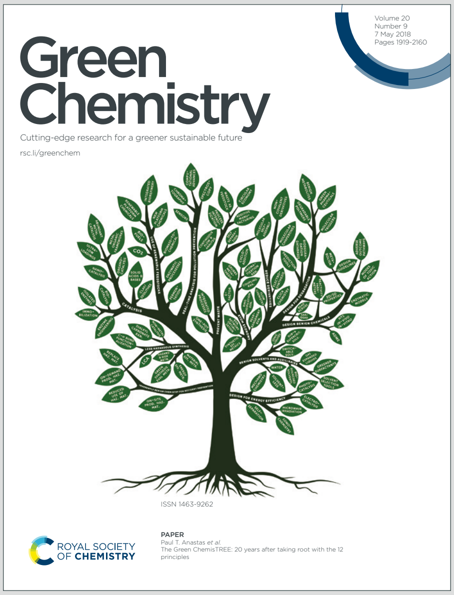
View Article Online
View Journal

Green Chemistry
Cutting-edge research for a greener sustainable future

This article can be cited before page numbers have been issued, to do this please use: Y. Shen, *Green Chem.*, 2025, DOI: 10.1039/D5GC03030G.



ROYAL SOCIETY OF CHEMISTRY

rsc.li/greenchem

View Article Online
DOI: 10.1039/D5GC03030G

1. Microwave-assisted pyrolysis is an emerging thermochemical technology that has gained significant attention for efficiently converting hydrogen-rich resources to H_2 and high-value carbon materials. The research progress in the microwave-assisted pyrolysis of hydrogen-rich resources for H_2 production were concluded.

2. This review discussed the microwave-assisted pyrolysis of waste polymeric wastes (lignocellulosic biomass and synthetic plastics), which were influenced by various operating parameters including the reaction temperature, the reaction time, the supply of microwave power, the origin of microwave feedstock, the particle size of feedstock, the mixing ratios of feedstock, the dielectric constant of feedstock, the feedstock pretreatment, the use of catalysts and microwave absorbers.

3. The challenges and future directions in microwave-assisted pyrolysis of biomass and plastic wastes were highlighted, thus promoting the H_2 production toward high-efficiency, energy-saving and low-carbon development.

View Article Online
DOI: 10.1039/D5GC03030G

Microwave-assisted Pyrolysis of Biomass and Plastic Wastes for Hydrogen Production

Yafei Shen [1, 2]*

[1] *School of Energy and Power Engineering, Nanjing University of Science and Technology, 210094 Nanjing, Jiangsu, China*

[2] *Jiangsu Purestar EP Technology Co., Ltd, No. 28 Gangao Road, ZJG Free Trade Zone, Jiangsu Province, China*

***Corresponding author**

Email: 376754097@qq.com; shenyf@njust.edu.cn (Y. Shen)

View Article Online
DOI: 10.1039/D5GC03030G

Abstract

The development of hydrogen energy is a key path to achieving carbon neutrality, providing zero-carbon and efficient clean energy solutions. Moreover, it can enhance energy security, promote the green transformation in industries, transportation and other fields, and form new economic growth points. Microwave-assisted pyrolysis is an emerging thermochemical technology that has gained significant attention for efficiently converting hydrogen-rich resources to H_2 and high-value carbon materials. Microwave heating enhances the uniformity of heat distribution. Electromagnetic energy is converted to molecular kinetic energy in microwave heating. Dielectric loss is the phenomenon in which a dielectric material dissipates its electromagnetic energy in form of heat or other forms. Dielectric loss is inherent to all materials and occurs naturally. This paper concludes the research advances and key challenges in the microwave-assisted pyrolysis of biomass and plastic wastes for H_2 production. In general, microwave pyrolysis is the selective heating of feedstocks. The parameters of microwave pyrolysis include the reaction temperature, the reaction time, the supply of microwave power, the origin of microwave feedstock, the particle size of feedstock, the mixing ratios of feedstock, the dielectric constant of feedstock, the feedstock pretreatment, the use of catalysts and microwave absorbers. The effects of these parameters on H_2 production from microwave-assisted pyrolysis are clarified. H_2 production through microwave-assisted catalytic pyrolysis of waste plastic and biomass has advantages in terms of lower energy consumption and potential for reducing tar formation, thus increasing the yield and selectivity of H_2 compared to conventional pyrolysis. Key challenges include achieving uniform heating in large reactors due to variable dielectric properties of feedstocks and limited microwave penetration, which risks hot spots and inconsistent product quality. Feedstock variability in composition, moisture, and size complicates stable material flow and continuous feeding systems. Microwave generation demands costly equipment and optimized energy use to ensure economic viability. Maintaining consistent product quality is difficult due to uneven heating and feedstock diversity, alongside managing the carbon byproducts. Furthermore, the future directions in microwave-assisted pyrolysis of each resource are discussed, thus promoting the H_2 production toward high-efficiency, energy-saving and low-carbon development.

Keywords: microwave heating; pyrolysis; hydrogen; plastic; biomass

View Article Online
DOI: 10.1039/D5GC03030G

1. Introduction

1.1. Hydrogen Energy

The challenge of climate change is promoting the present energy systems towards transition technologies that allow for decreasing greenhouse gas (GHG) emissions. Hydrogen (H_2) is used increasingly to different sectors from industry to transport [1]. Global H_2 use was around 120 Mt/a in 2020 [2] and will rise to 530 Mt/a in 2050 [3]. Recently, H_2 has been identified a renewable energy carrier/vector in a bid to reduce acute dependence on fossil fuels such as natural gas, petrol/gasoline, and diesel. In comparison to these fossil fuels, H_2 indicates the efficiency of a hydrogen economy (referred to a socio-economic system) in which H_2 is used as a primary energy carrier, replacing or complementing conventional fossil fuels [4]. Here a hydrogen economy envisions a transition from carbon-based energy sources to hydrogen-based energy infrastructure, to achieve a more sustainable, clean, and efficient energy system [5, 6]. As shown in Fig. 1, the successful implementation of a hydrogen economy requires advancements in H_2 production, transportation, storage, and utilization technologies, and the establishment of supportive policies and infrastructure to enable widespread adoption [7-9].

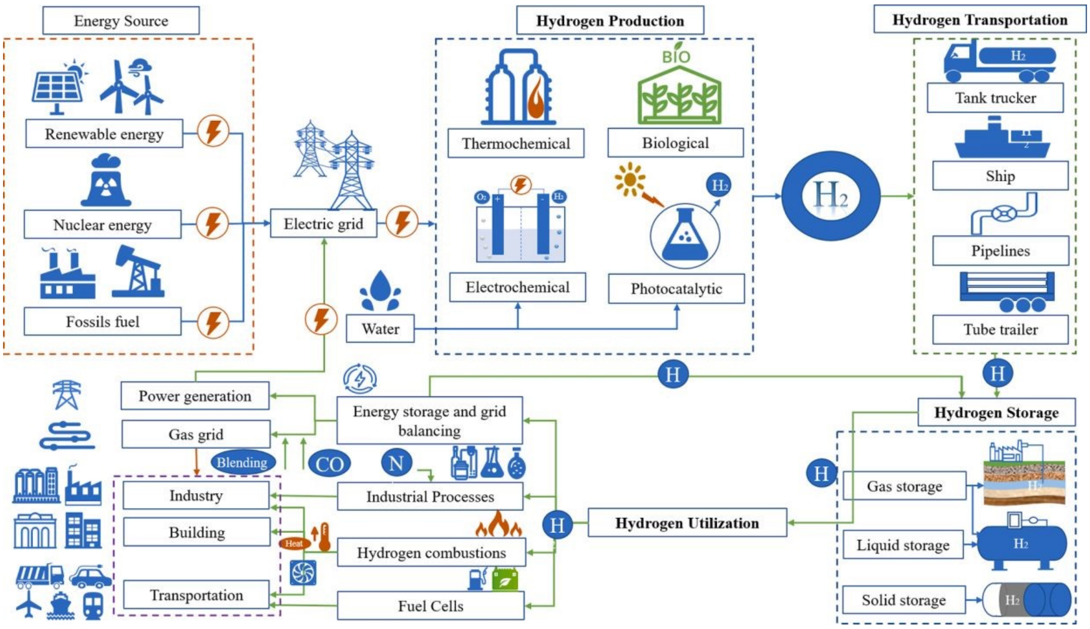


Fig. 1 Overview of a hydrogen economy including H_2 production, transportation, storage, and utilization technologies [9]

1.2. Hydrogen Production Technologies

View Article Online
DOI: 10.1039/D5GC03030G

Thermochemical, biological, electrochemical, and photocatalytic technologies can be used to produce H_2 from different resources [10]. Thermochemical technologies such as high-temperature pyrolysis and gasification are commonly used to produce H_2 from hydrogen-rich resources (e.g., natural gas, coal, petroleum, plastic, and biomass) [11]. Biological technologies such as microbial metabolism are used to produce H_2 from biomass wastes through water photolysis, photo-fermentation, dark-fermentation, and combined fermentation [12]. Electrochemical technologies such as electrocatalytic water splitting are used to produce H_2 [13]. Besides, photocatalytic technologies such as photocatalytic water splitting are used to produce H_2 [14]. H_2 is generally identified by thirteen color codes (i.e., green, blue, grey, brown or black, turquoise, purple, pink, red and white), which refer to the technology or resource used to produce it [15]. The production of brown, grey, and black hydrogen using fossil fuels (e.g., coal, methane) is an important source of GHG emissions. Grey hydrogen is made from fossil fuels, often through steam methane reforming (SMR), which releases carbon dioxide (CO_2). Black or brown hydrogen is made using bituminous coal (black) or lignite (brown), respectively. Coal gasification can produce hydrogen with releasing CO_2 and carbon monoxide (CO) [16]. Much effort has been made to develop technologies that can produce hydrogen without GHG emissions. Compared with black and grey hydrogen, blue hydrogen production is more sustainable but still releases CO_2. Green hydrogen production is a clean technology that uses renewable energy sources (e.g., solar panel, wind turbine) for electrolysis of water to generate hydrogen, which can achieve zero carbon emissions. However, green hydrogen production is currently more expensive than blue hydrogen production mostly due to the cost of electrolyzer materials [18]. In contrast to green hydrogen, blue hydrogen is produced using fossil fuels (e.g., natural gas), but the CO_2 produced is captured, stored or utilized [19]. This raises concerns about its long-term sustainability, given the world's goal of reducing reliance on fossil fuels [20-22]. The choice between blue and green hydrogen depends on factors such as cost, availability of resources, and environmental goals.

1.3. Thermochemical Conversion of Hydrogen-rich Resources

View Article Online
DOI: 10.1039/D5GC03030G

Thermochemical conversion technologies such as coal gasification and SMR have been widely employed for production of hydrogen from fossil fuels. Owing to their cost-effective and high technology readiness, they are still the predominant hydrogen production technologies in commercial application. Many companies have developed the CCUS technologies to reduce CO_2 emissions, reducing the environmental impact. In addition, researchers have taken effort in developing advanced thermal conversion technologies and exploring renewable resources (such as waste plastics and biomass) to promote the sustainability of hydrogen production. For example, methane pyrolysis can be used to produce hydrogen and solid carbon with zero-CO_2 emissions [23, 24]. Biomass with carbon-neutral property [25-28] and plastic wastes [29] can be used as sustainable hydrogen-rich resources replacing coals for hydrogen production through the pyrolysis or gasification process. In common, the gaseous products can be further reformed or upgraded into hydrogen and carbon materials under the catalytic effects. In recent years, conventional pyrolysis has been widely used for converting biomass and plastic wastes into various products, but the conversion efficiency is significantly affected by the heat transfer efficiency and the heating model [30]. Microwave can offer volumetric heating with a higher energy efficiency than conductive-convective heat transfer in conventional approaches [31]. Thus, microwave-assisted pyrolysis has received increasing interest because of its low thermal inertia, uniform and volumetric heating, high heating rate, and high efficiency, which can increase productivity and energy efficiency [32]. Microwave-assisted pyrolysis as an emerging thermochemical technology have been increasingly developed for converting hydrogen-rich resources into H_2 and other valuable products. H_2 production by microwave-assisted pyrolysis has advantages of reducing energy consumption and tar production. This paper will conclude the research progress in microwave-assisted pyrolysis of biomass and plastic wastes for H_2 production. The challenges and future directions in microwave-assisted pyrolysis of biomass and plastic wastes will be highlighted, thereby promoting the H_2 production toward high-efficiency, energy-saving and low-carbon development.

2. Microwave Pyrolysis

View Article Online
DOI: 10.1039/D5GC03030G

2.1. Principal Microwave Heating

Microwave refers to electromagnetic wave with frequencies of 300-3000 GHz [33]. The magnitude and spatial distribution of its energy depend on the transmission, reflection, and absorption of electromagnetic wave in the materials (Fig. 2a) [34]. Microwave transmissive materials including most polymer materials and some non-metallic materials can transmit electromagnetic wave without greatly changing its nature (including energy). Microwave reflective materials mainly consist of highly conductive metals. Besides, microwave absorbing materials are designed to neither easily reflect nor completely transmit microwave, necessitating good impedance matching and strong microwave loss, such as dielectric and magnetic loss. Dielectric loss includes interface polarization, dipole polarization, and conductive loss. Magnetic loss includes natural resonance, hysteresis loss, and eddy current loss. Microwave absorbing materials of dielectric loss include ceramic- and carbon-based materials such as silicon carbide and graphite. Microwave absorbents of magnetic loss mainly include ferrite and magnetic metal particles (Fe, Ni, Co and their alloys) [35].

The electromagnetic wave lost within the material is transformed into heat, making microwave heating a non-contact and volumetric heating method. Microwave heating occurs from the inside to the outside, leading to consistency in the direction of heat and mass transfer. Moreover, microwave with the characteristics of selective heating can result in a substantial overlap between the thermal sites in the reaction system and the material reaction sites, which eliminates the heat conduction process required by conventional heating method. Thus, microwave pyrolysis can accelerate the reaction rate and reduce the apparent activation energy [36]. The ability of materials to absorb microwave and convert it into heat is commonly represented by the magnitude of the loss angle tangent (tanδ). In general, tanδ greater than 0.5 indicates that the material has a strong microwave absorption ability, while value less than 0.1 suggests a weak microwave absorption ability [37]. Some common materials of different categories and their tanδ values are listed in Table 1. The electromagnetic energy is converted into heat by applying microwave susceptors that absorb the microwave radiation and

View Article Online
DOI: 10.1039/D5GC03030G

heat the feedstock such as biomass. Another reason for adding microwave susceptor is attributed to the low dielectric characteristics of biomass. In usual, carbon material or water having much higher dielectric loss can be added to the biomass for converting the microwave energy into heat [38].

Table 1. Representative materials with transmission, reflection, and adsorption effects on microwave [35]

Type of material		**Name of material**	**Loss angle tangent (tanδ)**
Microwave transmissive materials (mainly most polymers and some non-metallic materials)		Borosilicate glass	1.2×10^{-3}
		Teflon	4.8×10^{-4}
		Polystyrene	3.0×10^{-4}
		Alumina	1.0×10^{-3}
		Fused quartz	3.0×10^{-4}
		Silicon	$< 1.2 \times 10^{-2}$
Microwave reflective materials (mainly some metal materials with good electrical conductivity)		Al	/
		Cu	/
		Au	/
		Ag	/
		Zr	/
Microwave absorption materials	Dielectric loss type (mainly ceramic-based and carbon-based materials)	SiC	0.58-1
		Graphite	0.36-1
		Carbon black	0.35-0.83
		Activated carbon	0.57-0.8
		Charcoal	0.14-0.38
		Carbon nanotube	0.25-1.14
		Foam carbon	0.05-0.2
	Magnetic loss type (mainly ferrite and magnetic metal particles)	Ferrite	0.2-0.3
		Carbonyl iron powder	0.08-0.14

2.2. Microwave-assisted Pyrolysis

Conventional pyrolysis has been widely applied in the industry. Heat is transferred from the furnace to the particle surface through conduction, convection, and direct radiation and then through conduction from the surface to the core, thereby creating a temperature gradient from the outside to the inside of the particle (Fig. 2b) [32, 35]. However, the energy during microwave-assisted pyrolysis is directly delivered to the particle core that can form a temperature gradient from the particle core to the surface, without physical contact between the feedstock and the thermal source (Fig. 2c). This heating mechanism releases volatiles that are diffused from the inner core to the outer surface and from the high-temperature region to the low-temperature region, which greatly affects the product properties [32]. Another distinguishing characteristic of

View Article Online
DOI: 10.1039/D5GC03030G

microwave pyrolysis is the formation of micro-plasma during microwave reactions. This plasma region contains hotspots with higher temperature than the average [39]. The elevated temperature can stimulate the ionization of surrounding molecules, thus resulting in increased productivities. It was confirmed that microwave could generate micro-plasma and hotspots for promoting catalytic reactions and increasing hydrogen production [40]. Meanwhile, non-thermal effects of microwave reduce the activation energy of reactions. Compared to conventional pyrolysis, the activation energy can be reduced by 40-150 kJ/mol [36]. The low activation energy further promotes chemical cracking processes, resulting in greater operational efficiency.

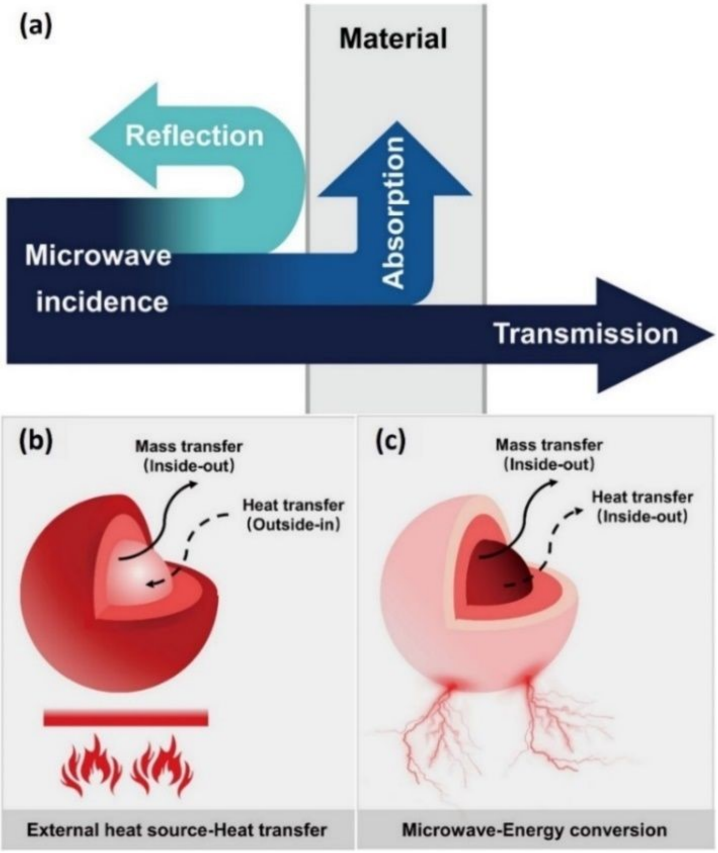


Fig. 2 (a) Transmission, reflection, and absorption of microwave in materials, (b) Conventional heating involving heat transfer with an external heat source, and (c) Microwave heating involving energy conversion (microwave energy to thermal energy) [35].

Microwave heating enhances the uniformity of heat distribution. Electromagnetic energy is converted to molecular kinetic energy in microwave heating. Dielectric loss is the phenomenon in which a dielectric material dissipates its electromagnetic energy

View Article Online
DOI: 10.1039/D5GC03030G

in form of heat or other forms. Dielectric loss is inherent to all materials and occurs naturally. In general, the microwave pyrolysis is the selective heating of feedstocks. The parameters of microwave pyrolysis include the reaction temperature, the reaction time, the supply of microwave power, the origin of microwave feedstock, the particle size of feedstock, the mixing ratios of feedstock, the dielectric constant of feedstock, the feedstock pretreatment, catalysts and microwave absorbers used [41]. The effects of these parameters on hydrogen production from microwave-assisted pyrolysis will be discussed in the following sections.

3. Microwave Pyrolysis of Plastic Wastes

3.1. Plastic Pyrolysis for Hydrogen Production

Plastic wastes such as polyolefins are considered promising resources that can be used for hydrogen production. Pyrolysis coupled with reforming process has been proposed as a suitable route to produce hydrogen from plastic wastes [42]. The gaseous product of plastic pyrolysis is normally rich in alkenes and alkanes that can be further cracked or reformed into hydrogen in the presence of catalysts. Co-production of H_2 and CNT over different Ni and Fe based catalysts has been widely studied [42-46]. In particular, the pyrolysis and in-line catalytic steam reforming of plastic-derived nascent volatiles are often performed in two individual reactors, which provides significant advantages. Firstly, an independent temperature optimization in the pyrolysis and reforming steps can be implemented. Secondly, the reforming temperature can be greatly reduced with respect to conventional gasification, allowing minimizing catalyst sintering problems. Thirdly, the direct contact of plastic charges and impurities with the reforming catalyst is avoided. Finally, the active reforming catalyst allows producing a tar-free gas [47]. Research works have focused on developing high activity and high stability catalysts [48, 49], as well as advanced reforming techniques such as plasma catalysis [50]. Recently, Wang et al. [48] utilized the hydrothermal synthesis of Ni- and Fe-loaded biochar catalysts for co-production of hydrogen and CNTs from plastic wastes by the pyrolysis-catalytic cracking process. Hydrothermal synthesis enhanced inherent metal dispersion by replacing native minerals through ion exchange, effectively purifying the biochar catalyst by removing inherent metals while simultaneously incorporating the active metal onto the support, thereby improving catalytic performance. Moreover, Liu et al. [49] designed a multilayer stainless-steel catalyst for the pyrolysis-catalytic reforming of plastic waste into hydrogen and CNTs. Compared to the particle catalyst, this monolithic catalyst could be easily recovered by an ultrasound separation method.

3.2. Microwave-assisted Plastic Pyrolysis for Hydrogen Production

3.2.1. Reaction mechanism

The two-step process of pyrolysis coupled with catalytic reforming (Fig. 3a) shows several advantages, but inevitably considerable energy input is required for the two reaction steps with the large volumes of CO_2 produced [51]. Moreover, the two-step process is invariably complicated. In recent years, the one-step process of pyrolysis under microwave radiation coupled with catalysis has attracted increasing attention for plastic cracking into hydrogen and carbon. Due to low dielectric characteristics of plastic wastes, microwave adsorbers such as SiC [52] and carbon-based materials [53-55] are commonly adopted in microwave pyrolysis. The gas products are significantly affected by the pyrolysis temperature, microwave power, and mass ratio of plastic to adsorber. Without addition of catalysts, the composition of gas products includes H_2, CH_4, C_2H_4, and C_3H_6 [52, 53], which are similar to the composition of gas products from the conventional pyrolysis. Recently, Zhang et al. [55] studied the temperature distribution and the energy transformation of activated carbon (AC) particles in the microwave-driven thermal-chemical system by experimental and numerical methods. The mechanism of microwave heating was revealed by two heating patterns including volumetric heating and localized heating. On the one hand, microwave energy was consumed and transformed into heat volumetrically via resistive and magnetic losses. The temperature distribution inside the particle was consistent with the microwave power dissipation density and affected by the electric field. This volumetric heating pattern tended to form a uniform temperature profile. On the other hand, microwave energy in the multiparticle system was consumed in the form of plasma discharging in

View Article Online
DOI: 10.1039/D5GC03030G

the localized region with massive heat bursts. When the gap distance of particles was narrow, the distorted electric field would lead to the breakdown of the gas medium with electron accumulation and avalanche. This localized heating pattern induced the local high temperature and led to the radical rise from the surface to the interior. The combination of volumetric heating by thermal and localized heating by plasma could contribute to the high performance on microwave pyrolysis of plastic waste (Fig. 4), resulting in the massive generation of hydrogen (280 mmol/$g_{plastic}$) and carbon.

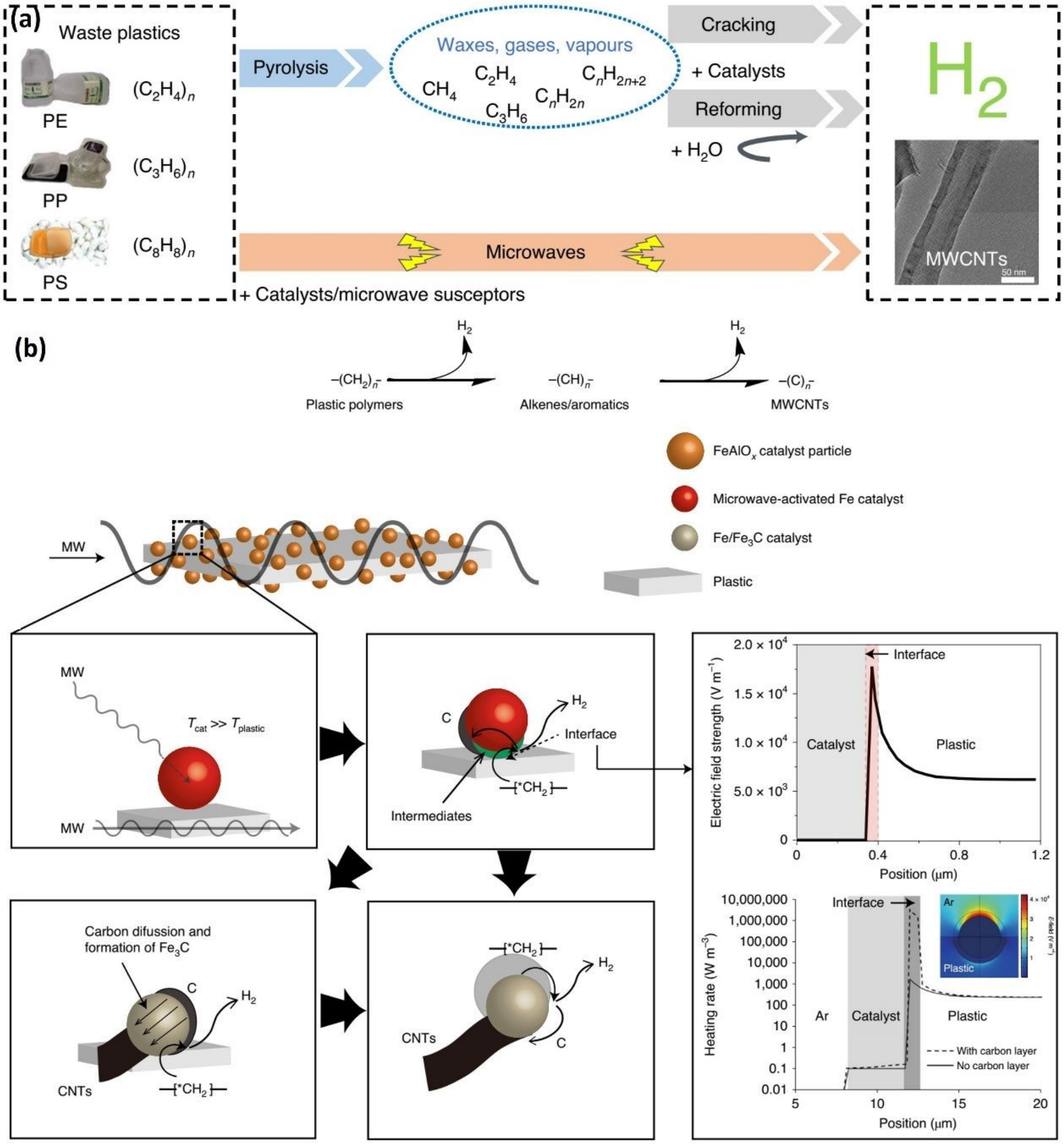


Fig. 3 (a) Schematic diagram of the two-step pyrolysis-catalytic reforming and the one-step microwave-initiated catalytic pyrolysis processes for conversion of plastic waste to hydrogen and CNTs, and (b) the mechanism illustration on the microwave-initiated pyrolysis of HDPE plastic over a $FeAlO_x$ catalyst [51]

View Article Online
DOI: 10.1039/D5GC03030G

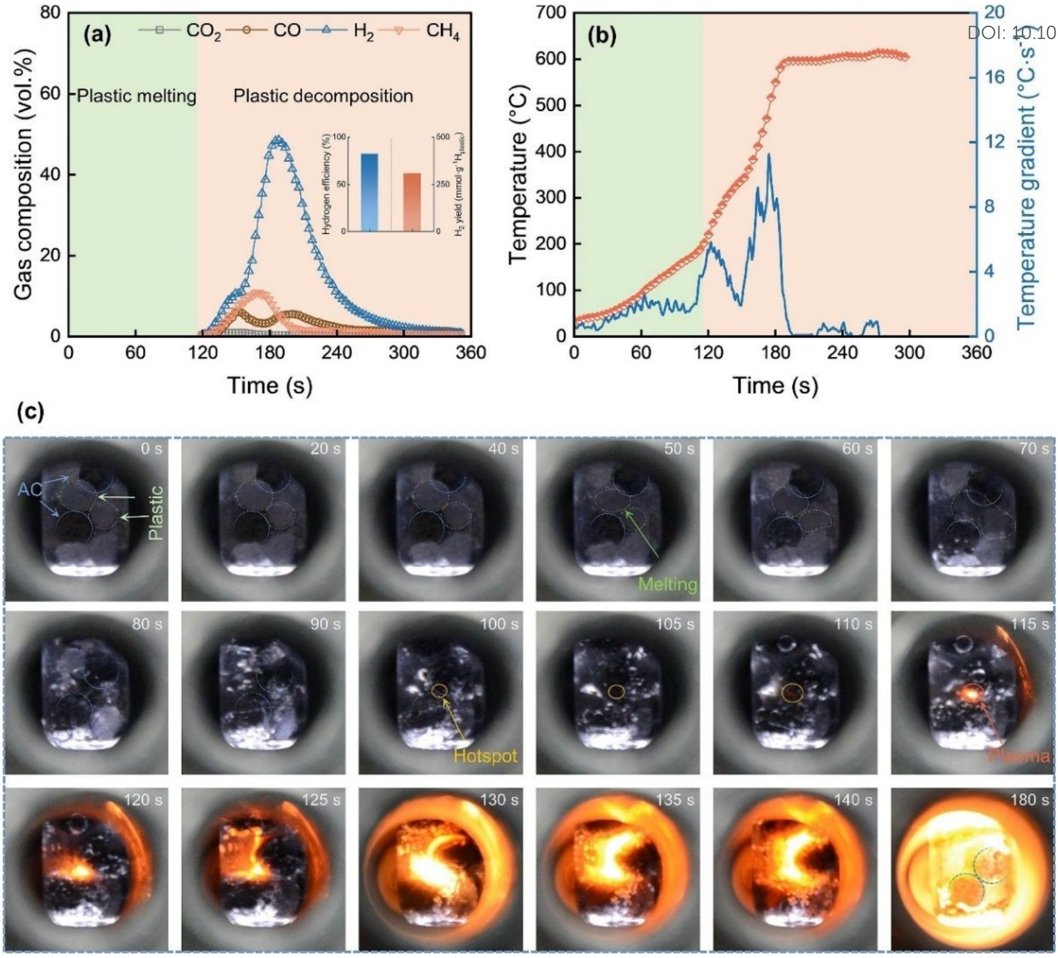


Fig. 4 Time on stream analysis of microwave-driven decomposition of plastic wastes: (a) gas composition, (b) temperature, and (c) images of the mixed PE and AC [55]

3.2.2. Catalyst development

Microwave catalytic pyrolysis of plastic into H_2 and high-value carbon has become a promising way for plastic waste upcycling. Transition metals especially for iron-based catalysts [51, 56-62] have been mostly employed for microwave catalytic pyrolysis of plastics for H_2 and CNTs production. Table 2 concludes research works on the carbon and hydrogen production from microwave catalytic pyrolysis of plastics. For example, Jie et al. [51] synthesized the $FeAlO_x$ particles for microwave catalytic pyrolysis of HDPE, which achieved the co-production of H_2 (yield: 55.6 mmol/$g_{plastic}$, selectivity: 97%) and CNTs (1560 mg/$g_{plastic}$). A mechanistic model was also proposed for the microwave-initiated solid-solid reaction using iron-based catalysts for H_2 and CNTs production from plastic (Fig. 6b). $FeAlO_x$ plays two roles in this process. Firstly, there is efficient energy absorption transfer from the incoming microwave electromagnetic radiation to initiate the physical heating process (driving force) of the catalyst particle.

View Article Online
DOI: 10.1039/D5GC03030G

Secondly, the catalytic reaction on the particle surface occurs as the particle reaches the required temperature. When microwave interacts with $FeAlO_x$ particles, heat is rapidly generated over the entire particles. Moreover, as microwave heating is itself a function of the electrodynamic properties of the catalyst (that is, the charge dynamics associated with the susceptibility of the catalyst), electromagnetic heating is closely connected to the material properties, which dictates the heating rate. In general, the very nature of microwave initiating these catalytic reactions substantially minimizes the competing chemical side reactions. Hence the catalytic process occurs only at the interface between the hot (and almost constantly heating) catalyst particle and the cold plastic (substrate or bath), and the cleavage of C–H bonds is dominant [51]. Further, Shen et al. [56] proposed a multistep mechanism based on the microwave-induced 'micro-hot spots' theory, indicating that the yield and main composition of pyrolytic products were determined by the microwave absorbing property and the catalysts activity. To validate the mechanism, iron-based catalysts with different microwave-absorbing properties were prepared using different catalyst supports (e.g., AC, SiC, and SiO_2). The catalysts with high dielectric loss enhanced the gas production and the CNTs growth owing to the local high-temperature generated over the catalyst surface under microwave irradiation. Besides, the catalytic activities of $FeAlO_x$ with different iron loadings showed that the increase of iron content from 7% to 22% improved the gas yield from 86.3% to 93.7% but had weak effect on the morphology of CNTs.

Table 2. Representative research works on the carbon and hydrogen production from microwave-assisted catalytic pyrolysis of plastic wastes

Plastic type	**Operating condition**	**Catalyst**	**H_2 conc. (vol.%)**	**H_2 yield ($mmol/g_{plastic}$)**	**Carbon yield ($mg/g_{plastic}$)**	**Ref.**
HDPE	Mass ratio of plastic to catalyst: 1, microwave power: 1000 W, time: 90 s	$FeAlO_x$	97	55.6	1560	[51]
HDPE	Mass ratio of plastic to catalyst: 30, microwave power: 800 W	$FeAlO_x$	96.82	-	-	[56]
PE	Mass ratio of plastic to catalyst: 1, microwave power: 900 W, time: 90 s	$FeAlO_x$@C	71	54.7	250	[57]
HDPE	Mass ratio of plastic	$Fe/FeAl_2O_4$	85	47.03	120	[58]

View Article Online
DOI: 10.1039/D5GC03030G

	to catalyst: 1, microwave power: 900 W					
LDPE HDPE PP PS	Mass ratio of plastic to catalyst: 1/2, microwave power: 800 W	Fe–Fe_3C@C	-	69.4 70.7 71.2 37.2	-	[61]
LDPE	Mass ratio of plastic to catalyst: 1/2, microwave power: 1000 W	$Al_iFe_jO_k$	87.5	60.2	571	[62]
PE	Mass ratio of plastic to catalyst: 1/2, microwave power: 700 W, time: 400 s	$FeNi/Al_2O_3$	96	415	-	[63]
LDPE	Mass ratio of plastic to catalyst: 1, microwave power: 500 W (800 °C)	$FeNi/Al_2O_3$	76	52.1	445	[64]
LDPE	Mass ratio of plastic to catalyst: 1/2, microwave power: 1000 W	NiFeAl	85.1	60.5	-	[65]
HDPE	Mass ratio of plastic to catalyst: 3/5, microwave power: 1000 W	Fe/Ni-CeO_2@CNTs	91.5	50.2	-	[66]
PE	Mass ratio of plastic to catalyst: 1, microwave power: 1000 W	$CoFeO_x$	75.51	61.6	-	[67]
LDPE	Mass ratio of plastic to catalyst: 2/1, microwave power: 700 W	Fe-Co-Al	-	61.39	-	[68]
PP	Mass ratio of plastic to catalyst: 1/3, microwave power: 900 W	10%Fe/Al_2O_3	92.05	43.02	-	[69]
HDPE	Mass ratio of plastic to catalyst: 1/2, microwave power: 750 W	$Co_1Fe_9O_x$	-	63.64	-	[70]
PP	Mass ratio of plastic to catalyst: 1, microwave power: 1100 W	$FeAl_2O_4/Fe_2O_3$	-	44.07	-	[71]
LDPE	Mass ratio of plastic to catalyst: 10/4, microwave power: 1000 W	MAX phase Ti_3AlC_2	78	46	-	[72]

Most of research works on the microwave-assisted pyrolysis of plastics has focused on the yield and quality of pyrolytic products, while it is difficult to directly capture the free radicals and intermediates generated during the reaction. Yao et al. [59, 60] studied the reactive molecular dynamic mechanisms of microwave-enhanced catalytic cracking of plastics for H_2 production over iron catalysts. Molecular dynamics (MD) simulations by the ReaxFF method were used to explore the mechanism of microwave enhanced iron-catalytic cracking of PE [60]. It was found that the adsorption amount between Fe and PE increased under the effect of a positive microwave electric field, and the H-C-C bond angle polarization was induced, resulting in a reduction of the activation energy (*Ea*) for C–H bond dissociation from 421 kJ/mol to 65 kJ/mol. The reaction kinetics revealed that C–C bond breakage primarily relied on temperature, with dissociated carbon atoms forming C chains on Fe, thus limiting hydrocarbon gas production. By backtracking H_2 molecules, the migration and collision of H radicals within the Fe catalyst were the predominant pathways among the four H_2 generation pathways (Fig. 5, a-d). The coupling mechanism of microwave and Fe catalysis could enhance hydrocarbon cracking, demonstrating the distinction between microwave and conventional heating at the same temperature [60]. The H_2 generation with H atoms dissociated by Fe catalysis (Path 1) accounted for 68% of the total H_2 yield (Fig. 5e). The interactions of the reactants under the microwave electric field showed that Fe and PE moved closer, enhancing their adsorption and increasing collision frequency between Fe and C–H bonds. Additionally, microwave irradiation altered the H–C–C bond angle, reducing C–H bond hybridization and promoting C–H bond dissociation, thereby enhancing hydrogen production (Fig. 5f). In general, the combined thermal and non-thermal effects of microwave facilitated the formation of H_2 and solid carbon while minimizing by-products (e.g., tar).

View Article Online
DOI: 10.1039/D5GC03030G

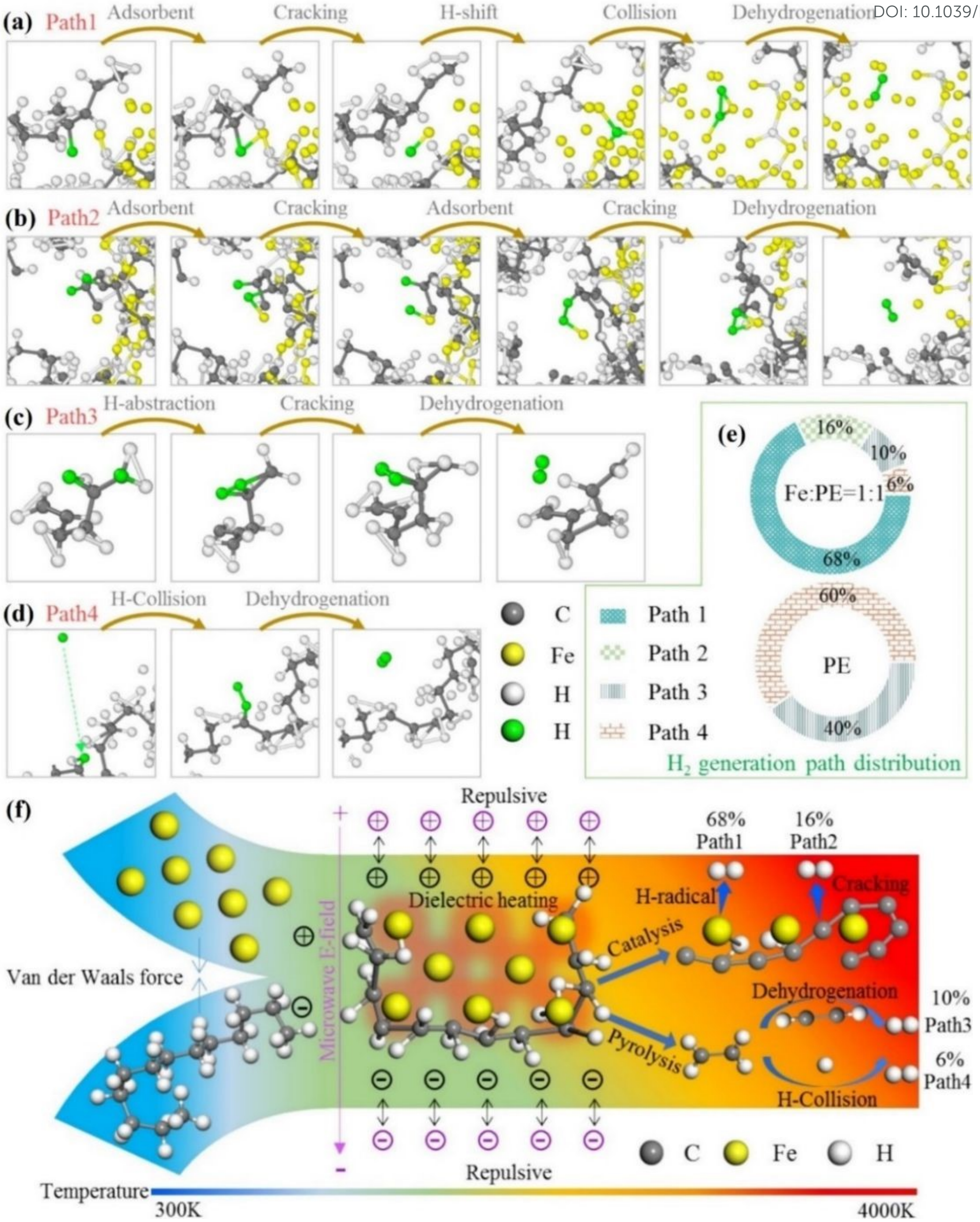


Fig. 5 Pathways of H_2 generation from PE by Fe catalytic pyrolysis under microwave: (a-d) four H_2 generation paths, and (e) the proportion of H_2 generated by each path with/without catalyst; (f) Action mechanism of Fe under microwave E-field. [60]

Polymetallic catalysts such as Fe-based bimetallic catalysts have attracted widespread attention owing to their higher catalytic activity than monometallic catalysts [63-74]. For example, Li et al. [68] found that Fe-Al catalysts could be rapidly converted into active Fe-Co alloys after Co doping under the microwave field for efficiently catalytic

View Article Online
DOI: 10.1039/D5GC03030G

dehydrogenation of plastic. Meanwhile, Co doping inhibited the formation of Fe_3C during the reaction, changed carbon diffusion pathways, and promoted the CNTs and H_2 production. Thus, the H_2 yield of LDPE increased from 47.10 mmol/g (Fe_1Al_2) to 61.39 mmol/g ($FeCoAl_2$). Also, Luo et al. [72] found that the microwave adsorbing property and catalytic activity of SiC were significantly improved after being loaded with Fe and Ni bimetals, which facilitates rapid heating and plastic dehydrogenation. The H_2 yield and the graphitization degree of CNTs can be modified by adjusting the type and proportion of active components in the catalyst. Polymetallic catalysts can effectively improve the catalytic activity and stability of iron-based catalysts, but the active metals usually require deposited on suitable supports to improve the dispersion, sinter resistance, and microwave adsorbing property for better catalytic performance. This process complicates the preparation process of the catalyst with additional costs. In addition, the support affects the adsorption and desorption of the products during the reaction, ultimately affecting the product's distribution and hampering the active component's evaluation and mechanism study. Zhao et al. [74] employed a one-step combustion method for synthesis of various self-dispersing Fe-Co-Ni mono- and bi-metallic catalysts that were applied for microwave catalytic upcycling of plastic to H_2 and CNTs. Compared to monometallic catalysts, higher H_2 yield and selectivity can be achieved through the microwave-intensified catalytic dehydrogenation of HDPE with $Ni_1Fe_3O_x$ (60.2 mmol/g, 79.4 vol.%), $Ni_1Co_3O_x$ (63.2 mmol/g, 81.4 vol.%) and $Ni_3Co_2O_x$ (63.5 mmol/g, 83.7 vol.%).

3.2.3. High-value carbon products

Plastic waste has become an alternative resource for producing carbon-free H_2 and high-value carbon. The challenge lies in the efficient catalytic pyrolysis of plastics, the energy-intensive nature of decomposition, and reactor configuration. Microwave-induced rapid pyrolysis decreases bulk temperature and minimizes random scissions, but the coexistence of solid plastic and catalyst leads to carbon block formation, thus hindering continuous interaction and CNTs growth [57]. Zhao et al. [74] also found that the microwave-assisted pyrolysis of LDPE over the $Ni_3Co_2O_x$ catalyst resulted in

View Article Online
DOI: 10.1039/D5GC03030G

41.5 wt.% solid residue, with carbon deposition on the catalyst of 21.3 wt.%, and 10.2 wt.% filamentous carbon. In a single-stage process, the presence of solid plastic with the catalyst leads to carbon block formation, inhibiting the growth of filamentous structure. Vatankhah et al. [64] proposed a two-stage process of microwave pyrolysis of LDPE at 500 ^{o}C followed by catalytic chemical vapor deposition (CVD) at 800 ^{o}C. Transition metals such as Fe, Ni, and Co, and their alloys were used as catalysts (Fig. 6a). The FeNi/Al_2O_3 catalyst exhibited the best performance owing to its optimized nanocrystalline size and interaction strength, which facilitated the production of CNTs (445 mg/g) and H_2 (52.1 mmol/g) (Fig. 6b). It also showed a sustained efficiency over ten consecutive cycles, yielding 513 mg/g of CNTs (Fig. 6c). In addition, Li et al. [71] studied the microwave-assisted catalytic pyrolysis of PP wastes for co-production of H_2 and bamboo-shaped CNTs employing various iron-based catalysts. The Al-Fe catalysts exhibited exceptional performance, achieving a H_2 utilization efficiency of 97.65% and a yield of 44.07 mmol/g PP. The gas yields increased from 19.99 to 94.21 wt.% compared to noncatalytic cases. The mechanism analysis on catalytic properties and product yields highlighted the significance of oxygen vacancies in selecting high-value products via two adsorption pathways. The variations in product distribution mechanisms between conventional and microwave pyrolysis showed that microwave conditions resulted in four times higher H_2 yields. The techno-economic assessment (TEA) and Monte Carlo risk analysis further compared the disparity. The microwave technique had a remarkable internal rate of return (IRR) of 39%, leading to an income of $577/t of plastic with a short payback period of 2.5 years. Therefore, this research offered sustainable solutions for the plastic crisis, validating the potential applicability of commercializing the research outcomes in real-world scenarios.

View Article Online
DOI: 10.1039/D5GC03030G

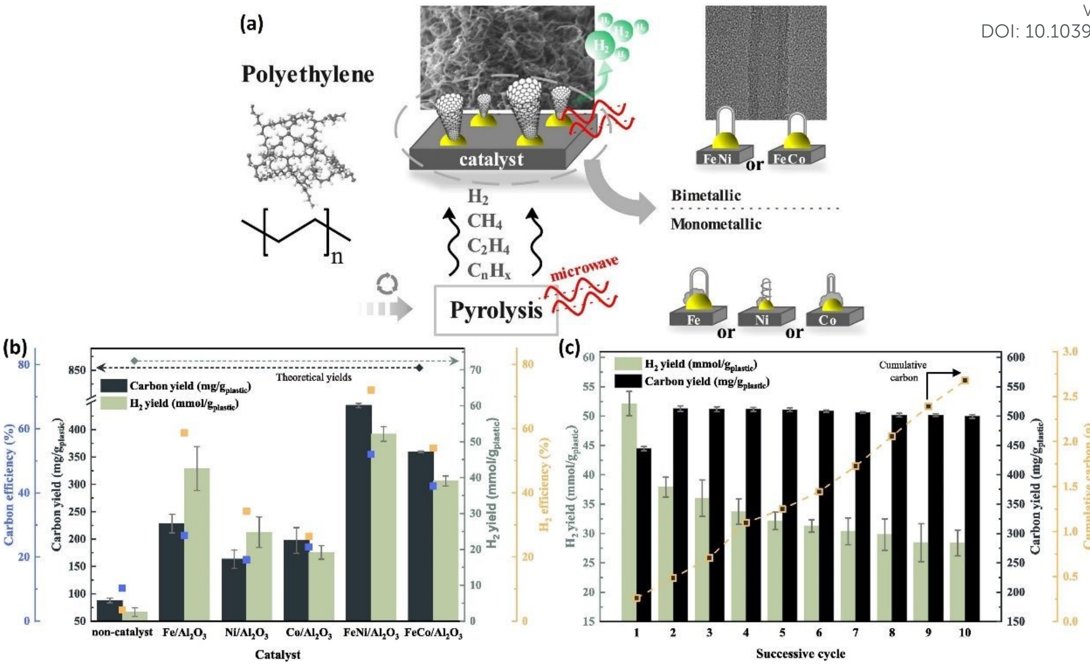


Fig. 6 (a) Schematic diagram of microwave-assisted catalytic pyrolysis of LDPE over mono- and bi-metallic catalysts for H_2 and CNTs production, (b) the yields of H_2 and carbon with overall process efficiency for various catalysts, and (c) the yields of H_2 and carbon during consecutive cycles of LDPE decomposition (0.5 g added per cycle) over 150 mg of the $FeNi/Al_2O_3$ catalyst [64]

3.3. Current Challenges and Future Directions

Microwave catalytic pyrolysis technology can selectively heat catalysts (e.g., Fe-Al oxides) for efficiently converting plastics to H_2 (with a yield of 46-71.4 mmol/g) and high-purity carbon materials (CNTs/graphene) at 800-1200 ^{o}C. The advantages of this technology include fast reaction speed, zero CO_2 emissions, 40%-60% reduction in energy consumption, and ability to directly process mixed plastics. This technology has the dual value of waste plastic treatment and clean energy/material production. Currently, the feasibility has been verified in the laboratory. To achieve large-scale operation, challenges such as the stability of the catalyst and the design of continuous reactors need to be addressed. The future breakthrough directions need to focus on three core areas: the analysis of the microwave-catalysis synergy mechanism, the design of large-scale reactors, and the high-value application of carbon materials. Several technical challenges need to be concerned. (1) Although iron-based catalysts (e.g., $Fe/FeAl_2O_4$) can enhance microwave absorption capacity, they are prone to metal sintering at high temperatures, resulting in a reduction of active sites and a

View Article Online
DOI: 10.1039/D5GC03030G

decrease in H_2 production from 55.6 mmol/g to 30 mmol/g. Insufficient dispersion of γ-Al_2O_3 supported catalysts can also affect the uniform growth of CNTs. (2) During the microwave cracking process, H_2, CNTs, graphene and incompletely decomposed tar-like substances may be generated simultaneously. The purity of H_2 fluctuates in the range of 79.82%-90%. The differences in plastic types (e.g., PE, PS) can greatly alter the product distribution, and targeted conversion can be achieved by precisely controlling the microwave power (2-5kW) and the catalyst ratio. (3) Plastic itself has a weak microwave absorption capacity, so microwave-absorbing materials (e.g., AC, $FeAlO_x$ composites) need to be added to assist in heating. However, if the proportion of the microwave-absorbing agent (5%-20%) is too high, it will reduce the effective volume of the reaction system, and the energy conversion efficiency will be less than 50% in large-scale production. (4) The actual waste plastics contain impurities (e.g., pigments, plasticizers), and need to be crushed and cleaned before processing. The energy consumption for pretreatment accounts for 30%-40% of the total cost. The cracking of mixed plastics may produce harmful gases (e.g., chlorides).

In the future directions, (1) it is necessary to develop polymetallic composite catalysts (e.g., Fe-Co/Al_2O_3), and screen highly active components in combination with density functional theory to enhance the anti-sintering ability; (2) it is necessary to regulate the dielectric-catalytic synergy effect, utilize the microwave field to enhance the electron transfer rate between metals and carriers, and achieve low-temperature and efficient cracking; (3) it is necessary to design a multi-cavity coupled microwave resonant system to break through the penetration depth limit of a single cavity and achieve a continuous production; (4) it is necessary to integrate in-situ infrared temperature measurement and AI dynamic control system, and adjust the microwave power pulse frequency (10-100Hz) according to the real-time product distribution; (5) it is necessary to prepare carbon materials with specific specifications by controlling the cracking temperature gradient (800-1200 ℃); and (6) it is necessary to establish a carbon footprint calculation model for plastic cracking and quantitatively compare the emission reduction benefits of traditional landfill/incineration processes.

View Article Online
DOI: 10.1039/D5GC03030G

4. Microwave Pyrolysis of Biomass

4.1. Pyrolysis of Biomass for H_2 Production

Biomass as a carbon-neutral feedstock can manage carbon with important potential for renewability, sustainability, recyclability, and natural availability [75]. Biomass is composed of every living material including non-lignocellulosic and lignocellulosic biomass [75]. These materials including forest woody biomass and industrial and agricultural waste, mainly contain cellulose, lignin, hemicellulose, ash, and various extractives [76]. In 2050, biomass will be expected to comprise around two-thirds of the whole consumption of renewable energy [76]. Indeed, the production of H_2 must come from renewable resources like biomass to meet the world's increasing energy demand. In recent years, biomass pyrolysis has gained increasing attention to obtain value-added products, thanks to the development of cutting-edge, innovative and cost-effective pyrolysis processes. Pyrolysis of biomass for syngas production has various technical obstacles. The composition of syngas is determined by several factors, such as temperature, residence time, and the characteristics of biomass feedstock [77]. The intricate interplay of these constituents results in a refined and interconnected formation of syngas such as H_2, CO, CH_4, CO_2, water vapor, and other hydrocarbons. The choice of biomass feedstock has a considerable influence on the composition of syngas, as different forms of biomass contribute unique characteristics to the syngas [78]. Compared to other methods of producing syngas, biomass pyrolysis has the benefit of using bio-oil, which serves as an extra source for H_2 generation and is more convenient to transport than solid biomass or H_2. The biomass fast pyrolysis and in-line steam reforming method for H_2 production has several benefits, including using mature biomass cracking technology, choosing processing plant locations flexibly, and the availability of the subsequent processing options for bio-oil [77]. However, the precise execution, effective generation of H_2, and intricate chemical makeup are crucial obstacles in biomass pyrolysis that must be overcome to fully exploit its potential as a versatile energy resource [77]. Advanced pyrolysis processes such as catalytic pyrolysis [79-81], hydropyrolysis [82], and microwave pyrolysis [83] are

View Article Online
DOI: 10.1039/D5GC03030G

usually adopted to achieve high yields and qualities of pyrolytic products. These advanced processes not only allow a better selectivity of pyrolytic products but also improve the process parameters by minimizing the reaction time and temperature and increasing the yields [84].

4.2. Microwave Pyrolysis of Biomass for H_2 Production

4.2.1. Reaction mechanism

Microwave heating is known for its rapid, uniform, volumetric, and selective nature. No direct physical contact between the material and microwave source is required, making it one of the unique indirect heating of the materials. Microwave heating has been applied for pyrolysis of various biomass feedstocks to produce biofuels, biochar, and syngas [85, 86]. The microwave pyrolysis of biomass to produce H_2-rich gas was firstly reported by Dominguez et al. [87]. Compared to conventional pyrolysis, microwave pyrolysis produces microplasma and hot spots, which enhance catalytic reactions and produce more H_2 in the syngas [83]. So far, the microwave pyrolysis of biomass for high-concentration H_2 production has been developed at the early stage. It is thought that the effectiveness of microwave heating for biomass pyrolysis depends on the changes in dielectric properties. Fan et al. [88] investigated the microwave dielectric properties and loss mechanism of biomass (tobacco industrial waste - TIW) at different frequencies (915 and 2450 MHz) and temperatures (25-800 ^{o}C) using the cavity perturbation method. The findings revealed that the dielectric properties and penetration depth of the biomass and biochar changed significantly during microwave pyrolysis. As illustrated in the pyrolysis mechanism (Fig. 7a) and the dielectric loss mechanism (Fig. 7b) during the heating process of TIW, the dielectric constant and dielectric loss coefficient first increased and then decreased in the drying stage, and they decreased continuously with the generation of volatile in the pyrolysis stage, while the formation and high conductivity of biochar promoted a sharp increase in dielectric properties in the carbonization stage. Here the loss tangent angle was 0.01-0.05 in the first two stages, while it increased to 0.10-0.25 in the carbonization stage, indicating that the biomass is a low-loss material. However, the microwave absorption

View Article Online
DOI: 10.1039/D5GC03030G

capacity was enhanced for biochar. Dipole polarization primarily contributed to the dielectric loss in the drying and pyrolysis stages, while interfacial polarization played an important role in the carbonization stage (Fig. 7b). The complex channels formed by the well-developed pore structure allowed for multiple reflections of microwave within the biochar, leading to gradual absorption (Fig. 7c). In addition, the porous structure could enhance the interfacial polarization of the biochar, further enhancing its microwave-absorption capacity [88].

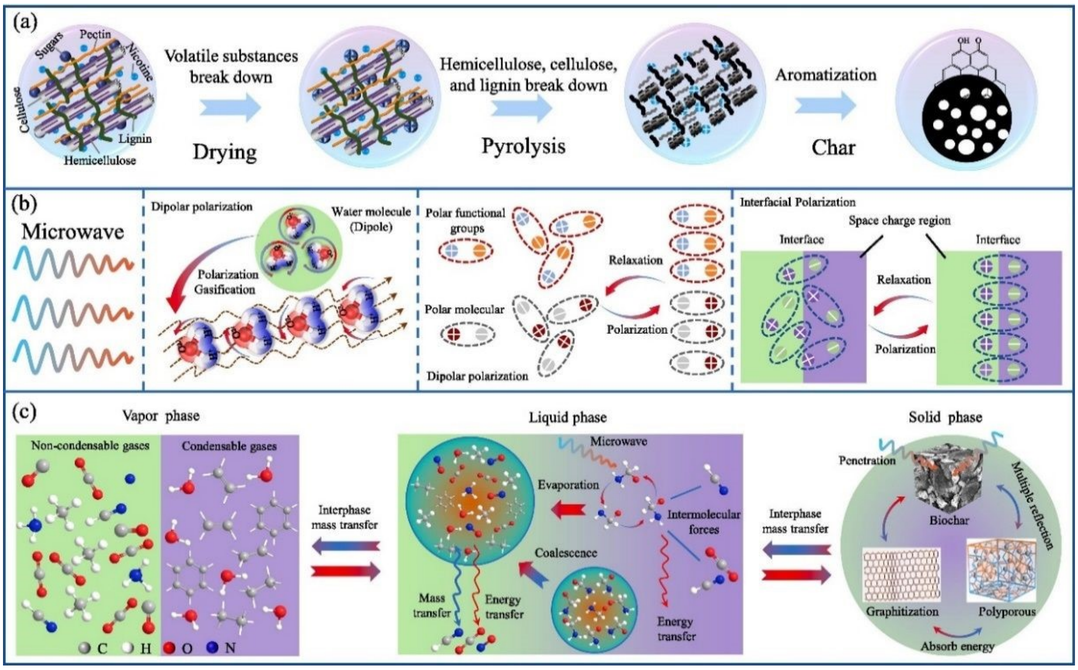


Fig. 7 (a) Pyrolysis mechanism of TIW, (b) dielectric loss mechanism and polarization effect in the heating process of TIW, and (c) physical phenomena and microwave losses on the gas-solid-liquid phases during the microwave heating of TIW [88]

4.2.2. Catalyst development

The production of H_2 from the microwave pyrolysis of biomass is generally affected by the properties of biomass feedstocks, the operating conditions of pyrolysis process, and the performances of catalysts used. Table 3 concludes the research works on the H_2 production from microwave-assisted catalytic pyrolysis of various biomass wastes. Compared to conventional pyrolysis, microwave pyrolysis of biomass can yield more gaseous products and higher H_2 yields. Particularly, the yields of total gaseous product and H_2 are enhanced by increasing the pyrolysis temperature, which is associated with the susceptors used and the microwave power [87-91]. In general,

View Article Online
DOI: 10.1039/D5GC03030G

high microwave power (or heating rate) and final pyrolysis temperature favors the high H_2 production owing to the cracking of macromolecules to small molecules and enhanced cracking of biomass [104-106]. Furthermore, microwave heating phenomena, i.e., the use of susceptors for better microwave heating, favor the production of H_2 through further cracking of the primary tar vapors. The detailed comparison of conventional and microwave pyrolysis of biomass wastes to H_2 can be referred to the literature [83]. Similar to the plastic pyrolysis, the development of low-cost, high-efficient, and sustainable catalysts (specifically biochar and its supported catalysts) has attracted increasing attention for the microwave pyrolysis of biomass [94, 98, 102, 107].

Table 3. Representative research works on the H_2 production from microwave-assisted catalytic pyrolysis of biomass wastes

Biomass type	Optimal conditions	Catalyst	H_2 concentration	Ref.
Coffee hulls	Temperature: 1000 ^{o}C, Microwave power: 420 W	-	40.6 vol.%	[87]
Rice straw	Microwave power: 300 W	-	50.7 vol.%	[89]
Dry banyan leaves	Microwave power: 1000 W	-	52.8 vol.%	[90]
Rice straw	Microwave power: 1000 W	-	56.1 vol.%	[91]
Rice straw	Temperature: 700 °C, microwave power: 2.5 kW	$ZnCl_2$	44.9 vol.%	[92]
Oil palm fiber	Temperature: 680 °C, microwave power: 800 W	-	32.9 vol.%	[93]
Spruce sawdust	Microwave power: 400 W	Char doped with Co	43.2 vol.%	[94]
Oil palm fiber	Temperature: 700 °C, microwave power: 508.36 W	-	-	[95]
Gumwood	Temperature: 800 °C	-	45.1 vol.%	[96]
Corn stalk	Temperature: 600 °C	-	22.2 vol.%	[97]
Pinewood			30.2 vol.%	
Algae			34.5 vol.%	
Douglas fir sawdust	Temperature: 700 °C	Biochar	87.1 vol.%	[98]
Anaerobically digested sludge	Temperature: 800 °C	-	50 vol.%	[99]
	Temperature: >1000 °C	Graphene aerogel		[100]
Bagasse	Microwave power: 800 W	Ni/SiC	38.13 g/kg $_{biomass}$	[101]
Wheat straw	Temperature: 400 °C	NiO/C	34.3 vol.%	[102]
Rice straw			44.3 vol.%	
Maize straw			41.4 vol.%	
Corn stover	Temperature: 600 °C, microwave power: 1100 W	P-CaO	42 vol.%, 257 NmL/g $_{biomass}$	[103]
Pinus			51 vol.%,	

DOI: 10.1039/D5GC03030G

massoniana	
Wheat straw	53 vol.%
Bamboo	51 vol.%
Cellulose	48.3 vol.%, 241.7 NmL/g $_{biomass}$
Lignin	55.4 vol.%, 249.4 NmL/g $_{biomass}$

Biochar can act the role of susceptor due to its high microwave absorption capacity, while transition metals such as Ni, Co and Fe can serve as the role of active sites for enhancing tar cracking [107]. More recently, Zeng et al. [103] developed a novel pearl-like calcium oxide (P-CaO) for microwave-assisted pyrolysis of lignocellulosic biomass, achieving high production of H_2-rich syngas owing to the dual roles of CaO in H_2 enhancement and CO_2 absorption (Fig. 8a). The P-CaO catalyst produced the highest H_2 yield (257 NmL/g$_{\text{corn stover}}$, 7.6 times higher than no-catalyst and 2.2 times higher than commercial CaO), and lowest CO_2 production (44 NmL/g$_{\text{feedstock}}$), with syngas purity exceeding 72 vol% at 600 ^{o}C. The increase in H_2-rich syngas production demonstrated universal applicability across other biomass feedstocks. Furthermore, the deep study on the microstructural changes and phase transition mechanisms of P-CaO shaded insights into the gas formation pathways. The P-CaO nanoparticles, with abundant alkaline sites, excellent adsorption capacity and large specific surface area due to aggregate, facilitate the secondary cracking of organic intermediates such as phenols, thereby promoting the production of H_2, while CO_2 adsorption favors the water–gas shift (WGS) equilibrium. Gas formation pathways from the microwave pyrolysis of cellulose and lignin over P-CaO are illustrated in Fig. 8b. Cellulose initially underwent depolymerization and intramolecular rearrangement, producing oligosaccharides or monosaccharides (e.g., glucose), accompanied by dehydration. Subsequently, the generated organic macromolecular intermediates underwent ring-opening reactions, resulting in the formation of small oxygenated compounds, such as linear ketones, cyclic ketones, acids, and esters. These products were then converted into aromatic compounds via further ring-opening or aromatization reactions, which were accompanied by substantial dehydration, decarboxylation, and dehydrogenation, resulting in the rapid release of gas products. Lignin initially underwent the reactions of debranching and decomposition. Under microwave induction, a portion of lignin decomposed to produce pyrolysis intermediates with benzene-ring structures, while another portion of the complex branched structures broke down into small molecules containing carboxyl or aldehyde groups (e.g., formic acid, acetic acid). This process involved significant dehydration and the generation of CO_2 and CO. In the pyrolytic lignin, the less-branched structures further decomposed, generating a large number of free radicals. The electron-rich –OCH_3 group was activated, resulting in free radical reforming reactions that produced gases such as CO, H_2O, and CH_4. A small portion of the remaining acidic compounds underwent high-temperature dehydrogenation and releasing a large amount of H_2 [103].

View Article Online
DOI: 10.1039/D5GC03030G

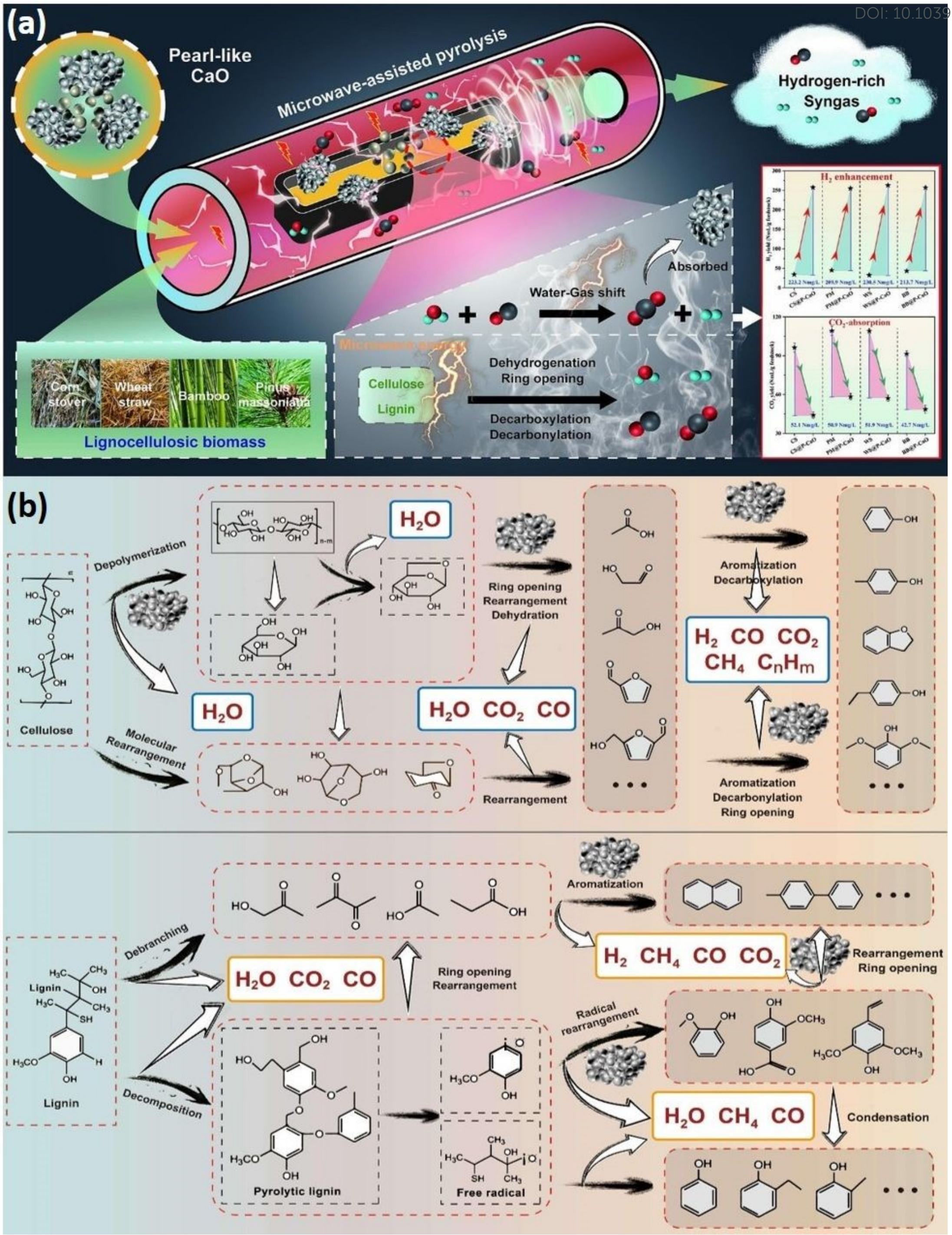


Fig. 8 (a) Schematic diagram of microwave-assisted pyrolysis of biomass for H_2-rich syngas production enhanced by P-CaO and (b) Plausible gas formation pathways from cellulose and lignin over P-CaO [103]

4.2.3. Variable-frequency microwave

In the field of biomass depolymerization, microwave-based techniques have emerged because of their ability to facilitate secondary cracking reactions and reduce tar yield without incurring issues such as coking or pollution in the reaction chamber [85].

Moreover, microwave exhibits metal discharge and plasma effects, which can greatly enhance catalyst activity in tar cracking [108]. Compared to the conventional heating, the pyrolysis of biomass by microwave heating typically at fixed frequencies (most commonly at 2450 MHz or 915 MHz) can yield more gaseous products and higher H_2 yields, but employing the fixed-frequency microwave restricts the investigation of how varying microwave frequencies impact temperature distribution and subsequent reactions involved in tar cracking. Wang et al. [108] employed a variable-frequency microwave (ranging from 2430 to 6000 MHz) pyrolysis of pine sawdust over AC to investigate the effect of microwave frequency on tar removal and H_2 production. Microwave frequencies greatly impacted the temperature distribution and heating rate of AC. At 4640 MHz, the AC rapidly reached 1145 ^{o}C with an ultra-fast heating rate (2022 ^{o}C/min), which contributes to 100% efficiency in tar cracking, resulting in a H_2 yield of 32.8 mmol/g. With a H_2 recovery rate over 94% (Fig. 9a), the 4640 MHz frequency showed a 15.4-fold increase compared to the 2450 MHz frequency. Within the context of tar cracking, this pronounced electric field effect functions as a swift and robust energy source, expediting the efficient cleavage of C–C and C–H bonds in biomass tar. Specifically, the localized high-temperature environment accelerates the dissociation and fragmentation of tar molecules, which mitigates the adhesion of tar to the catalyst surface, thus augmenting the rate of tar cracking (Fig. 9b). Furthermore, the intensified heating rate promptly offers significant thermal energy in a condensed timeframe, facilitating the rapid desorption of hydrogen molecules by enabling them to surmount surface adsorption barriers efficiently. To be specific, the gas yields reach 78.1, 77.0, and 68.4 wt% for pine sawdust, poplar wood, and corn straw, respectively, with a consistent H_2 recovery rate exceeding 93% across different biomass types. H_2 and CO are the predominant gas components, with total yields of 61.4, 57.6, and 52.3 mmol/g, respectively (Fig. 9c). Several challenges in the variable-frequency microwave system need to be concerned. Firstly, it is necessary to thoroughly assess the scalability of this system to industrial applications. The efficiency and economic feasibility of scaling up from laboratory to industrial scale is crucial for practical implementation. Secondly, it is necessary to investigate the long-term stability of this

View Article Online
DOI: 10.1039/D5GC03030G

system under continuous operation. Finally, life cycle assessment (LCA) is required to fully understand the environmental impact and sustainability of the process. Exploring the integration of this system with other renewable energy sources and carbon capture systems can further enhance its sustainability profile.

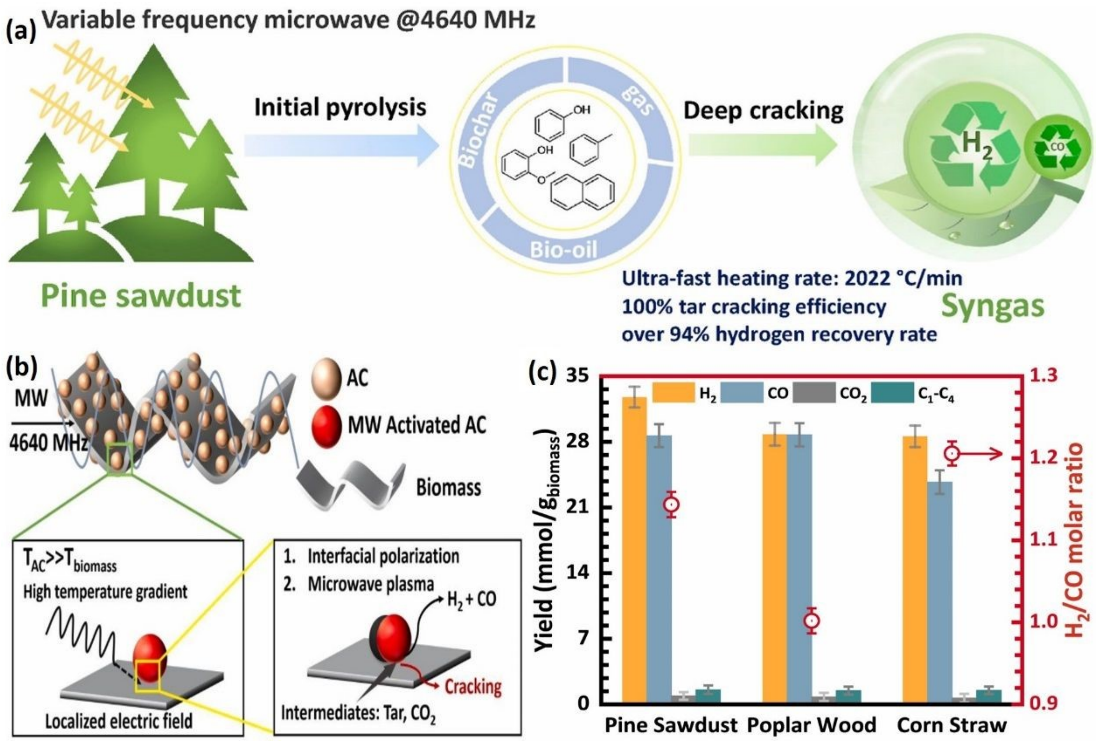


Fig. 9 (a) Schematic diagram of a variable-frequency microwave pyrolysis of pine sawdust over AC for H_2-rich syngas production, (b) the 4640 MHz microwave frequency induced tar cracking in biomass pyrolysis to H_2-rich syngas, and (c) the yields of gas products from microwave pyrolysis of different biomass feedstocks (microwave frequency: 4640 MHz, microwave power: 100 W, the mass of AC: 2 g, the mass of biomass: 0.5 g for each trial, the N_2 flow rate: 20 mL/min) [108]

4.2.4. Life cycle assessment (LCA) and TEA

LCA and TEA are crucial tools to evaluate the sustainability and economic feasibility of certain process/technology, playing pivotal roles in guiding decision-making and optimizing the overall performance of the microwave pyrolysis technology. LCA can assess the environmental impacts of a process throughout its entire life cycle, from raw material extraction to end-of-life disposal. With the systematic analysis of the factors and process inventories such as energy consumption, emissions, and resource usage, LCA provides a comprehensive understanding of the ecological footprint of the process. LCA performed for microwave pyrolysis technologies helps to identify areas where process/technology improvements can be made, guiding the development and implementation of more sustainable practices. TEA is a pivotal tool for evaluating the economic viability of a process. TEA involves the systematic assessment of costs and revenues associated with the technology, considering the factors such as capital investment, revenue streams from the sales of products or energy generated, and the operational expenses [109].

Microwave-assisted pyrolysis is a rapid, highly efficient, controllable, selective and adaptable conversion alternative as it is contrasted with conventional electric heating pyrolysis. Furthermore, the enhanced production of the resultant bioproducts from waste valorization *via* microwave-assisted pyrolysis, which is rich in soil-enriching nutrients, contributed to a net global warming potential (GWP) reduction, turning the values negative through carbon sequestration. Hence, integration of microwave in pyrolysis process can be accompanied by a reduced environmental footprint and energy consumption in comparison to its conventional counterpart. Considering that microwave-assisted pyrolysis is an emerging technology in advancing performance, there has been increasing investigations over the past few years that delves into the LCA, typically with respect to their energy efficiencies and environmental effects, albeit still scarcely available in comparison to conventional pyrolysis. The integration of microwave heating in pyrolysis process is beneficial to lower energy consumption and reduced environment impacts, which has been demonstrated in several studies [110-113]. Lin et al. [110] assessed microwave-assisted pyrolysis of waste sludge for H_2-rich gas production, which reported positive outcomes with much reduced GHG emissions of 385 kg-CO_2 eq. compared to conventional pyrolysis with drying and activation pretreatment, slow pyrolysis technology and fast pyrolysis conditions that exhibited 2350 to 2360 kg-CO_2 eq., 817 kg-CO_2 eq. and 431 kg-CO_2 eq., respectively. The enhancement in microwave-assisted pyrolysis in contrast to traditional process can be explained via its distinctive heating mechanism that expeditiously transformed sludge into bioproducts since the feedstocks directly absorbed the radiated energy, rapidly reaching the desired temperature with minimal heat transfer resistance. It was

View Article Online
DOI: 10.1039/D5GC03030G

reported that the major contributors to energy utilization and GWP were attributed to heating at microwave-assisted pyrolysis and drying stages. Besides, Zhu et al. [111] assessed the economic feasibility and environmental impact of a microwave-assisted catalytic pyrolysis of forest residues for co-production of biofuel and biochar. The cradle-to-gate (CTG) carbon intensity of biofuel ranged from −57.3 to 27.4 g CO_2-eq/MJ respectively as using either low-carbon electricity or carbon-intense electricity. Compared to petroleum fuels, a 43% to 162% reduction of GHG emissions could be achieved depending on electricity mix and methods to treat biochar co-product. The use of electricity to produce biofuel as compared to directly charge electric vehicles was justified as a preferred use based on the finding that the advanced utilization of waste biomass through microwave-assisted catalytic pyrolysis could contribute to a significant GHG reduction of transportation fuel without sacrificing the travel distance of vehicles. The minimum selling price of biofuel was \$1.02/L in the absence of any policy support and could be reduced to a comparable price of petroleum fuels at \$0.53/L or increased to \$1.32/L mostly depending on the co-product revenue from biochar's higher or lower-value applications. Therefore, this co-production of biofuel and biochar could bring flexibility to the biorefinery for seeking the highest possible economic and environmental benefits facing the changing market and policy.

4.3. Current Challenges and Future Directions

Microwave catalytic pyrolysis technology can selectively heat catalysts (e.g., Ni/AC, KOH modified carbon) for efficiently converting biomass to H_2 at 500-800 ^{o}C (with a yield of 50-80 mmol/g). This technology has the advantages of fast reaction speed (5-10 minutes), low energy consumption (30%-50% lower than conventional pyrolysis) and clean products (H_2 purity >90%). The catalyst can promote the cleavage of C-H and O-H bonds in biomass while inhibiting the formation of tar. Currently, issues such as catalyst deactivation and raw material pretreatment need to be addressed, but the dual value of resource utilization of biomass and green hydrogen production should be demonstrated. Several technical challenges need to be concerned. (1) In microwave catalytic reactions, nickel-based (e.g., Ni/AC) or modified carbon-based

View Article Online
DOI: 10.1039/D5GC03030G

catalysts are prone to deactivation due to carbon deposition, sintering or impurity adsorption, resulting in a decrease in H_2 production. (2) The uneven distribution of the microwave field affects the pyrolysis efficiency. Laboratory equipment is difficult to be directly scaled up, and the continuous feeding and product separation technologies are not yet mature. (3) The cost of biomass pretreatment (crushing and drying) is high, and the impurities in the product H_2 (e.g., H_2S and tar) need to be purified separately. The cost of unit hydrogen production is still 40%-50% higher than that of traditional methane reforming.

In the future directions, (1) it is necessary to develop anti-carbon deposit composite catalysts (e.g., metal-oxide bifunctional carriers), and combine them with microwave-responsive material (e.g., CeO_2 doped gadolinium) to reduce the reaction temperature below 600 ^{o}C; (2) it is necessary to explore the microwave-thermochemical coupling process to achieve self-sustaining pyrolysis by taking advantage of the microwave-absorbing properties of the semi-coke skeleton and maximize energy utilization; (3) it is necessary to formulate pretreatment standards for different biomass to reduce the interference of moisture content and ash on microwave absorption; (4) it is necessary to establish the thermodynamic model of C-H bond breaking in the microwave field effect for revealing the dynamic relationship between oxygen vacancy formation and hydrogen generation; (5) it is necessary to conduct more research works on the co-pyrolysis of biomass and hydrogen-rich waste (e.g., plastic) to enhance H_2 production [114, 115]; (6) it is necessary to conduct more research works on the in-situ capture of CO_2 for enhancing the production of H_2 and high-value carbons (e.g., CNTs) via the CVD process [116]; and (7) it is necessary to develop scale-up continuous microwave pyrolysis devices for practical applications [117]. In general, the field of microwave-assisted biorefinery requires interdisciplinary cooperation to break through technical bottlenecks for achieving large-scale production of green hydrogen with low cost and low energy consumption.

View Article Online
DOI: 10.1039/D5GC03030G

5. Conclusions and Outlooks

The development of hydrogen energy is a key path to achieving carbon neutrality, providing zero-carbon and efficient clean energy solutions. Moreover, it can enhance energy security, promote the green transformation in industries, transportation and other fields, and form new economic growth points. Microwave-assisted pyrolysis is an emerging thermochemical technology that have gained significant attention for efficiently converting hydrogen-rich resources to H_2 and high-value carbon materials. This paper concludes the advances and future challenges in the microwave-assisted pyrolysis of waste polymeric wastes such as biomass and plastic for H_2 production. In general, microwave pyrolysis is the selective heating of feedstocks. The parameters of microwave pyrolysis include the reaction temperature, the reaction time, the supply of microwave power, the origin of microwave feedstock, the particle size of feedstock, the mixing ratios of feedstock, the dielectric constant of feedstock, the feedstock pretreatment, catalysts and microwave absorbers. As for the microwave catalytic plastic pyrolysis for H_2 production, this technology can achieve a H_2 recovery rate of 97% within 30-90 s, which is faster than the traditional pyrolysis process. Fe-Al composite catalysts (e.g., Fe-Al oxides) exhibit optimal performance in microwave fields, achieving a high H_2 production rate of 62.3 mmol/g. The reaction also generates high-value CNTs, forming a resource recycling model of "plastic to H_2 and nano-carbon". Besides, the selective heating characteristic of microwave makes the energy consumption only 1/8 of the traditional method, and the Zn/ZnO catalyst system can achieve depolymerization of polyolefins at a low temperature of 280 ^{o}C. As for the microwave catalytic biomass pyrolysis for H_2 production, this technology can generate heat through the dielectric loss of polar molecules (e.g., water, oxygen-containing functional groups in biomass), achieving rapid internal temperature rise and shortening the reaction time (1/10-1/5 of the traditional heating). This technology can directly act on reactants and catalysts, reducing heat loss and lowering energy consumption by 30%-50%. Microwave fields can induce plasma effects or hot spot effects, accelerating the bond breaking of biomass macromolecules (e.g., cellulose,

View Article Online
DOI: 10.1039/D5GC03030G

lignin) and generating more small-molecular gases (e.g., H_2, CO, and CH_4). Great progress has been made in the catalysts design, process integration, and mechanism exploration. However, large-scale application still needs to overcome difficulties such as uniform heating and catalyst stability. In the future, it is expected to promote this technology to become one of the important paths for green hydrogen production through multidisciplinary integration (e.g., materials science, reaction engineering) and intelligent control (Al optimization parameters).

Four prospects are proposed for the microwave pyrolysis of waste plastics into H_2. In the direction of catalyst system innovation, it is necessary to develop atomic cluster-oxide co-catalysts (e.g., Zn/ZnO) to enhance the C-H bond breaking efficiency by utilizing the enhancement effect of the local electric field. It is also necessary to explore the non-precious metal multi-component composite catalyst (e.g., Fe-Co/Al_2O_3) and optimize the balance between microwave absorption and catalytic activity. In the direction of process integration, it is necessary to construct a continuous fluidized bed reaction system to solve the dynamic mixing issue of plastic powder and catalyst, and develop microwave-plasma coupling devices to enhance molecular bond breaking through discharge effects. In the direction of raw material adaptability expansion, it is necessary to develop a tolerant catalyst system for landfill mixed plastics and study the co-pyrolysis path of biomass and plastics to enhance the processing capacity of complex components. In the direction of scale-up application path, it is necessary to establish an energy consumption evaluation system based on LCA analysis and clarify the optimal power density range (currently at 400-800W). Four prospects are proposed for the microwave pyrolysis of biomass into H_2. In the direction of catalyst innovation, it is necessary to develop atomically dispersed NiO-CeO_2 and FeO_x-CeO_2 catalysts and enhance microwave absorption capacity using oxygen vacancies in cerium-based materials; Core-shell catalysts (e.g., Fe@C) are constructed to inhibit carbon deposit formation. In the direction of system integration optimization, microwave plasma technology can be coupled to generate high-energy electrons by the 2.45 GHz antenna to promote the breaking of C-H bonds. Moreover, mobile modular devices can be developed to meet the needs of distributed treatment of agroforestry waste. In the direction of raw material expansion, it is necessary to establish differential depolymerization pathways for lignocellulose and lipid biomass, especially to address the catalyst poisoning in raw materials with high ash content. In the direction of scale-up application path, the current laboratory-level H_2 production cost is $4.2/kg, and commercialization needs to be achieved by improving the energy efficiency of the microwave system to 53% (currently 44%). Meanwhile, the lifespan of the catalyst can be extended to over 1,000 hours.

References

[1] Hren R., Vujanovic A., Fan Y.V., Klemes J.J., Krajnc D., Cucek L. Hydrogen production, storage and transport for renewable energy and chemicals: An environmental footprint assessment. *Renew. Sustainable Energy Rev.* 2023, 173, 113113.

[2] International Energy Agency. Global Hydrogen Review 2021.

[3] International Energy Agency Net Zero by 2050: A Roadmap for the Global Energy Sector (2021).

[4] Guan D., Wang B., Zhang J., Shi R., Jiao K., Li L., Wang Y., Xie B., Zhang Q., Yu J., Zhu Y., Shao Z., Ni M. Hydrogen society: from present to future. *Energy Environ. Sci.* 2023, 16, 4926-4943.

[5] Hermesmann M., Müller, Green, turquoise, blue, or grey? Environmentally friendly hydrogen production in transforming energy systems. *Prog. Energy Combust. Sci.* 2022, 90, 100996.

[6] Rasul M.G., Hazrat M.A., Sattar M.A., Jahirul M.I., Shearer M.J. The future of hydrogen: Challenges on production, storage and applications. *Energy Convers Manage.* 2022, 272, 116326.

[7] Olabi A.G., Bahri A.S., Abdelghafar A.A., Baroutaji A., Sayed E.T., Alami A.H., Rezk H., Abdelkareem M.A. Large-vscale hydrogen production and storage technologies: Current status and future directions. *Int. J. Hydrogen Energy* 2021, 46, 23498-23528.

[8] Muhammed N.S., Gbadamosi A.O., Epelle E.I., Abdulrasheed A.A., Haq B., Patil S., Al-Shehri D., Kamal M.S. Hydrogen production, transportation, utilization, and storage: Recent advances towards sustainable energy. *J. Energy Storage* 2023, 73, 109207.

[9] Zhang L., Jia C., Bai F., Wang W., An S., Zhao K., Li Z., Li J., Sun H. A comprehensive review of the promising clean energy carrier: Hydrogen production, transportation, storage, and utilization (HPTSU) technologies. *Fuel* 2024, 355, 129455.

[10] Megia P.J., Vizcaino A.J., Calles J.A., Carrero A. Hydrogen production technologies: From fossil fuels toward renewable sources. A mini review. *Energy Fuels* 2021, 35, 16403-16415.

[11] Amin M., Shah H.H., Fareed A.G., Khan W.U., Chung E., Zia A., Farooqi Z.U.R., Lee C. Hydrogen production through renewable and non-renewable energy processes and their impact on climate change. *Int. J. Hydrogen Energy* 2022, 47, 33112-33134.

[12] Xu X., Zhou Q., Yu D. The future of hydrogen energy: Bio-hydrogen production technology. *Int. J. Hydrogen Energy* 2022, 47, 33677-33698.

DOI: 10.1039/D5GC03030G

[13] Aslam S., Rani S., Lal K., Fatima M., Hardwick T., Shirinfar B., Ahmed N. Electrochemical hydrogen production: sustainable hydrogen economy. *Green Chem.* 2023, 25, 9543-9573.

[14] Xu F., Weng B. Photocatalytic hydrogen production: an overview of new advances in structural tuning strategies. *J. Mater. Chem. A* 2023, 11, 4473-4486.

[15] International Energy Agency. Hydrogen. https://www.iea.org/reports/hydrogen. [Accessed 29 June 2022].

[16] Yu M., Wang K., Vredenburg H. Insights into low-carbon hydrogen production methods: Green, blue and aqua hydrogen. *Int. J. Hydrogen Energy* 2021, 46, 21261-21273.

[17] Ishaq H., Dincer I., Crawford C. A review on hydrogen production and utilization: Challenges and opportunities. *Int. J. Hydrogen Energy* 2022, 47, 26238-26264.

[18] Zainal B.S., Ker P.J., Mohamed H., Ong H.C., Fattah I.M.R., Rahman S.M.A., Nghiem L.D., Mahlia T.M.I. Recent advancement and assessment of green hydrogen production technologies. *Renew. Sustain. Energy Rev.* 2024, 189, 113941.

[19] Alhumaidan F.S., Halabi M.A., Rana M.S., Vinoba M. Blue hydrogen: Current status and future technologies. *Energy Conver. Manage.* 2023, 283, 116840.

[20] Ahmed S.F., Mofijur M., Nuzhat S., Rafa N., Musharrat A., Lam S.S., Boretti A. Sustainable hydrogen production: Technological advancements and economic analysis. *Int. J. Hydrogen Energy* 2022, 47, 37227-37255.

[21] Kannah R.Y., Kavitha S., Preethi, Karthikeyan O.P., Kumar G., Dai-Viet N. Vo., Banu J.R. Techno-economic assessment of various hydrogen production methods – A review. *Bioresour. Technol.* 2021, 319, 124175.

[22] Singla M.K., Gupta J., Beryozkina S., Safaraliev M., Singh M. The colorful economics of hydrogen: Assessing the costs and viability of different hydrogen production methods - A review. *Int. J. Hydrogen Energy* 2024, 61, 664-677.

[23] Pangestu M.R.G., Malaibari Z., Muhammad A., Al-Rowaili F.N., Zahid U. Comprehensive review on methane pyrolysis for sustainable hydrogen production. *Energy Fuels* 2024, 38, 13514-13538.

[24] Sanchez-Bastardo N., Schlögl R., Ruland H. Methane pyrolysis for zero-emission hydrogen production: A potential bridge technology from fossil fuels to a renewable and sustainable hydrogen economy. *Ind. Eng. Chem. Res.* 2021, 60, 11855-11881.

[25] Shen Y. Biomass pretreatment for steam gasification toward H_2-rich syngas production – An overview. *Int. J. Hydrogen Energy* 2024, 66, 90-102.

[26] Zhou Q., Shen Y., Gu X. Progress in torrefaction pretreatment for biomass gasification. *Green Chem.* 2024, 26, 9652-9670.

[27] Aziz M., Darmawan A., Juangsa F.B. Hydrogen production from biomasses and wastes: A technological review. *Int. J. Hydrogen Energy* 2021, 46, 33756-33781.

[28] Vuppaladadiyam A.K., Vuppaladadiyam S.S.V., Awasthi A., Sahoo A., Rehman S., Pant K.K., Murugavelh S., Huang Q., Anthony E., Fennel P., Bhattacharya S., Leu S-Y. Biomass pyrolysis: A review on recent advancements and green hydrogen production. *Bioresour. Technol.* 2022, 364, 128087.

[29] Chen Z., Wei W., Chen X., Liu Y., Shen Y., Ni B-J. Upcycling of plastic wastes for hydrogen production: Advances and perspectives. *Renew. Sustainable Energy Rev.* 2024, 195, 114333.

[30] Jiang Z., Liang Y., Guo F., Wang Y., Li R., Tang A., Tu Y., Zhang X., Wang J., Li S., Kong L. Microwave-assisted pyrolysis - A new way for the sustainable recycling and upgrading of plastic and biomass: A review. *ChemSusChem* 2024, 17, e202400129.

[31] Zhang Q., Li Z., Liu Z., Prasetyatama Y.D., Oh W.K., Yu I.K.M. Microwave-assisted

View Article Online
DOI: 10.1039/D5GC03030G

biorefineries. *Nature Reviews Clean Technology* 2025, 1, 269-287.

[32] Su G., Ong H.C., Cheah M.Y., Chen W-H, Lam S.S., Huang Y. Microwave-assisted pyrolysis technology for bioenergy recovery: Mechanism, performance, and prospect. *Fuel* 2022, 326, 124983.

[33] Zaker A., Chen Z., Wang X., Zhang Q. Microwave-assisted pyrolysis of sewage sludge: A review. *Fuel Process. Technol.* 2019, 187, 84–104.

[34] Zhang H., Ding J., Zhao Z. Microwave assisted esterification of acidified oil from waste cooking oil by CERP/PES catalytic membrane for biodiesel production. *Bioresour. Technol.* 2012, 123, 72-77.

[35] Ke L., Zhou N., Wu Q., Zeng Y., Tian X., Zhang J., Fan L., Ruan R., Wang Y. Microwave catalytic pyrolysis of biomass: a review focusing on absorbents and catalysts. *npj Mater. Sustain.* 2024, 2, 24.

[36] Luo H., et al. Microwave-assisted low-temperature biomass pyrolysis: from mechanistic insights to pilot scale. *Green Chem.* 2021, 23, 821-827.

[37] Mallakpour S., Rafiee Z. New developments in polymer science and technology using combination of ionic liquids and microwave irradiation. *Prog. Polym. Sci.* 2011, 36, 1754-1765.

[38] Allende S., Brodie G., Jacob M.V. Breakdown of biomass for energy applications using microwave pyrolysis: A technological review. *Environ. Res.* 2023, 226, 115619.

[39] Li J., Lin L., Ju T., Meng F., Han S., Chen K., Jiang J. Microwave-assisted pyrolysis of solid waste for production of high-value liquid oil, syngas, and carbon solids: A review. *Renew. Sustainable Energy Rev.* 2024, 189, 113979.

[40] Lestinsky P., Grycova B., Pryszcz A., Martaus A., Matejova L. Hydrogen production from microwave catalytic pyrolysis of spruce sawdust. *J Anal Appl Pyrolysis* 2017, 124, 175-179.

[41] Suresh A., Alagusundaram A., Kumar P.S., Vo D-V. N., Christopher F.C., Balaji B., Viswanathan V., Sankar S. Microwave pyrolysis of coal, biomass and plastic waste: a review. *Environ. Chem. Lett.* 2021, 19, 3609-3629.

[42] Williams P.T. Hydrogen and carbon nanotubes from pyrolysis-catalysis of waste plastics: A review. *Waste and Biomass Valorization* 2021, 12, 1-28.

[43] Wu C., Nahil M.A., Miskolczi N., Huang J., Williams P.T. Processing Real-World Waste Plastics by Pyrolysis-Reforming for Hydrogen and High-Value Carbon Nanotubes. *Environ. Sci. Technol.* 2014, 48, 819-826.

[44] Niu F., Wu Z., Chen D., Huang Y., Ordomsky V.V., Khodakov A.Y., Geem K.M.V. State-of-the-art and perspectives of hydrogen generation from waste plastics. *Chem. Soc. Rev.* 2025,

[45] Acomb J.C., Wu C., Williams P.T. The use of different metal catalysts for the simultaneous production of carbon nanotubes and hydrogen from pyrolysis of plastic feedstocks. *Appl. Catal. B* 2016, 180, 497-510.

[46] Yao D., Zhang Y., Williams P.T., Yang H., Chen H. Co-production of hydrogen and carbon nanotubes from real-world waste plastics: Influence of catalyst composition and operational parameters. *Appl. Catal. B: Environ.* 2018, 221, 584-597.

[47] Barbarias I., Lopez G., Artetxe M., Arregi A., Bilbao J., Olazar M. Valorisation of different waste plastics by pyrolysis and in-line catalytic steam reforming for hydrogen production. *Energy Convers. Manage.* 2018, 156, 575-584.

[48] Wang Y., Wang C-H. Sustainable production of carbon nanotubes from plastic pyrolysis using Ni- and Fe-biochar catalysts synthesized via hydrothermal treatment. *Appl. Catal. B* 2025, 373, 125340.

[49] Liu Q., Jiang D., Zhou H., Yuan X., Wu C., Hu C., Luque R., Wang S., Chu S., Xiao R.,

DOI: 10.1039/D5GC03030G

Zhang H. Pyrolysis–catalysis upcycling of waste plastic using a multilayer stainless-steel catalyst toward a circular economy. *PNAS* 2023, 120, e2305078120.

[50] Ma Y., Gao N., Quan C., Sun A., Olazar M. High-yield H_2 production from HDPE through integrated pyrolysis and plasma-catalysis reforming process. *Chem. Eng. J.* 2024, 479, 147877.

[51] Jie X., Li W., Slocombe D., Gao Y., Banerjee I., Gonzalez-Cortes S., Yao B., AlMegren H., Alshihri S., Dilworth J., Thomas J., Xiao T., Edwards P. Microwave-initiated catalytic deconstruction of plastic waste into hydrogen and high-value carbons. *Nature Catal.* 2020, 3, 902-912.

[52] Shi H., Cui Y., Zhang Y., Zhao W., Liu W., Ruan R. Gases production from microwave-assisted pyrolysis of polypropylene plastic. *J. Environ. Chem. Eng.* 2023, 11, 110851.

[53] Cui Y., Zhang Y., Cui L., Xiong Q., Mostafa E. Microwave-assisted fluidized bed reactor pyrolysis of polypropylene plastic for pyrolysis gas production towards a sustainable development. *Appl. Energy* 2023, 342, 121099.

[54] Felix M. de S., Hagare D., Tahmasebi A., Sathasivan A., Arora M. Microwave pyrolysis of polypropylene, and high-density polyethylene, and catalytic gasification of waste coffee pods to hydrogen-rich gas. *Waste Manage.* 2024, 187, 306-316.

[55] Zhang P., Liang C., Chen X., Liu D., Ma J. Insight into microwave heating patterns for sustainable decomposition of plastic wastes into hydrogen. *Appl. Therm. Eng.* 2025, 260, 124954.

[56] Shen X., Zhao Z., Li H., Gao X., Fan X. Microwave-assisted pyrolysis of plastics with iron-based catalysts for hydrogen and carbon nanotubes production. *Mater. Today Chem.* 2022, 26, 101166.

[57] Zhang B., Wang H., Yang Y., Zhou Y., Zhang B., Huang K. Microwave-carbon fiber cloth co-ignited catalytic degradation of waste plastic into high-yield hydrogen and carbon nanotubes. *J. Environ. Chem. Eng.* 2023, 11, 109710.

[58] Yao L., Yi B., Zhao X., Wang W., Mao Y., Sun J., Song Z. Microwave-assisted decomposition of waste plastic over Fe/$FeAl_2O_4$ to produce hydrogen and carbon nanotubes. *J. Anal. Appl. Pyrolysis* 2022, 165, 105577.

[59] Yao L., Zhang F., Song Z., Zhao X., Wang W., Mao Y., Sun J. ReaxFF MD simulation of microwave catalytic pyrolysis of polypropylene over Fe catalyst for hydrogen. *Fuel* 2023, 340, 127550.

[60] Yao L., Li H., Song Z., Wang W., Mao Y. Mechanism of microwave-enhanced catalytic of plastic cracking for hydrogen production over iron catalysts: A reactive molecular dynamics study. *Fuel* 2025, 389, 134646.

[61] Dong Y., Liu B., He M., Zhang Z., Tang C., Zhao J., Wu H., Fan Y., Ma W. Microwave-coupled recycling of plastic waste into hydrogen and carbon nanotubes over economical iron-based catalyst. *Int. J. Hydrogen Energy* 2025, 115, 24-36.

[62] Xie M., Xu H., Wang Y., Pan H., Duan D., Niu B., Long D., Zhang Y. Constructing bifunctional porous nanosheets for efficient conversion of waste plastics into valuable hydrogen and carbons. *Chem. Eng. J.* 2023, 471, 144460.

[63] Zhang P., Wu M., Liang C., Luo D., Li B., Ma J. In-situ exsolution of Fe-Ni alloy catalysts for H_2 and carbon nanotube production from microwave plasma-initiated decomposition of plastic wastes. *J. Hazard. Mater.* 2023, 445, 130609.

[64] Vatankhah F., Garcia A.C., Chaouki J. Hydrogen and carbon nanotube production from microwave-assisted catalytic decomposition of plastic waste. *Chem. Eng. J.* 2025, 503, 158189.

[65] Zhang Z., Chen H., Hu W., Xie M., Pan Y., Niu B., Duan D., Ding L., Long D., Zhang Y. Temperature-dependent NiFeAl catalysts for efficient microwave-assisted catalytic pyrolysis of polyethylene into value-added hydrogen and carbon nanotubes. *Fuel* 2024, 366, 131390.

View Article Online
DOI: 10.1039/D5GC03030G

[66] Wang J., Pan Y., Song J., Huang Q. A high-quality hydrogen production strategy from waste plastics through microwave-assisted reactions with heterogeneous bimetallic iron/nickel/cerium catalysts. *J. Anal. Appl. Pyrolysis* 2022, 166, 105612.

[67] Chen W., Zhou Y., Wang Y., Zhong Y., Yu Y., Huang K. Microwave-assisted pyrolysis of plastic waste with magnetic catalysts in a multi-ridge field compressed reactor. *J. Anal. Appl. Pyrolysis* 2024, 179, 106440.

[68] Li W., Qian K., Yang Z., Ding X., Tian W., Chen D. Promotion effect of cobalt doping on microwave-initiated plastic deconstruction for hydrogen production over iron catalysts. *Appl. Catal. B* 2023, 327, 122451.

[69] Parmar K.R., Tuli V., Caiola A., Hu J., Wang Y. Sustainable production of hydrogen and carbon nanotubes/nanofibers from plastic waste through microwave degradation. *Int. J. Hydrogen Energy* 2024, 51, 488-498.

[70] Zhang B., Li Y., Lu S., Hu Y., Li Y., Wang S., Liu J., Tang T., Li S. Co-, Ni-, and Cu-doped Fe-based catalysts for the microwave-assisted catalytic pyrolysis of polyethylene. *ChemSusChem* 2024, 17, e202301563.

[71] Li J., Chen K., Lin L., Han S., Meng F., Hu E., Qin W., Gao Y., Jiang J. Product selection toward high-value hydrogen and bamboo-shaped carbon nanotubes from plastic waste by catalytic microwave processing. *Environ. Sci. Technol.* 2024, 58, 14675-14686.

[72] Luo J., Gong G., Ma R., Sun S., Cui C., Cui H., Sun J., Ma N. Study on high-value products of waste plastics from microwave catalytic pyrolysis: construction and performance evaluation of advanced microwave absorption-catalytic bifunctional catalysts. *Fuel* 2023, 346, 128296.

[73] Cao Q., Dai H-C, He J-H, Wang C-L., Zhou C., Cheng X-F, Lu J-M. Microwave-initiated MAX Ti3AlC2-catalyzed upcycling of polyolefin plastic wastes: Selective conversion to hydrogen and carbon nanofibers for sodium-ion battery. *App. Catal. B* 2022, 318, 121828.

[74] Zhao J., Gao J., Wang D., Chen Y., Zhang L., Ma W., Zhao S. Microwave-intensified catalytic upcycling of plastic waste into hydrogen and carbon nanotubes over self-dispersing bimetallic catalysts. *Chem. Eng. J.* 2024, 483, 149270.

[75] Pal D.B., Singh A., Bhatnagar A. A review on biomass based hydrogen production technologies. *Int. J. Hydrogen Energy* 2022, 47, 1461-1480.

[76] Vuppaladiyam A.K., Vuppaladadiyam S.S.V., Awasthi A., Sahoo A., Rehman S., Pant K.K., Murugavelh S., Huang Q., Anthony E., Fennel P., Bhattacharya S., Leu S-Y. Biomass pyrolysis: A review on recent advancements and green hydrogen production. *Bioresour. Technol.* 2022, 364, 128087.

[77] Arregi A., Amutio M., Lopez G., Bilbao J., Olazar M. Evaluation of thermochemical routes for hydrogen production from biomass: A review. *Energy Conversion and Management* 2018, 165, 696-719.

[78] Damian C., Devarajan Y., Raja T., Jayabal R. A comprehensive review of biomass pyrolysis for hydrogen production in India. *Process Safety Environ. Pro.* 2024, 190, 646-662.

[79] Shen Y., Zhao P., Shao Q., Ma D., Takahashi F., Yoshikawa K. *In-situ* catalytic conversion of tar using rice husk char-supported nickel-iron catalysts for biomass pyrolysis/gasification. *Appl. Catal. B: Environ.* 2014, 152-153, 140-151.

[80] Shen Y., Zhao P., Shao Q., Takahashi F., Yoshikawa K. *In situ* catalytic conversion of tar using rice husk char/ash supported nickel–iron catalysts for biomass pyrolytic gasification combined with the mixing-simulation in fluidized-bed gasifier. *Appl. Energy* 2015, 160, 808-819.

[81] Shen Y., Zhang N., Zhang S. Catalytic pyrolysis of biomass with potassium compounds for Co-production of high-quality biofuels and porous carbons. *Energy* 2020, 190, 116431.

[82] Lee X.J., Ong H.C., Gan Y.Y., Chen W-H., Mahlia T.M.I. State of art review on conventional

DOI: 10.1039/D5GC03030G

and advanced pyrolysis of macroalgae and microalgae for biochar, bio-oil and bio-syngas production. *Energy Convers. Manage.* 2020, 210, 112707.

[83] Sridevi V., Surya D.V., Reddy B.R., Shah M., Gautam R., Kumar T.H., Puppala H., Pritam K.S., Basak T. Challenges and opportunities in the production of sustainable hydrogen from lignocellulosic biomass using microwave-assisted pyrolysis: A review. *Int. J. Hydrogen Energy* 2024, 52, 507-531.

[84] Nguyen V.G., Nguyen-Thi T.X., Nguyen P.Q.P., Tran V.D., Ağbulut Ü, Nguyen L.H., Balasubramanian D., Tarelko W., Bandh S.A., Pham N.D.K. Recent advances in hydrogen production from biomass waste with a focus on pyrolysis and gasification. *Int. J. Hydrogen Energy* 2024, 54, 127-160.

[85] Ren X., Ghazani M.S., Zhu H., Ao W., Zhang H., Moreside E., Zhu J., Yang P., Zhang N., Bi X. Challenges and opportunities in microwave-assisted catalytic pyrolysis of biomass: A review. *Appl. Energy* 2022, 315, 118970.

[86] Qiu B., Wang Y., Zhang D., Chu H. Microwave-assisted pyrolysis of biomass to high-value products: Factors assessment, mechanism analysis, and critical issues proposal. *Chem. Eng. J.* 2024, 498, 155362.

[87] Dominguez A., Menendez J.A., Fernandez Y., Pis J.J., Nabais J.M.V., Carrott P.J.M., *et al.* Conventional and microwave induced pyrolysis of coffee hulls for the production of a hydrogen rich fuel gas. *J Anal Appl Pyrolysis* 2007, 79, 128-135.

[88] Fan X., Li B., Zi W., Kang M., Wu H., Bian J., Sun M. Microwave dielectric characterization and loss mechanism of biowaste during pyrolysis. *Energy Conversion and Management* 2024, 301, 118075.

[89] Huang Y.F., Kuan W.H., Lo S.L., Lin C.F. Hydrogen-rich fuel gas from rice straw via microwave-induced pyrolysis. *Bioresour Technol* 2010, 101, 1968-1973.

[90] Lin Y.C., Wu T.Y., Jhang S.R., Yang P.M., Hsiao Y.H. Hydrogen production from banyan leaves using an atmospheric-pressure microwave plasma reactor. *Bioresour Technol* 2014, 161, 304-309.

[91] Lin Y.C., Wu T.Y., Liu W.Y., Hsiao Y.H. Production of hydrogen from rice straw using microwave-induced pyrolysis. *Fuel* 2014, 119, 21-26.

[92] Li H., Li X., Liu L., Li K., Wang X., Li H. Experimental study of microwave-assisted pyrolysis of rice straw for hydrogen production. *Int. J. Hydrogen Energy* 2016, 41, 2263-2267.

[93] Hossain M.A., Jewaratnam J., Ganesan P., Sahu J.N., Ramesh S., Poh S.C. Microwave pyrolysis of oil palm fiber (OPF) for hydrogen production: parametric investigation. *Energy Convers Manag* 2016, 115, 232-243.

[94] Lestinsky P., Grycova B., Pryszcz A., Martaus A., Matejova L. Hydrogen production from microwave catalytic pyrolysis of spruce sawdust. *J. Anal. Appl. Pyrolysis* 2017, 124, 175-179.

[95] Hossain M.A., Ganesan P., Jewaratnam J., Chinna K. Optimization of process parameters for microwave pyrolysis of oil palm fiber (OPF) for hydrogen and biochar production. *Energy Convers Manag* 2017, 133, 349-362,

[96] Parvez A.M., Wu T., Afzal M.T., Mareta S., He T., Zhai M. Conventional and microwave-assisted pyrolysis of gumwood: A comparison study using thermodynamic evaluation and hydrogen production. *Fuel Process. Technol.* 2019, 184, 1-11.

[97] Parvez A.M., Afzal M.T., Jiang P., Wu T. Microwave-assisted biomass pyrolysis polygeneration process using a scaled-up reactor: Product characterization, thermodynamic assessment and bio-hydrogen production. *Biomass Bioenergy* 2020, 139, 105651.

[98] Wang C., Lei H., Zhao Y., Qian M., Kong X., Mateo W., *et al.* Integrated harvest of phenolic monomers and hydrogen through catalytic pyrolysis of biomass over nanocellulose derived

View Article Online
DOI: 10.1039/D5GC03030G

biochar catalyst. Bioresour Technol 2021, 320,

[99] Kim D., Kim G., Oh D.Y., Seong K-W, Park K.Y. Enhanced hydrogen production from anaerobically digested sludge using microwave assisted pyrolysis. *Fuel* 2022, 314, 123091.

[100] Liu W., Jiang H., Zhang X., Zhao Y., Sun S., Qiao J. Less defective graphene aerogel and its application in microwave-assisted biomass pyrolysis to prepare H_2-rich gas. *J. Mater. Chem. A* 2019, 7, 27236-27240.

[101] Zhang Z., Huang K., Mao C., Huang J., Xu Q., Liao L., Wang R., Chen S., Li P., Zhang C. Microwave assisted catalytic pyrolysis of bagasse to produce hydrogen. *Int. J. Hydrogen Energy* 2022, 47, 35626-35634.

[102] Yue M., Cheng X., Jiang Q., Xu G., Wang J., Fu Y., Ye F. Enhanced hydrogen production from straws using microwave-assisted pyrolysis with NiO/C based catalyst/absorbent. *Int. J. Hydrogen Energy* 2024, 59, 535-550.

[103] Zeng C., Jiang Z., Zeng Y., Zhang S., Luque R., Yan K. Microwave-assisted pyrolysis of biomass for efficient H_2-rich syngas production promoted by calcium oxide. *Chem. Eng. J.* 2025, 506, 159905.

[104] Parvez A.M., Wu T., Hong Y., Chen W., Lester E.H., Mareta S., *et al.* Gasification reactivity and synergistic effect of conventional and microwave pyrolysis derived algae chars in CO_2 atmosphere. *J Energy Inst* 2019, 92, 730-740.

[105] Ferrera-Lorenzo N., Fuente E., Bermudez J.M., Suarez-Ruiz I., Ruiz B. Conventional and microwave pyrolysis of a macroalgae waste from the Agar-Agar industry. Prospects for bio-fuel production. *Bioresour Technol* 2014, 151, 199-206.

[106] Yin C. Microwave-assisted pyrolysis of biomass for liquid biofuels production. *Bioresour Technol* 2012, 120, 273-284.

[107] Zhang S., Dong Q., Zhang L., Xiong Y. High quality syngas production from microwave pyrolysis of rice husk with char-supported metallic catalysts. *Bioresour Technol* 2015, 191, 17-23

[108] Wang J., Wen M., Ren J., La X., Meng X., Yuan X., Ragauskas A.J., Jiang J. Tailoring microwave frequencies for high-efficiency hydrogen production from biomass. *Energy* 2024, 297, 131337.

[109] Foong S.Y., Chan Y.H., Yek P.N.Y., Lock S.S.M., Chin B.L.F., Yiin C.L., Lan J. C-W, Lam S.S. Microwave-assisted pyrolysis in biomass and waste valorisation: Insights into the life-cycle assessment (LCA) and techno-economic analysis (TEA). *Chem. Eng. J.* 2024, 491, 151942.

[110] Lin J., Liu S., Han Z., Ma R., Cui C., Sun S. Scaled-up microwave pyrolysis of sludge for hydrogen-rich biogas and life cycle assessment: Parameters synergistic optimization, carbon footprint analysis and technology upgrade. *Chem. Eng. J.* 2023, 452, 139551.

[111] Zhu H., Saddler J., Bi X. An economic and environmental assessment of biofuel produced via microwave-assisted catalytic pyrolysis of forest residues. *Energy Conver. Manage.* 2022, 263, 115723.

[112] Gallorini R., Rosi L., Galletti A.M.R., Licursi D., Antonetti C. Pyrolysis of Posidonia oceanica fibrous spheres: A comparative evaluation of conventional and microwave-assisted pyrolysis. *J. Anal. Appl. Pyrolysis* 2025, 191, 107206.

[113] Muniyappan D., Lima G.R., Junior A.O.P., Gopi R., Ramanathan A. Multivariate combined optimization strategy and comparative life-cycle assessment of biomass and plastic residues via microwave co-pyrolysis approach towards a sustainable synthesis of renewable hydrocarbon fuel.

View Article Online
DOI: 10.1039/D5GC03030G

J. Environ. Chem. Eng. 2023, 11, 111436.

[114] Abedin A., Bai X., Smith M., Muley P. Microwave-assisted co-gasification of mixed plastics and corn stover: A synergistic approach to produce clean hydrogen. *Energy Conversion and Management* 2023, 280, 116774.

[115] Chen Y., Wu X., Ma T., Chen W., Hu H., Chang C., Pang S., Li P. Synergistic effects of Fe@C catalysts prepared at different carbonization temperatures on microwave co-pyrolysis of biomass and plastic for high-value oil and gas production. *Fuel* 2024, 373, 132290.

[116] Veksha A., Tsakadze Z., Lisak G. Carbon dioxide capture from biomass pyrolysis gas as an enabling step of biogenic carbon nanotube synthesis and hydrogen recovery. *ChemSusChem* 2023, 16, e202300143.

[117] Lin J., Liu S., Han Z., Ma R., Cui C., Sun S. Scaled-up microwave pyrolysis of sludge for hydrogen-rich biogas and life cycle assessment: Parameters synergistic optimization, carbon footprint analysis and technology upgrade. *Chem. Eng. J.* 2023, 452, 139551.

View Article Online
DOI: 10.1039/D5GC03030G

Data availability

All data generated or analyzed during this study are available from the corresponding authors upon request.