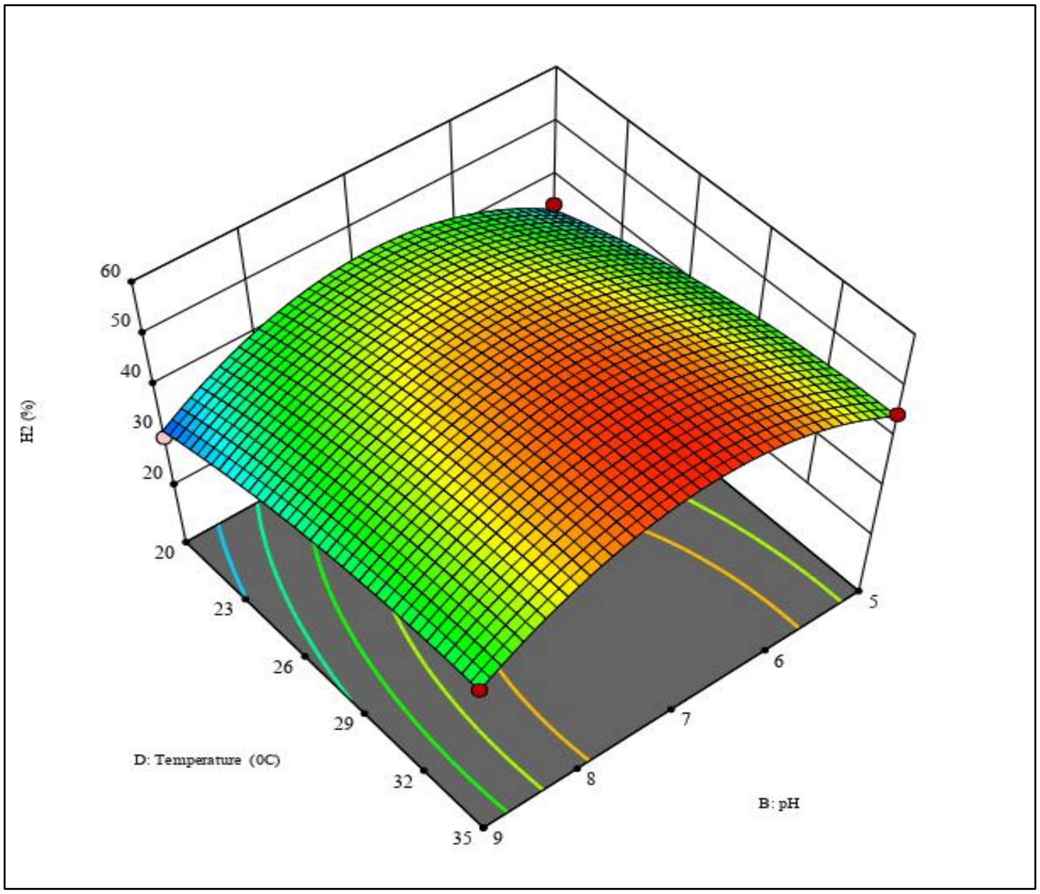

Figure 4.10 Temperature versus pH

The figure 4.11 below shows the interaction effect of temperature and biomass concentration on the hydrogen production rate. When temperature increased from 20^0C to 35^0C and biomass concentration increased from 10g/l to 5g/l the color of surface plot slightly changed from bluish to greenish. As I discussed before, the bluish color indicates the lowest production rate and the greenish color indicates highest. Thus, the production rate of hydrogen was increased when temperature and biomass concentration increased.

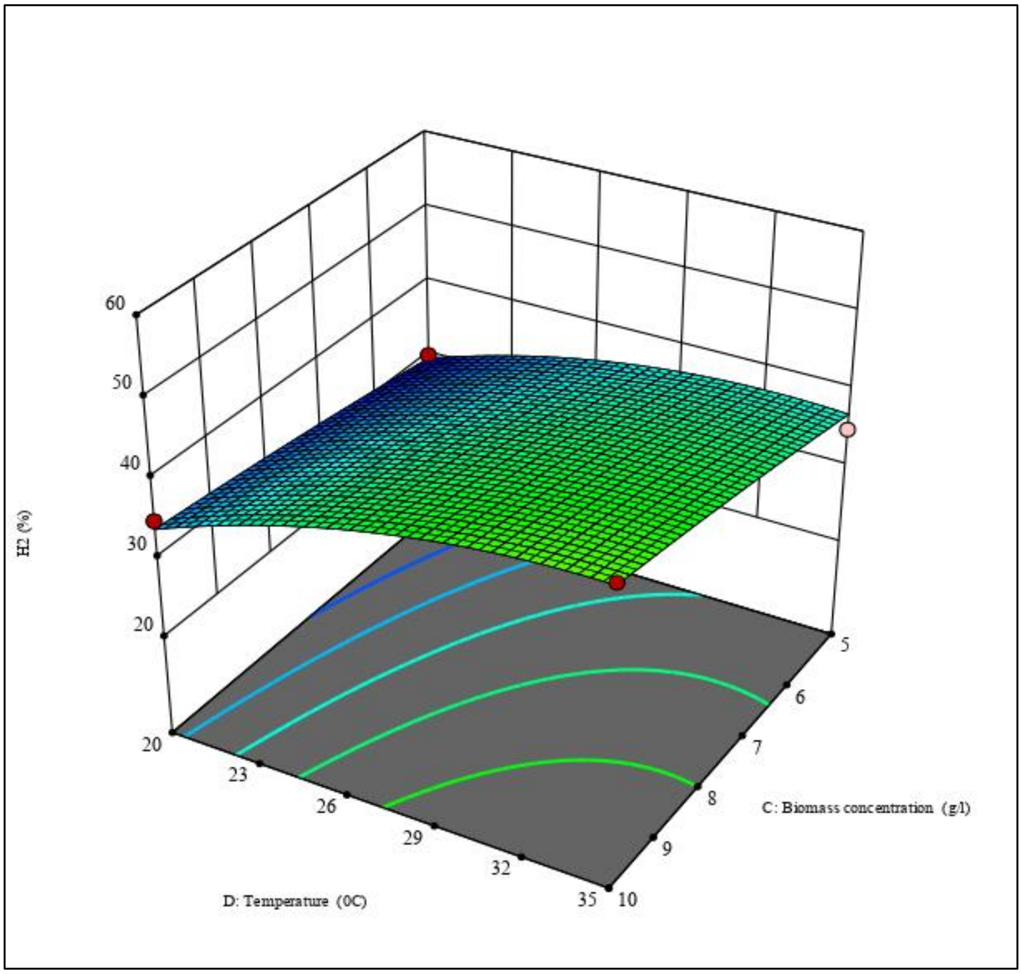

Figure 4.11Temperature versus Biomass concentration

4.3.9 Validations of operating parameters on hydrogen production

Since, the effect of all operating parameters was studied above there were criteria to select confirmation location of optimum production rate. According to the effect of operating parameters on the production the criteria to select confirmation location were minimizing time, pH in range, maximizing biomass concentration and also maximizing the solution temperature. Table 4.13 below shows the selection criteria to select the confirmation location.

Table 4.13 Criteria to select the confirmation point

Name	Goal	Lower Limit	Upper Limit	Lower Weight	Upper Weight
A:Time	Minimize	1	4	1	1
B:pH	Is in range	5	9	1	1
C:Biomass concentration	Maximize	5	10	1	1
D:Temperature	Maximize	20	35	1	1
H_2	Maximize	30	60	1	1

4.3.10 Confirmation and confirmation Location

The table 4.14 and 4.15 below shows that the confirmed values and the confirmation location from the solution. The optimum hydrogen was **59.7922%** at the optimum time of **1**hr, pH of **6.8662**, biomass concentration of **10**g/l, and temperature of **35**^{0}C. The criteria to confirm this location was according to the effects of different operating parameters. According to their effect on the quantum yield of hydrogen, the confirmation was by minimizing time, pH in the interval, maximizing biomass concentration and temperature. As table 4.14 below shows the selected yield which was selected by maximizing the H_2 response.

Table 4.14 Confirmation

Solution 2 of 100 Response	Predicted Mean	Predicted Median	Observed	SD Dev	SE Pred	95% PI low	95% PI high
H_2	59.7922	59.7922	30	2.1197	2.38335	54.7122	64.8722

Table 4.15 Confirmation location

Time	pH	Biomass concentration	Temperature
1	6.8662	9.99998	35

CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

5.1 CONCLUSIONS

Biomass have been changed over under fluid and vaporous biofuels through diverse methodology. In this study corn cob was used to produce hydrogen by photo electrochemical process. 4 kg of corn cobs has been collected in bag from local available agricultural lands of asendabo and has been taken to Jimma University, jimma institute of technology environmental engineering laboratory. Then the corn cobs has been crushed to fine size. These particles was sieved to 2mm in diameter by mesh sieve. After sieving the sample the solution of biomass with water was prepared from 2litters of pure water and at different level of operating parameters. Then stir with stirrer to mix the solution. Then after a direct current (DC) was applied to maintain the electricity balance and electrons flow from the negative terminal of the DC source to the cathode at which the electrons are consumed by hydrogen ions (protons) to form hydrogen. Biomass was oxidized in anode, hydroxide ions (anions), give away electrons and these electrons return to the positive terminal of the DC source. When light immersed into the solution the solution temperature increased this result expansion speedup the redox response.

Moisture content of corn cob beyond 20% would create difficulties, however in this study the moisture content of sample corn cob was (9.2%) which is desirable for the process to take place. The corn cob used in this study was characterized by relatively high volatile matter content (79.4%). The higher the volatile content of the biomass, the better rate because of the biomass yield up on carbonization. The ash content (2.4%) is less than 6% which indicates the corn cob is desirable for the process and also the fixed carbon content of corn cob was 9% which is enough. Hydrogen yield increases with time decrease which indicates the better hydrogen production when the time decrease and in the neutral solution with maximum biomass concentration and maximum temperature. Optimization of operating parameters is done by Design Experts version 11.1.2.0 with the study type of response surface and the design type is central composite with the quadratic design model. So, the optimum hydrogen **(59.7922%)** was located at time, pH, biomass concentration and temperature of **1hr**, **6.8662**, **10g/l** and **35^0C** respectively.

5.2 RECOMMENDATIONS

Based on the current investigation the following recommendations are forwarded:

- Different types of biomass, which are pollutant in the environment but they are the sources of energy were recommended to increase the yield of H_2 gas.
- Optimization of inter electrode distance were recommended to maximize the yield of H_2 gas from corn cobs.
- Different photo anodes were recommended to use, instead of stainless steel in this study to maximize the yield of H_2 gas.
- Chemical properties of corn cob characterization was recommended to determine their effect on the production rate.
- Optimization of the power consumption have to be carried out to minimize the cost of power consumption

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APPENDIX 1

Starting Points

Number of Starting Points: 125

Time (hr)	pH	Biomass concentration (g/l)	Temperature(^{0}C)
2.5	7	10	27.5
2.5	7	5	27.5
1	7	7.5	27.5
4	5	10	35
2.5	7	7.5	27.5
1	5	5	20
2.5	7	7.5	20
4	9	10	20
4	5	10	20
1	9	5	35
2.5	9	7.5	27.5
4	9	5	35
4	5	5	35
1	5	10	20
2.5	5	7.5	27.5
1	5	5	35
1	9	5	20
1	5	10	35
4	7	7.5	27.5
1	9	10	20
4	9	10	35
2.5	7	7.5	35
4	9	5	20
4	5	5	20
1	9	10	35

1.35465	8.17	6.65669	31.9328
3.42336	7.45582	7.07182	31.9522
1.69855	8.95236	9.28074	27.0681
3.75753	6.10705	7.94525	23.1898
2.21892	7.49006	6.45802	21.2869
2.185	6.98785	7.7073	23.9193
3.74373	6.34692	8.40897	24.0897
3.34261	6.09789	8.02916	22.4723
3.9983	5.94242	9.55425	24.3919
3.15261	8.91347	5.80368	25.2231
3.42345	8.56471	9.93995	28.0361
1.17924	6.40384	8.15995	22.3712
2.42493	7.48555	8.68796	34.5093
3.50752	6.8068	5.62138	22.4733
3.35602	8.70056	9.0297	31.0406
2.94737	7.22862	5.96417	26.9851
1.40953	5.49217	5.11641	27.9196
2.05525	6.18161	9.35104	32.6211
2.26958	8.14375	7.83301	33.0911
2.6019	6.68831	6.81797	21.6285
3.27284	6.77127	8.85003	23.0334
3.95082	8.35751	8.71457	22.3867
1.67261	8.80651	5.44112	32.8745
2.81017	8.40251	8.80353	22.2854
2.62106	6.81712	9.97684	30.2738
1.03562	6.73114	9.60071	32.8143
3.03736	8.66344	5.86084	26.0908
1.19534	7.63635	8.60246	34.867
3.4523	8.55631	5.44677	22.6899
1.65797	6.75455	7.6598	26.9649

2.28804	6.57694	5.69978	33.2841
1.06458	6.22771	5.05736	31.3076
2.07298	5.67199	5.86672	20.2164
3.91168	5.17751	8.42235	24.8268
2.33825	8.46135	5.2932	27.8341
1.81326	5.02902	9.21187	29.1851
2.3251	6.64198	6.86944	26.1601
3.27843	8.90947	9.85705	28.801
1.85122	6.1933	5.75933	22.2046
3.21827	8.07239	9.90015	26.7495
3.83548	6.93256	9.86717	31.76
1.59423	8.27026	5.04465	20.0428
2.63545	7.74151	7.21954	21.1535
1.59803	6.25367	5.34744	26.1351
3.57705	8.13191	9.99613	33.3751
3.69892	7.90905	5.6562	21.8139
3.93127	5.33204	8.34532	28.1492
2.30557	6.85602	7.26191	21.6233
3.39937	8.12804	7.84486	27.002
1.98813	5.10128	5.39734	25.697
1.06975	5.66578	5.93347	24.4911
2.60776	7.85595	8.87714	28.5469
3.43148	8.00942	6.73108	25.0408
3.03354	6.55657	9.04055	25.6065
1.04465	8.22366	5.54573	27.0175
1.43993	7.55568	6.36699	29.176
2.95811	5.92783	7.89892	33.4429
2.96636	5.99629	8.91127	28.2506
2.17175	5.99919	9.35705	21.3615
3.98162	5.74346	5.66916	26.9938

2.21209	6.28121	7.49144	24.1004
2.79575	5.3221	5.70059	24.2095
2.54332	8.88901	9.72192	29.3778
3.46242	7.3291	7.89145	28.6454
1.14402	6.14956	6.44022	25.5432
2.58604	6.63671	8.42707	20.7008
1.17886	8.105	7.3341	34.0598
2.1421	8.44322	8.1538	25.096
3.9968	8.08987	8.51417	29.0649
2.24668	6.72196	6.32347	22.402
2.03102	5.02313	8.10778	30.1832
3.46278	7.50075	9.77743	34.7888
1.75709	5.72039	7.36644	27.4199
2.91787	8.15075	6.94356	28.394
2.09109	5.82418	6.42496	26.6264
2.99572	8.6462	5.34089	24.6666
1.00452	8.05962	9.43111	25.0179
1.46023	6.39561	7.26834	30.901
3.97796	7.51925	9.88933	34.8993
2.59572	5.25241	7.49299	32.0606
3.81307	6.84526	9.53049	26.0516
1.36116	8.09961	7.23618	33.4564
2.3398	5.01467	8.21887	23.6364
3.00755	6.14766	9.52711	21.2896
1.43507	7.74064	6.7955	24.077
1.684	7.96597	6.64031	20.8481
1.70843	6.97651	7.89791	29.2051
2.11589	7.18165	6.9164	22.6588
3.88138	7.02846	8.48186	33.4068
2.26652	6.7834	5.95917	21.1991

3.84616	8.28635	7.49687	21.4714
1.8065	5.6342	9.12655	20.4917
3.90057	6.83831	9.88073	34.215
2.94063	8.01579	5.33831	33.6534
3.72233	7.94385	9.77257	31.3445
1.08018	6.82567	7.62684	31.0588
2.90954	7.41301	5.48208	27.3183
1.16813	8.4558	8.4503	25.0243
1.68504	5.04949	7.66149	31.5727
1.24456	7.48895	5.73242	32.2325

APPENDIX 2

Solutions

100 Solutions found

№	**Time (hr)**	**pH**	**Biomass concentration (g/l)**	**Temperature (^0C)**	**H_2**	**Desirability**	**Remark**
1	**1.000**	**6.865**	**10.000**	**35.000**	**59.792**	**1.000**	**Selected**
2	1.000	6.921	10.000	35.000	59.791	1.000	
3	1.000	6.951	10.000	35.000	59.783	1.000	
4	1.000	6.819	10.000	35.000	59.779	1.000	
5	1.001	6.841	10.000	35.000	59.785	1.000	
6	1.000	6.981	10.000	35.000	59.770	1.000	
7	1.000	6.796	10.000	35.000	59.767	1.000	
8	1.003	6.882	10.000	35.000	59.790	1.000	
9	1.001	6.770	10.000	35.000	59.749	1.000	
10	1.000	7.018	9.999	35.000	59.744	1.000	
11	1.000	7.051	9.999	35.000	59.718	0.999	
12	1.000	6.727	10.000	34.976	59.721	0.999	
13	1.000	6.986	10.000	34.940	59.787	0.999	
14	1.000	6.684	10.000	35.000	59.667	0.999	
15	1.000	6.875	9.980	35.000	59.766	0.999	
16	1.000	6.657	10.000	35.000	59.632	0.999	
17	1.000	6.637	10.000	35.000	59.603	0.998	
18	1.018	6.877	10.000	35.000	59.767	0.998	
19	1.000	6.937	9.971	35.000	59.747	0.998	
20	1.000	7.188	10.000	35.000	59.534	0.998	
21	1.014	6.932	9.999	34.926	59.792	0.998	
22	1.000	6.575	10.000	35.000	59.499	0.998	
23	1.000	6.899	9.955	35.000	59.731	0.997	

24	1.000	6.993	9.989	34.864	59.792	0.997	
25	1.000	6.828	9.955	35.000	59.718	0.997	
26	1.000	7.045	10.000	34.804	59.788	0.997	
27	1.021	6.685	9.989	35.000	59.623	0.996	
28	1.000	7.029	9.992	34.795	59.792	0.996	
29	1.040	6.925	10.000	35.000	59.732	0.996	
30	1.040	6.732	10.000	35.000	59.662	0.996	
31	1.005	6.487	10.000	35.000	59.304	0.995	
32	1.000	6.461	10.000	35.000	59.248	0.995	
33	1.000	6.791	9.928	35.000	59.661	0.995	
34	1.000	7.356	10.000	35.000	59.156	0.995	
35	1.000	6.767	9.955	34.812	59.742	0.994	
36	1.000	6.753	9.914	34.997	59.615	0.994	
37	1.063	6.921	10.000	35.000	59.699	0.994	
38	1.063	6.782	10.000	35.000	59.668	0.994	
39	1.038	7.002	9.959	35.000	59.644	0.994	
40	1.061	6.754	10.000	34.982	59.656	0.993	
41	1.069	6.852	9.999	35.000	59.686	0.993	
42	1.034	7.288	10.000	35.000	59.277	0.993	
43	1.000	6.343	10.000	34.999	58.907	0.992	
44	1.000	6.410	9.966	35.000	59.060	0.992	
45	1.000	6.669	9.890	35.000	59.488	0.992	
46	1.000	7.119	10.000	34.508	59.792	0.992	
47	1.001	6.283	10.000	35.000	58.700	0.991	
48	1.000	7.518	10.000	35.000	58.635	0.990	
49	1.000	6.822	9.832	35.000	59.540	0.989	
50	1.004	7.535	10.000	35.000	58.562	0.989	
51	1.000	6.641	10.000	34.348	59.792	0.989	
52	1.004	6.234	10.000	35.000	58.515	0.989	
53	1.000	7.167	9.999	34.248	59.792	0.987	

54	1.103	7.238	10.000	35.000	59.280	0.987	
55	1.006	6.624	10.000	34.208	59.792	0.986	
56	1.096	7.340	10.000	34.994	59.052	0.986	
57	1.000	6.288	10.000	34.592	58.834	0.985	
58	1.000	7.671	10.000	35.000	57.999	0.985	
59	1.028	7.377	9.984	34.510	59.188	0.984	
60	1.000	7.732	10.000	35.000	57.708	0.982	
61	1.000	6.578	10.000	33.931	59.782	0.982	
62	1.000	7.750	10.000	35.000	57.618	0.981	
63	1.035	7.054	9.743	35.000	59.303	0.980	
64	1.217	6.911	10.000	35.000	59.470	0.979	
65	1.000	7.271	10.000	33.756	59.711	0.978	
66	1.000	6.571	9.668	35.000	59.004	0.976	
67	1.000	7.374	9.997	33.753	59.450	0.976	
68	1.166	6.293	10.000	35.000	58.509	0.975	
69	1.000	7.328	10.000	33.382	59.652	0.971	
70	1.137	7.053	10.000	33.950	59.791	0.971	
71	1.268	7.372	10.000	35.000	58.688	0.968	
72	1.000	6.327	9.500	35.000	58.103	0.960	
73	1.000	7.434	10.000	32.801	59.441	0.958	
74	1.286	6.104	10.000	34.943	57.595	0.956	
75	1.000	7.107	9.328	35.000	58.700	0.956	
76	1.002	5.908	10.000	33.655	57.230	0.955	
77	1.301	6.060	10.000	35.000	57.349	0.953	
78	1.003	5.553	10.000	35.000	54.501	0.952	
79	1.000	6.759	9.623	33.288	59.624	0.950	
80	1.000	6.236	9.316	35.000	57.482	0.945	
81	1.000	6.267	10.000	32.153	59.096	0.943	
82	1.000	7.026	9.431	33.290	59.386	0.938	
83	1.001	8.407	10.000	35.000	53.008	0.937	

84	1.000	5.641	9.618	35.000	54.576	0.934	
85	1.000	6.757	9.166	33.750	58.879	0.928	
86	1.000	8.288	9.661	35.000	53.597	0.927	
87	1.000	5.750	10.000	32.402	56.341	0.925	
88	1.000	8.257	9.411	35.000	53.522	0.914	
89	1.674	5.977	9.998	35.000	56.395	0.910	
90	1.000	7.879	9.999	30.759	57.546	0.902	
91	1.000	5.402	10.000	32.228	53.600	0.896	
92	1.000	7.284	8.506	35.000	57.178	0.894	
93	1.000	6.109	8.632	35.000	55.834	0.891	
94	1.000	5.897	10.000	30.326	57.121	0.890	
95	1.000	5.437	10.000	31.114	53.844	0.878	
96	1.000	8.647	8.922	35.000	49.318	0.844	
97	2.221	7.735	10.000	35.000	55.510	0.844	
98	1.000	5.039	9.465	33.224	49.116	0.843	
99	1.000	5.057	9.078	32.792	48.724	0.813	
100	2.238	8.491	10.000	35.000	49.848	0.791	