Production of Hydrogen Gas from Biomass

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Abstract. Hydrogen, in contemporary times, is looked forward to being a great fuel for a wide range of applications. Production of hydrogen for further use as a fuel comprises various methodologies considering the raw material, temperature, pressure implications, and availability of the desired reactants. This project involves hydrogen production using the enzymatic methodology that theoretically involves the utility of Rhodobacter spheroids for biomass fermentation, mostly including canteen waste or food waste of other types. The biomass used for this project mainly comprises vegetables and fruit peels. As an alternative, on an experimental basis, the project undertook the use of Saccharomyces cerevisiae (yeast) for this process. The output of this project would be analyzed using various techniques to understand the composition of the output.

INTRODUCTION

The twentieth century has witnessed the entire world progress across various domains and bring about the technological and industrial development in different fields. The industrial revolution has impacted thousands of lives especially in the developing nations like India and the energy sector here has been one of its important pillars. The energy sector has a lion's share in driving a country's economy. According to some reports, with increasing industrialization and injection of revolutionary ideas into the market, global energy consumption continues to escalate. It is forecasted that the consumption levels will shoot up by 50% to 100% by 2050. It becomes very important for the mankind to explore and research energy sources for the better future. 'Hydrogen energy carrier' is one of the booming fields of research & development for scientists across the globe. Hydrogen on reaction with atmospheric oxygen gives water as product releasing large amount of heat. When the data of energy released by combustion of various fuels like LPG, methane etc. is compared we come to a conclusion that on mass for mass basis dihydrogen releases about 3 times energy than petrol. The reaction product is non-polluting as well which gives usage of hydrogen for power generation an upper hand. This makes it environment friendly. Sometimes due to presence of N2 as impurity along with dihydrogen, oxides of dinitrogen can be produced as pollutant by products. However, this can be restricted by injection of water to lower the temperature so that reaction between N2 and H2 does not take place. This simple combustion reaction is integrated into a fuel cell to revolutionize the energy sector which converts the heat released into electrical energy.

If hydrogen is to become a fundamental energy source for electrical power generation, as well as a transportation fuel, it is important to discover novel generation pathways to meet the increase in demand. One of the promising ways to produce hydrogen is to use biomass for the process. This is because biomass is abundant, clean and renewable.

LITERATURE REFERENCES

As a source of renewable energy, the generation of biofuels from agricultural waste, such as ethanol and hydrogen, is receiving attention. A by-product of the pineapple processing industry, pineapple peel makes up between 29 and 40 per cent (w/w) of the total pineapple weight. Pineapple peel underwent a 4-hour preparation with water and heat at 100°C to produce 36.252.87% per cent cellulose. Then, 0.5% (w/w) Aspergillus niger (Sigma) cellulase was added for enzymatic hydrolysis. After 24 hours of incubation, the maximal sugar production (34.03 1.30 g/L) was attained. Saccharomyces cerevisiae TISTR 5048 and Enterobacter aerogenes TISTR 1468 produced ethanol and hydrogen using the enzyme hydrolysate as the fermentation medium without adding any nutrients. Following the elimination of hydrogen generation by S. cerevisiae, the highest ethanol yield (9.69 g/L) was attained. [1]

This study utilized the principle that the bacteriorhodopsin (BR) produced by *Halobacterium* salinarum could increase the hydrogen production of Rhodobacter sphaeroides. *H.* salinarum are co-cultured with *R.* sphaeroides to determine the impact of purple membrane fragments (PM) on *R.* sphaeroides and improve its hydrogen production capacity.In this study, low-salinity in 14 % NaCl domesticates *H* salinarum. Then, 0–160 nmol of different concentration gradient groups of bacteriorhodopsin (BR) and *R.* sphaeroides was co-cultivated, and the hydrogen production and pH are measured; then, *R.* sphaeroides and immobilized BR of different concentrations are used to produce hydrogen to detect the amount of hydrogen. Two-chamber microbial hydrogen production system with proton exchange membrane-assisted proton flow was established, and the system was operated. As additional electricity added under 0.3 V, the hydrogen production rate increased with voltages in the coupled system. [2]

Waste biomass can be converted to hydrogen by microbiological processes. Dark fermentation is a process used to produce hydrogen from organic matter, including biomass. Dark fermentation is recognized as the most promising method due to its advantages such as relatively low energy demand. [3]

This paper highlights various processes for the conversion of biomass into hydrogen gas. Biomass and biomass-derived fuels can be used to produce hydrogen sustainably. Biophotolysis, photo-fermentation and dark fermentation processes can be practically applied to produce hydrogen. [4]

In order to produce H2, the dark fermentation (DF) process of food waste (FW) was used in this study to examine the effects of adding two different types of ash, fly ash and bottom ash. Using leftover forest biomass as fuel, both kinds of biomass combustion ash (BCA) were amassed in an industrial bubbling fluidized bed combustion device. Findings showed that when compared to the control test without the addition of BCA, adding BCA at various concentrations of 1, 2, and 4 g/L may effectively boost H2 generation. This energising impact was attributed to the significant contribution of metal elements released from BCA, such as sodium, potassium, calcium, magnesium, and iron, in the provision of buffering capacity and inorganic nutrients for the operation of hydrogen-forming bacteria. [5]

Hydrogen production from inexpensive abundant renewable biomass can produce cheaper hydrogen, decrease reliance on fossil fuels, and achieve zero net greenhouse gas emissions, but current chemical and biological means suffer from low hydrogen yields. Synthetic enzymatic pathway consisting of 13 enzymes for producing hydrogen from starch and water. The overall process is spontaneous and unidirectional because of a negative Gibbs free energy and separation of the gaseous products with the aqueous reactants. As technology improvements and integration with fuel cells, this technology also solves the challenges associated with hydrogen storage, and distribution in the hydrogen economy. [6]

Biomass has been recognized as a major world renewable energy source to supplement declining fossil fuel resources.
It will play an important role in the future global energy infrastructure for the generation of power and heat, but also for the production of chemicals and fuels.
The dominant biomass conversion technology will be gasification, as the gases from biomass gasification are intermediates in the high-efficient power production or the synthesis from chemicals and fuels. The scenario illustrates the key role of hydrogen in a long-term transition towards a clean and sustainable energy future. [7]

The use of hydrogen (H2) as a fuel offers enhanced energy conversion efficiency and tremendous potential to decrease greenhouse gas emissions, but producing it in a distributed, carbon-neutral, low-cost manner requires new technologies. Herein we demonstrate the complete conversion of glucose and xylose from plant biomass to H2 and CO2 based on an in vitro synthetic enzymatic pathway. Glucose and xylose were simultaneously converted to H2 with a yield of two H2 per carbon, the maximum possible yield. Parameters of a nonlinear kinetic model were fitted with experimental data using a genetic algorithm, and a global sensitivity analysis was used to identify the enzymes that have the greatest impact on reaction rate and yield. After optimizing enzyme loadings using this model, volumetric H2 productivity was increased 3-fold to 32 mmol $H2\cdot L^{-1}\cdot h^{-1}$. The productivity was further enhanced to 54 mmol $H2\cdot L^{-1}\cdot h^{-1}$ by increasing reaction temperature, substrate, and enzyme concentrations—an increase of 67-fold compared with the initial studies using this method. The production of hydrogen from locally produced biomass is a promising means to achieve global green energy production. [8]

In direct hydrogen fermentation, the microbes produce the hydrogen themselves. These microbes can break down complex molecules through many different pathways, and the byproducts of some of the pathways can be combined by enzymes to produce hydrogen. Researchers are studying how to make fermentation systems produce hydrogen faster (improving the rate) and produce more hydrogen from the same amount of organic matter (increasing the yield). [9]

In this study, the feasibility of biohydrogen production from enzymatic hydrolysis of food waste was investigated. Food waste (solid-to-liquid ratio of 10%, w/v) was first hydrolyzed by commercial glucoamylase to release glucose (24.35 g/L) in the food waste hydrolysate. Then, the obtained food waste hydrolysate was used as a substrate for biohydrogen production in the batch and continuous (continuous stirred tank reactor, CSTR) systems. It was observed that the maximum cumulative hydrogen production of 5850 mL was achieved with a yield of 245.7 mL hydrogen/g glucose (1.97 mol hydrogen/mol glucose) in the batch system. In the continuous system, the effect of hydraulic retention time (HRT) on biohydrogen production from food waste hydrolysate was investigated. The optimal HRT obtained from this study was 6 h with the highest hydrogen production rate of 8.02 mmol/(h·L). Ethanol and acetate were the major soluble microbial products with low propionate production at all HRTs. Enzymatic hydrolysis of food waste could effectively accelerate hydrolysis speed, improve the substrate utilization rate and increase hydrogen yield. [10]

The hydrogen economy presents an energy future featuring high energy efficiency and nearly zero pollution. For example, Toyota and Hyundai start selling affordable hydrogen fuel cell vehicles this year. However, most hydrogen is produced from fossil fuels, such as natural gas and coal, resulting in net greenhouse gas emissions. In addition, current hydrogen production facilities equipped with high-temperature and high-pressure reactors require very high capital investment and large scale facilities. They cannot be scaled down to produce affordable hydrogen to local users, such as hydrogen fuel cell vehicles. Although a few solutions are proposed to produce carbon-neutral hydrogen in distributed facilities, few solutions are practical by considering product yield, separation cost, and reaction rates, involving production costs and capital investment. For example, water electrolysis is too costly because of high price tags of electricity (i.e., more than 5 cents/KWh); solar spitting powered by sunlight suffers from too slow reaction rate and low photo-to-chemical energy efficiency. Producing hydrogen from less expensive and evenly distributed biomass is an attractive alternative, but current methods have not produced sufficient yields and/or fast enough to date. [11]

The multifariousness of biofuel sources has marked an edge to an imperative energy issue. Production of hydrogen from microalgae has been gathering much contemplation right away. But, mercantile production of microalgae biofuels considering bio-hydrogen is still not practicable because of low biomass concentration and costly down streaming processes. This review has taken up the hydrogen production by microalgae. Biofuels are the up-and-coming alternative to exhaustible, environmentally unsafe fossil fuels. Algal biomass has been considered an enticing raw material for biofuel production, these days photobioreactors and open-air systems are being used for hydrogen production from algal biomass. The formers allow careful cultivation control whereas the latter ones are cheaper and simpler. A contemporary, encouraging optimization access has been included called algal cell immobilization on various matrixes which has resulted in a marked increase in the productivity per volume of a reactor and the addition of the hydrogen-production phase. [12]

EXPERIMENTAL STUDY

Hydrogen has emerged as a promising alternative to conventional fossil fuels due to its potential as a clean and sustainable energy source. As the world strives to reduce greenhouse gas emissions and mitigate climate change, the production of hydrogen from biomass has garnered significant attention. Biomass, derived from organic matter such as agricultural waste, forestry residues, and energy crops, offers a renewable and abundant resource for hydrogen generation. Through various thermochemical and biochemical processes, biomass can be efficiently converted into hydrogen, unlocking a pathway towards a greener and more sustainable future. Now, the process of hydrogen production from biomass is mainly divided into two parts. One is "Thermochemical Process" and other one is "Biological Process". We will discuss about these processes in detail. Fig. 1. Possible technologies to produce hydrogen from biomass `8 3.1.1 Thermochemical Process Thermochemical Process in the production of hydrogen from biomass is the process that involves application of high temperatures to convert the biomass into hydrogen rich gases. This process involves subjection biomass, such as agricultural waste, forestry residues, or energy crops, to heat and perform chemical transformation resulting in release of hydrogen gas. Thermochemical processes involve various processes or operations like, Gasification, Pyrolysis, Steam Reforming, Partial Oxidation, Thermochemical Cycle.

i. Gasification :

Thermochemical gasification is a partial oxidation process whereby a carbon-rich material such as biomass is broken down to gas consisting of carbon monoxide, hydrogen along with carbon dioxide, methane and other gaseous hydrocarbons. It also consists of contaminants such as, tars, char, ash, etc. This mixture is known as syngas or synthesis gas. Gasification using air results in relatively low operating temperatures, higher amount of tar and about 50% nitrogen in the gas. This gas can be burned directly for heat or used for running engines after removing tar. The makeup of syngas will vary due to the different types of feedstocks, their moisture contents, the type of gasifiers used, the gasification agents and the temperature and pressure in the gasifier

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ii. Pyrolysis :

Pyrolysis is an essential thermochemical process used in the production of hydrogen from biomass. It involves the thermal decomposition of biomass in the absence of oxygen or with limited supply of oxygen. This process breaks down the complex organic molecules present in biomass into smaller, simpler molecules through heating. `9 During pyrolysis, the biomass is subjected to high temperature typically ranging 400°C to 600 °C in a reactor. The absence of oxygen prevents complete combustion and allows the formation of valuable products, including hydrogenrich gases. This thermal decomposition leads to the formation of solid char, liquid bio-oil, and a gas mixture known as syngas, which contains hydrogen, carbon monoxide, methane, and other gases. The syngas can be subsequently treated to separate and obtain hydrogen.

iii. Steam Reforming :

Steam reforming is another thermochemical process used in the production of hydrogen from biomass. It involves the reaction between biomass and steam at high temperatures, typically above 700°C, to hydrogen gas and carbon dioxide. In the steam reforming process, biomass feedstock is mixed with steam and introduced into a reformer, which is a reactor designed to facilitate the desired chemical reactions. Inside the reformer, the biomass undergoes a series of reactions, including gasification and water-gas shift reactions, resulting in the production of hydrogen-rich gas. The water-gas shift reaction is a subsequent reaction that occurs in the presence of a catalyst. It involves the conversion of carbon monoxide and steam into additional hydrogen gas and carbon dioxide. This reaction helps to maximize the yield of hydrogen and minimize the presence of carbon monoxide, which is undesirable in the final hydrogen product.

iv. Partial Oxidation :

Partial Oxidation involves controlled combustion of biomass in the presence of limited oxygen, resulting in the production of hydrogen gas and carbon dioxide. `10 In the partial oxidation process, biomass feedstock is introduced into a reactor along with a controlled amount of air or oxygen. The biomass is typically finely ground or pulverized to increase its surface area and facilitate efficient reactions. The introduction of limited oxygen creates an oxygen-deficient environment, promoting partial combustion rather than complete combustion.

v. **Thermochemical Cycle :**

It involves a series of interconnected thermochemical reactions that enable the conversion of biomass into hydrogen gas. The thermochemical cycle process typically consists of several stages, each with its own set of reactions. The main steps involved in the thermochemical cycle are, Biomass Gasification, which is partial combustion in the presence of limited oxygen or steam. The next step is Syngas purification and further steps involve hydrogen generation.

B**iological Conversion**

Biological hydrogen production processes are considered inexhaustible and environment friendly. It allows for the production of hydrogen that is both renewable and carbon neutral. Biological hydrogen production can be classified into five different groups:

(i) Direct bio-photolysis
(ii) Indirect bio-photolysis
(iii) Biological water – gas shift reaction
(iv) Photo-fermentation
(v) Dark fermentation

All processes are controlled by the hydrogen-producing enzymes, such as hydrogenase and nitrogenase. Commonly, microorganisms, such as micro-algae and cyanobacteria, produce the enzymes required to synthesize H2, including nitrogenases and hydrogenases. Nitrogenases reduce protons (H+) from adenosine triphosphate (ATP) and electrons and release H2, while `11 hydrogenases reversibly catalyse the conversion of protons to hydrogen. In contrast to thermochemical processes, biological conversion takes place at lower temperatures (30–60 ◦C) and pressures (1 atm), decreasing the energy cost. Moreover, the microorganisms used can be easily regenerated by replication, decreasing the turnover frequency compared with chemical catalysts easily deactivated during thermochemical conversions. Biological processes are particularly interesting in waste management and enable the conversion of agricultural waste, agri-food effluents, and solid residues, or municipal solid waste. Investigations of sewage sludge have increased in the last ten years because the nature of the material is favourable to its conversion through different biological processes.

Fermentation:

Fermentation is generally defined as a chemical change in organic substrates caused by microorganism activities. It can be classified into dark, and photo-fermentation based on the demand for light during the conversion for hydrogen and hydrogen-rich biogas generation. Dark fermentation, another biological option for producing H2, occurs when anaerobic microorganisms, such as micro-algae or specific bacteria, are sustained in the dark at temperatures between 25 and 80 ◦C, or even at hyper-thermophilic (>80 ◦C) temperatures, depending on the strains. Under these conditions, the gas produced contains H2, CO2, and small amounts of CH4, CO, and H2S, depending on the converted substrate.

Photofermentation is the fermentative conversion of organic substrate to biohydrogen by various photosynthetic bacteria through a sequence of biochemical reactions involving three steps, similar to anaerobic conversion. Photosynthetic bacteria such as Rhodobium, Rhodobacter, Rhodospirillum, and Rhod pseudomonas can produce hydrogen through the action of their nitrogenase. Photo-fermentation hydrogen production has received a worldwide research interest in recent years, owing to its main advantages of broad material supplies and comprehensive substrate consumption. Fig. 3. Basic mechanism of Photo-fermentation Photolysis refers to the chemical reaction or decomposition of a compound induced by light. It can occur through direct photolysis or indirect photolysis, depending on the mechanism involved.

Direct Photolysis: Direct photolysis involves the direct absorption of light energy by a compound, leading to its transformation or degradation. When a compound absorbs light, it undergoes an electronic excitation, which can trigger various reactions. For example, direct photolysis can lead to the breaking of chemical bonds, rearrangement of molecular structures, or the generation of free radicals. The specific photochemical reactions depend on the compound's chemical properties and the wavelength of light absorbed.

Indirect Photolysis: Indirect photolysis involves the transformation of a compound mediated by light-activated reactive species present in the environment, such as excited states of naturally occurring substances or pollutants. These reactive species can react with the target compound and cause its degradation. Common examples of indirect photolysis processes include reactions mediated by hydroxyl radicals (•OH), singlet oxygen ($^{1}O_2$), or other reactive species generated by the interaction of light with molecules present in the environment.

EXPERIMENTAL WORK

The experimental work aims to study the dark fermentation process for hydrogen production. Following steps were followed to design the experimental set-up. Food waste & remains were collected as biomass from the near-by canteens & juice centres. The collected biomass included: ¬ Banana peels ¬ Pineapple peels ¬ Orange & sweet-lime peels ¬ Pomegranate shells The biomass was then mixed with water & micro-organism yeast i.e. Saccharomyces cerevisiae is added to this mixture. The mixture composition on mass basis is as follows: ¬ Water: 300 grams ¬ Biomass: 1.5 kg ¬ Yeast: 100 grams . The biomass-water mixture was stored in airtight container & allowed to undergo fermentation under the action of yeast. A U-tube manometer calibrated to atmospheric pressure was also attached to this setup. The mixture was allowed to undergo fermentation for 30 days. The manometer readings were taken at regular intervals.

RESULTS AND DISCUSSIONS

BEFORE (16.6 cm) AFTER (17.7 cm)

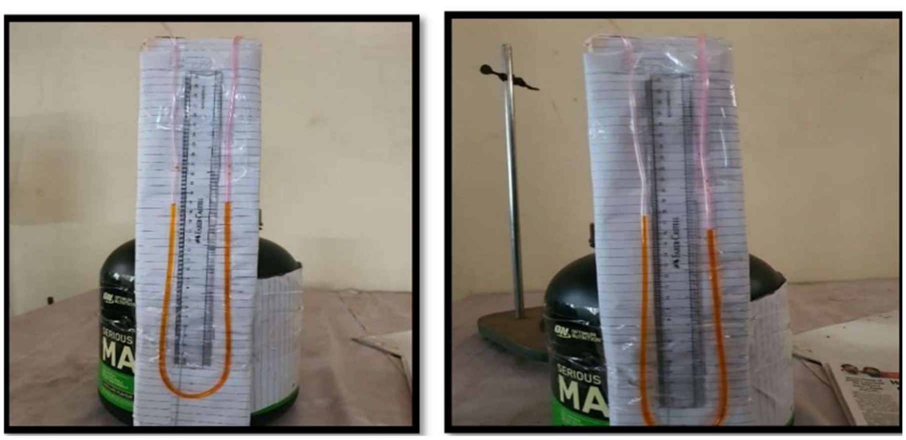

Fig. 1. Before and After deviation of manometer readings\

As from the above result we can see the comparison of two images above which clearly shows that there is a change in manometric level as the gas is formed in the container because of the dark fermentation process. As Gas is present inside that container it will fluctuate the level of fluid in the tube which is set from the datum line. The scale tells depicts there is increase in height as gas is present.

CONCLUSION

This project gave us an opportunity to study and understand all the process involved in the production of Hydrogen gas from biomass fully. This in depth study of all the processes made us aware of all the parameters involved in each process. Production of hydrogen gas from biomass on laboratory scale has many limitations, related to the temperature and pressure parameters. High temperature, pressure conditions are difficult to attain at laboratory scale. Due to this reason we have used method of Dark Fermentation, which can be possible at laboratory level temperature and pressure.

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