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# Study on Hydrogen Production From Solar Biomass Based on Fe-Ce Catalyst

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## **Abstract**

Hydrogen energy has a series of advantages, such as high energy density, high utilization efficiency, good storage and transportation performance, zero pollution to the environment and so on. Hydrogen energy has a series of advantages, such as high energy density, high utilization efficiency, good storage and transportation performance, zero pollution to the environment and so on. With the help of renewable solar energy to provide heat, this hydrogen production process is expected to truly realize the sustainable development of energy. Its research has important strategic significance and social value. Firstly, the progress on hydrogen energy production based on solar biomass is summarized. Secondly, the consumption mechanism of hydrogen production from biomass driven by solar energy is analyzed. Thirdly, the preparation of Fe-Ce catalyst is designed. Finally, the hydrogen production effect based on different catalysts is analyzed, results show that Fe-Ce catalyst can effectively improve the quality of hydrogen production based on solar biomass.

**Keywords:** Hydrogen energy, Fe-Ce catalyst, biomass energy, exergy.

## 1 Introduction

Biomass refers to the formation of various organisms through photosynthesis and the use of atmospheric, land, water and other conditions, that is, all living and growable organic substances, which are generally called biomass. At present, the utilization of biomass includes the following aspects: crop straw and firewood are directly used as fuel, methane is produced by anaerobic fermentation of biomass, methanol fuel and ethanol fuel can be produced by biomass, biochar, fuel gas and bio oil can be produced by pyrolysis, and energy plants can be cultivated by advanced biotechnology. However, there are few studies on the combination of solar energy and biomass energy to produce hydrogen [1].

At present, the research on solar thermochemical hydrogen production at home and abroad is mostly in the thermochemical hydrogen production of metal or metal oxide driven by solar energy, steam reforming gasification and thermal cracking gasification of petroleum coke, organic biomass, coal and hydrocarbons. Photochemical utilization of solar energy is the use of chemical reactions to convert solar energy into other energy and store it. However, due to the influence of various factors such as energy density, season, climate and location, the efficient utilization of solar energy is limited. It is precisely because of this that researchers are prompted to explore and find more direct and effective solar energy storage methods, that is, solar energy is efficiently converted into hydrogen energy [2].

Biomass energy is a renewable resource. Plants can regenerate biomass energy through photosynthesis. Together with solar energy and wind energy, biomass energy is a renewable resource. It is rich in resources and can ensure the long-term utilization of energy; The content of S and N in biomass is low, and only less SO<sub>x</sub> and NO<sub>x</sub> are produced in the combustion process; When biomass is used as fuel, because the CO<sub>2</sub> it needs during growth is equivalent to the CO<sub>2</sub> it emits during combustion, its net CO<sub>2</sub> emission to the atmosphere is close to zero, so that the greenhouse effect can be effectively controlled; For areas lacking coal, biomass energy can be fully utilized; Among the world's energy sources, coal, oil and natural gas are the three major energy sources, and biomass energy has become the fourth largest energy source. On land, the average annual biomass production is nearly 100~125 billion tons; The average annual biomass production in the ocean is nearly 50 billion tons [3, 4].

At present, the research on solar thermochemical hydrogen production at home and abroad is mostly in the thermochemical hydrogen production

of metal or metal oxide driven by solar energy, steam reforming gasification and thermal cracking gasification of petroleum coke, organic biomass, coal and hydrocarbons. Solar hydrogen production methods mainly include the following: solar thermal decomposition of water to produce hydrogen, solar thermochemical hydrogen production, solar photoelectrochemical decomposition, solar photochemical decomposition of water to produce hydrogen, etc [5].

Starting from the concept, the solar thermal decomposition of water to produce hydrogen is the simplest method in hydrogen production. It is a process that uses the solar concentrator to absorb solar energy, directly heat the water to make its temperature reach more than 2500K, and finally decompose into  $H_2$  and  $O_2$ . The problems of this method are: (1) the separation of  $H_2$  and  $O_2$  at high temperature; (2) Material selection of solar reactor at high temperature. Scientists from various countries have studied many ways to overcome the shortcomings of direct thermal decomposition of hydrogen, of which thermochemical cycle is a good solution. Scholars have developed hundreds of multi-step thermochemical hydrogen production systems. The well-known UT-3 cycle and iodine sulfur (IS) cycle can decompose under 1273K to produce hydrogen and oxygen. The predicted hydrogen production efficiency is 48% and 52% respectively. However, these processes are complex, and gas separation and material corrosion are still difficult problems. Knocke of Germany studied the cyclic reaction of iron and chlorine. Even though this method is feasible in both chemistry and practice, it lacks competitiveness due to its uneconomical nature. There are many types of photolysis solar cells. The main research direction is the development of semiconductor materials with high corrosion resistance and low band gap, and the optimization of the structure of the photoelectrode is the focus of the research of Photoelectrochemical decomposition. At present, many scientists have done a lot of research in order to find semiconductor materials that meet these conditions. Linkous and others of Florida solar energy research center have developed a hydrogen production system of double bed photocatalytic decomposition of water. Hydrogen is generated on the reduction reaction bed and oxygen is generated on the oxidation bed of the system, which prevents the combination of hydrogen and oxygen and improves the utilization efficiency of solar energy. The development of this new reactor can make dye photocatalysts and metal complexes well used in the system of solar water decomposition to hydrogen, improve the hydrogen production efficiency and inhibit the photodegradation reaction. So far, in improving the efficiency of solar energy conversion, it mainly focuses on

how to inhibit the reverse reaction, reduce the recombination of electron hole pairs, and develop new semiconductor photocatalysts [6–8].

In China, the research on hydrogen production by solar energy has also been widely concerned by scholars and research institutions. The main research directions are photosynthetic microorganisms and photocatalytic decomposition of water to produce hydrogen. In the 1960s, the hydrogen production method of photocatalytic decomposition of water developed rapidly. Many scholars were committed to the study of stable and efficient photocatalysts, all starting with ultraviolet catalysts. At present, Chinese scholars and research institutions have made great achievements in the three aspects of photocatalytic decomposition of water to produce hydrogen, photovoltaic cell electrolytic water to produce hydrogen and Photobiological Hydrogen, especially in the research of photocatalytic decomposition of water has reached the international top level. However, there is a lack of research on solar thermal driven hydrogen production in China. Domestic research on solar heating mainly focuses on solar energy and methanol reforming hydrogen production, solar heating and biomass supercritical water hydrogen production.

At present, biomass can be transformed into liquid fuel, gas fuel and chemicals through thermochemical conversion processes including pyrolysis and gasification, so as to realize high value-added, efficient and clean utilization. However, in this process, the reaction of biomass conversion is very complex, which is the coupling of cracking, reforming, polymerization and other reactions. Catalysts can effectively improve the rate of key chemical reactions and the selectivity of target products, and play an important role in the process of biomass conversion. At present, the commonly used catalysts in the field of biomass thermochemical utilization include alkali metal/alkaline earth metal oxides, transition metal oxides and molecular sieves. Due to the complex and changeable biomass utilization scenarios and mostly high-temperature reactions, the catalyst is easy to be inactivated due to carbon deposition and sintering, which will affect the thermochemical conversion efficiency of biomass. Iron cerium bimetallic oxide as catalyst has the advantages of simple preparation, high efficiency and easy recovery

$\text{Fe}_2\text{O}_3$  can activate the aldehyde group of benzaldehyde and the carbonyl group of cyclohexanone;  $\text{CeO}_2$  has superior storage and transfer effects on reactive oxygen species. In recent years,  $\text{CeO}_2$  has been applied in the research of CO oxidation, photocatalytic oxidation, electrocatalytic oxidation and organic pyrolysis. Therefore, iron cerium catalyst is feasible for hydrogen production from solar biomass.

## 2 Consumption Mechanism of Hydrogen Production From Biomass Driven by Solar Energy

Solar energy drives the biomass hydrogen production process, that is, the concentrated solar energy is used to generate high-temperature heat to provide the heat absorbed by the biomass hydrogen production process and high-temperature thermal environment (as shown in Figure 1). From the first law of thermodynamics, solar energy is stored in H<sub>2</sub> products in the form of chemical energy, and water vapor is used as gasification agent to increase the number of H atoms in the biomass gasification reaction process. Thus, the output of H<sub>2</sub> in syngas products is increased. Solar energy and biomass not only realize the cascade utilization of fuel chemical energy, but also store and utilize solar energy stably and efficiently in the form of chemical energy [9].

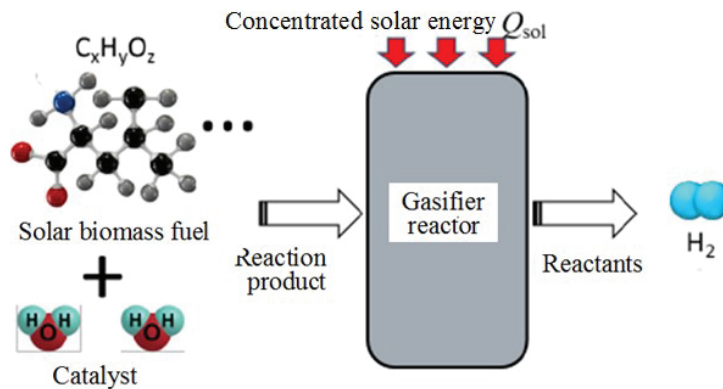
The energy conversion mechanism of biomass hydrogen production driven by solar energy can be analyzed from the perspective of energy and quality. Figure 2 shows the energy balance diagram of biomass hydrogen production driven by solar energy.

According to the first law of thermodynamics, the energy conservation formula is:

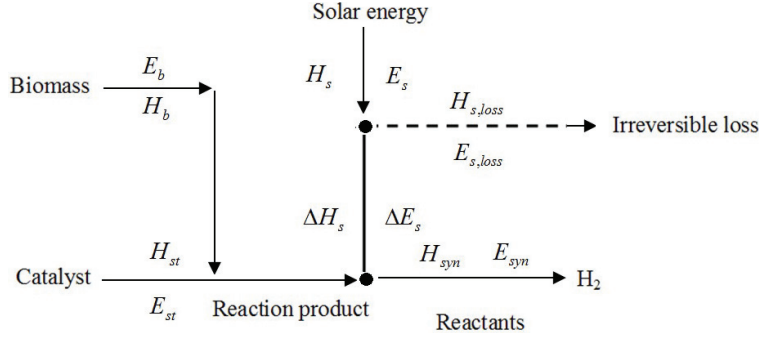
$$H_b + H_s + \Delta H_s = H_{syn} \quad (1)$$

$$\Delta H_s = H_s - H_{s,loss} = H_s \cdot \eta_t \quad (2)$$

where  $H_b$  denotes the high calorific value of biomass raw materials,  $H_s$  denotes the sensible heat energy of catalyst at preheating temperature,  $\Delta H_s$  denotes solar energy absorbed and converted by thermochemical gasification,



**Figure 1** Biomass hydrogen production process of solar energy.



**Figure 2** Energy balance diagram of biomass hydrogen production driven by solar energy.

$H_{syn}$  denotes the calorific value and sensible heat of syngas produced after hydrogen production from biomass.  $\eta_t$  denotes the thermal efficiency of solar energy conversion.

According to the second law of thermodynamics, the equilibrium analysis of biomass gasification process driven by solar energy is as follows [10]:

$$E_{syn} = E_b + E_{st} + E_s - E_{s,loss} - E_{r,loss} \quad (3)$$

$$\Delta E_s = E_s - E_{s,loss} = H_s \cdot \eta_t \left(1 - \frac{T_0}{T_C}\right) \quad (4)$$

where  $E_{syn}$  denotes the chemical and physical properties of syngas,  $E_b$  denotes the Chemical and physical properties of biomass fuels.  $E_{st}$  denotes the physical properties of catalyzer,  $E_s$  denotes the heat energy of concentrated solar energy,  $E_{s,loss}$  denotes the irreversible loss of solar thermal energy,  $E_{r,loss}$  denotes the irreversible loss in hydrogen production process,  $T_0$  denotes the environmental temperature,  $T_C$  denotes the condensing collection temperature.

The concentrating process of high-temperature solar energy mainly depends on mature concentrating equipment, such as heliostat, parabolic dish, etc. The collected effective solar energy can be calculated by the following formula:

$$Q_{s,r} = A_s T_s (1 - \eta_{o,loss}) \quad (5)$$

where  $Q_{s,r}$  denotes the collected solar energy,  $A_s$  denotes the area of solar concentrating equipment,  $T_s$  denotes the solar radiation intensity,  $\eta_{o,loss}$  denotes the total optical loss of condensing instrument mainly includes specular reflection loss, light scattering and overflow loss.

For the gasifier reactor, after receiving high-temperature solar energy, most of it is used for the heat absorption required by biomass hydrogen production, while the rest is irreversible heat loss due to the high temperature difference between the reactor and the ambient air. Therefore, the effective solar energy  $Q_{s,ab}$  absorbed by biomass gasification can be calculated by the following balance equation [11]:

$$Q_{s,ab} = Q_{s,r} - (Q_{con} + Q_{cov} + Q_{rad})_{loss} \quad (6)$$

where  $Q_{con}$  denotes the irreversible heat loss caused by temperature difference between gasifier reactor and ambient air,  $Q_{cov}$  denotes the irreversible heat loss due to convection caused by temperature difference between gasifier reactor and ambient air,  $Q_{rad}$  denotes the irreversible heat loss caused by temperature difference between gasifier reactor and ambient air.

The solar energy absorbed by the gasifier reactor is used to drive biomass to produce hydrogen, that is, the heat absorbed by each intermediate endothermic reaction in the process of hydrogen production, as shown in the following expression [12]:

$$Q_{s,ab} = m_{i,r} \sum_i^N \Delta G_i + v_j \left( \sum_j^J q_{s,T_g} - q_{s,T_n} \right) \quad (7)$$

where  $i$  denotes the intermediate reaction of the  $i$ th biomass hydrogen production reaction process,  $N$  denotes total number of reactions,  $m_{i,r}$  denotes mass of reactant participating in the  $i$ th reaction,  $q_{s,T_g}$  denotes sensible heat of the  $i$ th material output reactor,  $q_{s,T_n}$  denotes the sensible heat of the  $i$ th substance input into the gasifier.  $v_j$  denotes the amount of mol of a single substance in the reactor.

The share of solar energy is the ratio of input solar energy to total energy consumption  $\lambda_{Sol}$ , which can characterize the contribution of solar energy to the thermochemical energy conversion process, it is expressed by

$$\lambda_s = \frac{m_b \cdot H_b}{m_b \cdot H_b + T_s \cdot A_s} \quad (8)$$

### 3 Preparation of Fe-Ce Catalyst

A new catalyst was prepared by impregnation method, which mainly includes Fe and Ce. Dolomite has good catalytic performance, and dolomite is abundant, cheap and easy to obtain. Rare earth elements have been concerned

by researchers. They play a more and more important role in traditional chemical industry and many other high-tech applications. Ce is one of the most important elements in rare earth. In the past 40 years, ceria has become one of the main participants in catalytic science. Ceria plays a leading role in catalysis and cocatalyst, from environmental and energy applications to several important catalytic reactions of electrical, optical and biological reactions. Fe is also a common catalyst element in catalytic reaction. The addition of Fe can promote the cracking of liquid products and promote gas production. The catalyst prepared by impregnation has the advantages of high utilization of supported components, low cost, simple method and high production capacity. The two components were combined by impregnation to prepare Fe-Ce catalyst [13].

Fe-Ce catalyst was prepared by impregnation method. Weigh a certain amount of iron nitrate and cerium nitrate respectively and put them into deionized water. Stir to make cerium nitrate and iron nitrate evenly mixed and dissolved in deionized water. After uniform mixing, add the treated carrier dolomite particles into the mixed solution and stir on a constant temperature magnetic stirrer at room temperature for 12 hours, After mixing, it shall be soaked at room temperature for 12 hours, and then dried in a digital display blast drying oven for 12 hours. The dried catalyst shall be mixed with calcium bentonite in the ratio of 3:2, and a certain concentration of adhesive (35% sodium silicate solution, which is produced by Tianjin Tianda purification materials fine chemical plant) shall be added. After mixing evenly, it shall be extruded, pulled and granulated. In order to convert unstable salts loaded on dolomite into stable iron cerium oxide, it was calcined in a vertical heating furnace at 800°C for 3 hours to prepare seven catalyst samples with a total load of 10%, Fe<sub>2</sub>O<sub>3</sub> and CeO<sub>2</sub> loads of 8%, cool naturally to room temperature for standby [14, 15].

## **4 Effect of Fe-Ce Catalyst on Hydrogen Production of Solar Energy**

### **4.1 Effect of Fe-Ce Catalyst on Hydrogen Production Products**

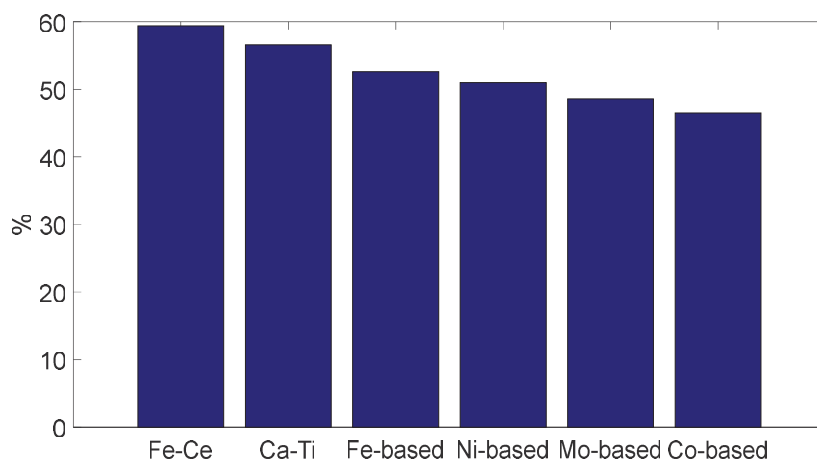
Fe-Ce catalyst can affect the hydrogen production products, therefore hydrogen production products with Fe-Ce catalyst and traditional catalyst are analyzed, and the analysis results are listed in Table 1.

As seen from Table 1, the hydrogen production products with Fe-Ce catalyst is highest, and the hydrogen production products with Co-based



**Table 1** Hydrogen production products with traditional catalyst

Catalyst	Volume Fraction/%					
	H <sub>2</sub>	CO	CH <sub>4</sub>	CO <sub>2</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>
Fe-Ce	28.5	32.5	10.3	35.7	0.82	0.91
Ca-Ti	26.4	30.8	9.53	33.1	0.77	0.87
Fe-based	24.8	28.1	8.51	31.7	0.66	0.79
Ni-based	22.5	26.4	7.44	28.5	0.62	0.73
Mo-based	21.7	24.8	6.32	26.4	0.56	0.66
Co-based	20.8	22.7	5.47	25.1	0.48	0.58



**Figure 3** Gasification rate of hydrogen production with different catalysts.

catalyst is least, The hydrogen production products with other catalyst is sorted in decrease turn: Ca-Ti catalyst, Fe-based catalyst, Fe-based catalyst, Ni-based catalyst, Mo-based catalyst and Co-based catalyst.

#### 4.2 Effect of Fe-Ce Catalyst on Gasification Rate of Hydrogen Production

The gasification rate of hydrogen production with different catalysts is shown in Figure 3. Gasification rate refers to the ratio of the total mass of the generated mixture to the dry mass of the raw materials participating in the reaction, which reflects the gasification degree of the raw materials. As seen from Figure 3, the gasification rate of hydrogen production with Fe-Ce is highest, and the gasification rate of hydrogen production with Mo-based catalyst is least.

**Table 2** Thermodynamic parameters of gasification products of hydrogen production system under different catalysts

Catalyst	Volume Fraction/%				
	Combustion Enthalpy	Formation Enthalpy	Apparent Enthalpy	Chemical Exergy	Physics Exergy
Fe-Ce	743.3	657.3	81.4	664.7	146.2
Ca-Ti	695.5	596.7	76.3	579.4	135.7
Fe-based	684.1	564.7	73.5	559.3	124.6
Ni-based	665.4	496.1	66.9	519.7	115.3
Mo-based	563.8	467.9	62.5	486.9	103.5
Co-based	529.4	437.2	56.8	453.6	98.4

### 4.3 Effect of Fe-Ce Catalyst on Fuel Efficiency and Fuel Exergy Efficiency in Hydrogen Production Process

In order to further compare the effects of different catalysts on the energy conversion before and after the reaction, the thermal calculation of gaseous products produced by different catalysts is carried out respectively, so as to obtain the enthalpy and exergy values of gaseous products for hydrogen production under different catalysts, and then analyze the fuel efficiency and fuel exergy efficiency. Analysis results are shown in Table 2. As seen from Table 2, the combustion enthalpy, formation enthalpy, apparent enthalpy, chemical exergy and physics exergy of gasification production of hydrogen production with Fe-Ce catalyst is highest.

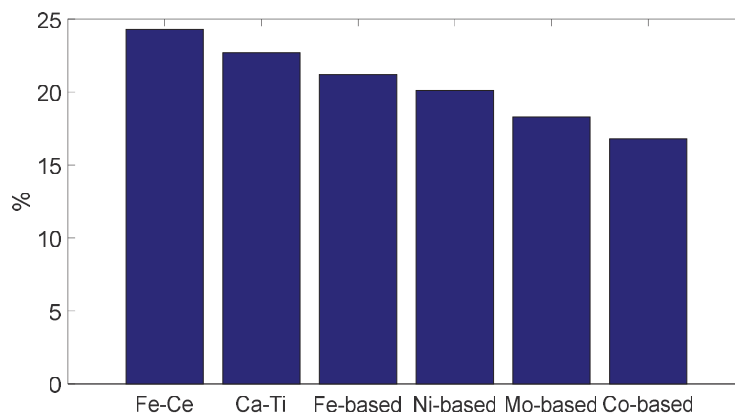
### 4.4 Effect of Fe-Ce Catalyst on Fuel Exergy Efficiency in Hydrogen Production Process

The fuel exergy efficiency refers to rate of chemistry of gas mixture exergy to chemistry of biomass exergy, and the fuel exergy efficiency with different catalysts is shown in Figure 4. As seen from Figure 4, the Fe-Ce catalyst can obtain the highest fuel exergy efficiency of hydrogen production.

As seen from the analysis results, the Fe-Ce catalyst can obtain higher gasification rate and hydrogen production, and the other gasification products has small fluctuation. The energy quality of hydrogen in the gas product with Fe-Ce catalyst is higher and the content of by-products is lower.

## 5 Discussion

Based on the analysis results, Fe-Ce catalyst can effectively improve the hydrogen production products comparing with other catalysts, Fe-Ce catalyst



**Figure 4** Fuel exergy efficiency with different catalysts.

can also enhance the gasification rate of hydrogen production, Fe-Ce catalyst can improve the combustion enthalpy, formation enthalpy, apparent enthalpy, chemical exergy and physics exergy of gasification production of hydrogen production, in addition, Fe-Ce catalyst can obtain higher gasification rate and hydrogen production, and the small fluctuation of other gasification products. The hydrogen production system using Fe-Ce catalyst has high energy utilization and hydrogen quality before and after gasification. Fe-Ce catalyst is conducive to the conversion of solar energy and biomass energy to hydrogen energy. This research offers an effective method of utilizing the hydrogen of solar energy, and can enhance the quality of solar energy hydrogen products.

## 6 Conclusions

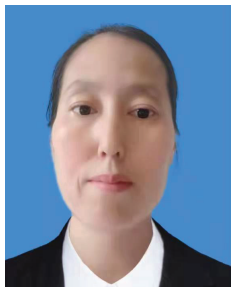
The utilization of hydrogen energy is an effective measure to reduce carbon dioxide emissions and protect the environment. Therefore, large-scale hydrogen production and the recovery and storage of gas and carbon dioxide are imperative. The vigorous development of hydrogen energy is of great significance to improve the economy and energy structure. The development of hydrogen production technology is a process of continuous demand for new energy support, and biomass hydrogen production by solar heating is conducive to building a resource-saving and environment-friendly society. Analysis results show that the hydrogen production system of Fe-Ce catalyst is conducive to the conversion of solar energy and biomass energy to hydrogen energy.

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## **Biography**



**Yanping Zhou** received the bachelor's degree in electronic information engineering from China University of Geosciences in 2005, the master's degree in earth exploration and information technology from Taiyuan University of Technology in 2009 respectively. She is currently working as a Lecturers at School of Chemistry and Chemical Engineering, Yulin University. Her research areas is hydrogen production from biomass.