

Generation of Bio-Hydrogen by Chemical Looping Water Splitting and Pyrolysis: Role of Catalyst and Recent Advancements

Mohamed Arshath S¹, Sahaya Michael Hayden R¹, Anandkumar P¹, Karthikeyan C^{2,*}

¹Department of Chemical Engineering, St Joseph's College of Engineering, Chennai 600119, Tamil Nadu, India

²Department of Chemical Engineering, Indian Institute of Technology Madras, Chennai, Tamil Nadu, India.

Corresponding Author: karthikeyanchemz@gmail.com

ABSTRACT

The increased population & advanced human lifestyle development led to new inventions. The consumption of fuels is increasing & the availability of fuels is decreasing daily. So far, the world is affected by severe global warming, loss of species, and more health risks. At this time, producing fuels from fossil is more toxic and non-eco-friendly. The best solution for this problem is Hydrogen, the alternative fuel from biomass and water. Hydrogen is a zero-emission fuel produced by pyrolysis, dark anaerobic fermentation, and water-splitting processes. Hydrogen can be played an essential role in future energy mixtures. Using the chemical looping water splitting and pyrolysis technique, we will determine the strength and productivity of Hydrogen. We use zeolite as the catalyst for efficient heating. Water splitting is also a recently developed method to produce Hydrogen from water. Several methods like electrolysis, photo electrolysis, photoelectrochemical (PCE), Etc., by using TiO₂ photocatalyst can produce Hydrogen. Our objective is to increase the yield of biohydrogen using the chemical looping water-splitting photoelectrochemical process and pyrolysis. It is economically feasible, with optimized process parameters, so this could be the better viable process for biohydrogen production.

Keywords: Fast Pyrolysis, Photochemical processes, Pyrolysis, Water Splitting, Zeolite.

INTRODUCTION

The world is critically facing severe global warming and the future demand for fossil fuels for energy production. Fossil fuels are hydrocarbon-containing substances that formed naturally in the earth's crust from the decomposition of dead plants and animals years ago. High demand for fossil fuels is expected to peak within 15 years, according to the report by the international energy agency. In the future, even though fossil fuel availability will be less, it will be challenging to consume economically as the price will be very high. With the various criticisms, we are looking for alternative energy production and consumption pathways, which should be environmentally friendly and not reflect any global warming effect. To ensure the route of producing green energy, and specifically, our ultimate requirement is Hydrogen; there is the possibility of producing green Hydrogen, which can be made from biomass that is abundantly available through an appropriate, feasible process (Balat *et al.*, 2010). Blue Hydrogen is also an emission-free one and not economically tricky, and it is from fossil fuel that will no longer be available. For green hydrogen production, we require biomass, which is readily available around the globe.

Various countries have come forward to implement the project of producing green Hydrogen for the welfare of people and the globe. Australia and Europe are the leading players; Saudi Arabia recently announced its intention to enter the market through solar power potential energy projects. Here we will discuss the pyrolysis and the water splitting process for green hydrogen production; even though various techniques and processes are available for green hydrogen production, we choose pyrolysis and water splitting, as it is practically possible and economically feasible (Konieczny *et al.*, 2008). Steam reforming is implemented for hydrogen production from fossil fuels, which is more process intensive and produces greenhouse gases. However, alternative resources like biomass for clean energy production using suitable catalysts and processes must be used to overcome this challenge.

HYDROGEN, A SUPPORTING ENERGY

There is an urgent requirement for developing a new possible route for the fossil fuels shortage and problems, and it should be technologically capable of workings. An alternative source is essential, and the method of producing and deriving the end product, which should be practically possible and economically feasible, is eco-friendly to easy handling. For that, Hydrogen is the replaceable one as it has a vast number of adding properties which are to be like it is the lightest element in the periodic table, it is colorless, tasteless, odorless, and it is available in high quantities very much abundant in the universal and also it is a nontoxic substance. As it has a higher energy density in vast, it is guaranteed for the required level of energy

delivery. Moreover, it is also to be found that Hydrogen contains a higher energy density than all other standard fuels. In general, Hydrogen exists as a gaseous phase concerning the range of temperature and pressure. There are several key characteristics of Hydrogen to be: high diffusivity, Excessive ignition temperature, Fast flame velocity, Requires less amount of ignition energy, and a wide range of flammability (Ni *et al.*, 2006). Furthermore, the manufacture of Hydrogen can be done from methods of different diversity is a major advantage. The main sources are fossil fuels, which are crude oil, coal, and natural gas.

The sources for the production of Hydrogen are to be:

- Natural biomass
- Water hydrolysis reaction
- Fission nuclear reactions
- By the water splitting from water
- Uncompressed hydrocarbons

Hydrogen Trade

The world is at the level of requiring a higher amount of Hydrogen as it is demand increases, and the market for it is to be estimated to greater than forty thousand billion dollars per year. This requirement is mainly due to the new and growing industries, which have many applications to produce a higher quality fuel processing. Future demand may be due to the expense of transportation of energy, higher economic amount of Hydrogen, decreasing availability of fossil fuels, technological error of producing, emission, and toxicity of the production process (Van Ruijven *et al.*, 2009). It is known that in the future, all vehicles will emerge with Hydrogen as fuels for transportation, so the feedstock quantity for production will be very vast and high around the globe. The main challenging factors for the production and trade of Hydrogen are possible pathways, feedstocks, storage, accessibility, and handling.

Hydrogen Application

Hydrogen is widely used in some industries and for the primary and secondary level ranges such as Hydrogen is used for exploring outer space, Hydrogen fuel cells produce electricity, and burning Hydrogen for electricity generation. Hydrogen is used in vehicles, Petroleum refining, Glass purification, Semiconductor manufacturing, Aerospace applications, Fertilizer production, Welding, annealing and heat-treating metals, Pharmaceuticals, As a coolant in power plant generators, commercial fixation of nitrogen from the air in the Haber ammonia process, Hydrogenation of fats and oils, Methanol production, in hydrodealkylation, hydrocracking, and Hydrodesulphurization, and also used as rocket fuel. The most crucial use of Hydrogen is ammonia synthesis. Essential advantages of direct hydrogen fuel in transmission are to be nontoxic and continuously burning—clean product combustion, High standard octane number, and Expanding gas range during cold weather.

Hydrogen Manufacturing Routes

There are many possibilities for hydrogen production where two primary feedstocks are available: fossil fuel and renewable sources. A major part of Hydrogen is manufactured from fossil fuel sources, and much less is produced from renewable sources (Sorrell *et al.*, 2010). In general, fossil fuels are the primary and renewable

sources are the secondary sources of hydrogen production. All the major parts of the industry use fossil fuels, with the steam reforming process for hydrogen production only on a small scale. The laboratory-scale renewable source is used for hydrogen production (Cherry *et al.*, 2004).

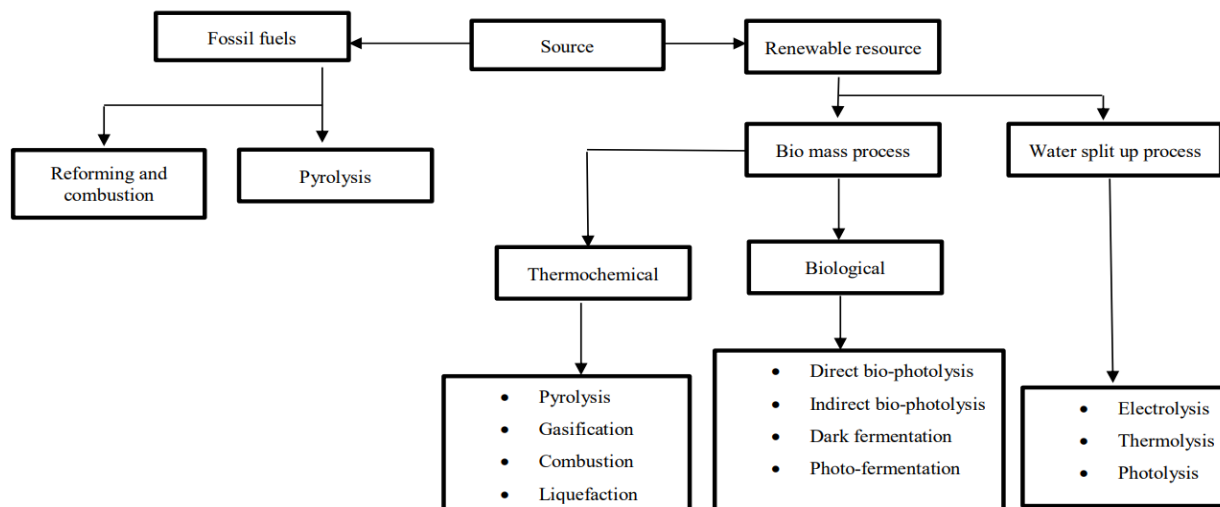


Figure 1. Classification of sources

1. Fossil fuel → pyrolysis
 - Hydrocarbon pyrolysis, Hydrogen sulfide pyrolysis
2. Renewable source → biomass process → Thermochemical
 - Pyrolysis, Gasification, Combustion, Liquefaction

The thermochemical method is the current most common method of producing Hydrogen. In this process, the required amount of Hydrogen is produced through the thermal-enhanced chemical reaction. The reaction occurs with the catalytic and noncatalytic possibilities (Armor *et al.*, 2005). The main advantage of this process is that it has higher overall efficiency and lower cost consumption. However, the production of Hydrogen is generated with the Product carbon dioxide. Now or in the future, a large amount of Hydrogen will be produced from biomass sources (Mangut *et al.*, 2006).

Biomass Routes:

Solid biomass: Crops, Fruits, Vegetable waste; Fermentation of liquid manure to Hydrogen.; Biological biomass of the hydrogen production.

PYROLYSIS

Pyrolysis is more cost-effective than wind electrolysis and photo-voltaic electrolysis systems. Pyrolysis is a practically applicable conversion of biomass to Hydrogen compared to the fermentation and biological routes because the practical and commercial route of

possibilities is to be taken care of in advance (Granovskii *et al.*, 2007). Just theoretical scripts are not required and recommended; in that point of view, we strongly found that the pyrolysis route of hydrogen production from biomass is more compatible and practicable. Woody biomass and the agricultural residue could be more economically converted to Hydrogen by the pyrolysis route (Tarnay *et al.*, 1985). Conversion of the biomass obtained from organic waste is also a route for economical and environmentally-friendly hydrogen production. The thermochemical process is far better and more effective since the biological route is more environmentally friendly and less energy-intensive, but they need to offer a higher production rate. In contrast, the other hand thermochemical process can fast process and a higher stoichiometric hydrogen yield.

Selection of Biomass

It is cheap, abundantly available, Renewable energy carriers, Plants, animal waste, and urban waste.

The primary sources are:

1. Waste substance: Crop residues, Agricultural residues
2. Products from the forest: Trees, Shrubs, Woods
3. Energy and starch crops: Corn, Wheat, sugar, Vegetable oil
4. Water-based substance: Algae, Water hyacinth

Biomass Categories:

Cellulosic Biomass

Cheap and abundant type. Conversion to the other product is constrained. Because It is in a solid state with a lower energy density level, it requires efficient technologies for biomass conversion. It is economically high. Gasification is the possible process for hydrolysis to generate aqueous sugar solutions and syngas.

Biomass Conversion

Conversion occurs with the liquid or gas phase, which has been converted to Hydrogen. In the gas phase, it is much easier and more economical for the hydrogen yield (Antonopoulou *et al.*, 2008). Starch and sugar gas biomass can be easily gained from the abundant vegetables. This biomass is easily converted to the required fuel with an easy process. Technology for transforming the solid phase to the fluid phase is.

1. Hydrolysis to generate an aqueous sugar solution
2. Pyrolysis and liquefaction to generate bio-oils and syngas.
3. Gasification to generate syngas

Triglyceride Biomass

- Vegetable oil, animal fats, and even water-based substance or even algae.
- Hydrogen is extracted from the biomass by using a catalyst upgrade. □
- The significant difficulties of proceeding with this process are higher cost, economical not feasible compared to the cellulose biomass.

Here we are extracting the Hydrogen from the bio-oil conversion. The biomass we use as feedstock needs to be converted to bio-oil. During the conversion process, the Hydrogen is released, and we capture and store it. Several processes are available to convert biomass to bio-oil, like reforming, pyrolysis, and gasification (Zakaria *et al.*, 2013). Here, we will analyze and use one of the liquefaction and pyrolysis processes.

Pyrolysis of Biomass

The biomass feedstock is to be heated with an anaerobic process which means the absence of oxygen at a higher temperature of 375°C to 525°C in a shorter period. It is a simple technique that converts the biomass into a gaseous phase. Two types of pyrolysis are available: fast pyrolysis and slow pyrolysis. Fast pyrolysis is used for the conversion of bio-oil, it has now accepted feasibility and viable routes for all renewable sources, and fast pyrolysis contains higher moisture levels and oxygen content lower than carbon and Hydrogen (Utgikar *et al.*, 2006), which tends to a lower heating and lower viscosity, a lower pH range of acid and finally the most crucial part higher efficient economy. Slow pyrolysis is used for biochar conversion. Reactors types and the heat transfer pattern are key factors to consider and design. We used the gas-solid convective pattern as the heat transfer strategy (Stedile *et al.*, 2015). Reactors 1 ablative fluidized bed. 2. Circulating fluidized bed. Fluidized bed reactors will be the most

suitable ones for the yield of Hydrogen due to their withstanding and producing higher heating rate, which is very much necessary for the pyrolysis process. The heat transfer pattern is to be the counter-current direction. As the temperature is proportional to the gas rate, the yield of the gaseous products through pyrolysis increases with the temperature corresponding to the liquid. The solid products are to be decreasing with the temperature increase. Residence time with the pyrolysis process tends to increase and fall in the volume of the product (Magrini-Bahr *et al.*, 2003). The product volume will increase with time after reaching the maximum value, concerning the further time it starts decreasing. In short, lengthening the residence time leads to the reduction of hydrogen yield. The higher residence time leads to the thermal cracking of the hydrocarbons. Pyrolysis of the birch wood biomass feedstock provides higher gaseous hydrogen production. When biomass composition is complex, it is challenging to determine the reaction in the processing route. There are different kinetics modules of pyrolysis reaction, which can be categorized as single-step global reactions with multiple-step models and single global models. The liquefaction process is hydrothermal, solvolysis, and hydrolysis, which is the opposite of the fast pyrolysis process in which a higher amount of hydrocarbon presents and a lower level of moisture and oxygen content are present, which leads to a higher heating value. It becomes difficult to handle, the efficiency drops to less, and it will become economical, not feasible (Elliott *et al.*, 1990). In the term process economy, the required capital cost for the high pressures equipment in the liquefaction process makes it less attractive for the industrial people to choose than the pyrolysis process. From the literature review, we are now seeing the hydrogen yield analysis from the process of fast pyrolysis from the biomass pine wood sawdust in a conical spouted bed reactor by using the catalyst Ni as it is to be commercially available. The operating temperature of the process is around 550°C - 900°C. At this condition, the continuous fast pyrolysis process has a higher impact on the hydrogen yield production from biomass. The maximum yield of Hydrogen is to be 64g per Kg of biomass at 550°C, and a possible yield of 110 per kg of biomass at 600°C-700°C. The pyrolysis gases and the char produced are removed and cleaned continuously from the conical spouted bed reactor. At the operating temperature of 800°C, hydrogen yield is 6.06%, carbon 49.33%, nitrogen 0.04%, and oxygen 44.57%, respectively. Furthermore, using steam or nitrogen as a fluidizing agent as required helps maintain the pyrolysis process's moderate temperature. Further, we proceed with a catalyst for higher effectiveness.

Biomass \rightarrow H₂ + CO + CO₂ + gas (hydrocarbon)

Factors Govern Hydrogen Production

Temperature, Residence time, Catalyst type, and type of biomass feedstock

A higher temperature with a shorter time will be the most suitable and appropriate for the processes.

Catalyst

Here we used titanium oxide and zeolite as a catalyst, where the size of its pores should be between 5.6Å and to 7.6Å. Furthermore, it is more effective and efficient at 650 C. The pore size is 2.5 Å to 3.4 Å at the higher temperature. Here we go to use the ZSM-5 catalyst, which is a form of one with a class of shape-selective catalysts with unique pores, and the structure designed, has high thermal stability to withstand the higher temperature. So these ZSM-5 catalysts produced higher aromatic yields (Vargas *et al.*, 1986). It is an optimal catalyst and satisfactory for deoxygenation and aromatic production. Since the zeolite catalyst plays a vital role, they help dictate the final product's chemical composition and yields. Bronsted acid sites are present internally and externally on the surface; the sites are active catalytic sites for the cracking deoxygenation, coking, and aromatization reaction. Surface chemistry and the pore structure are important properties influencing the conversion process. The formation of by-products is mainly due to the presence of a catalyst. Due to their surface characteristics, zeolite, and titanium oxide have better catalytic effects and a higher hydrogen production rate. Most researchers have found that chromium oxides are the most effective catalyst in the pyrolysis process of biomass feedstock, but it is not economically feasible.

Water Splitting

Photocatalyst semiconducting materials act as an absorber of photons from the visible spectrum of light. Photoinduced electrons transport the holes to the catalyst surface, which acts as an oxidation and reduction process. Each step in photocatalytic water splitting is critical and essential in higher-efficiency Hydrogen (Onay *et al.*, 2004). Surface adsorption, charge separation, charge utilization, and charge transport are important steps for the influence. The limitations arise from converting the laboratory scale to the pilot scale. A stable, recyclable, corrosive resistance photocatalyst is required, which is very crucial for pilot-scale production. Titanium oxide is the most widely studied photocatalyst for water splitting. It is abundant, inexpensive, noncorrosive, stable, and non-toxic.

Performance Enhancement

They enhance photocatalytic performance, including heterojunction formation, nanostructure design, dye synthesis, doping, and defect control. Theoretical and strategical understanding knowledge of the design will guide the path of the synthesis complement of the photocatalytic application (Reverberi *et al.*, 2016). Stability, recycling ability, and reusability are to be considered for the higher efficiency hydrogen production on the pilot scale.

Chemical Looping Water Splitting

Chemical looping water-splitting technology represents an energy-efficient and environmentally friendly method for hydrogen production. The chemical looping water splitting key section is the oxygen carrier for enhancing hydrogen performance. It uses metal oxides like titanium-based ones (Kaloidas *et al.*, 1987). Hydrogen production from direct water splitting is considered a sustainable approach. Chemical looping water splitting would provide roughly two to three percent of world hydrogen energy, and the purity is also much higher; chemical looping water splitting technology was initially designed as an advanced combustion method. Pioneering reports have verified that they enable efficient hydrogen production at around 1300°C temperature; as discussed earlier, the metal oxides are the oxygen carrier (Chiarioni *et al.*, 2006). Introducing the oxygen carrier as a redox catalyst significantly lowers the threshold to break the O-H bonds of the water and improve the reaction. It helps in the improvement of the redox activity of the process and the stability of the reaction.

Moreover, it helps to capture the carbon-di-oxide relatively during pure hydrogen production. Now we deal with the two steps thermochemical water splitting process proposed by Funk *et al.* in 1966. The main key in the process is the selection of oxygen carriers. Among the material used, Ni₂FeO₄ has shown the possible topmost hydrogen production of an average yield of 0.442mL/g. While using Ni as the promoter for the process, the maximum productivity of hydrogen increases to 10mL/g at the temperature of 1200°C. From the literature, we studied that the Ni is far better than the Mn and Co promoters.

As a conclusion from the literature review, we have studied that the hydrogen yield by using NiFe₂O₄ as oxygen carrier at 800°C-1200°C is 0.0197 m-mol/g, respectively at 1000°C-1400°C is found to be 0.535-0.714 m-mol/g respectively, Metal-based oxygen is used for the oxygen carrier to increase the reduction progress. Initially, the chemical looping process for hydrogen production was based on the "Steam-iron process," Water gas was invented in 1903 by British engineer Howard Lane. Though it is termed a Steam-iron process, it aims at generating heat and power Chemical-looping combustion or high-purity H₂ (Chemical-looping hydrogen) CLH (Chemical-looping water splitting) CLWS. Commonly, chemical looping denotes a cyclic process that is a solid material that circulates the oxygen required for fuel conversion. This solid material is called an 'Oxygen Carrier' and traditionally consists of metal oxide particles (Cox *et al.*, 1998). It not only supplies oxygen for the combustion of fuel but also the reduction of solid material. The chemical looping method uses a solid oxygen carrier, which supplies oxygen for fuel combustion and the solid material's reduction.

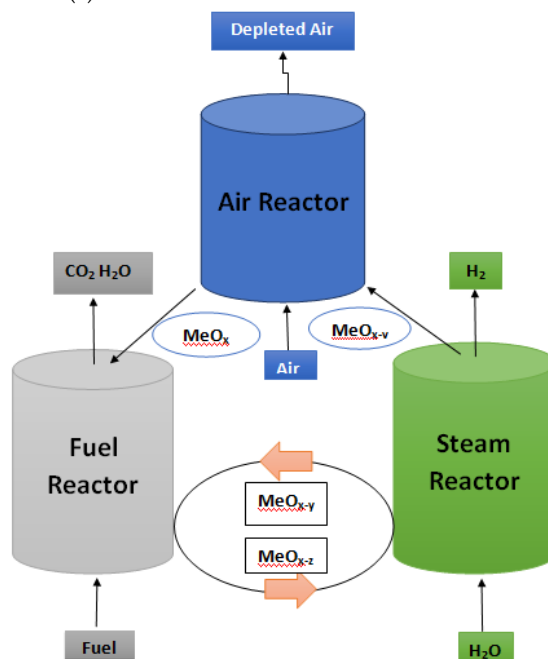
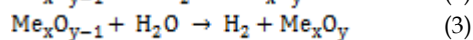
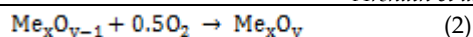
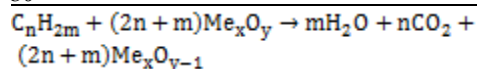


Figure 2. Process schematic of CLH production with alternative air oxidation

(Equation 1) It omits the utilization of air as an oxygen supply and thus enables the fuel conversion to a pure steam of CO_2 and H_2O , which can be easily separated by condensation. (Equation 2) The reduction in dissolved oxygen concentration in water is mainly due to pollution. Here, the solid material is re-oxidized with air to generate depleted oxygen (Equation 3).

Air oxidation might be executed to close the looping cycle. However, it reduces the hydrogen production rate and thereby the maximum efficiency of an integrated system as discussed by (in literature) with different fuels. Moreover, adding a third reaction step enables pure hydrogen production by re-oxidizing the oxygen carriers with water. From this process, we can understand that "Oxidation is the loss of Hydrogen, Reduction is the gain of Hydrogen" (Zanzi *et al.*, 2002).

Oxygen Carrier

The reactor's oxygen carrier is firstly reduced by fuel by generating H_2O and CO_2 . The oxygen carrier is also a transport intermediate to deliver pure oxygen without nitrogen dilution from the oxidizing stream, air, or water to the fuel (Rahimpour *et al.*, 2016). Oxygen carrier act as redox catalysts which helps to decrease the threshold energy for the O-H bond breaking of water. With the respective lattice, oxygen is to be abstracted from the oxygen carrier. One of the most significant and important chemical looping systems for hydrogen production is the utilization of suitable oxygen carriers (Rahimpour *et al.*, 2015). From the literature study, the suitable oxygen carriers for industrial applications should come under the

properties given below.

- Oxygen exchange capacity should be high.
- Favorable thermodynamics and reactivity regarding the selected fuel for the reduction reactions
- The risk of carbon formation should be low. Oxidation reactions reactivity should be high.
- Structural stability under continuous reduction and oxidation cycles
- Good fluidization properties and resistance to attrition are important in fluidized reactor systems
- Feasible material and production costs. Characteristics should meet environmentally friendly.

Metals such as Fe, W, Sn, Ni, Cu, Mn, and Ce have been tested. But it doesn't fulfill the requirements. To improve the chemical and mechanical properties of inert components, ZrO_2 , TiO_2 , SiO_2 , and Al_2O_3 , were used as an additive.

CONCLUSION

As natural gas or fossil fuel is not a permanent feedstock: Pyrolysis of biomass with lower we have studied the manufacture of Hydrogen and possible new pathways for the future. As Hydrogen will be the future fuel for that, we have just started to investigate and implement novel and advanced techniques for production. We have studied biomass types and their respective impact on both practical and economical hydrogen production. We have also studied the feedstock types, the catalyst characteristics, and the

selection process for the efficiency and feasibility of hydrogen production. We studied the possible processes like pyrolysis, water splitting, and chemical loop water splitting, which is practically possible and can also be improved in the future for the pilot scale production of Hydrogen. Fast pyrolysis is selected due to its higher heat transfer rate and the shorter residence time, and CLWS for its higher economic feasibility, as produced gas separation is unnecessary. We have come up with the possibilities. The defectives of the entire process start to form the selection of processes, then the feedstock categories, then the selective of the catalyst, which enhances the reaction for better quality.

In the future, we plan to design and improve green hydrogen production through simulation. The required reactors and respective parameters are to be designed in design software like ASPEN PLUS. Moreover, to work with the selection of advanced catalysts and their strategically role, which reflects in the performance improvement with the results improvement of reaction rate and the quality of the product. We aim to ensure an environmentally friendly and cost-effective water-splitting technique, utilizing suitable oxygen carriers to promote a sustainable economy.

ACKNOWLEDGEMENTS

I would like to thank my guide Mr Karthikeyan C, M. Tech, MBA, from the Department of Chemical Engineering, Indian Institute of Technology Madras, Chennai, Tamil Nadu, India and Mr Anandkumar P, M. Tech, (PhD) from Department of Chemical Engineering, St Joseph's College of Engineering, Chennai, Tamil Nadu, India.

REFERENCES

- Al-Kassir, A. Gañán, J, González, JF, González, CM, Mangut, V, Ramiro, A and Sabio, ER. 2006. Thermogravimetric study of the pyrolysis of biomass residues from tomato processing industry. *Fuel Processing Technology*. 87(2): 109-115.
- Amin, NAS, Linnekoski, J and Zakaria, ZY. 2013. A perspective on catalytic conversion of glycerol to olefins. *biomass and bioenergy*. 55: 370-385.
- Antonopoulou, G, Angelopoulos, K, Gavala, HN, Lyberatos, G and Skiadas, IV. 2008. Biofuels generation from sweet sorghum: fermentative hydrogen production and anaerobic digestion of the remaining biomass. *Bioresource technology*. 99(1): 110-119.
- Armor, JN. 2005. Catalysis and the hydrogen economy. *Catalysis letters*. 101: 131-135.
- Balat, H, and Kırtay, E. 2010. Hydrogen from biomass-present scenario and future prospects. *International journal of hydrogen energy*. 35(14): 7416-7426.
- Balat, M. 2008. Mechanisms of thermochemical biomass conversion processes. Part 1: Reactions of pyrolysis. *Energy Sources, Part A*. 30(7): 620-635.
- Baker, EG, Beckman, D, Elliott, DC, Gevert, SB, Kjellström, B, Solantausta, Y and Tolenhiemo, V. 1990. Techno-economic assessment of direct biomass liquefaction to transportation fuels. *Biomass*. 22(1-4): 251-269.
- Bentley, R, Brandt, A, Miller, R, Sorrell, S, and Speirs, J. 2010. Global oil depletion: A review of the evidence. *Energy Policy*, 38(9), 5290-5295.
- Chiarioni, A, Dovì, VG, Fabiano, B, and Reverberi, AP. 2006. An improved model of an ASR pyrolysis reactor for energy recovery. *Energy*. 31(13): 2460-2468.
- Chornet, E, Czernik, S, French, R and Magrini-Bair, KA. 2003. Fluidizable catalysts for hydrogen production from biomass pyrolysis/steam reforming. FY 2003 *Progress Report, National Renewable Energy Laboratory*.
- Cox, BG, Clarke, PF, and Pruden, BB. 1998. Economics of thermal dissociation of H₂S to produce Hydrogen. *International journal of hydrogen energy*. 23(7): 531-544.
- Dincer, I, Granovskii, M and Rosen, MA. 2007. Exergetic life cycle assessment of hydrogen production from renewables. *Journal of Power Sources*. 167(2): 461-471.
- Dydo, P, Konieczny, A, Mondal, K and Wiltowski, T. 2008. Catalyst development for thermocatalytic decomposition of methane to Hydrogen. *International Journal of Hydrogen Energy*. 33(1): 264-272.
- Ender, L, Meier, HF, Stedile, T, Simionatto, EL and Wiggers, VR. 2015. Comparison between physical properties and chemical composition of bio-oils derived from lignocellulose and triglyceride sources. *Renewable and Sustainable Energy Reviews*. 50: 92-108.
- Fabiano, B, Klemeš, JJ, Reverberi, AP and Varbanov, PS. 2016. A review of hydrogen production from hydrogen sulfide by chemical and photochemical methods. *Journal of cleaner production*. 136: 72-80.
- Honnery, D and Moriarty, P. 2022. When will the hydrogen economy arrive? *AIMS. Energy*. 10(6): 1100-1121.
- Kaloidas, VE, and Papayannakos, NG. 1987. Hydrogen production from the decomposition of hydrogen sulfide. Equilibrium studies on the system H₂S/H₂/Si_i (i= 1,..., 8) in the gas phase. *International journal of hydrogen energy*. 12(6): 403-409.
- Koçkar, OM and Onay, O. 2004. Fixed-bed pyrolysis of rapeseed (*Brassica napus* L.). *Biomass and Bioenergy*. 26(3): 289-299.
- Nate, M and Rahimpour, MR. 2016. Hydrogen production from pyrolysis-derived bio-oil using membrane reactors. In *Membrane Technologies for Biorefining* (pp. 411-434). Woodhead Publishing.
- Ni, M, Leung, DY, Leung, MK and Sumathy, K. 2006. The potential of renewable hydrogen production for energy supply in Hong Kong. *International journal of hydrogen energy*. 31(10): 1401-1412.
- Perlmutter, DD and Vargas, JM. 1986. Interpretation of

- coal pyrolysis kinetics. *Industrial & Engineering Chemistry Process Design and Development*. 25(1): 49-54.
- Rahimpour, MR. 2015. Membrane reactors for biodiesel production and processing. In *Membrane reactors for energy applications and basic chemicals*.
- Tarnay, DS. 1985. Hydrogen production at hydropower plants. *International Journal of Hydrogen Energy*. 10(9): 577-584.
- Utgikar, V and Ward, B. 2006. Life cycle assessment of ISPRA Mark 9 thermochemical cycle for nuclear hydrogen production. *Journal of Chemical Technology & Biotechnology: International Research in Process, Environmental & Clean Technology*. 81(11): 1753-1759.
- Van Ruijven, B and Van Vuuren, DP. 2009. Oil and natural gas prices and greenhouse gas emission mitigation. *Energy Policy*. 37(11): 4797-4808.