

Thermochemical Conversion of Agro-Waste for Green Hydrogen Production

Kunwar Pal^{a,*}, Abdul Rafey^b, and Kamal Kishore Pant^{b,*}

^a Thermochemical Conversion Division, Sardar Swaran Singh National Institute of Bio-Energy Kapurthala-144603, Punjab, India

^b Department of Chemical Engineering, Indian Institute of Technology Delhi, Hauz Khas, New Delhi-110016, India

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*Corresponding Authors Email: kkpant@chemical.iitd.ac.in; kunwar.pal@nibe.res.in

Abstract: The thermochemical conversion of agro-waste presents a sustainable pathway for green hydrogen production, addressing both energy and environmental challenges. Agricultural residues, such as crop straw, husks, and forestry waste, are abundant and rich in carbon content, making them viable feedstocks for hydrogen generation. Key thermochemical processes include pyrolysis, gasification, and hydrothermal liquefaction, each offering unique advantages in converting biomass into hydrogen-rich syngas. Gasification, in particular, operates at high temperatures with controlled oxygen or steam to enhance hydrogen yield while minimizing tar formation. Advanced catalysts and sorbents further improve hydrogen selectivity and carbon capture efficiency. Process optimization, including temperature control, catalyst selection, and reactor design, is crucial in maximizing hydrogen output and minimizing impurities such as CO and CH₄. Integrating carbon capture and storage (CCS) technologies enhances the sustainability of hydrogen production by reducing greenhouse gas emissions. Additionally, hybrid approaches combining thermochemical methods with biological or electrochemical processes offer the potential for improved efficiency and scalability. Despite its promise, challenges remain, including feedstock variability, high capital costs, and the need for technological advancements in process efficiency. Research efforts focus on developing cost-effective catalysts, optimizing reaction conditions, and utilizing artificial intelligence for process control. Policy support, investment in bio-refinery infrastructure, and life cycle assessment studies will be critical for commercializing this approach. Thermochemical conversion of agro-waste thus emerges as a promising strategy for producing green hydrogen, contributing to the global transition toward sustainable and carbon-neutral energy systems.

Keywords: Agro-waste, biomass, carbon-neutral, green hydrogen, sustainability, thermochemical conversion

1. Introduction

The petrochemical fertilizer and chemical processing industries have a significant share in the consumption of hydrogen produced worldwide. Due to the boost in the hydrogen economy, hydrogen as a future fuel in the automobile sector will also

stimulate the need for hydrogen [1]. However, hydrogen is the most abundant element in nature; it cannot be freely available, and thus, rather than fossil fuel, it must be produced from another renewable energy source. The most common technique for hydrogen production these days is hydrocarbon-steam

reforming or coal gasification for industrial processes, which require steam and hydrocarbons [2], [3]. Thus, hydrogen produced in this manner cannot be considered a renewable or clean gas as it is produced from hydrocarbon fuels and causes similar carbon dioxide emissions.

As the reduction of the greenhouse effect and independence from fossil fuels have become priorities for the world, new sustainable ways of hydrogen gas production need to be studied. In this direction, biomass gasification can produce hydrogen because it can recover energy from waste biomass [4]. Also, this process can be used to produce hydrogen, fuels, and many value-added chemicals. Thus, biomass gasification offers flexibility toward the input feedstock and output final products. The production of green hydrogen as fuel results in the generation of only energy and water as products without the emission of carbon or any toxic gas; thus, it is considered a clean fuel. Further, it is a much safer fuel than LPG, NG, gasoline, and diesel owing to its low density [5], [6], [7].

Biomass can be considered a prominent form of energy because it has around 10–14% share in the global energy supply [8], [9], [10]. Also, biomass contributes to up to 90% of total energy demand in the rural and remote areas of developing countries across the globe [11], [12]. In the coming future, it will remain the primary source of energy requirement for developing countries because it is expected that more than 80% of the world population will reside in the rural and remote areas of developing countries by 2050 [13], [14].

There are various methods available for biomass wastes to hydrogen production, but at present, most of the methods are either on a laboratory or pilot scale. The gasification of biomass to produce hydrogen is one of them. Gasification of biomass is a mature technology and has been used for more than 100 years for syngas and biochar

production with the help of various modes of gasifiers. The gasification process requires high temperature ($>700\text{ }^{\circ}\text{C}$) and a gasifying agent to convert the waste biomass into syngas, a mixture of carbon monoxide (CO), carbon dioxide (CO_2), methane (CH_4), and hydrogen (H_2) [15]. Tar and biochar are also produced during the gasification process. Thermal cracking in the presence of oxygen can be used to convert the tar, and a water gas shift reactor can be used to enhance hydrogen production. Pressure swing adsorption or membrane separation can separate the hydrogen from syngas. Hydrogen yield from gasification also depends on biomass's physical and chemical properties. So, the production of hydrogen from waste biomass requires process optimization and the identification and characterization of biomass through which the optimum yield of the hydrogen gas can be produced.

The use of hydrogen in the future will increase rapidly to overcome the problem of CO_2 emission and become a carbon-neutral environment worldwide. Global hydrogen demand was around 115 Mt in 2020, which is expected to increase to 200 Mt in 2030 and 530 Mt in 2050, and the demand for hydrogen in India would represent almost 10% of the global hydrogen demand [16]. India's annual demand for hydrogen was 6 MT in 2020, majorly for petro-refining, ammonia, and methanol production. These two applications currently account for more than 80% of the consumption of hydrogen, primarily derived from natural gas using steam methane reforming. As per the Ministry of Steel report, around 35% of the steel production in India is produced from the DRI-based plant only [17]. In India, most of the hydrogen (100%) is produced by using natural gas while simultaneously emitting the CO_2 into the environment. Around 11 kg CO_2 per kg of H_2 from SMR and 20 kg CO_2 per kg of H_2 from coal gasification are produced [18]. The use of up to 5 MT of green hydrogen per year

can reduce the 11 MT per year consumption of natural gas or around 25 MT of coal per year while simultaneously reducing the 34 million tonnes of CO₂ emission per year from natural gas or 57 million tonnes CO₂ emission per year from coal gasification by 2030, respectively [19], [20].


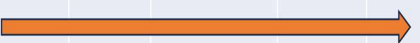
As can be seen from Table 1, if the current demand for all the fossil fuels, i.e., crude oil, coal, and natural gas, is hypothetically replaced by hydrogen, then about 276 MTPA of hydrogen will be needed. There will also be a corresponding reduction in CO₂ emission by about 2725 MTPA if the hydrogen is green. The prediction shows the strong need to replace fossil fuels in current applications with fuels like hydrogen.

Table 1: Market demand for green hydrogen and equivalent CO₂ savings per annum [21]

Fossil Fuel type	Annual Indian Demand	Green H ₂ requirement for replacement	Equivalent CO ₂ savings due to replacement
Coal	430 MTPA	143 MTPA	1625 MTPA
Crude Oil	250 MTPA	83 MTPA	740 MTPA
Natural Gas	130 MTPA	50 MTPA	360 MTPA
Total	810 MTPA	276 MTPA	2725 MTPA

Hydrogen from renewable energy via water electrolysis is one pathway for green hydrogen, but equally critical for India is to build a hydrogen economy using hydrogen from solid fuels like coal, pet coke, and solid waste, including MSW and biomass [22]. Based on preliminary analysis and the proposed technology route discussed in this chapter, hydrogen can be produced at a competitive cost—under ₹200/kg—nearly half the cost of hydrogen generated through renewable energy and water electrolysis using current state-of-the-art methods. The colour code of hydrogen with greenhouse gas emission from the production process and the

acceptance level of the different processes

Colour Code	Brown	Grey	Blue	Turquoise	Green
Energy Source	Coal or lignite	Natural gas	Any non-renewable energy source	Methane	Any renewable energy source
Process of getting hydrogen	Gasification	Steam methane reforming	Steam methane reforming and carbon capture & storage	Pyrolysis	Electrolysis of water and biomass gasification
Highest to lowest greenhouse gas emission					
Lowest to highest acceptable level					

can be seen in Table 2.

Table 2: Colour code of hydrogen with greenhouse gas emission and acceptance level of different processes

This study presents a comprehensive analysis of agro-waste thermochemical conversion for green hydrogen production, emphasizing the gasification pathway. Unlike conventional studies that focus on brief discussions related to individual thermochemical pathways, this work provides a detailed assessment of the gasification process and the reactions involved, hydrogen storage and safety, cost of production, and the challenges associated with the production. Further, an advanced gasification scheme is proposed for maximizing the hydrogen production from biomass through water gas shift reaction, tar conversion to yield more syngas through catalytic cracking, and separation and purification of the hydrogen through pressure swing adsorption techniques and other low-temperature separation methods. By addressing critical challenges such as feedstock variability, process economics, and environmental impact through a multidisciplinary approach, this study contributes to developing a cost-effective, scalable, and carbon-neutral hydrogen production pathway from agricultural residues.

2. Agro-waste feedstock potential

For hydrogen production, abundant and low commercial value agriculture waste such as crop residue waste, rice straw, wheat straw, sugarcane bagasse/trash, cotton stalk, sorghum stover, etc., can be used effectively. Using these materials as a feedstock for hydrogen production can solve waste management problems or stubble burning of agro residue in rural areas by simultaneously decreasing pollution and other environmental hazards. Various properties of agro-waste required to be considered during gasification are listed in the Fig. 1.

India, a major agrarian society, generates a lot of agro residues. Overall, India produces approximately 686 MMT (million metric tonnes) of crop residue biomass in the form of stacks, roots, trashes, husks, and yard trimmings on an annual basis, of which 234 MMT (34% of gross) are estimated as surplus for bioenergy generation and available in distributed form [23]. According to the MNRE report, it is estimated that 750 MMT of agricultural and forestry biomass is generated annually in India. The surplus biomass available in India is around 230 MMT out of the total available, with the potential of 28 GW of energy production [24]. From the observation of data from 2010–11 to 2015–16, the survey covered production statistics of the primary selected crops such as wheat straw, rice straw and husk, sugarcane leaf and bagasse, gram, soybean, groundnut castor, etc. Based on the survey, it is estimated that the annual average biomass generation from these crops was around 683 million tonnes [25]. It was also found that more than 80% of biomass is generally produced from rice straw and husk (33%), wheat straw (22%), sugarcane tops and bagasse (17%), and cotton (8%) [26]. The majority of biomass was produced in Uttar Pradesh, Maharashtra, Madhya Pradesh, Punjab, and Gujarat, and these all

were the top five states of India generating biomass [27].

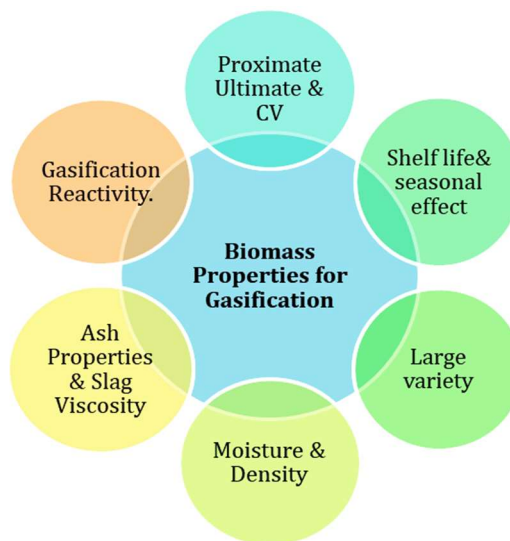


Fig. 1: Various properties of agro-waste

3. Gasification process for conversion of agro-waste

It is a thermo-chemical process involving multiple chemical reactions wherein a carbon-containing feedstock, such as agro waste, is converted into synthetic gas in a partial supply of air, oxygen, or steam. The process operates at sufficiently high temperatures ($>600 - 1000\text{ }^{\circ}\text{C}$) to thermally degrade the biomass waste to yield the hydrogen-rich syngas [15], [28]. Several advantages are associated with gasification, such as the increased heating value of fuel by the rejection of non-combustibles like nitrogen and water, reduction in oxygen content of the fuel, exposure to H_2 at high pressure or exposure to steam at high temperatures and pressures where H_2 is added to the product will raise the products relative hydrogen content (H/C ratio) [29]. Biomass feedstock has a variation in moisture content during the different seasons and in the different parts of the country. The feedstock quality, especially the moisture content, plays a significant role in the quality of the product after gasification; less than

20% moisture content generally seems reasonable for a good quality product [30], [31]. An overview of the different production processes, types of hydrogen storage, and various modes of hydrogen transportation with end applications can be seen in Fig. 2.

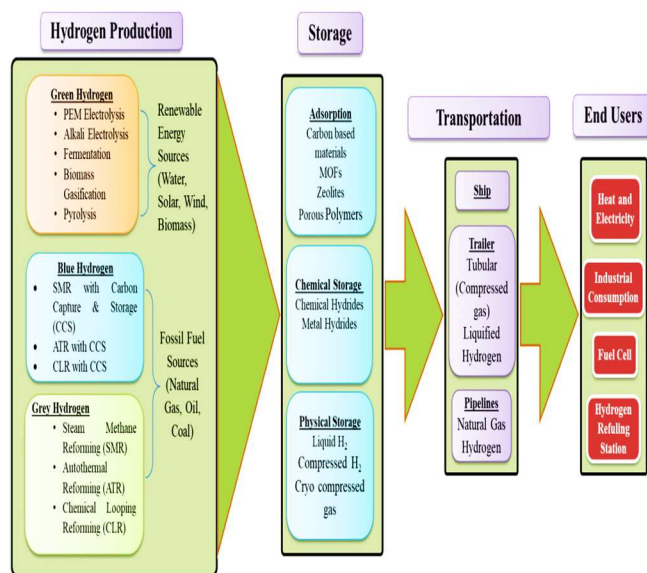
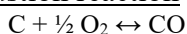


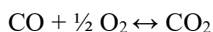
Fig. 2: Overview of hydrogen production to end-use

Conversion of biomass in a typical gasifier system is mainly carried out by four different stages: drying, pyrolysis, gasification, and combustion [32]. Many reactions of different natures (i.e., endothermic or exothermic, etc.) are simultaneously carried out in these four zones. The reactions inside the gasifier are complicated and can be found in reaction no. R1 to R8 [33], [34]. These reactions are generally classified into five types: i) carbon reactions, ii) oxidation reactions, iii) shift reactions, iv) methanation reactions, and v) steam reforming reactions [28], [35], [36], [37].

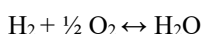
Combustion reaction



$$\text{Heat of Reaction} = -122 (\text{kJ/mol}) \quad (\text{R1})$$

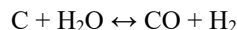


$$\text{Heat of Reaction} = -283 (\text{kJ/mol}) \quad (\text{R2})$$

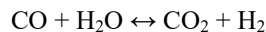


$$\text{Heat of Reaction} = -248 (\text{kJ/mol}) \quad (\text{R3})$$

Water gas shift reaction

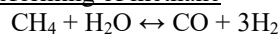


$$\text{Heat of Reaction} = +136 (\text{kJ/mol}) \quad (\text{R4})$$



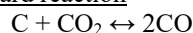
$$\text{Heat of Reaction} = -35 (\text{kJ/mol}) \quad (\text{R5})$$

Steam reforming of methane



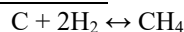
$$\text{Heat of Reaction} = +206 (\text{kJ/mol}) \quad (\text{R6})$$

Boudouard reaction



$$\text{Heat of Reaction} = +171 (\text{kJ/mol}) \quad (\text{R7})$$

Hydrogasification



$$\text{Heat of Reaction} = -74.8 (\text{kJ/mol}) \quad (\text{R8})$$

High purity near green hydrogen with a higher production rate can be produced from the advanced biomass gasification system, as can be seen in Fig. 3. The syngas produced after the gasification of biomass generally contain a high amount of tar, which can be converted into more syngas by increasing the temperature, and the process is called the thermal/catalytic cracking of tar. This can be done by adding oxygen to the gas, leaving the gasifier during thermal cracking. After the thermal cracking operation, the temperature of the gas stream will be lowered to around 250 °C by water quenching. Then, solid particles will be removed using a bag-house filter.

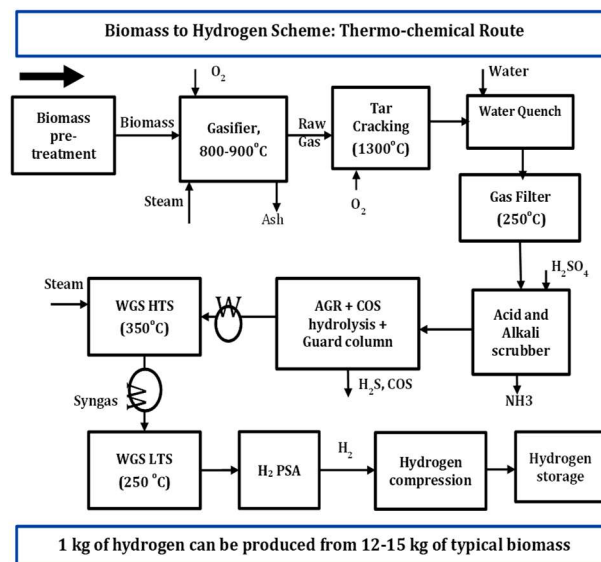


Fig. 3: Proposed route for biomass to hydrogen production

To maximize the yield of hydrogen, water gas shift (WGS) conversion process is

required. This conversion shifts the carbon monoxide (CO) present in the syngas to carbon dioxide (CO₂) and additional hydrogen (H₂) via reaction ($\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$), which is an exothermic in nature and known as the water gas shift reaction (WGSR). Typically, 1 kg of biomass feed requires 1 kg of steam during the WGSR. The reaction is favored at lower temperatures and higher steam content. Still, based on the varying temperature conditions, the WGSR can be called High-Temperature Shift Conversion (HTSC), Medium Temperature Shift Conversion (MTSC), Low-Temperature Shift Conversion (LTSC), and Sour Gas Shift Conversion (SGS) [26], [38]. Based on the syngas characteristics or as per final product quality requirements, any one or pair of shift conversion reactions can be used. The SGS conversion process typically utilizes a bed of cobalt molybdenum catalyst. The syngas typically enter the SGS reactor at 230-260 °C temperature. A high-temperature shift reaction is generally carried out at 350-450 °C, whereas a low-temperature shift can be carried out at 250 °C temperature [39], [40].

After WGSR, Pressure Swing Adsorption (PSA) is used to recover and purify the hydrogen from the hydrogen-rich gas stream coming from WGSR. PSA is an effective tool for producing pure hydrogen from syngas. The technology used in the PSA process generally relies on the differences in the adsorption properties of different gases to separate them under pressure. The PSA tail gas containing the impurities can then be sent into a burner for process heating and steam generation. The crude hydrogen obtained from the gasifier is a complex mixture of hydrocarbons, heavy chemicals, and moisture. Removal of such impurities from hydrogen is essential to hydrogen energy utilization. Other separation methods could also be employed for hydrogen purification and separation, such as low-temperature

separation methods (cryogenic distillation and low-temperature adsorption) and membrane separation methods (inorganic membrane and organic membrane).

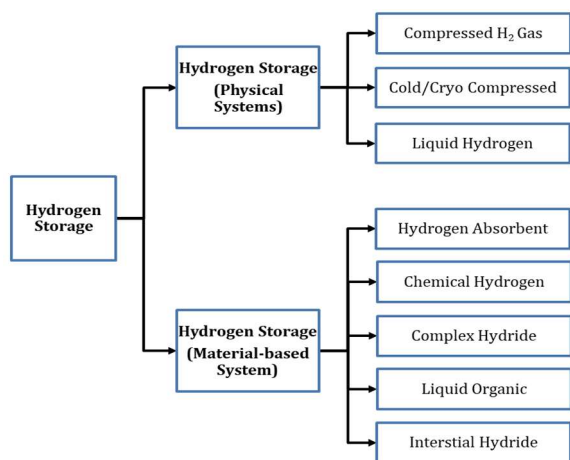
Applying a specific purification method depends upon the types and amounts of impurities. The impurities such as sulfide, HCHO, and HCOOH can be effectively eliminated using low-temperature adsorption. However, it is a complex method that requires high energy consumption and is suitable for small-scale operations. Metal hydride separation and palladium membrane separation methods are feasible when the separation of gas source with a high content of inert components is required, but the purification efficiency is low. New membrane technologies such as carbon molecular sieve membranes, ionic liquid membranes, and electrochemical hydrogen pump membranes have recently been developed, but their industrial implementation is limited. The pressure swing adsorption (PSA) technique is the most common and frequently adopted hydrogen purification technology widely used in coal gasification and natural gas reforming processes because of its long service life and economic feasibility [41]. In most PSA processes, activated carbon and zeolite have been used as an adsorbent to remove critical impurities of CO₂ and CO from the crude hydrogen [42], [43].

4. Hydrogen storage and safety

The pure hydrogen stream from the PSA can be compressed to the typical dispensing pressures of 350 or 700 bar using booster pumps and filled into the cylinders or storage tanks [44], [45]. These cylinders will then be dispatched to the customers. If the gas grid is available, the hydrogen will be boosted to a suitable pressure and injected into the gas grid. Hydrogen can operate fuel cell-based vehicles in either molecular form or combined form (say methanol, ammonia,

or DME). However, this would require suitable infrastructure for storing, distributing, and dispensing hydrogen (both in molecular and combined form).

Storage of hydrogen can be done either in the form of compressed gas or the form of liquid. High pressure of the order of 350–700 bar is required to store the hydrogen in the gaseous state [46], [47]. On the other hand, cryogenic temperature is required to store the hydrogen liquid state because hydrogen has a boiling point ($-252.8\text{ }^{\circ}\text{C}$) at atmospheric pressure. The other hydrogen storage options are adsorption on the solid surface or absorption within the solid [38], [48]. Different methods of hydrogen storage



are shown in Fig. 4.

Fig. 4: Various methods of hydrogen storage

Biomass gasification is a fairly complex technology, and hydrogen production plants based on biomass gasification must comply with various guidelines and national laws. Each process step has to be carefully considered for its Health, Safety, and Environmental constituents during the planning, engineering, construction, and operation stages. Identifying process safety and risk assessment is an essential activity during biomass gasification. Globally, it is gaining interest as the most cost-effective tool for

identifying safety requirements and reducing risk during operation. People dealing with gasification plant construction and operation generally recognize the risk assessment requirements, but due to lack of experience and resources, they did not assess the risk quantitatively. Using advanced safety techniques and tools during the gasification plant design and operation, many key issues related to safety can be easily identified. Implementing and incorporating essential safety features during the initialization step of plant design will result in safe operation during production. This will not only meet the necessary legislative standards but also satisfy the criteria of ALARP (As low as reasonably practicable) while handling the various raw materials properly. However, there can be several events of hazards that may occur with various consequences. But, the most critical issues are (i) fire and explosion hazards during the operation, (ii) operation failures due to various reasons, and (iii) unplanned release of hazardous liquids, chemicals, and gas.

5. Production cost of hydrogen from various methods

The cost of hydrogen production from different methods was analyzed based on various assumptions and market surveys, and the same is summarized in Table 3. It is possible to produce 1 kg of hydrogen from 12-15 kg of raw biomass followed by a thermochemical conversion route. The proposed technology (Fig. 4) for biomass waste gasification has some unique features, such as the capacity to produce 100 kg of hydrogen from 1.2-1.5 TPD of MWS/biomass with 85-95% conversion efficiency. With this high efficiency, the proposed pathway can convert all the available agricultural biomass to hydrogen energy. One kilogram of biomass is capable of producing approximately 85 grams of hydrogen. One kg of biomass can produce 0.6

Table 3: Cost of hydrogen production

Parameters	Water splitting (high-pressure electrolyzer) [49]	Steam-Methane reformation (SMR) [50]	Methane Pyrolysis (The new process)	Coal gasification (high ash India coal) [50], [51]	Biomass waste to hydrogen
Yield (kg of H₂)	1 kg of hydrogen /55-60 kWh	1 kg of hydrogen/3 kg of Methane	1 kg of hydrogen/ 4.2 kg of Methane	1 kg of hydrogen/19.2 kg of HAIC	1 kg of hydrogen/15 kg of biomass
Primary energy cost	At Rs 3/kWh	18 – 41.4 Rs/kg of natural gas	18 – 41.4 Rs/kg of natural gas	1.8-3.5 Rs/kg of HAIC Imported is nearly the same on eq. cal. basis	If the MSW cost is zero. Others are governed by policy
Energy costs/MJ	Rs 0.83/MJ _e	0.36-0.84 Rs/MJ	0.36-0.84 Rs/MJ	0.11-0.24 Rs/MJ	0-0.2 Rs/MJ
Cost of hydrogen	240-300 Rs/kg	200-300 Rs/kg	200 Rs/kg	120-160 Rs/kg	120-160 Rs/kg
CO₂ emission	Associated with electrolyzer manufacturing	8.07 kg of CO ₂ / Kg	1.67 kg of CO ₂ / kg of hydrogen	21 kg of CO ₂ per kg	Carbon neutral and hence zero

kWh of energy and may yield a maximum of 3 Rs. revenue; while converting it to hydrogen, we can get approximately proposed technology 0.093 kg of hydrogen and a revenue of 15/- Rs. five times higher revenue. After successfully demonstrating the indigenized technology, the total cost is Rs. 150 per kg.

6. Challenges linked with the implementation of green hydrogen

The development of low-cost indigenous technology for hydrogen production from biomass/agro-waste is hindered by several challenges, as summarized below [52], [53], [54], [55].

- **Feedstock Variability and Availability:** Agro-waste composition varies significantly based on crop type, location, and

seasonal changes, affecting process efficiency and hydrogen yield. High moisture and ash content in some residues can reduce conversion efficiency and lead to operational issues such as slagging and fouling in reactors.

- **High Capital and Operational Costs:** Thermochemical processes, especially gasification and hydrothermal liquefaction, require advanced reactors, catalysts, and separation units, increasing capital investment. The cost of biomass collection, transportation, preprocessing (drying, grinding, etc.), and storage adds to the overall expenses.
- **Process Optimization and Efficiency:** Achieving high hydrogen selectivity while minimizing by-products (CO, CH₄, tar, and char)

- requires precise temperature control, optimized catalysts, and effective reactor design. Tar formation in gasification remains a critical challenge, necessitating advanced tar-cracking catalysts or secondary reforming processes.
- **Catalyst Deactivation and Development:** Catalyst performance deteriorates over time due to sintering, carbon deposition, and poisoning from impurities in agro-waste feedstocks. Developing cost-effective, durable, regenerative catalysts is crucial for improving long-term process efficiency.
 - **Carbon Emissions and Sustainability Concerns:** Although thermochemical processes can integrate carbon capture and storage (CCS), ensuring a net-zero or negative carbon footprint remains challenging. Effective utilization of biochar and CO₂ by-products is essential to enhance overall sustainability.
 - **Integration with Renewable Energy and Hybrid Approaches:** Hybridizing thermochemical methods with biological or electrochemical processes can enhance efficiency, but technological integration remains complex. Ensuring a stable and renewable energy supply (e.g., for steam or plasma gasification) is necessary to maintain proper "green" hydrogen production.
 - **Policy, Economic, and Market Challenges:** Inconsistent government policies, subsidies, and carbon pricing mechanisms impact the economic feasibility of agro-waste-based hydrogen production. Competing with fossil-fuel-derived hydrogen, which remains cheaper due

to existing infrastructure and subsidies, presents a significant economic barrier.

- **Life Cycle Assessment and Environmental Impact:** Comprehensive life cycle assessments (LCA) are needed to evaluate the true environmental impact of thermochemical conversion, considering land use, energy input, and emissions. Managing waste by-products such as ash and heavy metals is crucial to minimize ecological risks.

7. Conclusions

The thermochemical conversion of agro-waste offers a sustainable and efficient route for green hydrogen production, utilizing abundant agricultural residues to address energy and environmental challenges. Processes such as pyrolysis, gasification, and hydrothermal liquefaction enable the transformation of biomass into hydrogen-rich syngas, with gasification being particularly effective in maximizing hydrogen yield while minimizing by-products. Despite challenges such as feedstock variability, high capital costs, and process optimization complexities, a key aspect for the future lies in exploring advanced catalysts and sorbents that could improve hydrogen selectivity while simultaneously capturing carbon emissions, thereby increasing overall process sustainability. Further, policy support, infrastructure investment, and life cycle assessment studies will be critical in facilitating large-scale commercialization. As the world transitions toward cleaner energy systems, thermochemical conversion of agro-waste presents a viable and impactful solution for achieving sustainable hydrogen production and reducing carbon emissions.

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