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Microwave-enhanced hydrogen production: a review

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Currently, the massive use of fossil fuels, which still serve as the dominant global energy, has led to the release of large amounts of greenhouse gases. Providing abundant, clean, and safe renewable energy is one of the major technical challenges for humankind. Nowadays, hydrogen-based energy is widely considered a potentially ideal energy carrier that could provide clean energy in the fields of transportation, heat and power generation, and energy storage systems, almost without any impact on the environment after consumption. However, a smooth energy transition from fossil-fuel-based energy to hydrogen-based energy must overcome a number of key challenges that require scientific, technological, and economic support. To accelerate the hydrogen energy transition, advanced, efficient, and cost-effective methods for producing hydrogen from hydrogen-rich materials need to be developed. Therefore, in this study, a new alternative method based on the use of microwave (MW) heating technology in enhanced hydrogen production pathways from plastic, biomass, low-carbon alcohols, and methane pathways compared with conventional heating methods is discussed. Furthermore, the mechanisms of MW heating, MW-assisted catalysis, and MW plasma are also discussed. MW-assisted technology usually has the advantages of low energy consumption, easy operation, and good safety practices, which make it a promising solution to supporting the future hydrogen society.

1. Introduction

Approaching the deadline for carbon neutrality draws attention to the urgent need for clean energies to substitute fossil fuels. These unrenewable energy sources generate greenhouse gas when consumed, which enhances the greenhouse effect, promoting global warming, and intensifying extreme weathers.[1–3] Besides the environmental hazards of using fossil fuels, their significance as raw materials in industries, pharmacies, agriculture, *etc.*, makes them too valuable to be depleted as energy sources in the expected future. These facts emphasize the necessity to find alternatives to fossil energy for future sustainable development.

Hydrogen energy is a promising substitution for carbon-based fuels owing to its abundance in nature, harmless

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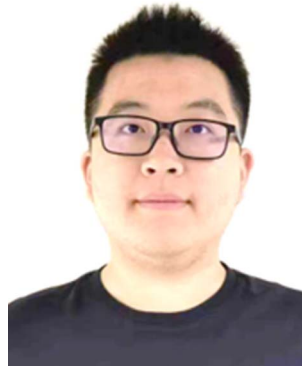
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emission,[4–6] and extremely high energy production per mass content (142 MJ), which is three times that of gasoline (44 MJ).[7–13] However, as a gaseous fuel, it has an extremely low mass density, which means a low energy density, whereby it produces a quarter of energy compared to gasoline per volumetric content. On the other hand, hydrogen is not an energy source like those fossil fuels harvested from nature, but is an energy carrier that is produced from consuming other sources.[14–16] It can be stored for subsequent uses as energy or in materials for use in fertilizer production, the oil refining industry, food, metal processing, and other fields.[17] As the most abundant element in the universe, its multiple access points, including water, minerals, and organic compounds, make hydrogen a highly desired energy source that will be essential for the future society.

While hydrogen has the potential to be an essential alternative to fossil fuels in our society, the currently reported hydrogen production methods mainly involve the classical fossil fuel steam conversion (accounting for over 80%) and natural gas-based conversion (accounting for over 70%).[17] The reason for this is that the low reliability of renewable energy sources requires high feasibility energy storage, but hydrogen

gas is not suitable for storage in terms of the transportation efficiency, facility safety, and construction costs of hydrogen facilities. This mismatch in generation and consumption hinders the transition to a hydrogen economy.[18–20] Therefore, a more flexible perspective of hydrogen production is required, which should not only focus on developing hydrogen production technologies from renewable energy sources but also on discovering a new route to release hydrogen from hydrogen-rich materials that can be synthesized by renewable energy sources, which can help realize the transportation of hydrogen in a non-gaseous form.[21]

The future hydrogen society will use hydrogen as the major energy carrier instead of gasoline or natural gas, especially for vehicles and factories,[14,15] but the most significant challenge in realizing this future is achieving efficient hydrogen storage. The direct increment in hydrogen density requires high-pressure compression at 700 bar (40 g H_2 per L) or low-temperature liquefaction at −253 °C (70 g H_2 per L) for hydrogen storage and transportation.[11,22,23] In principle, there are two hydrogen storage methods that could potentially solve the above problems, physical hydrogen storage and chemical hydrogen storage. Physical hydrogen storage involves adsorbing hydrogen

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in porous materials, like molecular sieves, MOFs, or carbon materials;[24–29] while chemical hydrogen storage aims to release hydrogen by decomposing hydrogen-rich molecules, and also a reversible hydrogen storage–release process under appropriate conditions. Chemical hydrogen storage could store a decent amount of hydrogen, but the key question is how to release the hydrogen. This concerns the material design, and may also influence current hydrocarbon material recycling.

Microwaves are electromagnetic waves with 0.001–1 m wavelength and 0.3–300 GHz frequency. Generally, mobile, radar and television satellite communications are all operated in this frequency band.[30] For microwave heating, two frequencies referred to as 915 MHz and 2.45 GHz are reserved by the Federal Communications Commission (FCC) for industrial, scientific, and medical purposes. Compared to traditional heating methods that rely on thermal conduction and convection, like oil baths or heating jackets, microwave heating or microwave dielectric heating pushes electromagnetic wave energy directly and preferentially to the absorbing media, which means that substrates are more evenly heated rather than heated from the surface to the core, external to internal.[31] This method began to be utilized by households in the 1970s, and in 1990 it was applied in many fields, especially material processing and microwave chemical reactions, including mineral processing,[32] metal oxide reduction,[33] leaching,[34] sintering, and the manufacturing of ceramic materials.[35] Currently, microwave-assisted pyrolysis technologies are rapidly growing, and playing a key role in the treatment of waste plastics,[36] rubber waste,[37] sewage sludge,[38] biomass,[39] and contaminated soil.[40] The key reason microwave heating is favored by industry is the high energy utilization and temperature elevation rate driven by well-distributed microwave absorbing media, which allows a high energy conversion efficiency and even heating of substrates.[41,42] Also, since the energy efficiency is higher and the system average temperature is reduced, there are fewer side reactions and better product selectivity. Besides the merits for the reaction progress, microwave reactors usually have compact structures, easy installation processes, simple operation methods, and good safety. Therefore, microwave-enhanced hydrogen production is a promising solution for the hydrogen society to support storing hydrogen in non-gaseous compounds and releasing it when needed in a convenient and affordable way.

In this paper, microwave-enhanced hydrogen production from plastic waste, biomass, low-carbon alcohols, and methane pathways are discussed. This paper aims to understand how microwave heating technology works and compares the differences between microwave heating and traditional heating methods in the hydrogen production process. At present, hydrogen is still mainly produced from non-renewable resources, such as steam reforming of coal, oil, and natural gas, so a full understanding and study of microwave heating technology will help to understand the advantages, disadvantages, and applicability of this technology in promoting the conversion of non-renewable resources to renewable resources for hydrogen production.

2. Mechanism of microwave heating

Microwaves are electromagnetic waves whose wavelengths range from 0.001–1 m and a corresponding frequency range of 0.3–300 GHz, and are composed of two perpendicular and oscillating electric (E) and magnetic (H) fields.[30,43] During the microwave heating process, the irradiated object interacts with the microwaves, and its temperature increases. The microwave absorption property of matter is related to the electric and magnetic loss tangents (tan δ_ε (eqn (1)) and tan δ_μ (eqn (2)), respectively).[44]

$$\tan \delta_\varepsilon = \frac{\varepsilon''}{\varepsilon'} \tag{1}$$

$$\tan \delta_\mu = \frac{\mu''}{\mu'} \tag{2}$$

where the real parts ε' and μ' represent the electromagnetic waves storage ability, and the imaginary parts ε'' and μ'' represent the attenuation ability of electric energy and magnetic energy, respectively. The greater the loss factor, the stronger the attenuation. In the microwave heating process, three types of materials are mainly involved that correspond to different heating mechanisms. For Class I (liquids such as water and alcohol), when microwave radiation acts on water molecules, the state of electron distribution of the water molecules will change rapidly, and then the polarization of the molecules will change due to the applied alternating electric field, resulting in orientation polarization, which induces a rotational motion of the molecules with the microwave frequencies. In this process, some friction between adjacent molecules may occur and will generate thermal energy. For Class II (inorganic solids), even though without molecules in this type of material, however, in a similar way as with liquids, the electrons and atoms (ions) in inorganic solids also can be excited by applied electromagnetic waves, and some friction will also exist during their motion, thus leading to a temperature increase. For Class III (metallic materials), microwave radiation will generate an induction current or a magnetic spin correlation phenomenon in the presence of an external magnetic field, then the electron motion and lattice vibration will be enhanced, which promotes heat generation.

3. Hydrogen produced from plastic waste

Owing to their light weight, good chemical resistance, flexible modifiability, and decent commercial accessibility, plastics have become ubiquitous in electronics, packaging, and construction. Since the 1950s, the rapid development of the plastics industry has made great contributions to the prosperity of human society. In 2018, global plastic production surpassed 350 million tons and has continued to increase. Despite the convenience brought by plastics, their negative impact on the natural environment and human health has become a growing concern, as evidenced by the mounting plastic pollution.[45–48] Although the gradual global awareness of the hazards of plastics

has now motivated the promotion of related activities, technologies, and policies, these are still far from sufficient, since recycling rates are as low as 20%.[45,49] Consequently, recycling through upcycling processes has become an urgent imperative to combat the harmful effects of plastic waste that would otherwise be relegated to landfills, incineration, or directly released into the environment.

Plastics are rich sources of hydrogen, which makes them ideal for microwave-assisted catalytic upgrading to produce hydrogen once discarded; hence not only generating profits but also contributing to pollution reduction.[50–54] Typically, iron-, cobalt-, and nickel-based catalysts are the most commonly used for this recycling due to their ability to activate carbon–hydrogen bonds. Specifically, these catalysts are capable of selectively promoting the cleavage of carbon–hydrogen bonds to generate hydrogen.[55–58] As magnetic substances, these three metal-based catalysts are highly responsive to microwaves, converting them into heat rapidly. Qian[59] et al. synthesized a Co-doped Fe–Al catalyst and used it in an LDPE dehydrogenation reaction, and found that the $Fe_1Co_1Al_2$ catalyst could yield 61.39 mmol (g plastic)$^{-1}$ hydrogen under microwave irradiation, which was almost two times higher than conventional heating. Meanwhile, Co-doping is not only conducive to the conversion of catalysts into FeCo alloys with enhanced activities but also can effectively inhibit the formation of Fe_3C, thereby altering the carbon diffusion pathway and promoting the formation of nanotubes and hydrogen production (Fig. 1a). Huang[60] et al. synthesized CeO_2 with iron/nickel nanoparticles-loaded carbon nanotubes (Fe/Ni–CeO_2@CNTs) substrates,

which could be used to effectively convert high-density polyethylene (HDPE) plastics to high-purity hydrogen (91.5 vol%, 50.2 mmol (g plastic)$^{-1}$) and carbon nanotubes under microwave radiation. The synergistic effect of Fe/Ni bimetallic particles and the CeO_2-induced reforming reaction significantly improved the selectivity and yield of H_2. It also achieved remarkable results in deconstructing low-density polyethylene (LDPE) and polypropylene (PP) waste as well, with hydrogen selectivities and yields up to 90.0 vol% and 48.31 mmol (g plastic)$^{-1}$, respectively, achieving near-zero carbon emissions (Fig. 1b). Song[61] et al. studied the effects of Fe and $FeAl_2O_4$ ratios and structure properties of the catalyst on the dehydrogenation efficiency of HDPE. The results showed that the best catalytic activity and absorption characteristics of the Fe–$FeAl_2O_4$ catalyst were achieved when the loading of Fe was 30 wt%, in which electromagnetic field distribution simulations proved that the catalyst was heated in the form of eddy current loss. A hydrogen yield of 47.3 mmol (g plastic)$^{-1}$ and hydrogen selectivity of 84.96 vol% were obtained in the HDPE plastic dehydrogenation reaction (Fig. 1c).

All the aforementioned catalysts for the dehydrogenation process are made from Fe and Ni because of their strong ability to activate carbon–hydrogen bonds. Alternatively, Ti_3AlC_2 (MAX) has decent dehydrogenation activity as well. Since titanium and iron belong to the same period of transition metal elements, Lu[62] et al. speculated that TiC in Ti_3AlC_2 could selectively catalyze the upgrading of plastics, like FeC_3, to produce H_2 and filamentous carbon. They found that Ti_3AlC_2 was capable of deconstructing LDPE, HDPE, and PP as
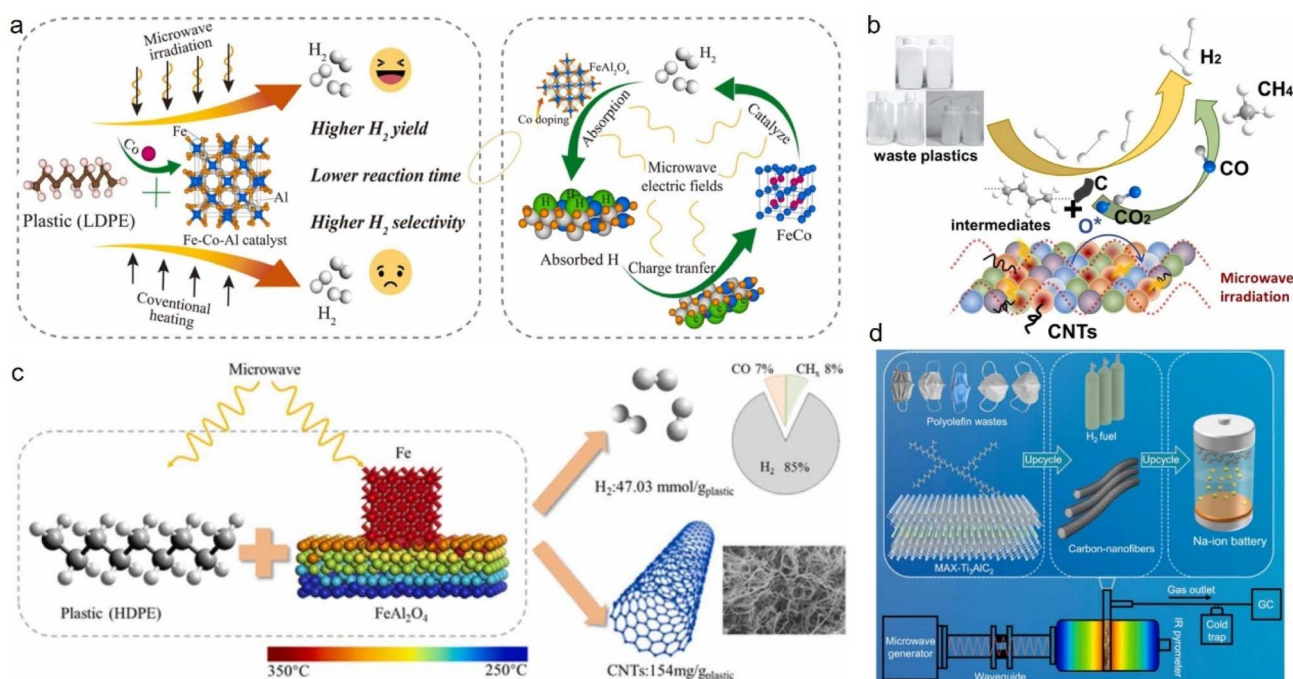

Fig. 1 Microwave-assisted enhanced hydrogen production from plastics *via* different catalysts. (a) Microwave-initiated decomposition of plastic over an Fe−Co−Al catalyst.[59] (b) Schematic diagram of the decomposition of waste plastics over Fe/Ni−CeO_2@CNTs catalyst in a microwave radiation field.[60] (c) Reaction mechanism of HDPE to prepare hydrogen and carbon nanotubes on Fe/$FeAl_2O_4$ under microwave irradiation.[61] (d) Microwave-initiated upcycling of polyolefin plastic wastes over MAX-catalyst and the application of carbon nanofibers.[62]

Table 1 Comparison of the catalytic performance of microwave heating and conventional heating methods in plastic dehydrogenation

Type	Plastic	Catalyst	Pyrolysis temp. (°C)	Catalytic temp. (°C)	Steam (Y/N)	H_2 yield (mmol $(g_{plastic})^{-1}$)	Ref.
Microwave (one-step)	LDPE	Fe–Co–Al	—	600–900	N	61.39	59
	HDPE	Fe/Ni–CeO_2@CNTs	—	800	N	50.2	60
	LDPE					48.3	
	PP					48.3	
	HDPE	Fe–$FeAl_2O_4$	—	300–450	N	47.3	61
	HDPE	Ti_3AlC_2	—	900–1000	N	49	62
	LDPE					51.3	
	PP					46	
	HDPE	$FeAlO_x$	—	300–380	N	55.6	64
	PP					51.4	
	PS					26.9	
	PE	Fe–Ni	—	400	N	51.8	65
Pyrolysis- reforming (two-step)	Plastic mixture	Ni–Fe/MCM41	500	800	N	38.1	66
	Plastic mixture	Ni–Fe	500	800	N	42.3	67
	PP	Fe, Ni	500	800	Y	25.14	68
	HDPE	Ni/ZSM_5	500	850	Y	66.09	69
	PP	NiMnAl 424	500	800	Y	56.6	70
		NiMnAl 444				37.2	
	PP	Fe/SiO_2-S	600	800	N	15.4	71
		Fe/SiO_2-L				25.6	
		Ni/SiO_2-S				18.1	
		Ni/SiO_2-L				22.6	

a microwave acceptor and a catalyst, giving H_2 yields of 51.3, 49, and 46 mmol (g plastic)$^{-1}$, respectively (Fig. 1d).

Table 1 presents a comparison between microwave heating and conventional heating methods in plastic dehydrogenation to illustrate the benefits of microwave-assisted catalytic technology. As mentioned, traditional heating methods typically employ a two-stage process involving plastic pyrolysis at high temperatures to produce low-molecular-weight hydrocarbon compounds, which are then subjected to a catalytic reforming method to generate hydrogen. However, this approach suffers from several significant drawbacks, including a high energy consumption, complex procedures, substantial carbon dioxide emissions (approximately 12 kg CO_2 per 1 kg of hydrogen produced), and low hydrogen selectivity.[63] In contrast, microwave heating methods facilitate the one-step production of high yields of hydrogen and offer numerous advantages, such as a low energy consumption and high efficiency.

4.   Hydrogen produced from biomass

Renewable resource biomass is another ideal source to generate hydrogen.[12,72–75] Currently, the main methods for converting biomass into hydrogen are biological and thermochemical methods. Despite the attractive prospect of generating hydrogen by the biological method in terms of its sustainability, the poor photosynthetic conversion and COD removal efficiency limit its practical application.[76] As mentioned, thermochemical methods usually require high temperature to activate the pyrolysis and initiate hydrogen production and are thus beset by the issues of high energy consumption and by-products generation.[77,78] Microwave-assisted pyrolysis can achieve rapid high-temperature heating, which can offer significant

advantages in transforming biomass into hydrogen. Qiao[79] et al. prepared a novel graphene aerogel with few defects by the microwave heating for chemically pre-reducing graphene aerogel. Under microwave irradiation, a high-temperature arc of more than 1000 °C (difficult to achieve by existing heating methods) could be generated by the aerogel, which could promote the rapid pyrolysis of biomass, whereby H_2-rich gas could be obtained with hydrogen yields of 3.31, 4.35, 2.25, and 2.90 g per g biomass from the microwave-assisted pyrolysis of four common solid biomasses (poplar branches, rice husks, straw, and corn Stover). Parvez[77] et al. compared the yield differences of gas, oil, and coke produced by the pyrolysis of Bakelite under conventional and microwave heating at 600 °C, 700 °C, and 800 °C, and found that the corresponding energy (higher heating value) of the produced gas under microwave heating was higher than those of conventional heating at the selected three temperatures. In addition, by using Aspen Plus™ for hydrogen plant simulation, the results showed that by producing 120 g H_2 per kg Bakelite, the microwave heating performance was 15% more efficient than conventional systems.

Therefore, microwaves can enhance the chemical reaction process, improving the hydrogen production efficiency of thermochemical methods (such as pyrolysis and gasification) and strengthening the energy efficiency in promoting biological hydrogen production.[80–82] However, further improvements are needed in the future to modify the advantages and limitations of the process. It is also necessary to perform a techno-economic assessment based on the production, costs, technical level, and industrial scalability in order to apply this technology to actual production.

5. Hydrogen produced from low-carbon alcohols

The reforming of low-carbon alcohols (methanol, ethanol, propanol, butanol, *etc.*) is a very promising approach for hydrogen generation, since their low sulfur contents, high volumetric energy density, high hydrogen/carbon ratio, and biodegradability make them desired media for energy transport.[83–86] Compared with other compounds (*e.g.*, that have a plastic reforming temperature above 700 °C),[58,67,87] low-carbon alcohols can be reformed at relatively low temperatures, for instance, methanol composed only of carbon–hydrogen bonds, and the hydrogen extraction process can be carried out at a low temperature of about 200–300 °C; while the reforming temperature of ethanol is only about 400 °C.[88–92] Besides, producing hydrogen from low-carbon alcohols has certain advantages: (1) in low-carbon alcohol compounds (which are easy to store and transport), reforming is expected to realize *in situ* hydrogen production, which helps to overcome the shortcomings of storage and transportation;[92–95] (2) availability of accessible and abundant resources;[96] (3) CO and CO_2 produced by the dehydrogenation of low-carbon alcohols can be used as raw materials to be reconverted into the initial compounds under appropriate conditions (temperature, pressure, *etc.*), so as to transport hydrogen on demand.[97–101]

An external energy supply is required for reforming low-carbon alcohols since it is an endothermic reaction. This could either involve using conventional heat sources (*e.g.*, steam, electric heating, or an oil bath) or alternative energy sources, such as plasma or microwaves in a reactor. Generally, the reaction rate depends on the energy induction rate, whereby the efficiency of conventional heating methods relies on the heat transfer efficiency and the system temperature usually has a low efficiency and poor selectivity for thermal conduction. In contrast, microwave-assisted heating can realize a rapid, selective, and volumetric heating process, which possesses benefits unachievable by traditional heating methods, namely a higher conversion and selectivity with a reduced system temperature required. Furthermore, microwave plasma exhibits a higher conversion rate (>90%) than DBD plasma technology due to its high stability and repeatability under various operating conditions and the possibility of operating at atmospheric pressure.[102]

When utilizing microwave plasma technology to reform low-carbon alcohols for hydrogen production, they operate in working atmospheres in nitrogen, argon, and oxygen gas, corresponding to nitrogen, argon, oxygen plasma,[103,104] *etc.* The corresponding plasma produces massive high-energy electrons, active groups, and excitation ions, thus promoting the reforming to produce hydrogen.[105–109] Fig. 2 illustrates a microwave plasma hydrogen production system; comprising a magnetron
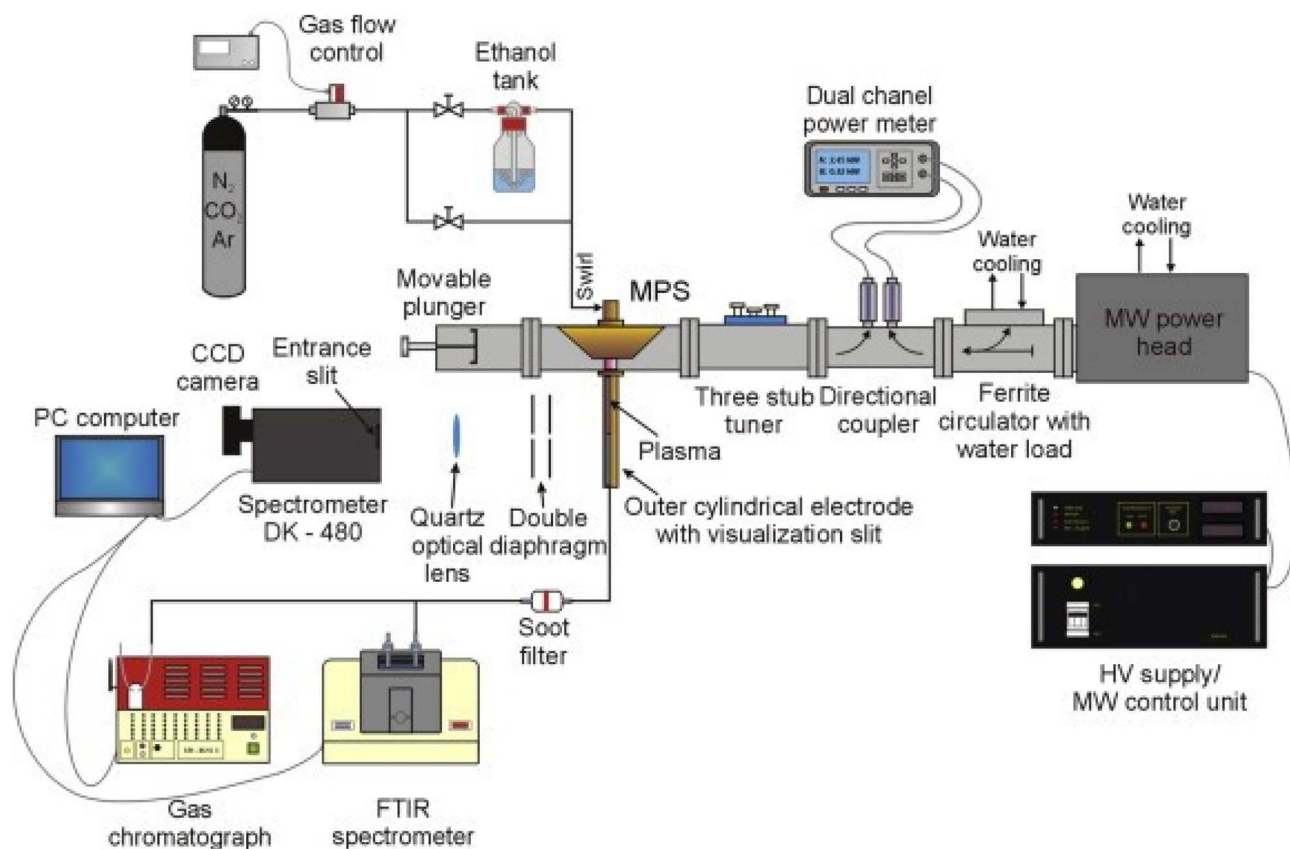

Fig. 2 Diagram of a microwave plasma hydrogen production system.[110]

Table 2 Summary of microwave-assisted hydrogen production from alcohols

Feed	Catalyst	Reaction parameters	H_2 selectivity (S)/production rate	Ref.
Methanol	—	Pressure: 1 atm Working gas: N_2	$S(H_2) = 85.5\%$	111
Methanol	CuO–ZnO–Al_2O_3	Pressure: 1 atm Working gas: N_2 Methanol : water: 1 : 1	$S(H_2) = 85$–96%	119
Methanol	CuZnO/Al_2O_3 PdZnO/Al_2O_3	Pressure: 1 atm Working gas: N_2	$S(H_2) = 70\%$	115
Ethanol	—	Pressure: 1 atm Working gas: N_2	728 NL h^{-1}	103
Ethanol	—	Pressure: 1 atm Working gas: N_2	1016 NL h^{-1}	104
Ethanol	—	Pressure: 1 atm Working gas: N_2/Ar/CO_2	210 NL h^{-1}	110
Ethanol	—	Pressure: 1 atm Working gas: N_2	1043 NL h^{-1}	113
Ethanol	—	Pressure: 1 atm Working gas: N_2/CO_2 Ethanol : water: 1 : 1	751 NL h^{-1}	120
Ethanol Isopropanol	—	Pressure: 1 atm Working gas: N_2/CO_2	1150 NL h^{-1} 1116 NL h^{-1}	121
Ethanol	Pyrolysis residue of sewage sludge	Pressure: 1 atm Working gas: N_2	$S(H_2) = 52.2\%$	122

generator, microwave power supplying and measuring system, microwave plasma source (MPS), impedance matching elements, gas supply and flow control system, gas analysis system, and optical emission spectroscopy (OES) system.[110] Wang[111] et al. used non-catalytic microwave plasma technology to refine methanol into hydrogen. A 3.3% molar fraction of methanol in the experiment showed a conversion rate greater than 97%, while the selectivity of H_2 increased from 77.5% to 85.8% when the applied power was increased from 800 W to 1400 W. Rincón[112] et al. found that low argon flow rates significantly promoted the hydrogen selectivity. Two atmospheric pressure microwave plasma sources could be used to withstand large ethanol flow rates, which enabled a nearly complete decomposition (>99%) of ethanol under various operating conditions while achieving high hydrogen yields. In addition, the technology is expected to be expandable to the industrial scale because of the relatively low specific energy required for ethanol decomposition. Compared with the steam reforming method, the direct introduction of liquid alcohols can save energy for gasification and improve the economic benefits. Czylkowski[113] et al. used nitrogen plasma to effectively decompose ethanol droplets into hydrogen-rich products while improving the production rate and energy efficiency.

Microwave plasma reforming technology is not limited to reforming single alcohols, like methanol,[114,115] ethanol,[110,116,117] propanol, and others, it can also simultaneously decompose low-carbon alcohol mixtures to prepare hydrogen,[102,118] which is more conducive to practical application without the expenditure for the separation and purification of alcohol mixtures. In addition, Table 2 also discusses the operating parameters and

hydrogen selectivity of microwave-assisted hydrogen production from alcohol compounds.

6. Hydrogen produced from methane

Methane is considered the second major greenhouse gas just following carbon dioxide, and the annual emissions of methane are yet to grow rapidly.[123,124] Thus, diversifying the utilization of methane is indeed essential to reduce methane emissions, address global warming, and carbon neutrality ultimately. As a high hydrogen-to-carbon compound, methane is naturally suitable as a feedstock to produce syngas: a mixture of hydrogen, carbon monoxide, and carbon dioxide gases.[125–128] Syngas can be transformed by a Fischer–Tropsch synthesis into raw materials required by various chemical products, like ammonia, methanol, and hydrocarbons,[129,130] achieving methane removal and resource utilization.

Methane reforming methods include the steam reforming of methane[131,132] (eqn (3)), the partial oxidation of methane[133–135] (eqn (4)), methane dry reforming[136–138] (eqn (5)), and methane thermal decomposition[139,140] (eqn (6)). Currently, methane steam reforming is still the main approach to produce syngas, but requires a large amount of superheated steam to maintain high temperature, resulting in huge energy costs. Meanwhile, the methane steam reforming process is a strongly endothermic reaction that usually needs to be operated at 800–900 °C high temperatures. Unfortunately, regular catalysts tend to be quickly inactivated under such harsh conditions.[141] Compared with the methane steam reforming method, the partial oxidation method with exothermic properties can be carried out under mild conditions; nevertheless, it is relatively difficult to
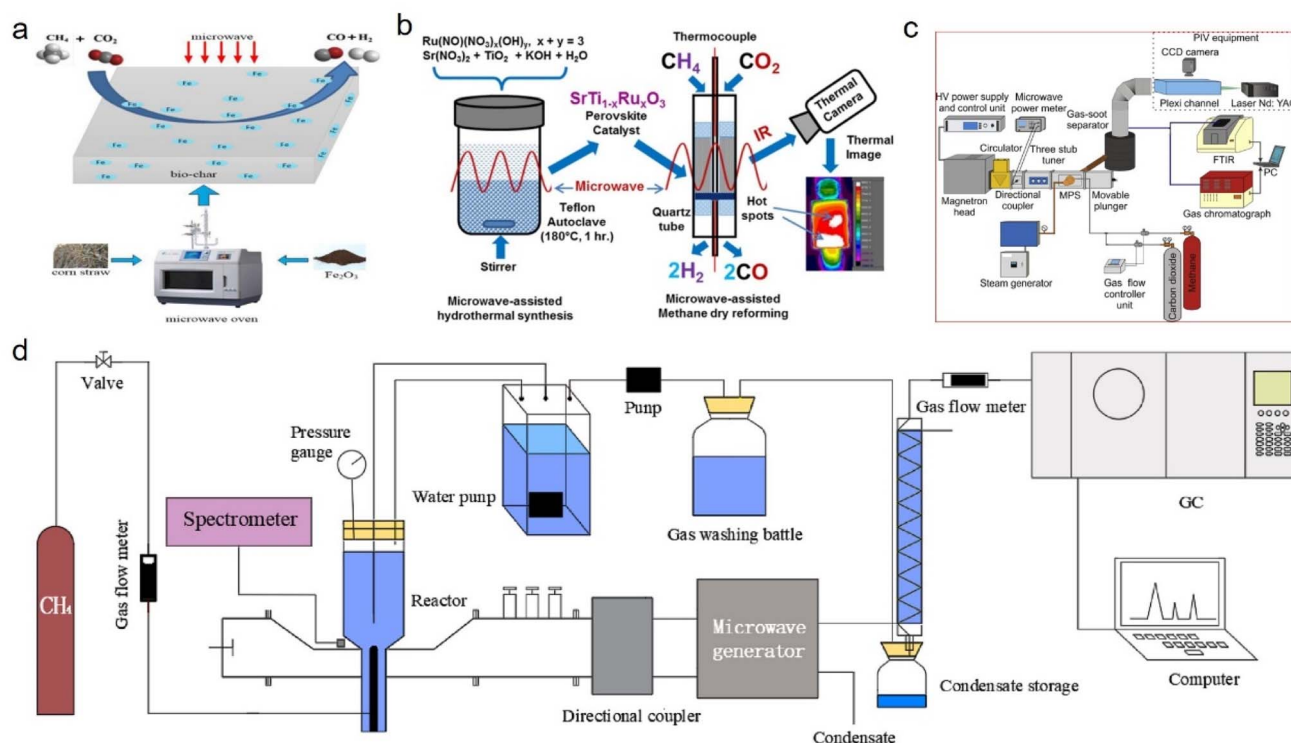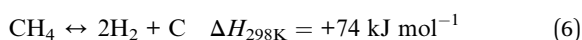
Fig. 3 (a) Porous Fe-rich biomass-derived carbon[142] and (b) ruthenium-doped strontium titanate (SrTiO₃) perovskite[143] catalysts applied for microwave-assisted methane dry reforming. (c) and (d) Sketch of microwave plasma enhanced hydrogen production *via* the steam reforming of methane.[144,145]

produce syngas from the partial oxidation method of methane. From an environmental aspect, methane dry reforming can convert methane and carbon dioxide into syngas, which utilizes greenhouse gases simultaneously, but the required reaction temperature is >700 °C, which incurs the same problem that catalysts may sinter and fail.

$$CH_4 + H_2O \leftrightarrow 3H_2 + CO \quad \Delta H_{298K} = +206 \text{ kJ mol}^{-1} \quad (3)$$

$$CH_4 + 1/2O_2 \leftrightarrow 2H_2 + CO \quad \Delta H_{298K} = -8.5 \text{ kJ mol}^{-1} \quad (4)$$

$$CH_4 + CO_2 \leftrightarrow 2H_2 + 2CO \quad \Delta H_{298K} = +247 \text{ kJ mol}^{-1} \quad (5)$$

$$CH_4 \leftrightarrow 2H_2 + C \quad \Delta H_{298K} = +74 \text{ kJ mol}^{-1} \quad (6)$$

The microwave-assisted heating method can efficiently restructure methane into syngas through catalytic or plasma pathways. Li[142] *et al.* primarily used Fe_2O_3 as a catalyst for the pyrolysis of biomass to obtain a large surface area, porous, Fe-rich biomass-derived carbon, and then applied this for microwave-assisted methane reforming and achieved a high methane conversion (800 °C). Furthermore, the conversion rate of CH_4 and CO_2 was relatively stable in a long–term reaction of 160 min, and the gaseous products contained a syngas content of 88.79% and H_2/CO ratio of 0.92 on average. Compared with traditional heating methods, microwave-assisted heating can not only play a significant role in enhancing chemical reactions, but also has a positive effect on catalyst preparation (Fig. 3a).

Stefanidis[143] *et al.* adopted conventional and microwave-assisted hydrothermal methods to prepare various ruthenium-doped strontium titanate (SrTiO₃) perovskite catalysts, and found that SrTiO₃ catalyst synthesis through microwave irradiation could efficiently convert CH_4 and CO_2 into syngas (H_2/CO = 0.9) (Fig. 3b). Furthermore, microwave plasma technology also exhibited excellent performance in methane reforming, and could be operated in catalyst-free conditions. For instance, Czylkowski[144] *et al.* studied the hydrogen production efficiency of methane by combining steam reforming (CO_2 and water steam) in a metal cylinder microwave plasma source (MPS) provided by waveguide, which could achieve a hydrogen production energy yield of 42.9 g (H_2) per kW per h by optimizing the absorbed microwave power, working gas composition and flow rate, and other process input parameters, while the plasma steam reforming of methane could operate stably at high gas flow rates (thousands NL per h) (Fig. 3c). Sun[145] *et al.* injected methane into water and realized the wet reforming of liquid phase methane by directly coupling liquid phase microwave discharge plasma. When the microwave input power was 900 W, the methane conversion rate and hydrogen concentration were 94.3% and 74.0%, respectively. In addition, through optimization of the electrode structure while improving the stability of the plasma system, a higher hydrogen yield and hydrogen energy efficiency were obtained, and the highest energy efficiency for hydrogen production was about 0.92 mmol kJ^{-1} (Fig. 3d). Moreover, the performance comparison of different catalysts has shown in Table 3.

Table 3 Summary of microwave-assisted methane dry reforming based on different catalysts

Catalysts	Temp. (°C)	VHSV (L g_{cat}^{-1} h^{-1})	Microwave-assisted heating		Conventional heating		H_2/CO	Ref.
			CH_4 conversion (%)	CO_2 conversion (%)	CH_4 conversion (%)	CO_2 conversion (%)		
Potassium-rich char	800	0.166	95	100	81	93	0.7	146
Activated carbon	600–900	0.16	100	100	72	80	0.7–1.4	147
Biochar	800	0.6	93.8	89.4	79	71.2	0.71–0.88	148
$SiC \cdot SiO_2$	810	—	27	17	—	—	0.97	149
12%Fe–SiC·SiO$_2$			>95	>95				
FY5	800	0.3	>96	>97	—	—	0.67	150
50% FY5 + 50% Ni/Al$_2$O$_3$		3	>88	>93	—	—	1	
Biochar	600–1000	—	40–100	45–100	—	—	0.91–3	151
Ni–CeO$_2$	850	—	65	84	—	—	1.1–1.5	152
2Ta–Ni			82	83				
2Cr–Ni			92	99				
2Fe–Ni			79	85				
7Ru/SrTiO$_3$	700	3	90.2	88.5	—	—	0.88	143
		4.5	91.7	89.4			0.9	
		6	93.9	90.3			0.89	
		7.5	93.4	90.4			0.89	
		9	94	91.2			0.89	
		10.5	94.6	91.8			0.89	
		12	61.8	63.6			0.85	
		13.5	53.5	64.9			0.86	
Char + Na	975	2.4	72	93	—	—	—	153
Char + K			73	92				
Char + Ca			79	83				
Char + Mg			80	82				
Char + Ni			92.7	86.7				
CoMo$_2$/Al$_2$O$_3$	—	10	80	93	—	—	0.8	154

7. Conclusion

Microwave-assisted technology offers an effective and cost-efficient means of generating hydrogen. During microwave-assisted heating, the heating characteristics of materials rely on their loss factor, and high loss factors are advantageous for achieving increased heating rates and reaction temperatures. Various literature reviews have indicated that electromagnetic waves are capable of selectively interacting with catalysts in the process of hydrogen production from waste plastics, which leads to a rapid heating of the catalyst particles and the catalytic cracking of carbon–hydrogen bonds in plastics to produce hydrogen. Additionally, the resulting hydrogen can quickly dissociate from the active sites on the catalysts to avoid undesirable side reactions. The utilization of microwave-assisted technology in enhancing biomass hydrogen production provides a promising avenue for sustainable hydrogen generation, since biomass resources are abundant worldwide, and as the bed temperature can quickly attain the required temperature for thermochemical reactions, thereby reducing the energy consumption of the reactions and side reactions. In contrast, low-carbon alcohol reforming can be conducted at a lower temperature, and low-carbon alcohols possess abundant resources and high hydrogen content, which makes them suitable for on-demand hydrogen production, thus overcoming the challenges related to hydrogen storage and transportation. Furthermore, carbon monoxide and carbon dioxide produced during methanol reforming can be converted back into methanol directly by industrial direct hydrogenation methods. Based on this, the selective decomposition of methanol into hydrogen and carbon monoxide using microwave catalysis or microwave plasma technology can help achieve a reversible hydrogen storage system by hydrogenating the separated carbon monoxide. Finally, microwave catalysis and microwave plasma technology can efficiently convert the two main greenhouse gases into synthesis gas under low energy consumption conditions in methane reforming, which can be utilized to synthesize high-value chemicals.

This literature review suggests several recommendations for future research endeavors:

(1) Due to the difficulty in obtaining pure plastic and biomass in practice in real life, it is essential to focus on hydrogen production by mixed impure organic sources to actually assess practical feasibility, thereby reducing the sorting cost and improving the universality of microwave-enhanced hydrogen production in the future. Second, more extensive research is required on the reaction mechanism of the process to facilitate the development of catalysts that can demonstrate stable performance, high dehydrogenation activity, and resistance to impurities. Furthermore, to improve the efficiency of co-processing biomass and plastic waste, further research needs to be conducted on various factors, such as the particle size, heating rate, microwave power, heating mode (continuous or intermittent), and mass ratio, to ultimately aid the

understanding and for guiding catalyst design to realize ideal performance, gas composition, and hydrogen production, and leading to an enhancement in the co-processing efficiency.

(2) Biomasses are renewable resources whose efficient development and utilization can play a pivotal role in addressing global energy and ecological environmental concerns. Nonetheless, the direct use of biomass as a hydrogen storage medium to enable on-demand hydrogen production remains challenging. To promote the advancement of a hydrogen-based society, establishing and evaluating the following technical issues need to be addressed: converting biomass into syngas *via* microwave-assisted pyrolysis technology, followed by transforming the syngas into high-hydrogen-content methanol that is easily storable and transportable; studying the feasibility of *in situ* hydrogen production by combining the advantages of microwave reactions with regard to the compact structure, easy installation, and ease of operation; methodically investigating the factors that influence the preparation of syngas from biomass, methanol production from syngas, and hydrogen production from methanol decomposition (*e.g.*, catalyst particle size, specific surface area) to achieve the optimal efficiency.

(3) The preparation of syngas through methane reforming usually requires high-temperature conditions, which imposes limitations on traditional heating methods. Fortunately, microwave plasma technology presents notable advantages over traditional techniques, including higher conversion rates and energy efficiency, better chemical selectivity, greater processing capacity, and improved discharge uniformity in methane reforming reactions. Microwave plasma is capable of effectively catalyzing methane and carbon dioxide in a non-equilibrium state. Nonetheless, to advance this technology from the laboratory scale toward commercialization, optimization of the process parameters, such as microwave power, pressure, reactant composition, flow rate, catalyst composition, preparation method, and the cost, is required to achieve greater energy and conversion efficiency, and to surmount the technical and economic obstacles.

In short, although microwave-assisted methods have already played a significant role in the domain of hydrogen production to date, further developments necessitate a meticulous optimization of the key parameters, such as microwave power, catalyst structure, and reaction pressure, to achieve better products. Additionally, an economic assessment of the microwave-assisted hydrogen production process is required to fully ascertain its benefits and promote its implementation in large-scale production.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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