



REVIEW

Plasma-electrified up-carbonization for low-carbon clean energy

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Abstract

Low-value, renewable, carbon-rich resources, with different biomass feedstocks and their derivatives as typical examples, represent virtually inexhaustive carbon sources and carbon-related energy on Earth. Upon conversion to higher-value forms (referred to as “up-carbonization” here), these abundant feedstocks provide viable opportunities for energy-rich fuels and sustainable platform chemicals production. However, many of the current methods for such up-carbonization still lack sufficient energy, cost, and material efficiency, which affect their economics and carbon-emissions footprint. With external electricity precisely delivered, discharge plasmas enable many stubborn reactions to occur under mild conditions, by creating locally intensified and highly reactive environments. This technology emerges as a novel, versatile technology platform for integrated or stand-alone conversion of carbon-rich resources. The plasma-based processes are compatible for integration with increasingly abundant and cost-effective renewable electricity, making the whole conversion carbon-neutral and further paving the plasma-electrified up-carbonization to be performance-, environment-, and economics-viable. Despite the chief interest in this emerging area, no review article brings together the state-of-the-art results from diverse disciplines and underlies basic mechanisms and chemistry underpinned. As such, this review aims to fill this gap and provide basic guidelines for future research and transformation, by providing an overview of the application of plasma techniques for carbon-rich resource conversion, with particular focus on the perspective of discharge plasmas, the fundamentals of why plasmas are particularly suited for up-carbonization, and featured examples of plasma-enabled resource valorization. With parallels drawn and specificity highlighted, we also discuss the technique shortcomings, current challenges, and research needs for future work.

KEYWORDS

carbon-rich resources, discharge plasmas, low-carbon energy, power-to-X, process electrification

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1 | INTRODUCTION

According to recent estimates, the global daily consumption of fossil oil has exceeded 100 million barrels to satisfy the dramatically increasing energy demands and is projected to increase by 41% from 2012 to 2035.¹ Global energy crisis (diminishing petroleum reserves) and environmental challenges (global warming and climate changes) resulting from the excessive use of nonrenewable fossil fuels drive the search for more sustainable energy alternatives. Low- or even negative-value carbon-rich resources, such as renewable biomass, organic industrial, municipal and food wastes, unprocessed or used (cooking) oils, and many others, represent abundant and virtually inexhaustive sources of carbon-based materials, energy, and platform chemicals on Earth.^{1,2} Owing to the favorable combination of affordability, CO₂ neutrality and renewability, carbon-rich precursors or feedstocks, particularly the biomass and its derivatives, have long been proposed as promising resources for the production of aviation fuels (such as bioalcohols and jet fuels), industrial chemicals, polymeric materials, and energy (heat and combustible gases) with different up-carbonization processes, which enable the conversion of these feedstocks to their high-value forms.^{3,4}

Natural, renewable carbon-rich feedstocks generally contain polymer blocks that show structure and component complexity. For example, the main components of lignocellulose, the most abundant renewable organic carbon source on Earth, are cellulose (40–50 wt% based on dry mass), hemicellulose (20–40 wt%), and lignin (20–35 wt%), whereas algae and animal feedstocks mainly consist of lipids, proteins, and saccharides.⁵ These feedstocks also contain higher oxygen contents (30–40 wt%) than fossil fuels, making the removal of most, or all, of the oxygen in the raw feedstock necessary to form molecules that have desirable properties such as for being used as biofuels. Besides oxygen, carbon is the most important element (and usually the largest one taking up 30–60 wt%), the content of which usually determines the quality of the upgraded products.^{6,7}

Over the recent decades, the valorization of natural carbon-rich feedstocks has been addressed from various angles, with several promising technologies developed to allow the conversion process to occur.^{7–9} However, to become sustainable alternatives and gain wide acceptance in today's markets, thus-obtained fuels and chemicals must become cost- and performance-competitive compared to petroleum-derived equivalents.^{9–11} Most current technologies and processes still lack sufficient energy, cost, and material efficiency, and fail to output market-sought products. This is partly due to the cost of collecting

and incomplete utilization of these feedstocks, and, more importantly, to the natural feedstocks' recalcitrance. The latter refers to raw feedstocks usually possessing physiochemical, structural, and compositional features that make it notoriously difficult to transform using mild physical, chemical, or biological means, with significant cost and efficiency challenges associated with converting such a material.^{7,9,12} Taking biomass as an example, biomass energy (bioenergy) currently accounts for only about 10%–14% of global energy usage. Bioenergy utilization is less than 4% of its total annual amount globally.^{6,8,9} Many countries have initiated extensive research and development programs in bioenergy. For example, a scenario has been developed by the U.S. Department of Energy Office of the Biomass Program for supplying 30% of the 2004 motor gasoline demand (60 billion gallons per year) with biofuels by 2030.¹⁰ Similar plans will see one-fourth of the transportation fuels in the European Union being derived from bioenergy.¹¹ For China, the proportion of nonfossil fuels in primary energy consumption aims to target over 25% by 2030; and it is estimated that China's bioenergy can contribute greatly not only to its carbon peaking and carbon neutrality targets but 6%–21% to a global carbon mitigation goal in 2050.¹³ These ambitious goals highlight the crucial importance and potential of natural carbon-resource conversion, with cutting-edge and efficient tools required to address significant challenges of current processing technological platforms.¹⁰

Plasma, that is, ionized but electrically neutral matter, is the fourth state of matter with the highest averaged energy per particle.¹⁴ There are many types of plasmas existing, both natural and artificial. With the sun as a typical example, natural ones occupy over 99% of the visible universe. Besides the naturally occurring plasmas, various artificial discharge plasmas have been manufactured and widely used for different applications. Based on the thermodynamic equilibrium states, plasmas are normally grouped as thermal plasmas (ThPs, or high-temperature plasmas) and non-ThPs (or possibly more general nonequilibrium plasmas).¹⁵ Plasmas, requiring only injecting energy, typically electricity, heat, or electromagnetic fields, enable resource-saving or chemical-free processing with high energy utilization efficiency, and thus, are inherently clean and environment-friendly technologies.¹⁶ Additionally, the easy accessibility of plasmas, due to the various discharge types and diverse systems (dielectric barrier discharges [DBDs], with different reactors, corona discharges, plasma torches, plasma-based UV-lamps, etc.), makes them able to be scaled up (or scaled down) to match the small or large facility production requirements, unlike conventional thermal or chemical processes, which generally require large-scale plants to be

economically viable.¹⁷ Plasmas can also be integrated with other enabling or even industrialized processes, such as catalysis, adsorption, or biological treatment, providing further feasibility for their implementation and commercialization. Besides the well-recognized ThPs used to control and harvest energy from nuclear fusion processes, plasma technologies are playing increasing roles in modern industries and societies. For example, plasma-based processes take up to one-third of the steps in manufacturing microelectronic circuits and microprocessors.¹⁸ Plasmas for environmental applications have been industrially implemented for over a century, with DBD-ozone generators and electrostatic precipitators (ESPs) as successful examples. The world market for ESPs alone was estimated to be over USD 15 billion by 2014.¹⁸ Another typical industrial installation example is surface modification or engineering based on etching, plasma-enhanced chemical vapor deposition (PECVD), and other plasma-assisted processes, which provide a cost-effective and ecologically benign alternative for wet chemical processing, and enable the production of many today's photovoltaic coatings and many plastics and textiles commodities. Due to the rapid development of applications in these industries, with only cold plasmas considered, the global market size is expected to reach USD 3.3 billion by 2026 from USD 1.6 billion in 2021.¹⁹

Owing to their unique physicochemical properties, such as high energy content and the rich assortment of reactive components, including free electrons, energetic radicals, ions and neutrals, and excited species and photons, discharge plasmas are also gaining increasing interest for different energy conversion purposes, not only for gas conversion applications but also for liquid and/or solid treatment.²⁰ Recently, plasma reforming or processing of carbon-rich precursors has emerged as a promising new technology platform, which may become a green complementary alternative to existing valorization processes. For example, ThPs with substantial heat and fast temperature increases have been widely used for direct gasification, pyrolysis, and combustion for syngas, heat, and electricity generation.²¹ Non-ThPs, with unique chemical activity enabling many chemical reactions to occur that may not be attainable in other processing environments, can assist or directly drive carbon-rich precursors conversion and upgradation, either dry processing or wet reforming, while requiring much easier system designs and fewer reaction steps.²² Plasma-enabled up-carbonization or conversion is considered to have no adverse effects on the environment. For example, no further cleaning is required for the off-gases from ThPs-gasification before being

discharged or used. Plasmas are capable of converting almost all sorts of feedstocks, such as low- or negative-value wastes and plastics, in particular, providing an ideal platform to alleviate environmental burdens from landfills. Also, the products in the forms of gas/liquid fuels, chemicals, and functional materials, such as the low- or zero-carbon hydrogen from plasma pyrolysis of biogas and reforming of bioalcohols, are clean, zero-carbon, and environment-friendly since many of them are commonly derived from nonrenewable and nonsustainable fossil fuels by heavy refining industry with obvious environmental pollution.^{23,24} Another important advantage of plasma reforming, especially using non-ThPs, is that it can be run “on-demand”, with the power consumption, thermal effects, and plasma chemistry being well-tuned and adapted to the specific targeted reaction or application requirements. In addition, plasmas can easily be switched on/off; therefore, they are suitable to combine with renewable electricity, making the plasma-integrated electrified up-carbonization more sustainable and cost-effective.²⁵

This paper aims to give an overview of the applications of reactive discharge plasmas for the valorization of carbon-rich feedstocks or precursors, outlining the basic scientific knowledge and technological aspects of this emerging topic. Figure 1 shows the basic structure of this

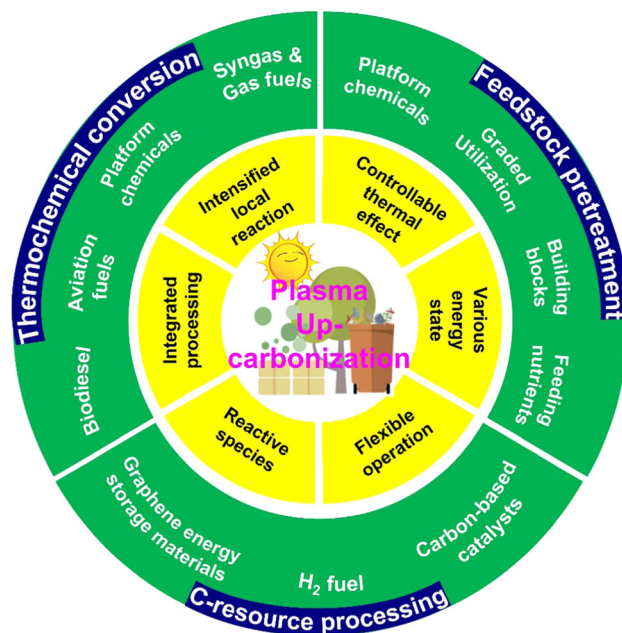


FIGURE 1 Plasmas, with the unique electricity-enabled physicochemical properties, electrify the conversion and up-carbonization of carbon-rich feedstock into the higher-energy state and further create value-added products, such as clean energy, high-performance advanced carbon-based energy materials, high-value platform chemicals, customized manufactured products, and several others.

review. We first briefly introduce common processes for natural solid carbon-rich feedstocks utilization and the discharge plasma technique, emphasizing the technical aspects of plasmas generation and the plasmas' unique physiochemical properties and reasons why they are well suited for up-carbonization. Next, we give selected examples of plasma up-carbonization processes to value-added end products (gas/liquid fuels, chemicals, functional materials, etc.), particularly on gasification, pyrolysis, liquefaction, feedstocks pretreatment, and derivatives upgradation, with particular focus on the chemistry and mechanisms of plasmas-carbon-feedstocks interactions and the superior features compared to conventional processes. It is worth mentioning that this review focuses mainly on renewable carbon-rich feedstocks, particularly different biomass sources and their derivatives. However, we also want to emphasize that more attention is needed to other carbon-rich resources. We expect this review could provide basic knowledge and insights to guide future research and translation of plasma-enabled up-carbonization.

2 | TECHNOLOGICAL OVERVIEW

2.1 | Carbon-rich feedstock conversion

The main components of natural, pristine, renewable carbon feedstocks generally are high molecular polymers, such as cellulose, hemicellulose, lignin, lipids, and proteins, which usually entangle together to create resistant structures (Figure 2A), posing extra and significant difficulties for their conversion, degradation, and upgradation, especially under mild conditions.^{12,26} How to destroy the internal structure and decompose solid macromolecules into reactive liquid or small gaseous molecules, and thus, transform these stubborn feedstocks into a clean and efficient energy source is the key problem related to their utilization and up-carbonization.^{12,26,27} As illustrated in Figure 2B, a wide range of technologies, which can be roughly classified into thermochemical, biochemical, and electrochemical conversions, have been developed over the past century to allow this conversion to occur.

The term 'thermochemical conversion' covers a range of technologies where feedstocks are converted through chemical reactions under controlled thermal conditions, mainly combustion, gasification, pyrolysis, and liquefaction. These can be configured to produce outputs of energy (heat and electricity), gaseous and solid fuels, biocrudes, and other platform chemicals.^{1,28,29} Combustion, the simplest and earliest method humans use to utilize dry carbon resources, is still the dominant bioenergy conversion worldwide, especially for domestic

heating in developing areas and electricity production.³⁰ However, the complex kinetics of chemical reactions involved and the high-water content and the wide existence of S and N in natural feedstocks make complete feedstock combustion difficult to achieve. This, in turn, often leads to the release of pollutants like CH₄, CO, SO_x, NO_x, and particulate matter into the environment.³¹ Gasification is the process of converting carbon-rich materials under optimized heating conditions into gaseous products (syngas or producer gas) rich in CO, H₂, and low molecular hydrocarbons with high yields. Although gasification is significantly different due to various factors, the basic reaction process can be summarized as water evaporation, thermal decomposition, reduction, and oxidation.³² The products can then be used as engine fuels or further upgraded to liquid fuels and chemical feedstocks through biological fermentation³³ or via the Fischer-Tropsch process.³⁴⁻³⁶ Currently, gasification is one of the best-developed solid carbon-feedstock conversion processes and has been industrialized for heating and power supply worldwide.^{30,31} However, the production of quite a large amount of tar from higher molecular weight (M_w) volatiles is inevitable. The presence of tar is a big fouling challenge, as it directly leads to blocking of the gas path and seriously damages the equipment; furthermore, it is a potential source of persistent environmental pollutants, such as polycyclic aromatic hydrocarbons (PAHs).³⁷

Pyrolysis and liquefaction are two other thermochemical processes that produce a mixture of gaseous products, biochar, and biocrude (or bio-oil). The studies into these two approaches are now leading the trend in thermochemical conversion.³⁸ Pyrolysis, that is, thermal decomposition of dehydrated feedstocks in the absence of oxygen, is usually performed at a temperature of 500-900 °C, the latter being considerably higher than that used in liquefaction, while the exposure time in pyrolysis is usually less than several minutes.^{7,39} However, it should be noted that the drying process typically required for the preparation of dehydrated source material is a significant extra cost to the pyrolysis conversion.¹¹ As an environment- and cost-benign solvent, water is almost the first used solvent (dating back to the year 1994) and widely applied in liquefaction, and thus a term—hydrothermal liquefaction (HTL)^{40,41} has been given to this conversion method and if not technically be deemed as the general designation of solvent-thermal liquefaction.

Biological conversion refers to the refining of the carbon-rich feedstocks into diverse products, including bioenergy (bioethanol, long-chain alcohols, biodiesel, biogas [hydrogen, methane-rich gas], etc.), bulk chemicals (organic acids [acetic acid, lactic acid], olefins), and

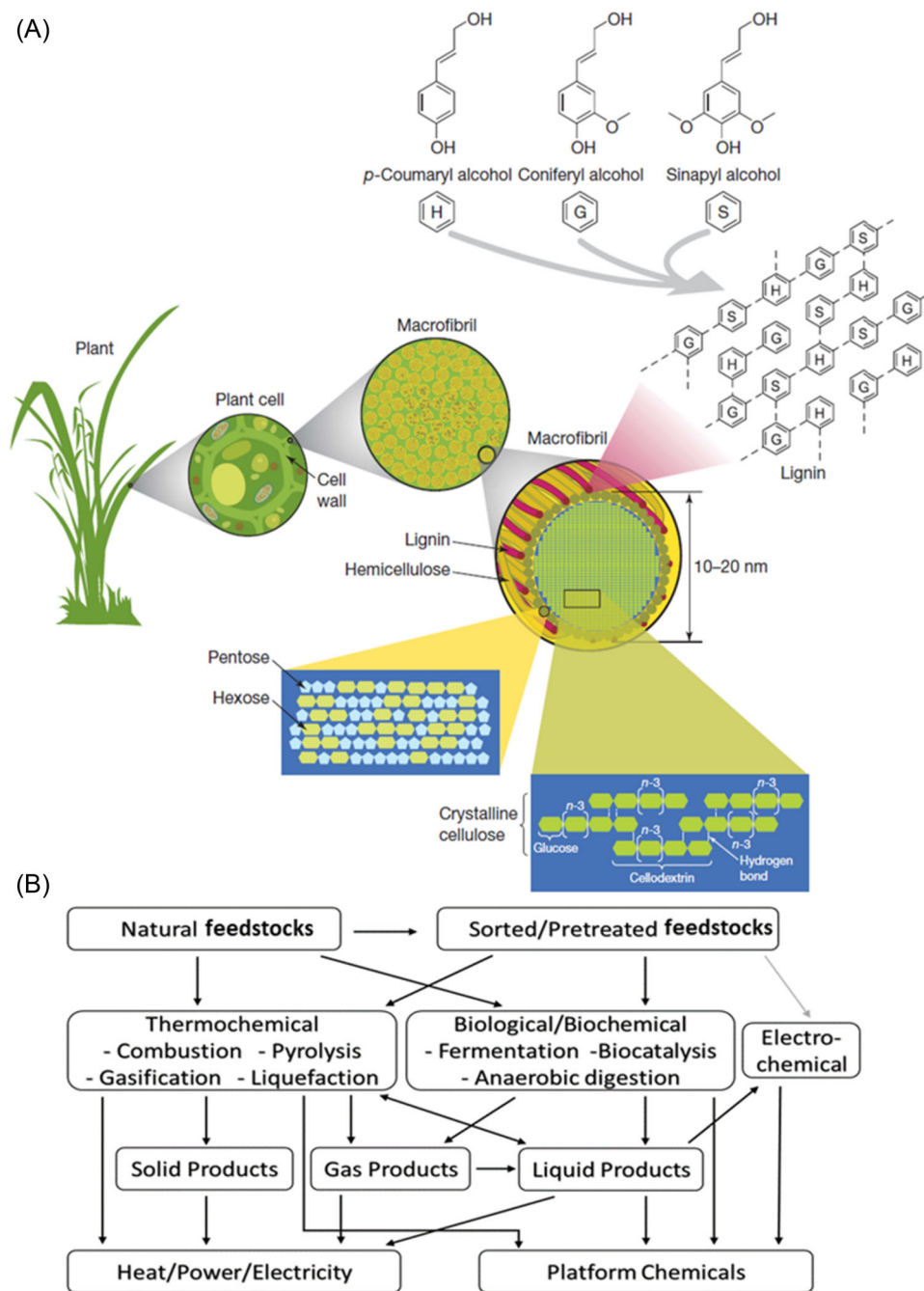


FIGURE 2 Basic structures and conversion techniques of renewable carbon-rich feedstocks, exemplified by lignocellulosic biomass resources. (A) General structures of lignocellulose in plant cell walls, representing the natural carbon-rich feedstock recalcitrance. Reproduced with permission: Copyright 2008, Springer Nature.¹² (B) Overview of the current conversion technologies.

fine compounds (amino acids, antibiotics, botanical drugs) mainly via enzymatic and microbial (or fermentative) processes.^{42–44} Such conversion mainly involves anaerobic digestion,⁴⁵ microbial fermentation,⁴³ and increasing innovations on using enzymes and even the microbes as novel biocatalysts for assisting/enabling chemical reactions.^{46,47} Biological/biochemical technologies generally occur under moderate conditions and harvest products with superior selectivity.^{42,47} However,

these processes usually take longer processing times, and each of them requires special operating conditions and/or different microbes, which leads to the process with poor versatility.⁴² Moreover, when processing complex raw materials, such as lignocellulosic and microbial biomass, there is often a need for a previous step, which is usually costly, to breakdown the matrix to provide suitable substrates for further conversions.^{42,43} Recently, (photo)electrochemical technologies (such as fuel cells,

organic electrosynthesis, electro-oxidation, and electrolysis) have also been trailed for direct electricity and chemicals generation from some feedstock fractions (usually lignin only) and, in particular, from biomass-derived compounds.^{48–50} Electrochemical conversion is still at its early research stage and, usually, requires involving other conversion techniques.⁵¹

2.2 | Discharge plasma techniques

2.2.1 | Plasma introduction

With energy introduced, the substance will change from solid to liquid, and then from liquid to gaseous. Suppose the energy input is large enough for the electrons in gas to overcome the electrostatic potential barriers, the gas will be ionized and converted into another aggregate state in which charged particles and neutral particles coexist, that is, the plasma state.⁵² Plasmas widely produced for experimental and industrial applications can be classified into two main categories: ThPs and non-ThPs. If gas is continuously heated at a sufficiently high temperature for achieving and sustaining the ionization, such plasmas are referred to as ThPs.^{21,23,53} In ThPs, all the constituent chemical species, electrons, and ions exist at least locally in thermodynamic equilibrium. In contrast, non-ThPs are characterized by a significantly higher temperature (T_e up to 15,000 K) than that of other heavy species (T_h 300–500 K). Electricity is the most commonly used energy for inducing plasma discharges and is most suited to be coupled with other renewable energy sources. Electrical energy for plasmas is generally supplied with different power forms, including direct current (DC), alternative current (AC), radiofrequency (RF), and pulsed microwave (MW).^{23,53} These power sources have outstanding features for specific applications, but unfortunately, they also have unavoidable drawbacks. For example, DC power, with a power supplying efficiency of up to 90%, can be easily controlled to deliver accurate inputs and drive both ThPs and non-ThPs using simple reactor configurations. However, electrode erosion in DC discharges is common, limiting long-term uses, and DC-ThPs generally require intensive water cooling.^{23,53} AC power with a wide operation frequency can sustain almost all sorts of non-ThPs discharges, but the power supplying efficiency is generally low. With electrode-free configurations, RF and MW are featured by high purity and low gas velocity when providing high energy density; but both use more complicated reactor designs, and the plasma ignition is difficult, especially under ambient pressure.^{23,53} Pulsed power, the nanosecond one in

particular, is featured by a high reduced electric field (E/N , up to 2000 Td in the air), a high electron density and energy, more uniform discharges, and enhanced energy efficiencies; however, the manufacturing is still costly, and the use in large-scale applications has not yet been implemented.⁵⁴ Thus, hybrid plasma systems are designed to compensate for the limitations of individual systems. For example, a combination of DC and RF was developed, in which a DC plasma jet was used as the auxiliary and was proved able to assist the ignition and stabilization of RF discharges.⁵⁵

Figure 3 summarizes the plasma reactors most often used to treat solid and liquid carbon-rich precursors. Based on the contact of plasmas and processed samples, these reactors are roughly classified into two groups: pure gas discharges and discharges closely in contact with liquids (samples placed in liquids). Gas discharges can be generated by many systems, such as plasma jet/torch (Figure 3A–C,F), DBD (Figure 3D), gliding arc (GA) discharge (GAD; Figure 3E), and MW discharge (Figure 3G).^{56–60} Whether dried or wet, samples can be carried into discharge zones by the inducer gas, placed directly in the reactor or underneath to contact with plasmas. For in-liquid processing, the plasmas can be generated over the liquid surface (Figure 3H,I; the plasma jet, DBD, and torch are also suitable for such treatments with liquid samples placed in or underneath plasma zones), in gas bubbles (Figure 3J,K), or directly in liquids.⁶¹ Furthermore, based on their physical performance, non-ThPs are also well known as many other types of discharges, such as corona, glow, spark/arc and diffuse discharges, which have specific features and extend the applications of non-ThPs in biorefinery and beyond (Table 1).

2.2.2 | Diverse energy levels and reactivity in plasmas for up-carbonization

As introduced above, a wide variety of plasma systems, with tunable energy outputs, a wide range of heating effects, and a rich assortment and abundant reactive species, provide feasibility for treating carbon-rich feedstocks and their derivatives in different physical states and shapes. These systems then fulfill different treatment or conversion purposes, mainly based on interactions of plasma-to-gas (vapors), plasma-to-liquids and solids. Different plasmas with operating pressures varying from vacuum or near to high pressures (up to 10 atm) possess different energy levels and reactivity (Figure 4A and Table 1), directly reflected by the heavy particle temperature (T_h), electron densities (n_e), rotational temperature (or gas temperature when discharging under

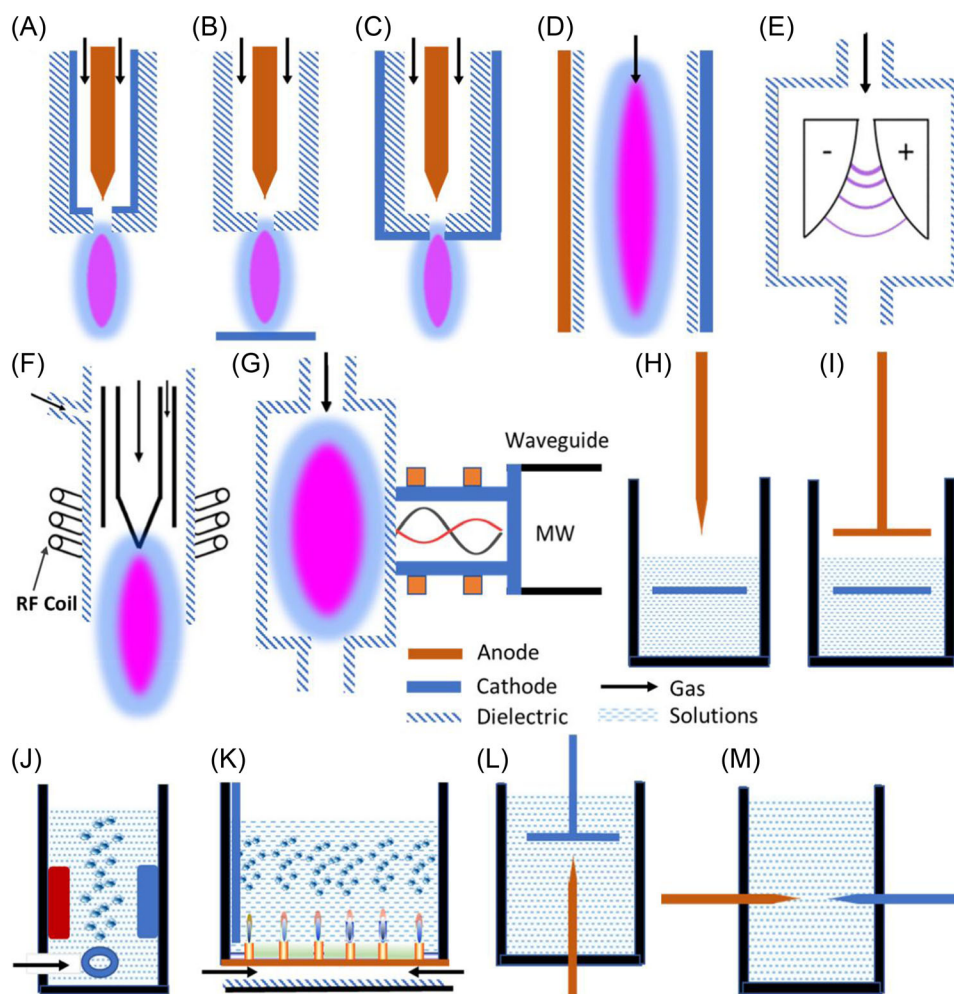


FIGURE 3 Schematic illustration of plasma reactors most commonly used for carbon-rich, solid feedstock processing applications. Gas discharges only: (A) nontransferred plasma jet/torch, (B) transferred plasma jet/torch, (C) DBD-like plasma jet, (D) DBD with traditional configuration, (E) GA discharge, (F) RF torch, and (G) MW discharge. Biomass samples, both dried or containing water, can be carried into plasma areas by the inducer gas, placed directly in the reactor or underneath for contact with plasmas. Discharges for liquid-involved processing of biomass samples: over liquid surfaces (H) needle-to-plate discharge and (I) plate-to-plate discharge over liquid surfaces, (J,K) gas bubbling discharge, and in-liquid (L) needle-to-plate discharge and (M) needle-to-needle discharge. DBD, dielectric barrier discharge; GA, gliding arc; RF, radiofrequency; MW, microwave.

TABLE 1 Energy in typical non-ThPs discharge plasmas and common chemical bonds with organic substances^{54,62}

Plasmas	T_g (K)	E (V/cm)	n_e (cm^{-3})	ϵ (eV)	Bond	D (eV)	Bond	D (eV)
Corona	<400	$\sim 2 \times 10^4$	$< 10^6$	<3	C–O	0.95–3.0	C–H	3.2–4.7
Glow	<700	$50\text{--}10^4$	$10^7\text{--}10^{10}$	2–8	O–O	1.6–2.5	C=C	3.3–7.5
DBD	<300	$10^3\text{--}10^5$	$10^{10}\text{--}10^{11}$	<10	N–H	2.1–4.7	O–H	3.4–5.2
Spark	>1000	<20	$> 10^{14}$	>1	C–C	2.6–5.2	C=O	5.5
Diffuse	<3000	$> 10^3$	$10^{10}\text{--}10^{13}$	>10	C–N	2.9	C≡C	8.4

Abbreviations: ϵ , electron energy; D , bond energy; DBD, dielectric barrier discharge; E , electric field strength; n_e , electron density; T_g , rotational temperature; non-ThPs, non-thermal plasmas.

high pressures, T_g), electric field strength (E), and averaged electron energy (ϵ), respectively.^{54,63} When processed under normal pressure, the T_h in the range of room temperature to more than 10,000 K and the high

values of n_e ($10^{15}\text{--}10^{20}/\text{m}^3$) give further possibility and flexibility for many applications with various aims. The electron energy (ϵ) of such plasmas is measured to be 1–10 eV with different processing conditions, indicating

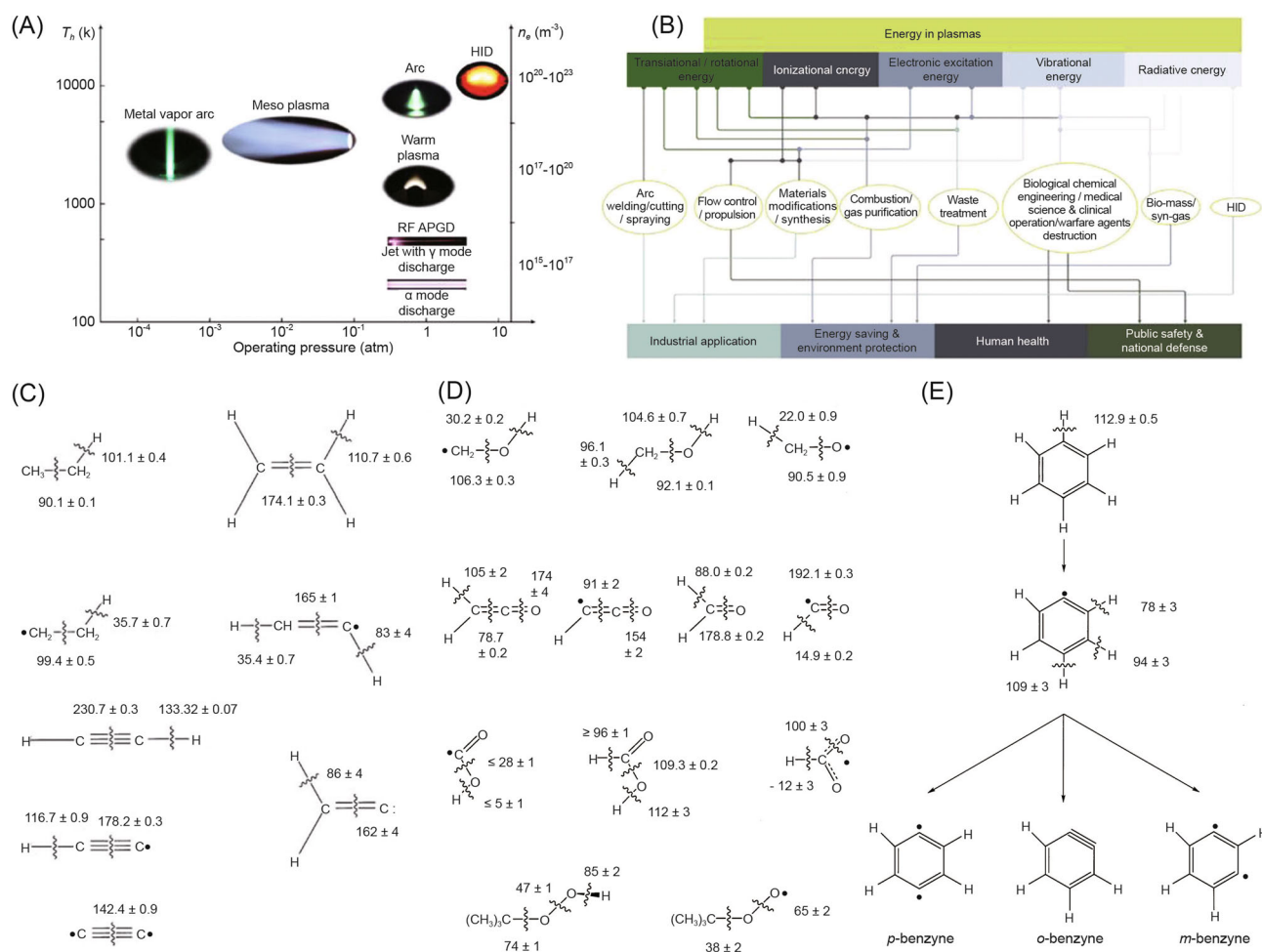


FIGURE 4 Energy distributed in various plasmas and experimental chemical bond enthalpies (DH_{298} , kcal/mol). (A) Heavy particle temperature (T_h) and electron density (n_e) with plasmas at different operating pressure, and (B) uses of energy distributed over various degrees of freedom for some typical collision-dominated plasmas. Reproduced with permission: Copyright 2018, Elsevier.⁶³ DH_{298} for (C) hydrocarbons and hydrocarbon radicals, (D) oxycarbons and oxycarbon radicals, and (E) benzene and phenyl radicals. Reproduced with permission: Copyright 2003, to American Chemical Society.⁶⁵

that the electrons in plasmas have an energy of up to 230.6 kcal/mol.^{25,54,63} Furthermore, in plasmas, there exist many other high-energy physical and chemical effects, such as ultraviolet (UV) ray with the energy of >5 eV (115.3 kcal/mol), shock wave, ions, and reactive oxygen and nitrogen species (RONS), such as OH and O radicals, which are with strong oxidation capacity.^{22,54,64} The energy can be further partitioned over various degrees of freedom, for example, translational, electronically, vibrationally, or rotationally exciting energies and radiation, suitable for many practical applications (Figure 4B).⁶³ For example, plasmas with a high translational energy density or a high heavy particle temperature for melting the materials are suited to the welding, cutting, and spraying process. Those with abundant reactive species and a low value of T_h close to or even lower than the room temperature show great

potential in biomedical applications. In addition, those with an appropriate translational energy density and abundant reactive particles are ideal for achieving high-performance feedstocks/waste and gas conversions.

For the carbon-rich feedstocks to be efficiently reformed into higher-value bio-based products, they must break the chemical bonds in raw materials selectively and with minimum energy inputs. The energy of the vast majority of the active particles in plasmas, up to 230.6 kcal/mol for electrons, and strong oxidizing species, is higher than that of common chemical bonds in organic substances and carbon precursors (Figure 4C–E and Table 1). These reactive plasmas are then capable of bond breaking for feedstock depolymerization and/or for oxidation to produce platform chemicals (Figure 4B), and thus are with broad application potential in up-carbonization, with increasing reports validating the

feasibility (direct thermochemical conversion, feedstocks pretreatment or surface modification, microorganism treatment for ethanol production enhancement, etc.).^{63,65} Moreover, the discharge reactivity can also be easily controlled by using different sorts of carrying gases or liquids. For example, O₂ or air containing gas creates an oxidative environment for surface functionalization and oxidation conversion with less or without the extra addition of strong chemical oxidants. H₂, NH₃, ethanol, and other H-rich gases support a discharge suitable for reductive upgradation.^{66,67} And others such as F-, Cl-, and Si-based gases are able to bring further functionality and initiate or facilitate downstream reactions.^{68,69}

ThPs, in local thermodynamic equilibrium, enable fast system temperature increases and extremely high heat transfer due to their super high enthalpy, thermal conductivity, and radiation intensity, and sustain high temperatures with the power supplying efficiency of up to 90% (generally 50%–70%).²³ These features make ThP an upcoming and promising technique to treat all sorts of organics and wide varieties of solid waste to produce heat and fuel gas, with several ThP-based systems implemented in industrial applications.^{23,70} In all plasmas, inelastic electron collisions result in the formation of other active species that sustain the plasma and create a chemically enriched environment, in particular, free electrons, atomic radicals (O, N, and others), O₃, and OH if with humidity, which are regarded as the most important species for dry processing. Under the action of the electric field, thus-formed active species can gain sufficient kinetic energy to initiate a wide range of chemical reactions.⁶³ For in-liquid discharges, plasmas normally activate the liquids first, leading to increased solution temperature and the formation and retaining of highly reactive species to further interact with suspended particles or dissolved bio-derived components.^{71–73} With

air discharge as an example, the basics of plasma–liquid interactions and species formation are illustrated in Figure 5. For more details on discharge features, physiochemical properties, mechanisms, reaction pathways, and applications in other fields of plasma–liquid systems, readers are encouraged to refer to some prestigious review articles.^{71–73}

Currently, non-ThPs for direct carbon-rich feedstocks conversion are still in their infancy. The recalcitrance structure and the complex composition of macromolecules again pose significant challenges for the plasma-generated species to be precisely delivered and effectively involved in raw materials conversion. However, there are also huge possibilities. In the next section, practical examples of plasma-involved up-carbonization processes are outlined and concluded to better understand plasma effects and potentials.

3 | APPLICATIONS OF REACTIVE PLASMAS ON UP-CARBONIZATION

The plasma technique has been widely employed for various up-carbonization purposes, with several practical plasma-enabled, assisted, or integrated processes developed. This section provides an overview of this emerging field based on state-of-the-art studies and discusses the mechanisms and further possibilities of these plasma-powered processes. The selected examples, basically using renewable biomass and its derivatives as the raw feedstock due to the literature availability and the aim to give a better comparison of the plasma-integrated processes, are classified into three groups: direct thermochemical conversion, mainly including gasification (Section 3.1), pyrolysis (Section 3.2), and liquefaction (Section 3.3); feedstock pretreatment and microbe

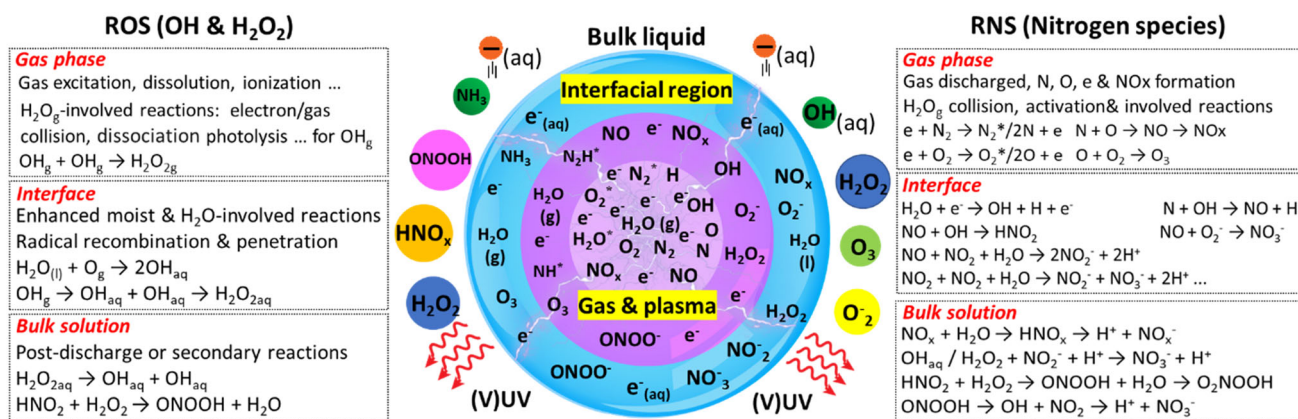


FIGURE 5 Air plasma–water interactions and typical reactions and chemistry involved at different stages for the formation of ROS and RNS. Reproduced with permission: Copyright 2021, Springer Nature.⁷⁴ RNS, reactive nitrogen species; ROS, reactive oxygen species.

engineering for enhancing bio-derived energy/chemicals (bioethanol, as a typical example) production (Section 3.4); and processing or upgradation of other derivatives, such as heavy/waste oil reforming, tar removal, and beyond (Section 3.5).

3.1 | Gasification

Gasification enables the direct conversion of carbon-rich feedstocks with limited oxidation (by controlling gasifying agents, such as air, O₂, steam, or a mixture of those in N₂) at high temperatures (over 1000 K) into gas mixtures as the main products, and generally, is the most efficient process for harvesting gas fuels, particularly syngas and those rich in H₂.⁷⁵ Gasification is also a best-developed thermochemical conversion process, which has been implemented at pilot or even industrial scales. The overall gasification is endothermic and can be expressed as C-feedstocks → char + tar + H₂O + gas (H₂, CO, CO₂, CH₄, and H₂O). As shown in Figure 6A, the main stages of the gasification generally involve oxidation (C complete or partial oxidation and H combustion), drying, pyrolysis, and reduction (C gasification reactions, i.e., Boudouard reaction, steam gasification, methanation, homogeneous volatile reactions such as water–gas shift reaction), and often tar reactions (formation and decomposition).⁷⁶ The economic performance of gasification is limited by the requirements in feedstock drying, specific high operating pressures and long preheating time, and more importantly, some technical challenges due to the formation of tar and/or soot, which leads to inadequate carbon yields and agglomeration and slagging.^{77,78} The complex feedstocks structures and the polymer-based basic components with aromatic nature or easy to be cyclized or aromatized are natural tar precursors, such as lignin and cellulose (Figure 6B,C). The primary tars with high reactivity are the intermediates directly formed from lignocellulosic biomass, such as lignin-derived vanillin and guaiacol and cellulose-derived levoglucosan. If failed to be fast and fully degraded, they are quickly transformed into secondary tars, such as phenolics and olefins, which will further develop into tertiary or end tars (methyl derivatives of aromatic compounds and PAHs).⁷⁹

Plasma-based gasification, with a basic system design and discharge photos shown in Figure 6D–F, is an ideal alternative able to solve almost all of the limitations mentioned above and is the best-established and most-mature plasma process in waste utilization with increasing commercialized plants being set up (Figure 6G,H). Currently, most applications of plasma technology for gasification as well as pyrolysis (discussed in Section 3.2) use ThPs.^{23,53} Compared with traditional gasification

with fire or electricity heating, ThPs have several outstanding advantages. First, ThPs offer a reaction environment with extremely high enthalpy under room pressure, creating and sustaining much higher operation temperatures (easy to reach over 3000 K) for fast depolymerization and fragmentation with much-improved yields, and high heating rates (up to 10⁴ K/s, 100-time higher than conventional heating) or short housing times required, which limits side reactions and energy loss while enhances product yields and selectivity.^{23,53,87} Second, ThPs are in local thermodynamic equilibrium resulting in a super high heat transfer and a uniform temperature distribution, which is also a challenge, especially for conventional fixed bed gasifiers.⁸¹ Third, the discharges of carrying gases and thus-forming gaseous products (H₂ in particular) create a highly reactive environment, facilitating high-temperature endothermic reactions and allowing plasmas to participate in many reactions, particularly tar decomposition, as a reactant.^{87,88} Thus, the production of tar, soot, or ash, the greatest hindrance to traditional gasification, can be well solved both by plasma gasification, which has been demonstrated to provide products with much less or even without unexpected tar.^{87–90} The use of discharge plasmas for tar (models) and heavy/waste oils reforming and upgradation has emerged as a hot research topic. We separate tar removal into an independent section (Section 3.5.1).

For plasma gasification, feedstocks can be placed directly in the discharge zone or supplied continuously, either in manual way or gas-carrying methods and the discharges used are normally DC or AC arc ThPs (photos of a plasma torch with air and stream discharge shown in Figure 6C,D, respectively) and partly electrode-free RF- and MW-plasmas.^{23,53} Table 2 presents some experimental studies on plasma gasification of some typical biomass. Basically, all studies show that the conversion can be fulfilled within minutes or even tens of seconds, including system heating and biomass reactions. Syngas is the main product, with a content of over 90% in all gaseous products in many studies. Air, O₂, and steam (with varying H₂O contents) are the most used agents to sustain an oxidation environment. For example, a jet-transferred-arc plasma torch capable of running over 700 kW using air or operated in the open air for sawdust and rice hull gasification gave a syngas yield of over 90%.⁹¹ Compared to pristine sawdust (without drying) with a water content of 40%, the dried sawdust generated a gasification product with increased CO (24.8%–28%) and CH₄ (0.16%–1.46%) but decreased H₂ (61.5%–51.8%) and CO₂ (7.3%–2.3%), indicating that increasing H₂O contents to some extent contributes to an enhanced H₂ mass yield,⁹¹ well consistent with other investigations,

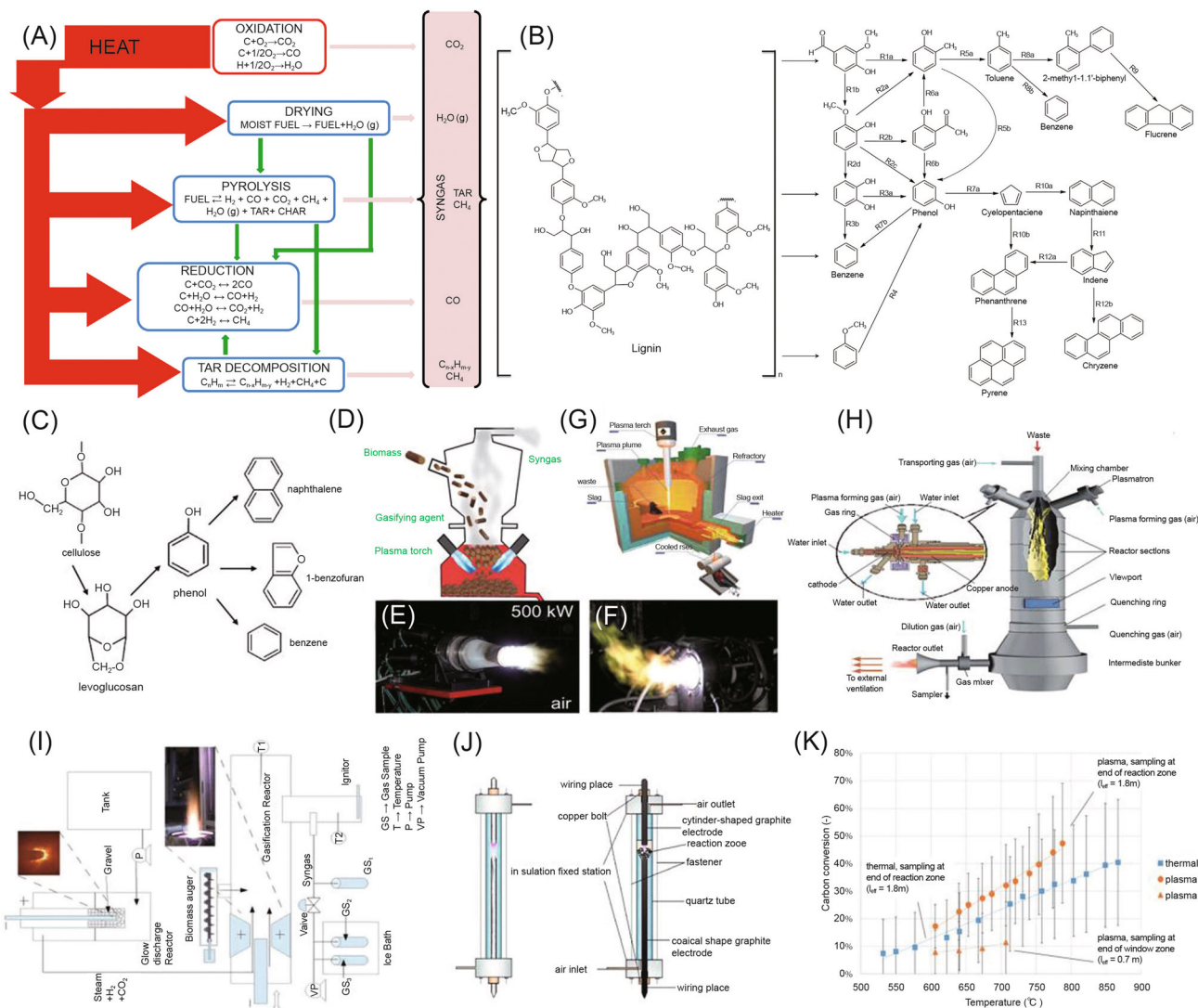


FIGURE 6 Biomass gasification without or with plasmas. (A) Main stages and reactions of biomass gasification. Reproduced with permission: Copyright 2016, Elsevier.⁸⁰ The proposed pathways for the tar formation during traditional gasification, which poses a great challenge, from (B) lignin (Reproduced with permission: Copyright 2018, Elsevier⁸¹), and (C) cellulose (Reproduced with permission: Copyright 2018, Elsevier⁸²); (D) a basic illustration of plasma biomass gasification (Reproduced with permission: Copyright 2020, Elsevier⁸²). Photos of a plasma torch used with (E) air and (F) stream discharge. Reproduced with permission: Copyright 2017, Elsevier.⁸³ Examples of ThPs used at pilot scale: (G) the Europlasma reactor with 500 kW plasma torch (Reproduced with permission: Copyright 2008, IOP Publishing^{23,53}) and (H) a three-jet reactor (200 kW) with electric arc plasma generators (Reproduced with permission: Copyright 2020, Elsevier^{23,84}). Examples of innovation on enhancing biomass gasification performance with non-ThPs: (I) a two-step combining glow discharge electrolysis and steam ThP for enhancing H₂ content (Reproduced with permission: Copyright 2015, Elsevier⁸⁵) and (J) a non-thermal arc discharge for gasification (Reproduced with permission: Copyright 2015, Elsevier⁵⁹). (K) A non-thermal steam discharge integrated with conventional thermal gasification of wood power enhanced carbon conversion. Reproduced with permission: Copyright 2018, MDPI.⁸⁶ ThP, thermal plasma.

such as an N₂ RF plasma torch with a controlled steam supplied (H₂O from 5% to 55%) for the gasification of rice straw or raw wood from municipal solid waste.⁹⁰ The increase in H₂ with increasing steam content can be explained by the decomposition of H₂O as well as CH₄ via steam methane reforming reaction, hydrogasification, and the Boudouard reaction, while the enhanced water–gas shift reaction leads to the increased CO₂

production.⁹⁰ Another feature of ThPs biomass gasification is the reduced formation of tar and soot. For rice hulls with a high ash content of 18%, after gasification with an air torch, the ash left was made of inorganic components only, particularly Si with a mass content of 40%.⁹¹ For wood, only less than 5% of residue was formed with an RF N₂ torch, and the residue was nonhazardous, nonleachable verified lava.⁸⁹ Increasing the H₂ fraction

TABLE 2 Experimental studies on plasma gasification and pyrolysis

Biomass	System and discharge conditions	Results	Ref
Gasification			
Sawdust and rice hull	A jet-transferred-arc air plasma torch or arc operated in the open air; dozens to 100 kW	≥90% Of syngas; dried sawdust for a gas product with increased CO and CH ₄ but decreased H ₂ ; no C left in residue; ash after hull gasification rich in Si (40%).	91
Rice straw	RF torch, N ₂ and steam (H ₂ O from 5% to 55%); 2–6 kW for temperatures of 700–1000 K	≥91% Of CO and H ₂ in gas within 1–4 min; no tar formed; H ₂ mass yield increased with higher H ₂ O, but syngas fraction decreased.	90
Raw wood	RF plasma torch; N ₂ and steam; 10 kW capability, with a continuous feeding process	CO and H ₂ as major components; 90% of yield obtained in 2 min; maximum energy yield of 111.89%; ≤5% nonleachable verified lava.	89
Paper mill waste	Air/O ₂ DC torch (3 tonnes/day); energy efficiency of 70%; 200 A 350 ± 10 V; T, 1673–1723 K, with an H ₂ recovery system	Syngas (~75%, vol/vol) passing a bag-filter and wet scrubber with water-gas shift and pressure swing adsorption; H ₂ (20 N m ³ /h) with purity over 99.99% and a cost of 1.74 USD/(N m ³) obtained.	93
Charcoal	Air and steam MW; 5 kW; varying O ₂ /fuel ratios	Syngas with hydrogen contents over 60% and H ₂ /CO ratios greater than three.	92
Cellulose	Air MW, 2.45 GHz; up to 6 kW; room pressure	Energy of gas 1.84 times higher than MW energy supplied; heating value of the gas yield up to 84% of the net MW energy transmitted	94
Corn cob	Arc plasma (nonthermal) 25.2 W	79% Of gas yield using N ₂ as a carrier gas; energy cost is 5328 kl/kg H ₂ .	59
Wood powder	N ₂ /H ₂ O gliding arc (GA; non-ThP) assisted, ~1 kW	10% Increase in carbon conversion and 30% increase in reaction rate	86
Pyrolysis			
Wood and rice husk	DC arc plasma; H ₂ /Ar, 40.5 kW; biomass fed at 1–4 g/s	Higher H ₂ , CO, C ₂ H ₂ , and lower CH ₄ , CO ₂ contents than conventional lower-T pyrolysis; C and O conversion of 79% and 72%, respectively.	95
Fir sawdust	RF (13.56 MHz) plasma jet; 1.6–2 kW; N ₂ 0.5 L/min; biomass fed at 0.3 g/min; 3–8 kPa	Gas yield of 66 wt% with total CO and H ₂ content up to 70 vol%; Biochar with C content of 83%, heating value of 29 MJ/kg, enhanced surface area (278 vs. 115 m ² /g for char from conventional pyrolysis) and developed microporous structures.	96
Waste wood	MW-induced jet, Ar discharge, 1 SLM N ₂ , preventing unwanted oxygen; 1 kW; water-cooling	Complete pyrolysis (a mean mass loss of 79.6%); liquid, solid, gas mass ratio found to be 66:20:13; CO in gas over 50%.	97
<i>Spirulina algae</i> (dry)	Atmospheric-pressure MW discharge; N ₂ 12 SLM; 0.8–1 kW, 1063–1121 K	Time required for complete conversion of algae to H ₂ almost independent of the reaction temperature; higher power for higher H ₂ yield; H ₂ , CO ₂ , and CO as main gas products; maximum H ₂ volume fraction of about 45%.	98

TABLE 2 (Continued)

Biomass	System and discharge conditions	Results	Ref
Waste rapeseed oil	Rotating GA-assisted pyrolysis; Ar or N ₂ , 2 or 5 L/min; 66–141 W	Arc behaviors changed with oil added; conversion up to 74%; activate species facilitating bond breaking of long-chain fatty acids into alkanes, cycloalkanes, olefins, and aromatic hydrocarbons; CO and C ₂ in gas; char with more developed graphitic structures.	99,100
Carambola leaves	AC arc plasma (nonthermal); Ar or N ₂ , 1–5 SLM; ~30 W; 7 min	Gas yield peaking at ~68%; good metal (Zn, Fe, Cu, and Cd) fixing efficiency of up to 90% with N ₂ discharge; biochar with C content over 60%, more dense structure and higher pore volume.	101
Rice straw	RF (nonthermal) 357–664 W	Gas yield increases with the increase of input power, 66.5% at 664 W; no tar is produced.	102
Cellulose	Air/Ar DBD, 2.1–2.3 W for cellulose pretreatment (10–60 s) before pyrolysis (350–450 °C)	The DBD-pretreated cellulose yields higher levoglucosan (78.6% vs. 58.2%); pretreated cellulose yields levoglucosan at a lower pyrolysis temperature.	103

Abbreviations: AC, alternative current; DBD, dielectric barrier discharge; DC, direct current; MW, microwave; RF, radiofrequency; ThP, thermal plasma.

in gaseous products is of particular and practical interest, such as for fuel cell applications. It has been proved that by tuning the ratio of O₂, syngas with a high hydrogen content of over 60% and an H₂/CO ratio greater than three could be obtained.⁹² A two-stage plasma system (Figure 6I) was designed to enhance hydrogen content.⁸⁵ The first stage is an electrolytic cell operated in glow discharge mode to generate steam. The second comprises a DC arc discharge for direct contact with biomass. H₂ molar fractions of over 50% were obtained by using this design.⁸⁵ Also, coupled with an H₂ recovery system, which enables water–gas shift reaction and pressure swing adsorption (PSA) for H₂ recovery, to an air DC plasma torch (at 3 tonnes/day scale), extra pure H₂ with a purity of over 99.999% at a rate of 20 N m³/h was obtained from paper mill waste.⁹³

Although conversion energy yields of over 100% have been increasingly reported and verified in the lab, pilot, and/or industrial scale, indicating their energy feasibility, such as energy yield of ~112% with an RF torch for wood gasification⁸⁹ and energy of the outlet fuel gas 1.84 times higher than MW energy supplied for cellulose,⁹⁴ ThPs are linked to high energy inputs and extra cooling systems required to protect plasma generators and reactors, which have been the major considerations. Attempts to use low-temperature or nonthermal discharges were then made. Corn cob gasification for hydrogen generation was conducted using a non-ThP AC arc plasma (Figure 6J).⁵⁹ A gas yield of the gasification of corn cob reached 79.0% of the feeding feedstocks without drying at a discharge power of 25.2 W when N₂ was used as the carrier gas. Under these conditions, the energy cost of H₂ produced was estimated to be 5328 kJ/kg. Meanwhile, a carbon conversion rate of 82.9%, CO selectivity of 39.9%, and a ratio of H₂/CO greater than 1.5 were obtained. The presence of moisture improved the gas yield, carbon conversion rate, and molar ratio of H₂/CO.⁵⁹ Nonthermal discharges can also be coupled into conventional thermal gasification, termed plasma-assisted gasification. Pang et al.⁸⁶ compared wood thermal gasification to non-ThP-assisted gasification in steam in a drop tube reactor at atmospheric pressure. A GA steam plasma increased ~10% the carbon conversion and ~30% the reaction rates over all-thermal gasification (Figure 6K).⁸⁶

3.2 | Pyrolysis

Pyrolysis is another widely investigated, well-developed, and commercialized thermochemical technique, and generally shares similar basics of gasification, except operated under more moderate temperatures (≥400 °C) but in an oxygen-starved atmosphere.¹⁰⁴ Not only gas

fuels but liquid fuels (bio-oil), rich in oxygenates, such as aromatic compounds, phenols, aldehydes, levoglucosan, hydrocarbon chains, and many other value-added chemicals, as well as solid residues (biochar), are the targeted products. Pyrolysis is generally run with the protection of inert gases (N_2 and Ar) and requires the raw feedstocks to be dried (with water content less than 10%) to obtain bio-oils with higher yields and higher quality. Based on the heating rate and feedstocks residence in reactors, pyrolysis is further categorized into slow (normally <500 °C, heating rate <2 °C/s, residence up to hours and days), fast (heating rate of 10–200 °C/s, residence ~ 1 s), and flash (fast heating rate up to 2500 °C/s, residence 0.1 s) pyrolysis. Fast pyrolysis is now of particular interest due to its technoeconomic advantages, especially for producing liquid fuels with lower costs, while slow pyrolysis is used more for biochar formation and flash pyrolysis is more similar to gasification and has more specific requirements on the ignition and heating techniques.¹⁰⁴ Besides fast harvesting bio-oils in seconds and with high yields (up to 80%), thus-obtained pyrolytic liquids can be easily and simultaneously upgraded to higher-valued transportable fuels with energy density increased by such as coupling with catalytic reforming (hydrogenation, deoxygenation, etc.).¹⁰⁵

Many chemical reactions occurring during pyrolysis, as well as the complexity of the feedstocks structure and components, make the understanding of the pyrolysis mechanisms a significant challenge and research hotspot. Once the system reaches and sustains at high temperatures (i.e., >300 °C), thermal depolymerizations of raw feedstocks occur and oxygenates and/or intermediates with smaller Mws are formed. Further heating, the temperature increase, and extension of residence time result in a more complete cracking and conversion of raw feedstocks, and further decomposition of the intermediates into lighter oils and even gaseous products or condensation into biochar or tar, especially with the actions of highly reactive radicals.¹⁰⁴ With the development of analysis techniques, such as Py-GC-MS/FID, TG-MS/TG-FTIR, in situ electron paramagnetic resonance (EPR), and many others for online monitoring of key intermediates and end-products, and theoretical calculation methods, including advanced kinetic modeling and molecular simulation (density functional theory [DFT]), more reasonable mechanisms have been proposed and verified to further guide the research, optimization, and up-scale applications pyrolysis for energy and resources harvesting from low-valued carbon-rich feedstocks, especially biomass and wastes.^{75,106} Figure 7A–C shows selected examples proposed or elucidated in previous studies for the pyrolysis pathways of basic components (cellulose,

hemicellulose, and lignin).^{97,99} For more details and research results on the reaction mechanisms and kinetics, please refer to dedicated reviews available in the literature.^{75,104,106} Moreover, unlike gasification requiring super high reaction temperatures, pyrolysis is operated under moderate temperatures, which fits the ideal working temperatures of many catalysts. Thus, specific catalysts are coupled either directly involved in pyrolysis reactions (in situ catalysis) or the postpyrolysis area (ex situ catalysis), assisting dehydration, decarboxylation, decarbonylation, C–C cracking, aromatization, and other advanced reactions, as so to enhance conversion rate, oil yield, and oil quality (Figure 7D).^{107–109}

As illustrated in Figure 7E, due to their superior features, discharge plasmas are suited to be integrated and used at different stages of pyrolysis, including the pretreatment of feedstocks before thermal treatment (plasma for feedstocks treatment detailed in Section 3.4), direct pyrolysis, catalytic pyrolysis, and posttreatment/upgradation. Coupling with catalysts directly in the discharge zone for solid feedstocks pyrolysis is feasible in principle but lacks experimental supports and verifications, possibly due to the too high temperature with plasmas. More commonly, the plasma-catalysis is used when the feedstocks are fed in a gaseous or liquid state, and importantly, it is used for enabling postreactions of pyrolytic heavy oil and tar by creating a unique, reactive environment for catalyst activation and tar/heavy oil reforming to enhance conversion and harvest finer products, such as enhanced H_2 production while reducing or transforming tar.¹⁰⁹ This emerges as an interesting research area, and further introduction is provided in Section 3.5.1 based on recent research outputs.

Plasmas for direct pyrolysis, again, are mainly based on the application of fast heating and heat transfer associated with ThPs, similar to gasification. Thus, those discharges used for gasification can be directly employed for pyrolysis in the absence of oxidative agents (air and steam, in particular), but simply controlling or lowering the input/discharge power to output a more moderate thermal effect for fitting the temperatures is required for pyrolysis. Using similar reactors/processes generally leads to a lower oil yield but higher gas production than conventional thermal pyrolysis. For example, a DC arc plasma using H_2/Ar as the inducer and carrying gas operated at 40.5 kW was used for pyrolysis of wood and rice husk fed continuously at 1–4 g/s. Due to the high input power and high temperature sustained, the conversion for carbon and oxygen shortly reached 79% and 72%, respectively. Compared to conventional pyrolysis, the gas products were rich in H_2 , CO, and C_2H_2 , while CH_4 and CO_2 contents decreased.⁹⁵ An RF (13.56 MHz) N_2 plasma jet run at lower powers

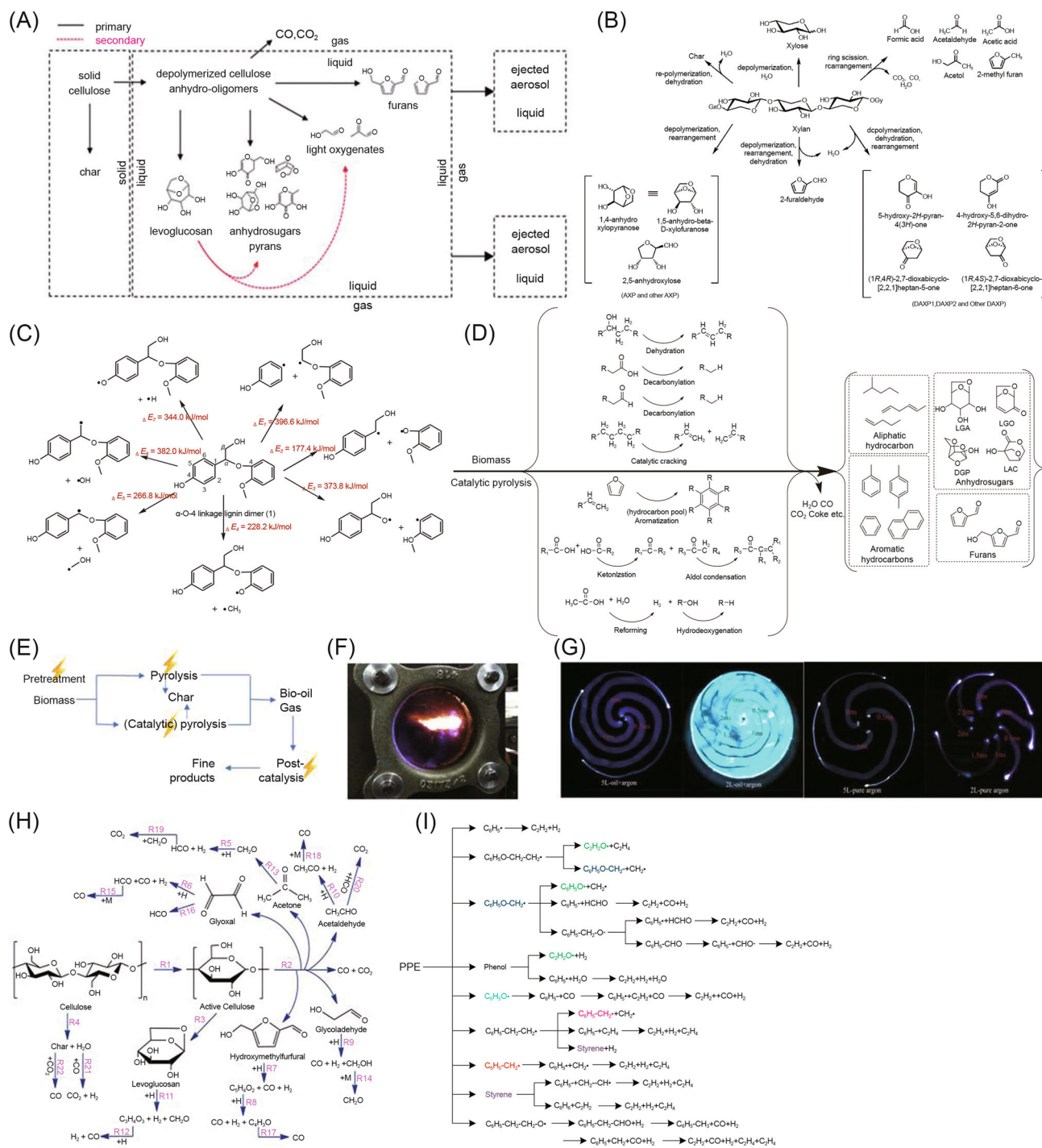


FIGURE 7 Biomass pyrolysis (A-D) without or (E-I) with plasmas. Proposed reaction pathways or pyrolysis mechanisms with raw materials of (A) cellulose (Reproduced with permission: Copyright 2012, The Royal Society of Chemistry¹⁰⁵), (B) hemicellulose (Reproduced with permission: Copyright 2011, Wiley¹¹⁰), (C) lignin (Reproduced with permission: Copyright 2015, Elsevier¹¹¹), and (D) schematic of the reactions for biomass catalytic pyrolysis for enhancing oil yield and quality (Reproduced with permission: Copyright 2017, Elsevier¹⁰⁶). (E) Illustration of in what stage of biomass pyrolysis plasmas can be integrated: warm plasmas such as (F) MW-induced discharge (Reproduced with permission: Copyright 2012, Elsevier⁹⁷) and (G) gliding arc discharge used for biomass gasification (Reproduced with permission: Copyright 2016, Elsevier⁹⁹). (H) Proposed reactions of cellulose pyrolysis using an MW discharge. Reproduced with permission: Copyright 2015, Elsevier.⁹⁸ (I) Hydrogen-based plasmas for the pyrolysis of phenethyl phenyl ether (PPE), a lignin model compound. Reproduced with permission: Copyright 2013, American Chemical Society.¹¹² MW, microwave; PPE, phenethyl phenyl ether.

(1.6–2 kW) was employed for fir sawdust pyrolysis. The gas yield peaked at 66 wt% with a total CO and H₂ content over 70 vol%, when the sawdust was fed slowly (0.3 g/min) and the discharge (1.8 kW) and pyrolysis occurred at reduced pressure (5 kPa). Besides gas products, biochar with a carbon content of 83% (heating value of 29 MJ/kg) was the other important product.⁹⁶ The biochar showed enhanced surface area (278 vs. 115 m²/g for that from conventional pyrolysis) and developed porous structures, possibly due to the surface functionalization or etching induced by the plasma-generated reactive N-species, which further facilitates biochar activation with the presence of inorganic metals and the newly formed CO₂ (Table 2).⁹⁶

Also, from the concern of requiring a lower temperature for pyrolysis, more plasmas supplying lower-temperature, such as the MW-induced discharge at lower powers (Figure 7F), GAD (Figure 7G, but mainly for liquid feedstock), and non-ThPs, are also proved effective for pyrolysis purposes.^{97,99} For example, an MW-induced plasma jet with Ar discharge at 1 kW was proved to achieve complete pyrolysis of waste wood with a mean mass loss reaching 79.6 wt%. CO, with a volume content of 50%, was the main gas product. The liquid, solid, and gas ratio was found to be 66:20:13 on a mass basis.⁹⁷ Another MW N₂ discharge operated under atmospheric pressure employed a reduced power (800–1000 W) and a high gas flow of 12 L/min to maintain the system temperature at 1063–1121 K. The residence time for complete conversion of dry *Spirulina algae* to H₂ was found almost independent to the reaction temperature provided. An increased power led to higher H₂ yields with H₂, CO, and CO₂ as the main gas products. GADs are increasingly used, especially when gaseous or liquid feedstock is introduced. A rotating GA was used to assist the pyrolysis of waste rapeseed oil, with Ar or N₂ as the carrying gas at a discharge power of 66–141 W. The overall waste oil conversion reached 74%. CO and C₂ dominated the gas products. Activated species were believed able to facilitate the bond breaking of the long-chain fatty acids into alkanes, cycloalkanes, olefins, and aromatic hydrocarbons, which were the main products in liquid after pyrolysis (Table 2).^{99,100} Providing and sustaining a more reductive environment, such as adding NH₃ and H₂, during pyrolysis is expected to enhance the production of higher-quality oils by facilitating a series of reactions leading to hydrogenation and/or deoxygenation. H-donators are also crucial in catalytic pyrolysis. H radicals are generally largely formed during plasma pyrolysis due to the dissociation of H₂, either from the carrying gas containing a certain amount of H₂ or from the just-formed H₂ product. These reactive radicals gain further energy under a strong electric field, which can initiate many reactions toward raw feedstock, intermediates, or

end-products, making the pyrolysis mechanisms more complicated and ongoing challenges. Reaction pathways for cellulose based on experimental investigations and a lignin model compound according to DFT calculations are shown in Figure 7H.I.^{98,112}

Non-ThPs are also increasingly used for carbon-feedstocks pyrolysis. The setup shown in Figure 6J generating nonthermal arc discharge was also used for carambola leave pyrolysis, by replacing air/steam with Ar or N₂. With a discharge power of ~30 W and a residence of 7 min, the gas yield was measured at 68%, and the metal (Zn, Fe, Cu, and Cd) was well fixed with a fixing efficiency reaching 90% with N₂ discharge. The biochar with a carbon content of over 60% was also characterized to be with denser structures and higher pore volumes.¹⁰¹ An RF plasma with low discharge powers also gave satisfactory gas yields (66.5% at 664 W), while no tar formation was found during rice straw pyrolysis.¹⁰² More recently, a study by Lusi et al.¹⁰³ provided experimental results supporting that non-ThPs with simple configurations (air or Ar DBD) could be an effective pretreatment method for levoglucosan production from cellulose pyrolysis, even with low discharge powers (~2 W) and short exposure (less than 1 min). Compared to direct cellulose pyrolysis with a maximum levoglucosan yield of 58.2%, DBD-treated cellulose generated a much-enhanced levoglucosan at 78.6% (Table 2). The enhancement was attributed to the homolytic cleavage of glycosidic bonds and possibly free radicals trapped within the cellulose structures playing further actions during pyrolysis.¹⁰³

3.3 | Liquefaction

Liquefaction is a solvent-based thermochemical conversion under mild temperatures (200–400 °C) with varying pressures (room pressure to ≥20 MPa), harvesting mainly bio-oils (liquid-phase products) as well as gas and biochar. The basic reaction pathways of carbon-rich feedstocks generally include three steps: (i) depolymerization into its forming monomers and oligomers; (ii) decomposition of thus-forming monomers/oligomers to form light fragments or intermediates with small molecules; and (iii) rearrangement of these fragments through condensation, cyclization, and polymerization into end compounds.⁷ Solvents are crucial in liquefaction. Water is green and cost-effective (or zero-cost) and widely used for liquefaction (termed HTL), and more importantly, it can avoid the costly feedstocks drying step. But the liquefaction using water is usually accompanied by several shortcomings, such as challenging operating conditions (higher temperature and pressure up to 24 MPa, requiring pressure-

resistant devices) and low yields of water-insoluble bio-oil low-heating values of the resulting bio-oil.^{7,113} To enhance the water-insoluble bio-oil yield with lower oxygen content, organic solvents, such as ethanol, methanol, and so forth, have been utilized as the reaction medium instead of water or as mixtures. The presence of organic solvents with lower critical points enables the feedstocks liquefaction into bio-oils, occurring under milder reaction conditions. Some other organic solvents with higher boiling points, such as phenols, polyols, and cyclic carbonates, have also been applied to liquefy biomass with/without the presence of catalysts. Such liquefaction usually occurs under relatively milder conditions (normal pressure, less than 200 °C) with a conversion yield of more than 90% (on a residue mass basis).^{7,113}

Integrating discharge plasmas into direct biomass liquefaction has been proposed for several years and is still in its infancy, with limited studies published. The plasmas used are mainly based on in-liquid discharges, sharing similar theories and techniques with the better-known and developed plasma electrolytic technology (PET) for the cleaning and coating of materials (metals, in particular). Thus, such liquefaction is also termed plasma electrolytic liquefaction (PEL). Unlike conventional electrolysis using low electrical potentials, PEL processing requires a much higher potential, which leads to excess gas evolution at the working electrodes, with continuous gas enveloped formed around the electrode (either cathode or anode), and a luminous discharge accompanied.^{114,115} The ability to form discharge plasmas in the solution on the surface of the materials treated or surrounding enables further applications, including biomass liquefaction by intensifying and sustaining a highly reactive environment. The current-voltage characteristics and basic processing mechanism (based on bubble behaviors) of PET are illustrated in Figure 8A,B.¹¹⁵ Generally, there are four stages in PET with the voltage increasing. At low potentials (U_1 stage, Figure 8A), the current increases linearly with voltage increases, following Faraday's law, enabling gas liberation.¹¹⁵ Further voltage increases lead to solution vaporization due to enhanced Joule heating, and thus, the occurrence of breakdown and presence of luminous gas (U_2). With the potential further increased (U_3), continuous gas bubbles and discharges are observed with a quick drop in current. Hereafter discharges develop into more intensive arcing (U_4).¹¹⁵

Such characteristics were also observed with PEL when a needle-needle reactor (Figure 8C) with a DC source was used for solid carbon-feedstocks (bamboo shoot sheet, sawdust, algae, etc.) liquefaction with polyols, such as ethylene glycol (EG), glycerol, poly EG (PEG), or their mixture used as the solvent.¹¹⁶ The four

stages reflecting I-V changes (Figure 8D) and the photos showing the bubble and discharge behaviors under the four stages in the absence of solid feedstocks (Figure 8F-I) confirm the PET-based properties.^{116,118} Using this design with the integration of plasma electrolysis, the polyol-based biomass liquefaction could be completed within several minutes with a small amount of acid (H_2SO_4) or KOH added under room pressure without extra external heating.^{119,120} For example, PEL in an EG/PEG mixture H_2SO_4 gave a conversion of 97% in 3 min toward bamboo shoot shell liquefaction, much faster than the conventional process using external heating, which generally requires a reaction time of over 20 min without considering the time taken for preheating the system to the set temperature.¹¹⁹ Similar results were confirmed with the pine sawdust, corn cob, corn stalk, and rice straw in glycerol/PEG and microalgae in EG.^{116,120,121} Taking the microalgae liquefaction as an example, the algae conversion increased sharply at the beginning. With the acid of 4 mmol and KOH of 8 mmol, the conversion peaked at 92% and 82% at 3 and 7 min, respectively, with the liquid yield up to around 70%. The mechanism behind the much-enhanced reaction kinetics was directly linked to a quick increase in the system temperature. A dramatic increase in the solution temperature was observed after introducing plasma discharge, especially in the acid process, where the temperature increased to around 190 °C after 2 min (microalgae in EG).¹¹⁶ To better understand the heating process in PEL, the changes in heating efficiency and the solution resistance over the processing were studied.¹¹⁷ As shown in Figure 8E, electric field heating (Joule heating) dominated in the initial stage of the process, while plasma discharge heating became the more obvious thermal source for longer processing and increased power inputs.¹¹⁷ Adding homogeneous acids or bases was proved crucial since they could assist in bond breaking (hydrolysis and depolymerization). More importantly, they enhanced the solution conductivity and decreased resistance, facilitating electron transfer, heat transfer, and thus, bubble formation and gas discharge development.¹¹⁶

Another feature of the PEL is that it can intensify the heat and mass transfer, and thus, reduce the solvent amount required for the liquefaction, due to the inside-out heating and the strong shock wave, kinetic force, and explosive impact induced by the plasma and bubble bursting (Figure 8D).¹¹⁵ Liquefaction is a typical liquid-solid reaction. The reaction efficiency of this process largely depends on the feedstock-to-solvent ratio. A higher solvent usage generally ensures better heat and mass transfer and liquid-solid contact/reaction for faster and more complete conversion. However, if the solvent dosage

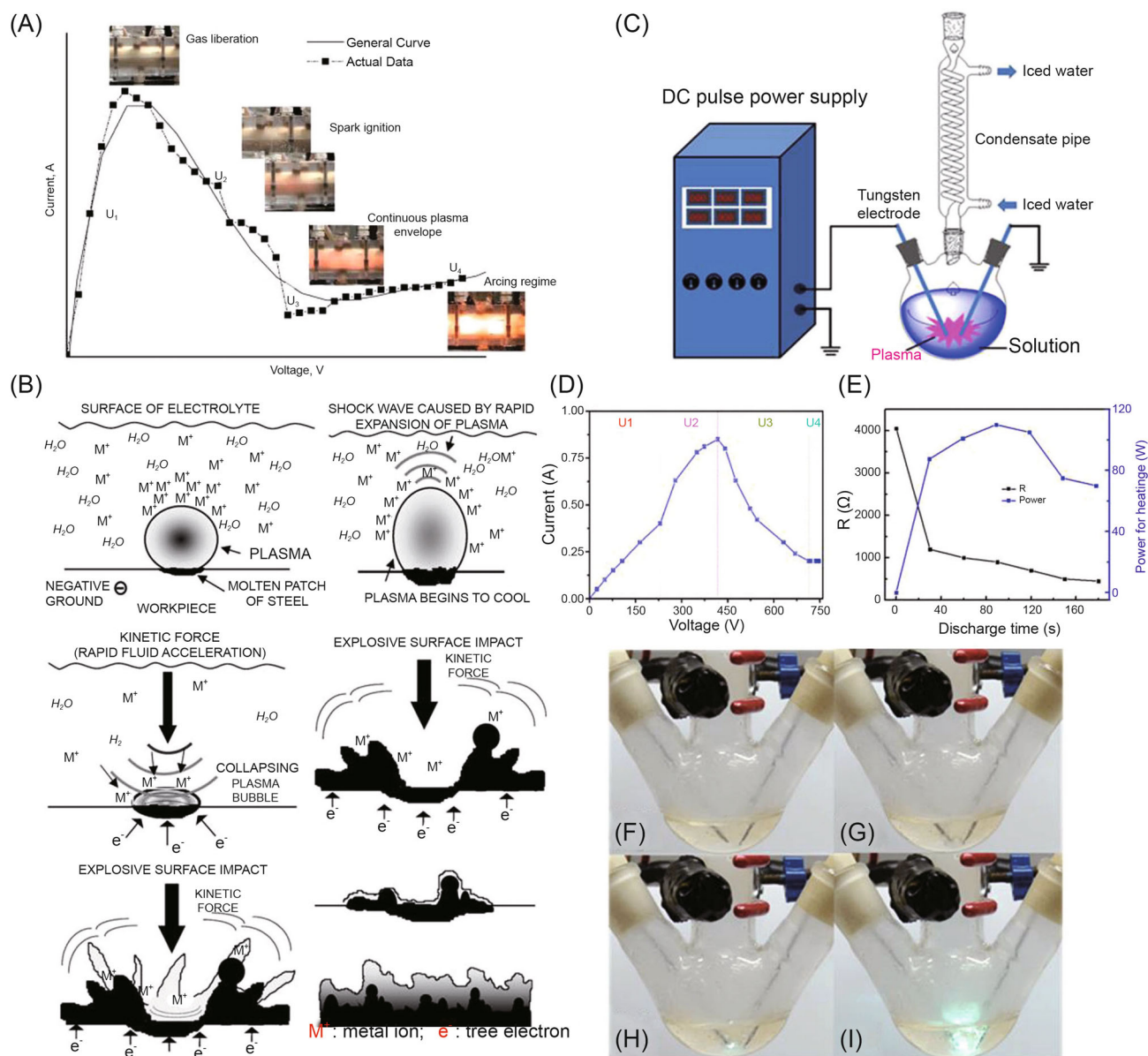


FIGURE 8 Biomass liquefaction using plasma electrolytic technology (PET). (A) Current-voltage characteristics and (B) processing mechanisms for metal cleaning and coating with PEF. Reproduced with permission: Copyright 2007, Elsevier.¹¹⁵ PET with a needle-needle configuration developed for direct biomass liquefaction, termed plasma electrolytic liquefaction (PEL) or plasma catalytic liquefaction (PCL). Reproduced with permission: Copyright 2019, Wiley.¹¹⁶ (C) Schematic of the setup, (D) I-V curve observed, and (E) discharge power and solution resistance changes during discharge. Reproduced with permission: Copyright 2019, IOP.¹¹⁷ (F-I) Photos of the discharge without biomass added. Reproduced with permission: Copyright 2019, Wiley.¹¹⁶ PCL, plasma catalytic liquefaction; PEF, polyethylene furanoate; PEL, plasma electrolytic liquefaction; PET, plasma electrolytic technology.

could be reduced, the following procedures for solvent recovery and recycling could be simplified and the economic benefits would be enhanced. With PEL for microalgae, an algae-to-solvent ratio of 1:6 (mass to volume) gave high conversions at 92%. While with the solvent dosage halved (1:3 of ratio), a conversion of ~85% was observed, indicating that the PEL might have further potential to intensify other in-liquid reactions.¹¹⁶ Recent studies also proved that PEL is also feasible for the direct

liquefaction of carbon-rich feedstocks containing significant moisture.^{116,118} The only effect of using wet feedstock or adding extra water was that a longer time was required for achieving full conversion since more time would be taken for water evaporation.^{116,118} Further, the increased moisture content sustained a more oxidative reaction environment, as observed from the optical emission spectra collected during the discharge, where the characteristic peak for OH radicals at 309 nm was greatly enhanced.¹¹⁸

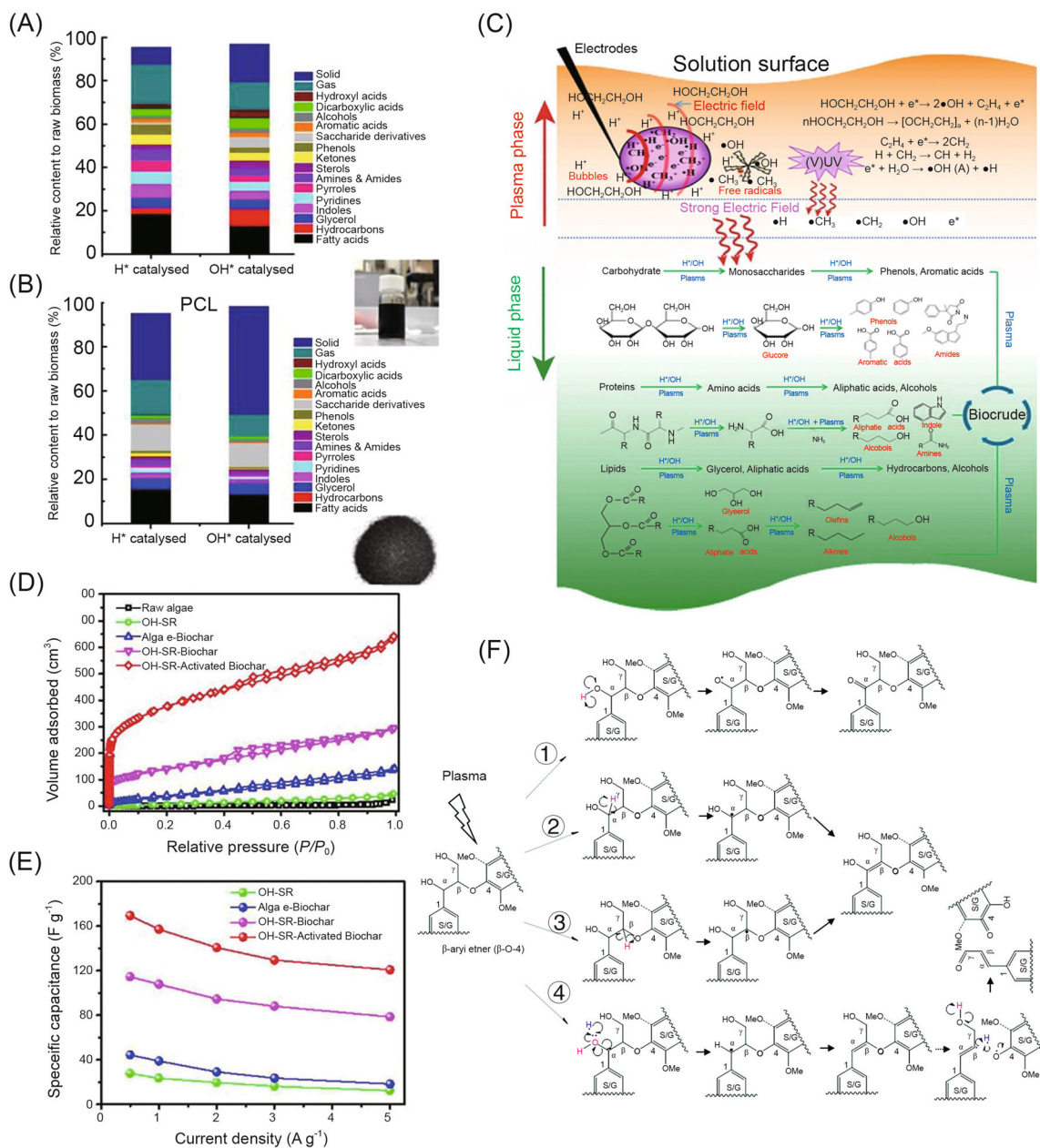


FIGURE 9 Products and proposed reaction mechanisms of biomass PEL. Product distribution of microalgae liquefaction using (A) plasma electrolysis and (B) conventional liquefaction; (C) proposed mechanisms for algae liquefaction; (D) Ar adsorption/desorption isotherms and (E) performance in energy storage of the solid residues from PEL of microalgae. Reproduced with permission: Copyright 2019, Wiley.¹¹⁶ (F) Proposed lignin modification during oxygenated monomers production using plasma electrolysis. Reproduced with permission: Copyright 2021, The Royal Society of Chemistry.¹²⁴ PCL, plasma catalytic liquefaction; PEL, plasma electrolytic liquefaction.

Zhou et al.¹¹⁶ also conducted a comparative study of microalgae PEL to conventional liquefaction of microalgae using EG in an autoclave with the same catalyst load and imitating temperature as those in PEL, with the liquid products characterized by gas chromatography–mass spectrometry (GC–MS) after silanization and categorized (Figure 9A,B).¹¹⁶ With the reaction extended to 30 min, the conventional conversions were still much lower. The authors concluded that the temperature increase in PCL might not be the only reason for fast liquefaction and

plasma-generated reactive species (particularly electrons, ·H, ·CH_x, and ·OH) might be involved in the feedstocks depolymerization (Figure 9C). However, no further experimental supports were provided due to the challenges of in situ observation of in-liquid discharge and product separation and characterizations. The authors also demonstrated that mild heating to PEL-generated residues could significantly increase the surface area, total volume, and mesopore volume of the solid residue (Figure 9D), and the electrochemical performances of thus-obtained biochar were also

largely improved when used as a supercapacitor electrode (Figure 9E). These results indicate that PEL may also serve as an effective pretreatment method as it produces a large number of active radicals, ions, and molecules, especially oxygen-containing species, which would enhance the functionality of the feedstock/substrate, which participates in subsequent heat treatment to further alter the morphology of the biochar.^{116,122,123} More recently, using the same reactor configuration driven by an AC source, plasma electrolysis successfully demonstrated the ability to obtain oxygenated cellulose monomers and high-quality lignin from red oak with the γ -valerolactone, a biorenewable chemical available from biomass conversion, and sulfuric acid as the electrolyte.¹²⁴ Benefited by the Joule heating and a large amount of highly reactive species generated during plasma electrolysis, rapid and complete biomass solubilization could be achieved. Levoglucosenone and furfural were recognized as the main oxygenated monomers, with a yield of 44.9% and 98.0% on a mole basis, respectively. Moreover, the PEL also generated high-purity lignin, which could produce much higher yields of phenolic monomers than the natural lignin or the lignin isolated if subjected to further solvolysis. Further characterizations of the lignin suggested that benzylic carbon of the natural lignin was selectively modified during plasma electrolysis to limit the formation of interunit C–C bonds, significantly improving the subsequent lignin valorization to aromatic monomers, as a proposed mechanism illustrated in Figure 9F.¹²⁴

3.4 | Feedstock pretreatment

Currently, the most widely available bio-derived liquid fuels (bioethanol, in particular) and platform chemicals are mainly produced from sugar-, starch-, and corn-based raw materials.^{125,126} The world is still facing severe challenges on population growth and food shortage. Waste lignocellulose, with an estimated annual production of $>10^{10}$ MT worldwide, has been regarded as an ideal non-food resource of sugars and others to produce such fuels and chemicals.¹²⁵ However, a significant challenge is the complex composition of lignocellulose (including cellulose, hemicellulose, lignin, wax, and many others) and, more importantly, the recalcitrant structures (Figure 2A). Such structures greatly hinder the extraction of lignocellulosic sugars and other resources under mild conditions and require effective solutions or techniques to the slow kinetics of raw feedstock breaking down into ready-usable monomers and/or oligomers, typically cellulose-to-sugars, their low yields, and the interference and further value-added utilization of other substrates (lignin in particular).^{10,43,126} The physico-chemical pretreatment is an essential step in breaking

down the robust and recalcitrant structure of the feedstock to increase the accessibility of cellulose and hemicellulose polymers (by increasing surface area, porosity, and sites for enzymes, and removing obstructing components) to enzymes and/or other hydrolysis chemicals and to change substrate affinity.¹²⁷ The main shared goal of biomass pretreatment is to reduce recalcitrance by depolymerizing or solubilizing lignin and hemicellulose and thus expose the crystalline cellulose core, making it more accessible for the subsequent catalytic or enzymatic process and ideally lowering dosages of the enzyme (or other chemicals) as well as shortening process times. Current pretreatment, using mechanical (milling, extrusion, steam explosion), chemical (dilute acid, alkaline, ammonia, ionic liquid, etc.), biological methods, or their combinations, is still one of the most energy-consuming and complicated processing steps in biomass valorization, and is also associated with other challenges such as the extensive formation of inhibitors (e.g., furan derivatives, aliphatic acids, and phenolic compounds) for the downstream processing (saccharification and fermentation), limiting further and larger-scale applications.^{125,127,128} For example, due to the high cost of the processes responsible for the release of sugars (the cost of the pretreatment, detoxification, and hydrolysis operations in a biorefinery) and the successive fermentation, the current price for 2G bioethanol is 0.57–1.20 USD/L, much higher than that for conventional bioethanol (<0.40 USD/L).¹²⁵

Plasmas, especially non-ThPs, provide both performance- and cost-effective solutions to these challenges, and are regarded as a new group of green biomass pretreatment technological platforms. Termed plasma pretreatment, this strategy has emerged as a new stand-alone process since it can induce chemical and physical changes in the lignocellulose structure without using additional chemicals or organic solvents. As discussed previously, the discharges use only electricity as the energy source and can be turned on/off easily, making them highly suited to be coupled with renewable, intermittent electricity, contributing to further cost reduction and environmental footprint enhancement.²⁵ Also, the treatment operating at ambient conditions can be easily integrated with other modern biorefinery processes.

Feedstocks can be treated directly by gas plasmas (dry treatment; Figure 10A,B) or indirectly in the liquid phase, where the discharges are sustained by bubbling gas (Figure 10C) or directly formed in liquids.^{129–132} Table 3 summarizes some applications of non-ThPs in lignocellulose pretreatment, which can be roughly divided into three categories based on the used gas: nitrogen/air plasma, argon plasma, and ozone plasma.²⁵

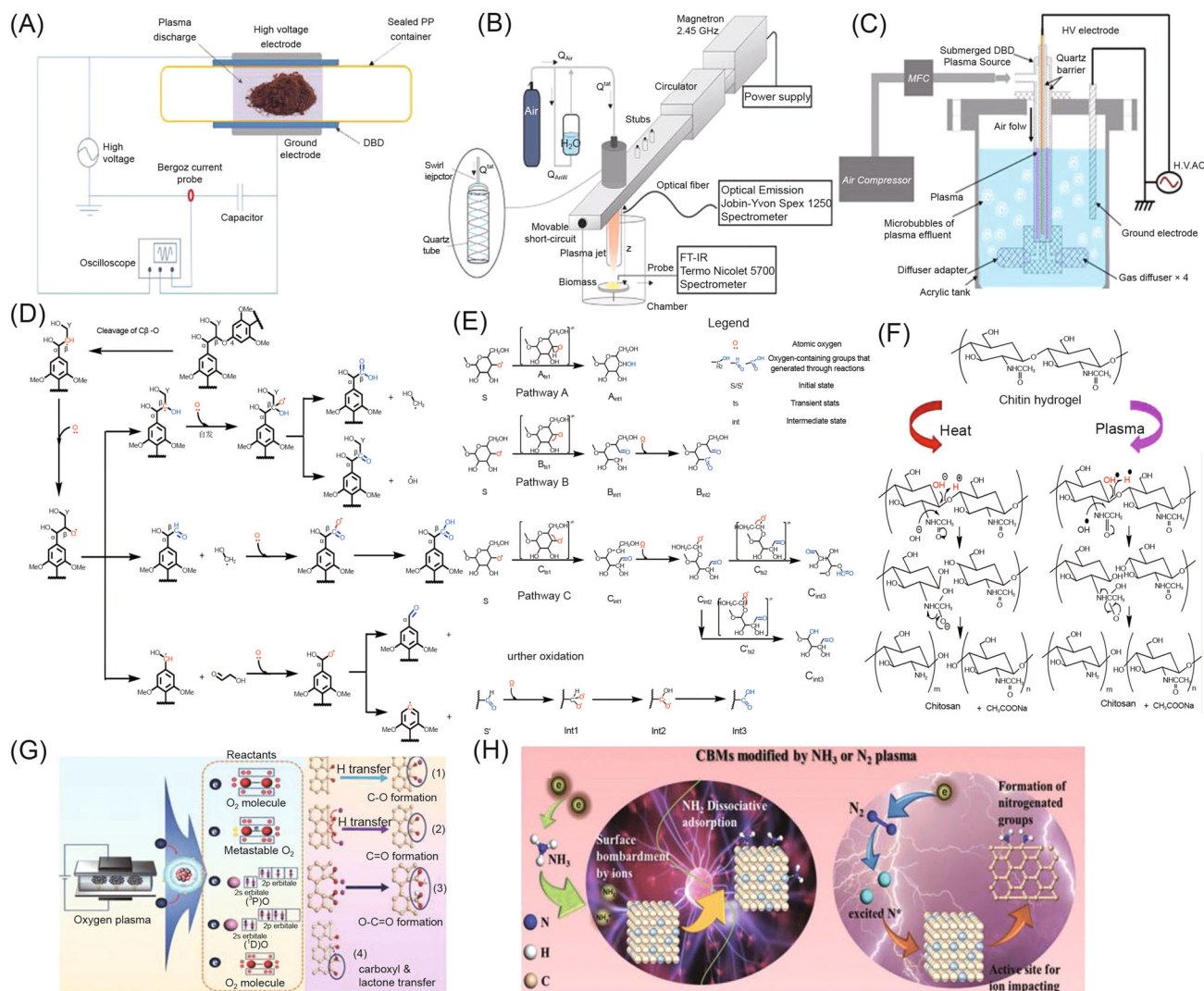


FIGURE 10 Non-thermal discharge plasmas for biomass pretreatment and microbial engineering. Schematic illustrations of plasma systems using (A) DBD (Reproduced with permission: Copyright 2017, Elsevier¹²⁹) and (B) MW discharge (Reproduced with permission: Copyright 2013, IOP¹³⁰) for dry pretreatment, and (C) gas bubble discharge (Reproduced with permission: Copyright 2019, Elsevier¹³¹). Free radicals (O and OH) involved reaction chemistry during plasma interacting with (D) lignin (Reproduced with permission: Copyright 2019, American Chemical Society¹⁴⁰), (E) cellulose (Reproduced with permission: Copyright 2006, IAEA¹⁴¹), and (F) chitin (Reproduced with permission: Copyright 2020, Elsevier¹⁴²). Schematic of the mechanisms of (G) O₂ and (H) NH₃ or N₂ plasmas for bio-carbon surface modification, Reproduced with permission: Copyright 2020, Wiley.¹⁴³ DBD, dielectric barrier discharge; MW, microwave.

Discharges for biomass pretreatment can be generated in different reactors, typically as a plasma jet, DBD, and MW plasma, with the reforming efficiency and the quality of by-products significantly influenced by gas composition, operating pressure, the content of water, and so on.²⁵ Plasmas have been demonstrated to affect any type of lignocellulose, and O₂-containing plasma shows the best effectiveness, especially at a suitable moisture content, mainly because of the generation of oxidative species leading to bleaching and delignification reactions. Water is proved to be an accelerator in pretreatment efficiency. First, water allows the formation of a proton-containing active layer around the

lignocellulose, which would then act as a catalyst for the hydrolytic breakage of glycoside bonds.^{133,134} Second, with the addition of water, which is introduced with the carrying, from wet feedstocks or solvents when the pretreatment is conducted in solutions, more reactive species, such as singlet delta oxygen, OH radicals, hydrogen peroxide, and acids like HNO₂ and HNO₃ capable of rapidly breaking C-C, C-O, and C=C bonds and initiating oxidation reactions, would be produced especially when the feeding gas contains O₂ or N₂.¹³⁰ Third, water is beneficial to the diffusion and penetration of reactive oxidation species like ozone into the raw materials, where these species would attack the aromatic

TABLE 3 Experimental studies on plasma-feedstock pretreatment

Biomass	Plasma type and conditions	Results	Ref
Wheat straw	Coaxial DBD; air + water; 230 W, 0.5–2 h	95% Lignin degradation; 78% glucose yield; 52% ethanol yield (only 6% to untreated biomass).	135
Spent coffee waste	Parallel-plate DBD, FeCl ₃ , H ₂ SO ₄ , air, AC HV 70 kV, 50 Hz, 2 min	Lignin removal/0.496 g reducing sugar per g waste after enzymatic hydrolysis/74% fermentation efficiency (twofold).	129
Wheat straw	DBD; air, N ₂ , and CO ₂ ; power ~0.01 W/cm ³ ; 10–300 s	High biomass/sugars recoveries at 90 s; glucan, xylan, and total sugar yield after enzymatic hydrolysis at 89.6%, 69.03%, and 84%, respectively. Competitive energy-processing costs of PT and subsequent EH are estimated to be \$0.052 MJ/kg glucose and xylose.	144
Sugarcane	Tornado-microwave; dry air; 2.45 GHz, 200–700 W	Lignin and hemicellulose degradation; reactive species identified.	130
Wheat straw	DBD; O ₂ /N ₂ ; 40/60; 18.4 kHz, 1–7 h	Removal of waxes, cutin, and lignin; glucose yield increased from 21% (untreated) to 67%.	136
Gray cotton	Plasma jet; He/O ₂ atmospheric pressure	Hydrophilicity increased by 10–100 times.	138
Sugarcane bagasse	Remote DBD; air; 230 W, 1–7 h, 1 bar	65% Lignin degradation without compromising the structure of cellulose and hemicellulose.	137
Wood	Ozone plasma; glass ozonizer	Enzymatic hydrolysis increased by 10 times; sugar yield increased from 13% to 63%; reduce in particle size and an increase in specific surface area.	145
Corn stalk	DBD; N ₂ + water; 3.0 kV, 2 h, 0.9 bar	76% Sugar yield; 32% sugar selectivity; drop in crystallinity of cellulose.	146
Brewer spent grain	Air plasma bubble; up to 15 min	2.14-Fold increase in yield of the reducing sugar; 36% decrease in the total lignin content using water as solvent.	131
Miscanthus grass	DBD + microbubbles; wet treatment; 3 h	Microbubbles for enhanced mass transfer of ROS and mixing; 26% sugar released with only 0.5% acid-soluble lignin, 2.5-fold increase in enzymatic hydrolysis.	147
MCC	Air DBD, 3 h	Glycosidic bonds partly cleaving; decrease in DP from 200 to 120; CI increased slightly (78%–81%); much-enhanced glucose yield (25 wt%).	137
Cellulose	DBD; air + water; 26 W, 2 kHz, 3 h	Strong capacity of cleaving covalent bonds and oxidation; increased O/C ratio by twofold; CI reduced (58%–39%); Mw decreased; DFT suggesting cleavage of C ₄ -O as the first step, followed by pyranose ring-breaking reaction.	141
MCC	Air DBD over water containing MCC; 80 W; 3 min	DBD acidification of water (pH to 1.35); tuned plasma acidification (at pH 1.42) obtaining 46% glucose yield.	148
Kraft lignin	Air-pulsed corona discharge; lignin in alkaline solution; 30 min	Oxidation energy efficiency increased with the O ₂ content (82 g/(kWh) at 89% O ₂); 70% of lignin degradation and oxidative converted.	149
Corn cob lignin	Dry treatment, DBD in continuous mode, air, 4.5 kW, 1.5 s	~2.5-Fold increase in O/C ratio, drop of Mw, from 12,378 to 9357, and β-O-4 linkages from 65.1 to 58.7 per 100 Ar.	140
Isoeugenol	“Face” discharge (direct in-liquid); NaOH solution, ~1 A, 20 min	Plasma-solution system in NaOH followed by a second NaOH boiling leading to aromatic structure breakdown, with the actions of OH, H, e, and H ₂ O ₂ .	150

Abbreviations: AC, alternative current; CI, crystallinity index; DBD, dielectric barrier discharge; DFT, density functional theory; DP, polymerization degree; MCC, microcrystalline cellulose; Mw, molecular weight; ROS, reactive oxygen species.

lignin structure.¹³⁰ Non-ThPs are highly effective in removing lignin, waxes, and other inherent antidegradation barriers of lignocellulose, with the treatment also leading to an increase in the specific surface area and total pore volume of lignocellulose, which produces a more accessible purified cellulose feedstock.^{130,135–137} Other beneficial effects relate to the changes in cellulose structure, in particular to the reduction of the degree of polymerization, and the formation of polar surfaces, which increase the solubility of cellulose.^{138,139} After plasma pretreatment, lignocellulosic samples are usually susceptible to subsequent chemical and biochemical treatments, such as acidic or enzymatic hydrolysis, to get high sugar yields and fermentative processes enhance fermentation efficiency and ethanol yields.

Shaghaleh et al.¹⁴⁴ used a DBD for wheat straw pretreatment before being subjected to enzymatic hydrolysis using air, N₂, or CO₂ as the inducer gas. With a power density, 90 s of treatment gave a total sugar yield of over 84%. The energy cost of the processing by combining a plasma discharge was estimated to be \$0.052 MJ/kg glucose and xylose, which is very competitive comparing other processes, showing the potential plasma pretreatment to be further scaled up and integrated into current biorefineries at the industrial level.¹⁴⁴ Wet processing is gaining increasing interest due to requiring no extra drying and is easy to sustain a more oxidative condition; however, one of the key issues is how to enhance the delivery, formation, and retaining of reactive and functional species in liquids. Direct in-liquid discharge offers an option. But the breakdown voltages of liquids are much higher than that of gas, leading to further challenges in plasma ignition and characterizations. Using commercially or industrially used bubble techniques, particularly the bubble column and microbubble, has been proved highly effective to enhance the mass transfer of gaseous plasma species through the gas–liquid interfaces and thus enhance treatment performance. This has also been confirmed for biomass pretreatment for enhancing yields of reducing sugars.^{131,147}

Investigations using the basic components (cellulose and lignin) were largely conducted to better illustrate the reaction mechanisms and pathways of plasma pretreatment. For the cellulose-to-sugar conversion, the treatment can be categorized in terms of the biomass state and the following hydrolysis: dry or wet treatment followed by acid/enzymatic hydrolysis^{137,141} and one-pot pretreatment and hydrolysis based on in-liquid plasmas,¹⁴⁸ which are capable of acidifying the solutions under N₂-containing atmosphere due to the large formation of HNO_x. Collectively, the main effects of plasmas for cellulose treatment include reducing the polymerization degree (DP) and/or M_w, changing crystallinity index (CI), increasing surface energy and water

solubility (oxygen-containing functional groups increased after plasma exposure in an oxidizing atmosphere), improving the contact and reaction efficiency with acids or enzymes, and thereby improving sugar yields and conversion rates.²⁷ For example, Benoit et al. investigated the efficiency of an air plasma (NTAP) for dry microcrystalline cellulose (MCC) pretreatment and found that the NTAP was capable of partly cleaving the glycosidic bonds, confirmed by the decrease in DP from 200 to 120. A much higher glucose yield of (25 wt%) was observed after further acid hydrolysis.¹³⁷ Wang et al.¹⁴⁸ used air plasma acidification for MCC processing and confirmed that effective hydrolysis could be obtained using the acid from air discharge. This plasma-based pretreatment without adding extra acids for hydrolysis is regarded as an environmentally friendly and effective method to hydrolyze cellulose. Cao et al.¹⁴¹ confirmed that air discharge (as an oxidative plasma) could reduce the hydrogen bonding and facilitate the cleavage of covalent bonds (β -1,4 glycosidic bond, in particular) by free radicals (reactive oxygen species [ROS]) by a series of structural characterizations. Theoretical analysis (DFT) revealed that cleavage of the C₄–O covalent bond was the first-step reaction during plasma-induced oxidation due to its low bond dissociation energy (229.2 kJ mol⁻¹). Pyranose ring-breaking reaction dominated dynamically and thermodynamically in next steps, with proposed reaction pathways shown in Figure 10D,E.

Lignin, accounting for ~30 wt% of lignocellulose, is the largest resource of natural aromatics, presenting a significant portion of lignocellulose¹⁵¹; yet, it is underutilized in current lignocellulose biorefineries, where lignin is usually slated for combustion. The depolymerization of lignin into its phenolic building blocks, drop-in chemicals, and functional materials, has been regarded as a key step in enhancing the cost-, environment-, and efficiency-competitiveness of a lignocellulosic biorefinery.^{152,153} Oxidized lignin has been proved with enhanced processability for being further depolymerized into valuable platform chemicals¹⁵⁴ and advanced materials.¹⁵⁵ This features the possibility of non-ThPs, especially those offering high-activity ROS, toward greener lignin processing and upgradation, requiring no additional specific oxidative chemicals. Many studies have been reported with different lignin sources tested in dry state or in-liquid. Panorel et al.¹⁴⁹ employed the pulsed corona discharge (PCD) to treat coniferous kraft lignin aqueous solutions and found that the rate and the energy efficiency of lignin oxidation increased with increasing oxygen concentration reaching up to 82 g kW⁻¹ h⁻¹ in 89 vol% O₂. Oxidation energy efficiency in PCD treatment exceeds the one for conventional ozonation by a factor of two under the

experimental conditions. Oxidation at low oxygen concentrations showed a tendency of the increasing aldehydes (vanillin and syringaldehyde) and glyoxylic acid formation yield. Cao et al.¹⁴⁰ investigated plasma-induced changes in the chemical structure of lignin, which showed that plasma possesses a strong capacity to cleave C–C covalent bonds in the aliphatic region of lignin, accompanied by oxidation, leading to the degradation and fragmentation of lignin (Figure 10D). According to the DFT analysis, the oxygen atom of β -O-4 aryl ether is the most likely potential reaction site, and the C $_{\beta}$ -O covalent bond exhibits the lowest decomposition free energy (50.5 kcal mol⁻¹), which will easily be cleaved in plasma. The dominant reaction pathway of lignin degradation is the cleavage of the C $_{\beta}$ -O covalent bond followed by the cleavage of the C $_{\beta}$ -C $_{\alpha}$ bond. Titova et al.¹⁵⁰ investigated the chemical transformations of isoeugenol (2-methoxy-4-propenylphenol, a model lignin compound) under the combined action of an atmospheric pressure discharge initiated in the volume of an electrolyte and alkali treatment using UV spectrophotometric analysis. They found that plasma-solution activation was an initiator of the oxidative breakdown of the aromatic structure of the compound during alkali treatment. Based on all the results discussed above, it could be concluded that plasma treatment enhances lignin transformation through lowering DP, increasing surface energy due to oxidation, improving solubility, and selectively cleaving C $_{\beta}$ -C $_{\alpha}$ bonds by radicals (O and OH, in particular).

Besides lignocellulose, discharge plasmas are also capable of pretreating and functionalizing other sources of feedstocks. For example, an in-liquid plasma in an NaOH/MeOH/water solution was proved highly efficient in simultaneous deacetylation and degradation to chitin, the most abundant aminopolysaccharide in nature (Figure 10F). The integration of plasma led to a significant decrease in NaOH concentration required compared to the conventional deacetylation (12% vs. >40%). The active species, OH radicals, in particular, formed in situ during the solution discharge, were believed to be involved in deacetylation and degradation of chitin hydrogel, resulting in the conversion of chitin hydrogel to chitosan with good solubility in the dilute acetic acid solution and sufficiently high antibacterial activity.¹⁴² Also, plasma technology is an effective and promising surface modification and functionalization process for all sorts of (bio)-carbons, allowing for chemical-free and greener treatment, mainly due to the abundant existence of free electrons (with energy up to dozens of electronvolt), reactive atomic and radical species (RONS in particular), and energetic photons (Figure 10G,H).^{143,156,157} It has been widely proved that plasma processing has outstanding performance in material modification/functionalization,

including etching of the surface, doping of (hetero)atoms, enriching of vacancies and functional groups, and fabricating of nanostructures.^{143,156,157} For example, O₂ or air plasmas effectively introduce O-containing groups, such as C=O, -COOH, and OH, to biochar surfaces, while discharges with N-based inducer gas lead to the formation of nitrogenated groups.¹⁴³

In addition, non-ThPs, cold ones in particular, from DBD or plasma jets, are featured by a gas temperature of lower than 40°C.^{25,52,63} Thus, direct thermal damage to the strains used for fermentation may not be significant to lead to organism death. Furthermore, the high-concentration active particles and moderate UV radiation from these discharges can produce desirable stimulation of metabolic activity in the strains of fermenting microorganisms.^{158,159} This provides an avenue for integrating plasma treatment into the fermentation process in a way that both make lignocellulose more degradable and make the microorganisms more effective in consuming lignocellulose-derived sugars and further converting them into end products. DBD, plasma jet, and RF atmospheric and room-temperature plasma, in particular, have also been applied to treat microorganisms as a new powerful tool for mutagenesis and select or enhance specific cell performances. For example, in yeast fermentation, desirable enhancements may include an increase in the rate of secondary metabolism and yield of metabolite (e.g., ethanol) production and an increase in the activity of enzymes associated with fermentation. This is because the multiple agents in cold plasmas, such as charged particles, free radicals, excited neutral species, high electric field, UV radiation, and so forth, possess significant and variable biological activities, with the capacity to induce changes in the permeability of the membrane, metabolic signaling pathways and enzymatic activities, and even alterations in genes.^{159,160} However, it should be noted that this approach relies on the plasma conditions necessary for the two processes above to be similar to enable the simultaneous application of plasma to substrate and culture in the pretreatment/refining processes. Otherwise, applying plasmas to the lignocellulose/yeast mixture may lead to undesirable effects, for example, mutagenesis (strain instability) and/or downregulation of pathways associated with glycolysis. Indeed, mutagenesis and selection of microorganisms using non-ThPs are promising strain development tools.¹⁵⁸

3.5 | Other processing of biorenewable feedstocks-derived resources

As previously mentioned, the recalcitrance structure of the raw carbon-rich feedstocks still poses great barriers to their direct conversion. While plasma processing of the

carbon-rich feedstocks-derived resources, especially those liquid substances with simpler structures and components, such as unwelcomed tars from biomass gasification and pyrolysis, low-grade biocrudes from biomass liquefaction, plant essential oils, and bioethanol, for the production of cleaner energy and/or higher-value goods, is causing chief interests. Indeed, in recent years, there have been tremendous growth and breakthrough in applying plasma-only and plasma-catalysis techniques to upgrade these bioresources. A short overview of selected but typical application examples is provided in this section.

3.5.1 | Tar removal and oil upgradation

Tar is a complex mixture of condensable hydrocarbons, including aromatics and PAHs. Tar can be classified based on the formation temperature (Figure 11A), types of waste, and the M_w of tar compounds.^{161,162} The tar formation causes major process and syngas end-use problems, including tar blockages, plugging, and corrosion in downstream fuel lines, filters, engine nozzles, and turbines.¹⁶³ Since tar can be easily condensed even at high temperatures or very small concentrations, tar removal is quite challenging and is an unfeasible option. Therefore, the efficient removal of tars from the product gas is crucial for high-temperature biomass utilization, such as gasification and pyrolysis. Apart from the conventional thermal cracking,¹⁶⁴ mechanical separation,¹⁶⁵ and catalytic reforming,¹⁶⁶ low-temperature plasma technology provides a promising alternative to the conventional approaches for converting tars into clean chemicals under mild conditions.¹⁶⁷ In non-ThPs, the overall gas temperature can be as low as room temperature, while the electrons are highly energetic with typical energy ranging from 1 to 10 eV. As a result, the plasma species can easily break most chemical bonds and overcome the disadvantage of the high temperature required by thermal or catalytic processes, and enable thermodynamically unfavorable chemical reactions to occur under ambient conditions.⁵² Elliott et al.¹⁶⁸ used an MW plasma torch for converting tars into CO, H₂, and carbon at high temperatures, incurring high energy cost. Nair et al.¹⁶⁹ developed a high voltage (80 kV) PCD to decompose model tar compounds—mixed naphthalene and phenol, which also suffered from the low energy efficiency. As shown in Figure 11B, GAD has been considered as a transitional plasma and can be generated by applying an electrical field across two or more electrodes in a laminar or turbulent gas flow,¹⁷⁰ which offers high flexibility for working in a wide range of flow rates and elevated power levels (up to several kilovolt) efficiently.

More recently, the plasma-enabled/assisted or integrated catalysis (also known as plasma catalysis), including (i) plasma catalyst pretreatment, (ii) in-plasma catalysis, and (iii) post-plasma catalysis (Figure 11C), offers a more feasible option to overcome the detriment of poor gas reactivity for plasma breakdown and thermal treatment catalyst fast neutralization. The plasma catalyst pretreatment gives rise to improved catalytic effectiveness by transforming the chemical makeup of the catalyst surface at room temperature,¹⁷⁵ presenting catalyst materials that can enhance the catalytic selectivity, reduce catalyst particle size, change the pore structure, and promote the reduction of active metals.¹⁷⁶ For example, glow discharge plasma pretreatment of NiMgSBA-15 catalysts improved activity compared to the untreated ones,^{177,178} together with smaller particle size, good catalyst dispersion, and enhanced catalyst stability for tar conversion. In-plasma catalysis, referred to as the synergistic plasma and heterogeneous catalysts, can enhance the tar cracking and offer minimal coke production in the presence of a catalyst. For example, Liu et al.¹⁷⁷ studied toluene steam degradation under Ni-ZSM-5 catalyst in three techniques of plasma only, post-plasma catalysis, and in-plasma catalysis, and they found a higher toluene conversion rate under in-plasma catalysis, unlike the other configurations. Lu et al.¹⁷⁹ also developed in-plasma catalysis based on the DBD plasma to ascertain execution and approach of toluene expulsion of catalyst FeO_x/SBA-15 under atmospheric pressure and room temperature, and they postulated that electrons collision plus oxidation of toluene through OH and O radicals in excited states, as well as premium oxygen affinity by catalyst Fe²⁺ in FeO_x/SBA-15 and excellent adsorption ability of SBA-15, contributed to the direct toluene degradation on the catalyst surface.

In the post-plasma catalysis, plasma discharge is normally employed to enhance the subsequent catalytic system. For instance, Bo et al.¹⁸⁰ developed a hybrid and unique process combining solar irradiation and post-plasma catalysis to efficiently oxidize toluene over a highly active and stable MnO₂/graphene fin foam catalyst. They found that the prominent synergistic effect of solar irradiation and postplasma catalysis with a synergistic capacity of ~42% can be mainly attributed to the solar-induced thermal effect on the catalyst bed, boosting ozone decomposition to generate more oxidative O radicals and enhancing the catalytic oxidation on the catalyst surfaces, as well as the self-cleaning capacity of the catalyst at elevated temperatures driven by solar irradiation. Yang et al.¹⁷³ also employed the three-dimensional (3D) hollow urchin α -MnO₂ for postplasma catalytic decomposition of toluene, and they found that the hollow structure with an enlarged contact surface

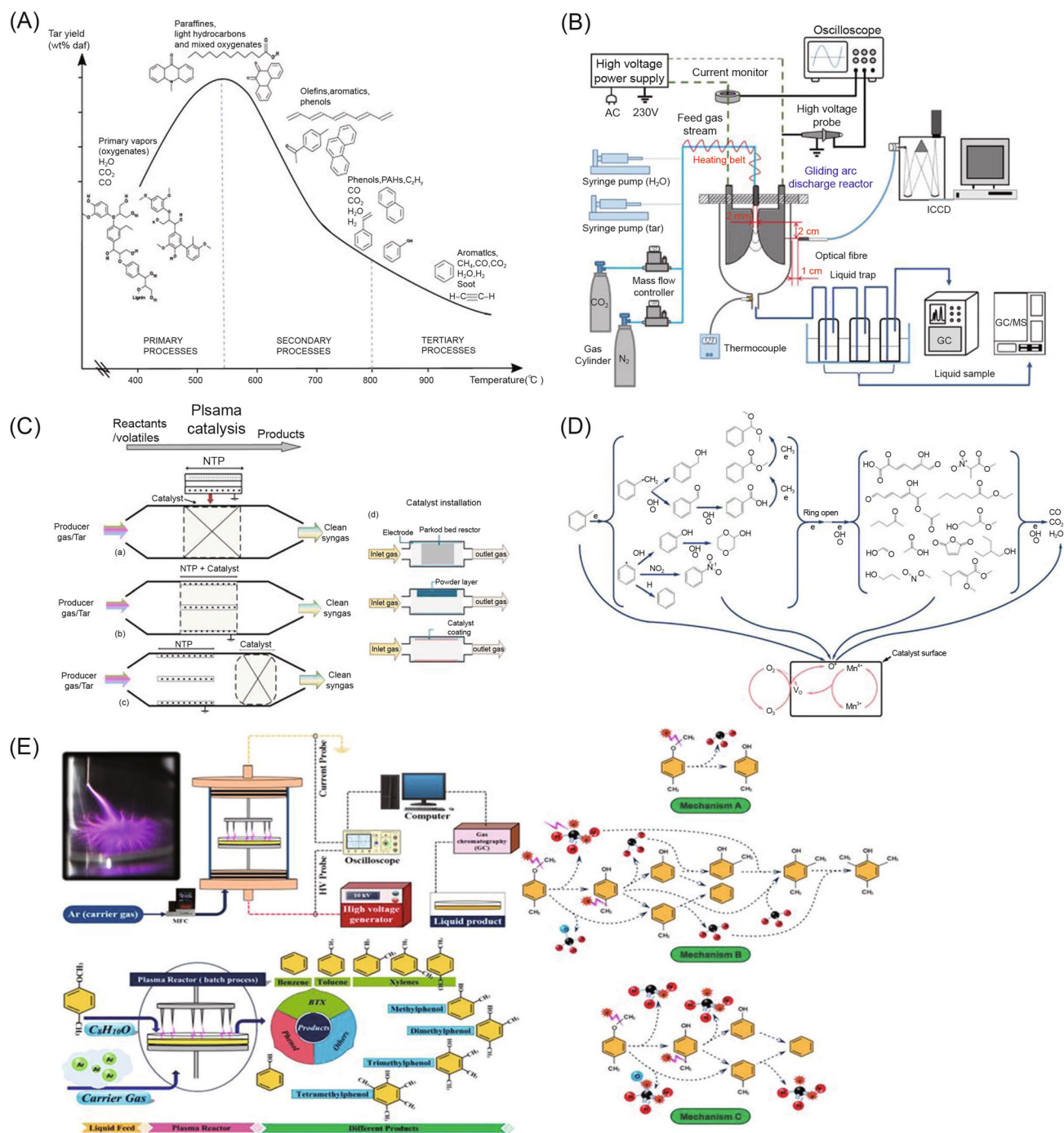


FIGURE 11 Tar and oil upgradation using discharge plasmas. (A) Tar formation with different processing temperatures during biomass valorization. Reproduced with permission: Copyright 2014, Elsevier.¹⁶¹ (B) Schematic of a GAD used for tar processing. Reproduced with permission: Copyright 2019, Elsevier.¹⁷¹ (C) The integration methods of catalysis with plasmas, termed plasma catalysis. Reproduced with permission: Copyright 2022, Elsevier.¹⁷² (D) Reaction pathways of plasma-MnO₂ catalysis enabled tar model degradation. Reproduced with permission: Copyright 2020, Elsevier.¹⁷³ (E) Pulsed corona plasma reactor used for the upgradation of a biocrude model (4-methylanisole) and proposed reaction mechanisms. Reproduced with permission: Copyright 2017, Elsevier.¹⁷⁴ GAD, gliding arc discharge.

area could enhance the adsorption toward gas and prolong the retention of gas on the catalyst surface.^{64,167} Furthermore, the fully exposed nonagglomerated 1D α -MnO₂ nanorods can promote oxygen vacancy density and low-temperature reducibility, facilitating the

adsorption and conversion of ozone into active oxygen species, which leads to the deep decomposition of toluene in postplasma catalysis (Figure 11D). Currently, the synergistic effects between the plasma and catalyst are still challenging to investigate due to the multi-

interactions during various plasma catalytic processes that occur. Though in its early stages of development, the technology provides a breakthrough for effective tar reforming and future commercial implementation due to the high tar conversion efficiency and selectivity of syngas, and further consented efforts should be directed at the successful development of hybrid plasma catalysis technology for tar removal. For further details on process design, reaction mechanisms, energy efficiency, and more on tar removal and/or upgradation using both plasma-alone and plasma-catalysis, readers can refer to many review papers recently published.^{167,172,181}

Bio-oils (or biocrudes) from liquefaction and/or pyrolysis of lignocellulosic biomass are potential energy carriers for future uses, but usually with unsatisfactory properties (thermal instability, high viscosity, corrosiveness, and low heating value [LHV]) due to high oxygen contents (10–45 wt%), which requires further upgradation mainly via zeolite cracking and/or hydrodeoxygenation (HDO).¹⁸² Oil from zeolite cracking is of a low grade with heating values nearly 25% lower than that of crude oil. This process is almost unfeasible due to the low H/C ratio and very short catalyst lifetime. The HDO upgradation is better than the zeolite cracking due to producing oils of an acceptable grade. However, HDO is feasible but not economical due to the limitation of high-pressure H_2 (75–300 bar) that requires a sustainable hydrogen supply.^{174,182} As discussed in Figure 6C, plasma-generated reactive species theoretically are apt to break the side-bonds of aromatic compounds instead of the benzene itself, which has also proved and validated effective for lignin-derived oil (using anisole, guaiacol, 4-methylanisole or others as the model compounds for simplifying the studies and understanding mechanisms) upgradation by removing extra oxygen. Figure 11E shows an example in which a pin to plate corona argon discharge was used to treat the model molecule of 4-methylanisole.¹⁷⁴ The operating and design parameters, including carrier gas flow rate, pulse repetition frequency, and the reactor configuration, would alter the electron and energetic species density and affect the conversion and product selectivity. The required hydrogen was generated in situ via methyl decomposition to H_2 , and the upgrading mechanism involved demethylation, transalkylation, hydrogenolysis, demethoxylation, and methane decomposition. The plasma upgradation led to a conversion of up to 70% and deoxygenation of 20%, with the most valuable and abundant products characterized to be benzene, toluene, and xylene (BTX) and phenol with a maximum selectivity of 15% and 46%, respectively.¹⁷⁴ Other studies were also conducted and proved that the HDO efficacy of bio-oils during plasma upgradation could be significantly

improved with tunable product selectivity by combining with specific catalysts.¹⁸²

3.5.2 | Fuel hydrogen production from bioethanol

Noteworthy, current ethanol reforming processes generally use petrol-based ethanol. But, we wish to provide a short introduction on plasma-enabled ethanol for fuel H_2 productions, considering that (i) the increasingly available bioethanol with decreasing prices is now serving the global energy market with a more than 100 billion liter scale^{183,184}; and (ii) ethanol is a commonly used solvent in many solid waste upgradation processes, such as liquefaction. Ethanol has also been regarded as a promising feedstock to produce higher-value and cleaner energy carrier hydrogen (H_2) and is expected to contribute to a more economical and competitive “hydrogen economy.”^{183,184} The most widely studied approaches for converting ethanol into H_2 are steam-based reforming (SR) processes, where ethanol and water at a specific ratio are vaporized into the reactor heated to high temperatures ($>700^\circ\text{C}$) for reactions with or without specially selected or designed catalysts. As the SR of ethanol is highly endothermic, a large amount of energy supplied by high temperatures and/or high pressures is indispensable, which requires higher energy consumption and requirements on reactors and process control, thus greatly hindering practical H_2 production.

Plasmas offer unique physiochemical environments due to the enrichment of energetic electrons and reactive particles, enabling thermodynamically unfavorable reactions to occur at ambient conditions (low temperatures and pressures) and have been widely applied in ethanol reforming for hydrogen production, mainly by two categories of discharge modes.^{184,185} The first mode is based on the gas phase discharges in which the ethanol is evaporated in advance or in the discharge zone due to thermal effects. This discharge mode dominates current research due to the well-established and easily available knowledge and diagnosis technologies on gas discharges, the flexibility with the choice of reactors and power supplies, the controllability, and the feasibility of combining with catalysts. The alcohol reforming by plasmas has been proved effective by using GAD, MW discharge, DBD, corona discharge, glow discharge, and others.^{184,186,187} As illustrated in Figure 12A, where the influencing factors, reaction process, intermediate species, and end products are summarized in plasma ethanol reforming systems with or without catalysts, the plasma alcohol reforming generally involves several reaction pathways, such as dehydration, decomposition, dehydrogenation, and coking, which are usually initiated and sustained by

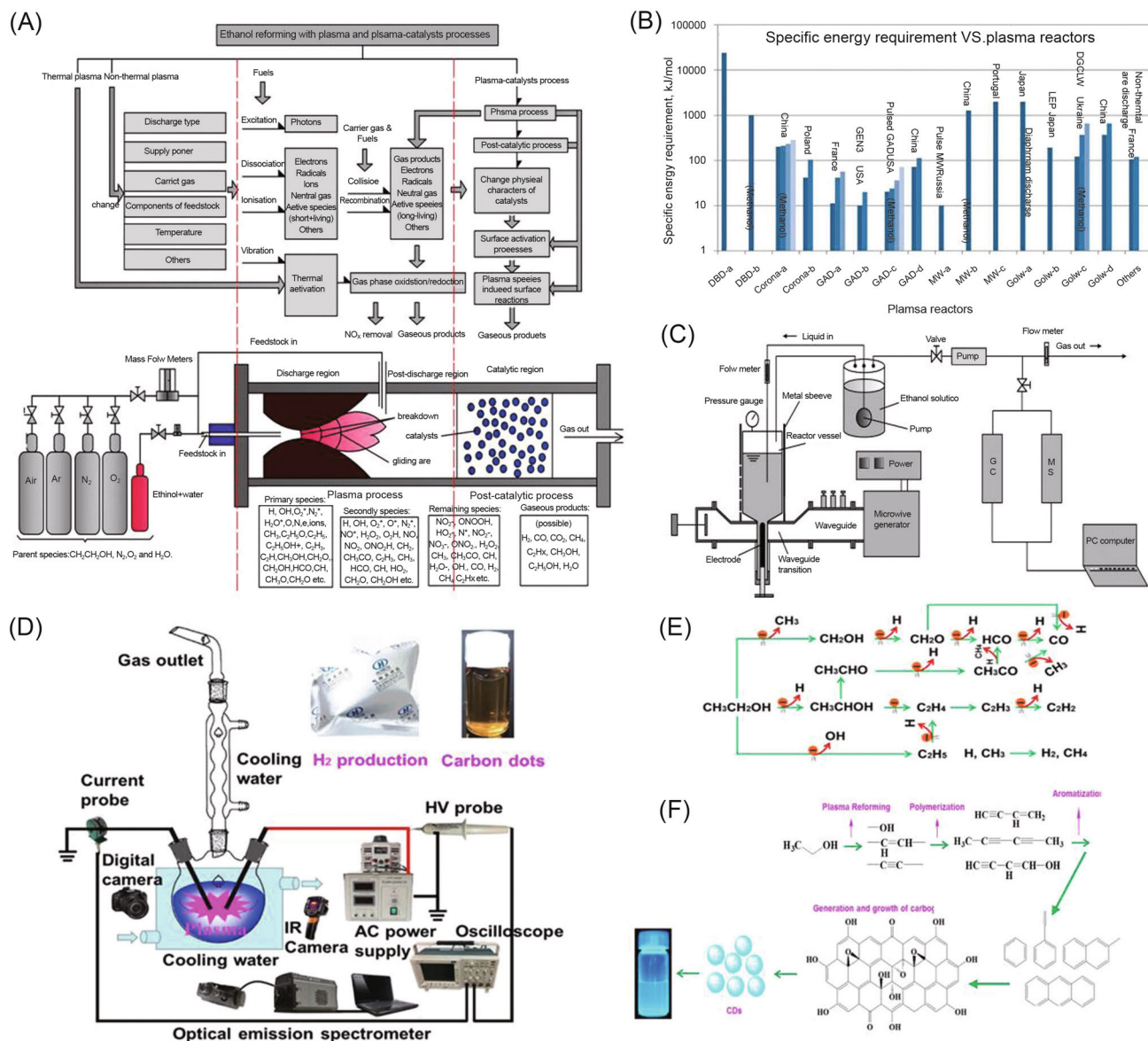


FIGURE 12 Discharge plasma for ethanol reforming. (A) Schematic summary of gas-phase ethanol reforming by plasma-only and plasma-catalytic technologies, and (B) specific energy requirement with various plasma reactors. Reproduced with permission: Copyright 2015, American Chemical Society.¹⁸³ (C) Schematics of the experimental setups for in-liquid ethanol conversion using MW discharge. Reproduced with permission: Copyright 2017, Elsevier.¹⁸⁸ (D) Schematics of the needle-to-needle pulsed discharge and proposed pathways of (E) ethanol dissociation and (F) C-dots formation during in-liquid plasma ethanol reforming. Reproduced with permission: Copyright 2020, Elsevier.¹⁸⁹ MW, microwave.

plasma-generated free electrons and reactive species.^{184,186,187} Many catalysts able to assist ethanol dehydrogenation, C–C bond breaking, and/or C1 product reforming, such as Ni, Cu, Mn, Re, and other metals supported on metal oxides including TiO_2 , Al_2O_3 , and CeO_2 , have been trailed to accelerate the conversion and/or enhance conversion and product selectivity.^{184,186,187} Figure 12B further summarizes the energy requirement and conversion efficacy in different plasma reactors, indicating that this technique can obtain overall alcohol conversion (even ~100%) while keeping economic viability (with a

general energy requirement 10–1000 kJ for producing 1 mol of H_2).¹⁸³ However, there are several unsettled issues with the gas-phase discharge reforming. For example, the purity of obtained H_2 is usually lower than 70% (vol/vol), limiting such a product's application. More importantly, different carrying gases are usually required, posing an extra challenge to gas product purification.

The second mode lies in the in-liquid discharges for direct ethanol reforming, which eases using carrying gases. Moreover, with energy (electricity, power, or

others) rapidly delivered to the liquid, a highly reactive environment and energy-concentrated will be locally created. Such localization of energy and reactive species is well suited for ethanol reforming while reducing energy waste.⁷² Typically used reactors of in-liquid discharges for ethanol reforming include MW and pulsed discharges (Figure 12C,D).^{188,190} The highest energy efficiency for hydrogen production directly from ethanol by in-liquid discharges was $>2\text{ m}^3\text{ H}_2/\text{kWh}$, showing superiority over the efficiencies for water electrolysis and catalytic ethanol reforming (0.2 and $0.5\text{ m}^3\text{ H}_2/\text{kWh}$, respectively). The plasma-enabled ethanol conversion is believed to be achieved mainly by electron and free-radical-induced reactions (Figure 12E). However, the H_2 contents from in-liquid discharge-based reforming are usually low ($<70\%$) and await further improvement. Recently, by accurately controlling the energy inputs, the discharge modes of in-ethanol pulsed discharge (Figure 12D) could be tuned over three modes observed, termed single spark mode (SSM), multiple spark mode (MSM), and gliding spark mode (GSM), with a discharge power of 4, 6, and 10 W, respectively. A gas production rate of $\sim 20\text{ mL}/\text{min}$ was measured for SSM, while 120 and $500\text{ mL}/\text{min}$ for MSM and GSM, accordingly. The H_2 volume contents for both SSM and MSM were over 90%, showing a great enhancement to other reported values. Unlike the case of GSM, where most carbons in the ethanol were converted to CO and solid carbons, in SSM and MSM, some carbons were retained in the liquids in the form of carbon dots, with a size of $\sim 3\text{ nm}$ and strong fluorescence, the strongest peak centered at 365 nm achieved with excited of 330 nm. The carbon dots further proved low cytotoxicity and good biocompatibility and could be used for cell imaging. Based on GC-MS results on the liquid after discharge, the authors also proposed a possible formation mechanism of carbon dots (Figure 12F). First, plasma generated in liquid forms localized energy and abundant reactive species to form C double and triple bonds. Under the plasma conditions, these bonds are very active for further reactions (polymerization and aromatization) to form further conjugate structures with enhanced FL properties.¹⁸⁹

3.5.3 | Plasma-cracking of biogas

Biogas rich in methane is also a carbon-rich resource widely available in nature. Plasma-enabled methane cracking, particularly by plasma pyrolysis powered by MW discharges, is an effective approach for extracting hydrogen, as well as hydrocarbons in some cases, from methane while converting the elemental carbon into

functional materials such as high-performance graphene.²⁴ It is estimated that plasma pyrolysis of methane favors a more competitive hydrogen production cost than water electrolysis (2–3 vs. 3.5–4.5 €/kg of hydrogen).¹⁹¹ Furthermore, if biogas is used as the methane source or the process is sustained by renewable energy, the plasma conversion can be regarded as a zero- or even negative- CO_2 emission process, and thus is expected to be an ideal technological platform for a sustainable hydrogen economy, largely contributing to the decarbonized global energy markets.

Jasiński et al.¹⁹² proposed a waveguide-based nozzleless cylinder-type microwave plasma source (MPS) to convert methane into hydrogen. It has been found that the waveguide-based nozzleless cylinder-type MPS has many advantages: stable operation in various gases (including air) at high flow rates, no need for a cooling system, and impedance matching. The plasma generation was stabilized by an additional swirled nitrogen flow (50 or $100\text{ L}/\text{min}$). The methane flow rate was up to $175\text{ L}/\text{min}$. The absorbed MW power could be changed from 3000 to 5000 W. The hydrogen production rate and the corresponding energy efficiency in the waveguide-based nozzleless cylinder-type MPS presented methane reforming were calculated to be $255\text{ g}/\text{h}$ and $85\text{ g}/\text{kWh}$. These parameters are better than those typical of the conventional methods of hydrogen production (steam reforming of methane and water electrolysis). Czyłkowski et al.¹⁹³ investigated the efficiency of hydrogen production via combined steam reforming (i.e., with the addition of CO_2 and water vapor) of methane in a waveguide-supplied metal cylinder-based MPS. The operating parameters were as follows: MW frequency of 2.45 GHz, maximum absorbed MW power of 6 kW, and working gas (methane + CO_2 + water vapor) flow rates up to $9000\text{ NL}/\text{h}$. It was proven that using the MW system, the plasma steam reforming of methane can be run stably at high gas flow rates (several $1000\text{ NL}/\text{h}$). By optimizing the process input parameters, that is, the absorbed MW power, working gas composition, and flow rate, the energy yield of hydrogen production of $42.9\text{ g}/\text{kWh}$ could be achieved. This study showed that MW plasma is a feasible system for H_2 production from methane.

Wang et al.¹⁹⁴ developed a directly coupled liquid-phase MW discharge plasma to realize liquid-phase methane wet reforming to produce hydrogen. When methane gas is injected into the water in the reactor, plasma is generated in the water by MW discharge. When the MW power was 900 W, the optimal methane conversion rate reached 94.3%, and the highest concentration of hydrogen reached 74.0%. In addition, by optimizing the electrode structure while improving the stability of the plasma system, a higher yield of hydrogen and energy efficiency of hydrogen production

were obtained, and the highest energy efficiency of hydrogen production was approximately 0.92 mmol/kJ. This investigation provides a new method for hydrogen production by liquid-phase plasma methane wet reforming.

Choi et al.¹⁹⁵ reported methane reforming in a steam plasma generated by MWs at atmospheric pressure without catalysts. The plasma reforming system comprises a 2.45 GHz MW plasma torch and a plasma nozzle. Methane gas is introduced into the steam MW plasma, stabilized by a swirl flow. The steam MW plasma provides highly reactive species and a high-temperature plasma flame, enhancing the chemical reaction rate and eliminating the need for catalysts. Using a specially designed plasma nozzle, high hydrogen concentrations (>70 vol%) in the effluent streams were achieved. Wang et al.¹⁹⁶ proposed a methane steam reforming process for producing mainly hydrogen in an atmospheric-pressure MW plasma reactor. Nanocarbon powders, CO_x, C₂H₂, C₂H₄, and HCN were also formed. The selectivity of H₂ was greater than 92.7% at inlet H₂O/CH₄ molar ratio (R) \geq 0.5 and was higher than that obtained using decomposition of methane (termed methane plasmolysis) because steam inhibited the formation of C₂H₂. The highest methane conversion was obtained at R = 1, reaching 91.6%, with the lowest specific energy consumption of H₂ formation at [CH₄]_{in} = 5%, 1.0 kW, and 12 L/min.¹⁹⁶

Graphene is a novel 2D nanomaterial composed of sp²-hybridized carbon atoms. Due to its excellent physical, chemical, and mechanical properties, graphene is expected to have promising applications in energy, machinery, environment, and biology. Recently, MW plasma has proven to be feasible to generate graphene materials from a carbon-containing precursor, such as methane (biogas), with selected examples shown in Figure 13. Unlike other methods, MW plasma is a single-step, rapid, and continuous technique that does not require catalysts, substrates, solvents, or acids.¹⁹⁷

Singh et al.¹⁹⁸ investigated the effect of hydrogen concentration on graphene synthesis using MW-driven plasma-mediated methane cracking. It has been found that nanographene consisting of 2–6 sheets per stack with dimensions between 100 and 500 nm formed, and its respective oxidative reactivity is comparable to commercially available similar carbon products (Figure 13A–D). Yuan et al.²⁰¹ synthesized high-quality graphene sheets (GS) on stainless steel substrates at ~500°C by MW plasma chemical vapor deposition (CVD) in a methane/hydrogen mixture atmosphere. The GS product was characterized to contain mostly 1 or 2–3 layers (Figure 13I,J). The preferential etching of the interplanar carbon species/bonding by excited hydrogen atoms in the plasma was considered essential for forming

graphene structures. This study showed that the CVD approach can produce graphene with high yield and high purity with no carbon impurities such as carbon nanotubes. Gudaitis et al.¹⁹⁹ synthesized graphene on the Si(100) substrates from a mixture gas of methane and hydrogen via direct MW plasma CVD (Figure 13E). The synthesized graphene exhibited intrinsic n-type doping due to the charge transfer from Si(100). The presence of compressive stress was revealed in the synthesized graphene. It was presumed that induction of thermal stress took place during the synthesis process due to the large lattice mismatch between the growing graphene and the substrate. Importantly, it was demonstrated that continuous horizontal graphene layers can be directly grown on the Si(100) substrates if the appropriate configuration of the protective enclosure is used in the MW PECVD process.

Mehedi et al.²⁰² studied the significant roles of process parameters in the deposition of graphene films via cobalt-catalyzed decomposition of methane diluted in hydrogen using PECVD. Growth temperature is one of the most influential parameters in minimizing the number of graphene layers, whereas MW power has the second largest effect on the crystalline quality and a minor role in the thickness of graphene films. The PECVD graphene obtained with optimized synthesis conditions has a continuous film consisting of 2–7 high-quality graphene layers. Fang et al.²⁰⁰ applied MW plasma CVD to realize the large-scale production of high-quality graphene from methane mixed with hydrogen (Figure 13F–H). The results demonstrated that the in situ hydrogen plasma posttreatment strongly influences the graphene films, such as the number of layers, defect density, and surface morphology. At the early stage, the residual carbon species could be used to further the growth of graphene films in the hydrogen plasma environment, resulting in the lowest I_{2D}/I_G and I_D/I_G value and the highest C/Cu atomic ratio. Subsequently, the main role of in situ hydrogen plasma was the gradual etching of the topmost graphene layer. Monolayer graphene films with smooth surface and low defect density could be obtained at the growth time of only 10 s and the hydrogen plasma posttreatment time of 150 s.²⁰⁰

3.5.4 | Plasma-made functional carbons from bioresources

Nanocarbons have experienced a tremendous increase in the variety of morphologies over their relatively short history, including 0D sphere, 1D tube, 2D graphene, and 3D carbon structures (nanodiamond or carbon nanobelt). However, most of the existing chemical synthesis

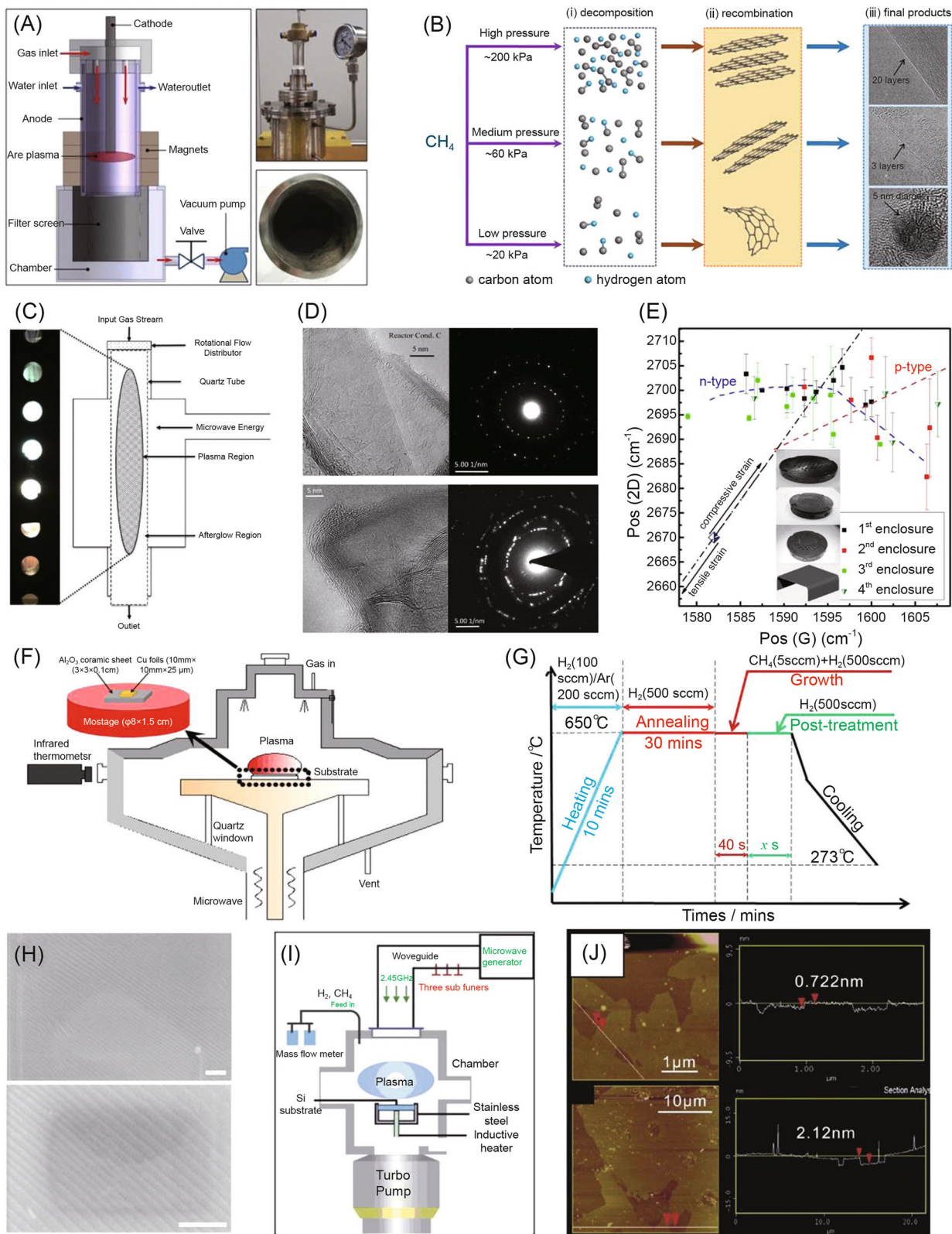


FIGURE 13 (See caption on next page)

processes for carbon material synthesis are often energy-inefficient and rely on toxic and nonrenewable chemicals or sources. This is why sustainable, low-carbon-imprint production and processing of functional nanomaterials is a highly topical issue. A viable solution is to engage green chemistry to reform minimally processed, renewable natural resources, such as biomass or other waste materials, into high-quality functional materials. However, due to the multicomponent and highly variable nature of such precursors, it is extremely challenging to achieve this goal using conventional (e.g., wet chemistry) approaches.

Currently, increasing attention has been paid to the direct conversion of natural carbon-rich feedstocks into value-added carbon materials, though most of the precursors used are still some model chemicals or reagents derived from bioresources. It is worth noting that the plasma pyrolysis or liquefaction of biomass can directly produce biochar, which can be further activated or functionalized to act as high-performance energy storage materials or catalyst supports. Another promising option is directly synthesizing the advanced carbon materials based on the novel plasma technology. The main generation methods include DBD, MW discharge, RF discharge, and more often-used, PECVD. The CVD process has been widely used to synthesize many advanced and functional materials. However, several barriers exist, including wasteful system heating, high temperature (~ 1000 °C), long heating, dwelling and cooling times, breakdown of precursor on the catalysts, very few controllable parameters, loss of catalyst, and slow, toxic chemical-based transfer. PECVD has been widely approved as an effective method toward these challenges, by significant reduction in temperature required, direct and fast surface heating, and plasma-induced reactions on catalysts, enabling better control and recycling of catalysts/supports.²⁰³ One good example is from van der Laan et al.,²⁰³ who demonstrated and explained how, through the use of a plasma, a graphene film containing

single-layer graphene could be grown at a temperature as low as 220 °C. The process could also be controlled, and an instant and water-mediated decoupling mechanism was realized.

Highly reactive, nonequilibrium plasma-enabled chemistry provides an environment- and human-health-friendly, energy-efficient, low-carbon-imprint route for the single-step fabrication of functional nanomaterials directly from low-cost natural resources, with the outcomes often superior, or even unprecedented, compared to conventional chemistry methods. Wang et al.²⁰⁴ developed a rapid and single-step process based on the atmospheric-pressure DBDs to reform yolk and white fractions of chicken eggs for amphiphilic C-dots production (Figure 14A,B). In this case, the reactive plasma environment served to reform abundant, unprocessed carbon precursor (chicken egg) into relevant hydrocarbon building units under ambient conditions (vacuum-free, solvent-free, and external-heating-free). Other types of natural precursors can also serve as a carbon precursor in place of the egg for the synthesis, and the composition of the starting material and the processing conditions determine the properties of C-dots.²⁰⁴ Seo et al.²⁰⁵ proposed a single-step, plasma-enabled, catalyst-free strategy to convert a range of pure and mixed natural precursors, including honey, butter, sugar, milk, and methane, into few-layer vertical graphene directly onto Si/SiO₂ substrates within a few minutes (Figure 14C). These functional vertical graphenes show reliable biosensing properties, strong binding with proteins, and improved adhesion to substrates. Seo et al.²⁰⁶ also developed a plasma pathway to synthesize synergistically integrated natural-resource-based vertically oriented graphene nanosheets and carbon nanotubes for high-performance supercapacitor electrodes (Figure 14D–H). Another work from Jacob et al. shows that *Melaleuca alternifolia*, a volatile natural extract from the tea tree plant, can also be used as the precursor through a fast and sustainable bottom-up process to grow large-area, high-quality graphene films without the aid of any catalyst.²⁰⁷ The as-fabricated graphene films with a

FIGURE 13 Microwave plasmas for graphene synthesis from biogas. (A) Schematic diagram and photos of the experimental apparatus and (B) schematic illustration on mechanism of graphene nanoflakes synthesized from methane by microwave plasma. Reproduced with permission: Copyright 2016, AIP Publishing.¹⁹⁷ (C) Schematic of the novel microwave plasma reactor and (D) the selected area electron diffraction (SAED) spot pattern indicative of high-crystallinity of the synthesized graphene from biogas. Reproduced with permission: Copyright 2019, Elsevier.¹⁹⁸ (E) Protective enclosures used for direct synthesis of the graphene from methane on Si(100) by direct microwave plasma-enhanced chemical vapor deposition (PECVD) and the Pos(2D) vs. Pos(G) plot of the obtained graphene. Reproduced with permission: Copyright 2020, MDPI.¹⁹⁹ (F) Schematic diagram of the microwave plasma chemical vapor deposition (MPCVD) chamber, (G) experimental protocol, and (H) plan-view FESEM micrographs of the MPCVD-grown graphene films (scale bar of 1 μm). Reproduced with permission: Copyright 2016, Elsevier.²⁰⁰ (I) Schematic of microwave plasma chemical vapor deposition (CVD) and (J) the AFM images of the synthesized graphene in an atmosphere of methane/hydrogen mixture by this method. Reproduced with permission: Copyright 2009, Elsevier.²⁰¹ AFM, atomic force microscopy; CVD, chemical vapor deposition; FESEM, field emission scanning electron microscopy; MPCVD, microwave plasma chemical vapor deposition; PECVD, plasma-enhanced chemical vapor deposition; SAED, selected area electron diffraction.

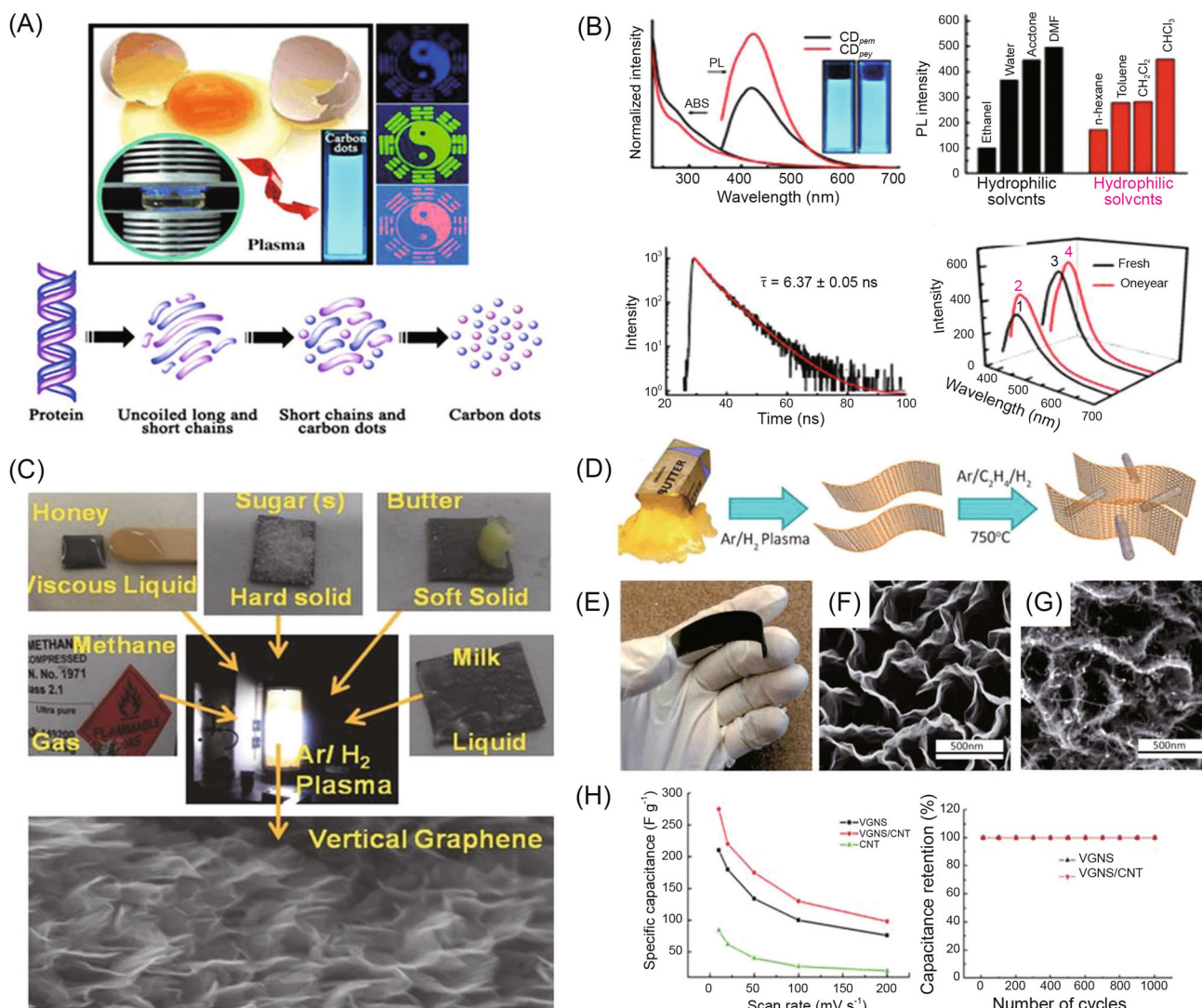


FIGURE 14 Discharge plasmas for advanced carbon material synthesis from raw carbon-rich feedstocks. Carbon dots synthesis from egg protein using a DBD plasma: (A) schematic and reaction pathway and (B) FL characteristics. Reproduced with permission: Copyright 2012, Wiley.²⁰⁴ (C) Vertical graphene harvested with Ar/H₂ plasma-enhanced CVD from different feedstocks including honey, sugar, butter and milk. Reproduced with permission: copyright 2013, Wiley.²⁰⁵ Vertically oriented graphene nanosheets (VGNS) and carbon nanotubes (CNTs) from Ar/H₂ plasma and a subsequent Ar/C₂H₄/H₂ plasma: (D) schematic for the direct growth of CNTs onto VGNS, (E) photo of the as-grown VGNS/CNTs hybrid on a flexible graphite substrate, SEM images of (F) VGNS and (G) VGNS/CNTs, and (H) application performance as supercapacitors. Reproduced with permission: copyright 2014, Wiley.²⁰⁶ CNT, carbon nanotube; CVD, chemical vapor deposition; DBD, dielectric barrier discharge; SEM, scanning electron microscopy; VGNS, vertically oriented graphene nanosheets.

stable contact angle of 135° can be potentially applied in highly hydrophobic coatings, and the electronic devices formed by sandwiching pentacene between graphene and aluminum films demonstrated memristive behavior, and hence, these graphene films could find use in nonvolatile memory devices.

Muvhiiwa et al.²⁰⁸ employed a nitrogen plasma reactor to obtain biochar from wood pellets. It has been found that the amount of biochar and its sieve particle size distribution decreased with an increase in oxygen feed for gasification and an increase in temperature for both biomass conversion processes. The biochar

exhibited a more broken and nonparallel structure than the feed wood pellets. During plasma gasification, all the particles of size <300 μm were entrained in the product stream while those with particles >2 mm remained in the reactor chamber. All the obtained results are vital to understanding practical process flow distributions and product separation mechanisms resulting from the transportation of biochar within biomass systems to improve their design. Al-Jumaili et al.²⁰⁹ used the PECVD system at different applied RF power to fabricate vertical graphene nanowalls on silicon and quartz substrates from an inherently volatile carbon precursor

without the use of any catalyst. Further biological studies suggested that significant morphological damage to bacterial cell walls by the sharp edges of graphene walls contributed to the cells appearing abnormal and deformed. Chen et al.²¹⁰ proposed a one-pot approach via MW heating in humidified N₂ combined with water vapor plasma modification to obtain lignin-based porous carbon. Humidified MW heating could produce hierarchical porous carbon with a high specific surface area (SBET) of 2866 m²/g and a high mesopore content of 68.16%. Water vapor plasma modification not only resulted in further development of the porosity with an increase in SBET by 11.6% but also the doping of oxygen (up to 33.43%). These characteristics ensure a high energy storage capacity and an excellent rate capability for the prepared supercapacitor, which exhibits the highest specific capacitance of 254.6 F/g at 0.5 A/g with a retention rate of 75.6% at 10 A/g. Karim et al.²¹¹ used ThPs processing (1200–1500 °C) to treat a mixture of potassium (K) containing banana peduncle and phosphorus (P)-rich effluent sludge (chemical fertilizer industry) wastes for the development of biochar complex fertilizer. Plasma processing produced biochar with higher total P (8.53%–11.81%) and K (17.13%–21.9%) than slow pyrolysis at 700 °C (P-4.2% and K-11.5%). Bioavailable phosphorus of effluent sludge (600 mg/kg) enhanced to 4500–6000 mg/kg in plasma-derived biochars. X-ray diffraction analysis indicates the presence of P as hydroxyapatite in sludge and biochar.

Notably, an increasing number of studies demonstrate that the plasma-enabled up-carbonization can simultaneously extract hydrogen fuel from the carbon precursors and reform the cracked carbon into value-added carbon materials as well as other fine chemicals. It has been proved that coalbed methane surrogates could be well reformed for coproduction of hydrogen and GS/carbon aerosol using a rotating GA plasma.^{212,213} Tang et al.⁹⁶ employed an RF capacitively coupled plasma pyrolysis reactor to process fir sawdust, providing guidelines for the utilization of biomass material for the cogeneration of syngas and char. The results showed that the yield of syngas containing H₂ increased due to the high plasma reactivity and thermal efficiency at a medium temperature, which favors hydrocarbon cracking. Meanwhile, the high heating rate of the plasma results in the production of a char with a higher porosity compared with those produced by the classical slow pyrolysis. Zhou et al.¹⁸⁹ developed a novel concept, “carbon to carbon and hydrogen to hydrogen” bioethanol reforming based on in-liquid plasma discharges (Figure 12D). Results show that clean hydrogen gas and smart nanocarbons could be produced by controlling energy transfer and distribution processes. The as-

synthesized carbon dots with low cytotoxicity have been successfully applied in biological applications. Without the use of any catalysts, Al-Jumaili et al.²⁰⁹ proved that the PECVD system with varying RF powers could harvest vertical graphene nanowalls and H₂ from an inherently volatile carbon precursor. Blanquet et al.¹⁰⁹ introduced a pyrolysis-non-ThP-catalytic system for the increased production of hydrogen-rich gas and hydrocarbon tar from waste wood sawdust. It has been found that H₂ yield increased from 1.0 mmol g⁻¹ biomass in the absence of plasma to 4.0 mmol g⁻¹ biomass with plasma-catalysis while more efficient recovery of hydrocarbon tar was achieved. These interesting demonstrations highlight the feasibility of implementing plasma as a green technology for sustainable carbon reformation to harvest both energy and materials, thus effectively “killing two birds with a stone.”

3.5.5 | Numerical simulations and machine learning for mechanism studies

As discussed in the above sections, plasma is suitable for a wide range of applications for the up-carbonization of a series of carbon-rich feedstocks. However, the performance or the efficiency of this technology depends on many factors, such as characteristics of the starting materials (moisture and composition), plasmas (discharge type, energy density, and reactive species etc.), and the operational conditions (gas flow rate, temperature, pressure, etc.); therefore, by experimental evaluations solely, it is always of great challenge to find the optimal conditions for the most efficient reformation of feedstocks, understand the kinetics and mechanisms that underpinned the plasma-induced reactions and the interactions between plasmas and feedstocks, and verify the technical feasibility, especially under real-world reaction conditions. Numerical simulations or mathematical modeling studies have long been regarded as time- and resource-saving tools to accomplish these goals without the need to build experimental facilities, although in general, not as accurately as direct experimental investigations.

Theoretical modeling, including thermodynamic, molecular dynamic, chemical kinetic and fluid flow calculations, and discharge simulations, have been conducted and reported for further understanding and performance-improving of the plasma-based conversion.²¹⁴ Modeling the detailed plasma chemistry of the conversion in actual reactors, with the realistic reactor geometries considered for the design improvement and energy efficiency enhancement, is generally challenging, even when using a simple starting model feedstock, such as methane or CO₂. And thus, typically, using a combination

of two or more different types of models (0D kinetics models for the detailed chemistry, 2D or 3D fluid models for studying reactor features) is necessary.²¹⁵ Below, we briefly introduce selected examples with the starting feedstocks ranging from gas to liquid and solid phases to highlight the merits of computational chemistry and engineering and encourage multidisciplinary collaborations for furthering applications of plasma technology for clean energy harvesting and utilization. Readers are encouraged to refer to the original references for more details on the relevant results and models.

Mao et al.²¹⁶ developed and validated a kinetic model incorporating the key excited species for methane pyrolysis with N₂/Ar/He diluents in a nanosecond pulsed discharge. Calculated by a 0D hybrid ZDPlasKin-CHEMKIN model and developed kinetic modeling, consisting of a plasma kinetic mechanism, including 468 reactions, and a kinetic mechanism of ground states with 245 reactions, which reveals the time evolutions of the excited species, radicals, ions, and electrons.²¹⁶ The calculations validated that H₂ and C₂H₆ were the major products of all mixtures and a three-stage effects of the plasma formed species were involved on the conversion: S1, representing the discharge where electron impact reactions dominate the species production, S2 the early stage of afterglow when the quenching of electronically excited states and ions of diluents occurs, contributing to the production of radicals and fuel ions, and S3, the later period of afterglow where the dissociative recombination of electrons and fuel ions occurs, leading to the formation of solid carbon.

Petitpas et al.²¹⁷ used a 1D phenomenological model to simulate the reforming of ethanol and E85 (15% gasoline and 85% ethanol) by a nonthermal arc discharge. A perfectly stirred reactor (PSR) with an input heating power equal to the electric power and a plug flow reactor were used to model the plasma region and postdischarge region, accordingly, with the mixture temperature calculated from the global enthalpy balance using the PSR outflow and the remaining cold gas. The model was implemented in FORTRAN code using the PSR and SENKIN modules of the CHEMKIN II package. The simulation results exhibited a good correlation to the experimental investigations, confirming the effects of supplied power, air/fuel ratio, and water addition during the reforming and the action of reforming and the key actions induced by electrons and charge radicals for enhancing reaction kinetics. Miotk et al.²¹⁸ studied similar alcohol reforming using MW plasma at atmospheric pressure both experimentally and mathematically, with the alcohols being introduced into the discharge zone by a heating vaporizer and nitrogen or carbon dioxide employed as the working gas. The

modeling of chemical reactions was conducted using a two-step method: plasma formation in alcohol flowing axially and then mixing with a CO₂/N₂ swirl afterward. A commercial software (Chemical WorkBench) was used for the calculations, where the plasma formation was simulated with a thermodynamic equilibrium reactor followed by a calorimetric bomb reactor, and the resulting gas mixture in a model of a well-stirred reactor. As a result, the chemical composition and temperature at the plasma outlet were determined, and the main reaction pathways were given. However, compared to experimental data, there was some discrepancy, especially the methane concentration, and the authors suggested using a sophisticated plasma fluid dynamics model for further explanation.

To address the insufficient conversion rate and energy efficiency of low-temperature plasma-enabled direct liquid cracking, Liu et al.²¹⁹ proposed a liquid-phase methane bubble plasma discharge for processing ethylbenzene, a model compound of heavy oil, and conducted detailed plasma kinetics modeling and DFT calculations for the validation of the process and the understanding of the conversion mechanisms. The results confirmed that ·H and ·CH₃ radicals were the main species active in the hydrogenation of ethylbenzene. The spatial distribution of ·H and ·CH₃ in bubbles determined their reaction rates with the ethylbenzene and the reaction direction toward ethylbenzene hydrogenation or free radical recombination. Furthermore, the H density could be well tuned by changing the bubble properties. For example, with selected bubble number and discharge parameters, the H density increased from 1.4×10^{20} to $3.88 \times 10^{21} \text{ m}^{-3}$. Such increase also led to the number of hydrogenated aromatic rings increasing by ~58%, indicating the outstanding performance of the proposed plasma-bubble design in chemical regulation and specifically in heavy oil upgradation.

As shown in Figures 7H,I and 10D, the reaction mechanisms behind the plasma pyrolysis and pretreatment of biomass (cellulose, lignin, or hemicellulose) were studied; DFT is a highly useful approach to understanding the reaction pathways and conversion routes of feedstocks.^{98,140,220,221} Different reactions involving plasma-forming radicals and chemicals are generally considered, compared, and then calculated, with the results in the form of Gibbs free energy, activation energy, enthalpy, or others provided for further evaluation and selection of the most favorable route(s), providing important guidelines for process optimization, reaction engineering, and also catalyst design.

Owing to the complexity of the feedstocks, reactor geometries, and plasma physiochemical properties in

practical uses, reasonable assumptions, simplification, and trade-offs are required for performing modeling, which may compromise the calculation accuracy, and current plasma modeling is still unable to capture the multiscale or multiphase plasma up-carbonization processes. Recently, machine learning (ML), as well as artificial intelligence, has attracted increasing interest as powerful tools for the prediction and optimization of a range of chemical processes, which also showed potential in better understanding plasma-reforming mechanisms.

A three-layered back-propagation artificial neural network (ANN)-based ML has been developed and trained to simulate and predict the complex plasma chemical reactions in the nonoxidative conversion of methane in a DBD reactor, with the discharge power recognized as the most influential factor on the process while the frequency as the least.²²² There is a good agreement between the experimental investigations and predicted data in terms of the CH₄ conversion, product selectivity and yield, and energy efficiency. Using a hybrid ANN and nondominating sorting genetic algorithm II, Tang et al.²²³ conducted a study on the simulation and optimization of a postplasma-catalytic system for toluene degradation. The method provided reliable predictions on the effects of four experimental parameters (discharge power, initial concentration of toluene, flow rate, and relative humidity) on the postplasma toluene removal over MnCoO_x/γ-Al₂O₃ catalysts.

Wang et al.²²⁴ developed a hybrid ML model to predict and optimize a genetic algorithm (GA) plasma tar reforming process using naphthalene as a tar model compound. A linear combination of three well-known algorithms, including ANN, support vector regression, and decision tree, was established to deal with the multiscale and complex plasma tar reforming process. The optimization of the hyperparameters of each algorithm in the hybrid model was achieved by using the GA, which shows a fairly good agreement between the experimental data and the predicted results from the ML model. The steam-to-carbon (S/C) ratio is the most critical parameter for the conversion with a relative importance of 38%, while the discharge power is the most influential parameter in determining the energy efficiency with a relative importance of 58%. The optimal processing parameters were identified, achieving the maximum tar conversion (67.2%), carbon balance (81.7%), and energy efficiency (7.8 g/kWh⁻¹) simultaneously when the global desirability index I_2 reached the highest value of 0.65.

More recently, Chu et al.²²⁵ applied stepwise linear regression (SLR) and ANN methods to develop quantitative models for eight kinds of syngas characteristics and

explored the simultaneous effects of input parameters during the plasma gasification by compiling 112 research cases. The ANN model demonstrates better performance than the SLR model for low heating value (LHV), dry gas ratio, and volume fraction of H₂ and CO, with $R_{\text{testing}}^2 = 0.807\text{--}0.939$. According to the reported results, flow rates of the work gas-N₂, feedstock type, flow rates of the work gas-steam, and input power are the most critical parameters for LHV, gas yield, and volume fraction of CH₄ and H₂, respectively. Input power and specific energy requirements are the most influential factors affecting volume fractions of H₂ (25.7–57.3 vol%) and input power plays a dominant role.

4 | CONCLUSION AND OUTLOOKS

Sustainable production of chemicals, fuels, and materials from carbon-rich, natural-abundant, and renewable precursors are of great importance due to the abundance, renewability, and CO₂-neutrality of raw feedstocks. Gas or in-liquid discharge plasmas convert electric energy to thermal, and, more importantly, chemical energy, providing efficient and fast temperature increases and a mixture of physiochemically reactive species, to drive chemical transformations in carbon-rich feedstocks. Electricity delivered in a promising form of plasma provides a potential alternative to conventional thermal energy for initiating reactions, which enables both large- and small-scale, electrified up-carbonization with potential economic viability, eliminates or reduces the CO₂ emission, and mitigates the environmental footprint. Further, the plasma processing is highly suitable to combine with and be powered by renewable, intermittent energy sources, thus making the whole process more sustainable and cost-effective.

As a state-of-the-art overview of results on plasma-enabled up-carbonization of natural-abundant, low-value, renewable carbon-rich feedstocks, this paper outlines the basic scientific knowledge and technological aspects of this emerging topic, and summarizes typical application examples and the chemistry and mechanisms of plasmas-carbon-feedstocks interactions. Due to the extremely intensified energy density, which enables super heating rates and short feedstock residence time, high reactivity, higher syngas, and light hydrocarbon yields while much lower or even zero tar formation can be obtained by using ThPs-based gasification and pyrolysis. In-liquid discharges, sharing similar basics of plasma electrolytic process, with the electricity or pulsed energy precisely and rapidly delivered to liquid precursors, create an energy-localized, high-reactive

environment for liquid activation and reactions/decomposition initiation to the feedstocks present in the liquids, and enable fast, complete, and external heating-free feedstock upgradation (liquefaction, in particular). The most significant feature of non-ThPs is the feasibility of providing a rich assortment of reactive chemical and physical species under atmospheric pressure with only very limited heat generated. This is perfectly suited for feedstocks pretreatment and modification, enhancing their surface functionality, removing barriers or unwanted substrates, and thus promoting the subsequent processing to get end products with higher values and yields. Moreover, due to the easy availability, diverse discharge and energy types, and facile integration with other processes or catalysis (termed plasma catalysis), discharge plasmas also show great potential to one-pot harvest clean fuels (H_2 , in particular) from processed or pretreated carbon-rich feedstocks or their derivatives, and various high-performance functional carbon-based materials or catalysts, effectively, “killing two birds with a stone.”

Owing to the compact design, wide technical universality, adaptive processing capacity, and low or even zero environmental side effects, the global market of plasma up-carbonization or processing of low-value carbon-rich feedstocks and various solid wastes to high-value chemicals, fuels, and materials is rapidly gaining momentum, with an ever-increasing number of commercial systems for the industrial-scale treatments. Most current successful implementations are based on ThPs, suited for industrial uses and the compatibility of the plasma systems to the current facilities in the factories. More specifically, arc plasmas and DC/RF torches, as well as some MW discharges, are preferable compared to other sources of plasmas due to their processing conditions, tuneable plasma powers and volumes, and high heating efficiencies. Typical technological examples include the first developed and successfully implemented gasification systems by Tetronics, Europlasma, Westinghouse, and several other companies that implement the further process and technology innovations. These advances are at high technology readiness levels (TRL 8: first demonstration of a commercial system and TRL 9: system proven in operational environment) or even industrially tested by companies, such as Advanced Plasma Power, Sunbay Energy Corp., and Enviropark Ltd. More details on the design, manufacturing, and engineering aspects, especially for waste utilization purposes, have been well elaborated and documented elsewhere.^{23,53} A key factor for ThPs-based systems to be economically viable is that the reactors should be upscaled to high processing capacities (multiple tonnes of feedstocks per hour) and continuously sustained with high powers (up to hundreds of kW or even MW). For

plasma gasification, the current highest capacity is 480 (oven-dried) tonnes/day realized by the Solena Group, and by operating several modular units, the throughputs of the plasma gasifier reach over 1000 tonnes/day, comparable to conventional gasification technologies at industrial scales, such as the circulating fluidized bed and bubbling fluidized bed.²²⁶ Plasma pyrolysis (bio)methane for zero-carbon hydrogen production is also a successful pilot-scale demonstration that is close to commercialization. The Monolith Materials runs a plant Olive Creek with plasma methane pyrolysis technique and is able to produce 5000 tons of zero-carbon hydrogen per year, deploying this technology at TRL 9, while the methane thermal pyrolysis and catalytic pyrolysis are still at TRL 3 (proof-of-concept demonstration) or TRL 4 (prototype at lab scale).^{24,227}

Although these demonstrations are successful and encouraging, it should be noted that the industrial-scale plasma-enabled up-carbonization and waste-to-energy or profit facilities are still limited, and plasma is normally regarded as a niche field with plasma-enabled conversion processes normally not being the technology of the first choice.^{16,18} There remain many technological bottlenecks and economical challenges. First, the handling efficacy and efficiency of large volumes (gas, liquid, solid, etc.) using plasmas is always a major concern. For example, for the ThPs, avoiding the existence of cold spots or maximizing the feedstocks' residence in the energy-intensified hot zones for complete conversion is an obvious technological challenge. Also, the corrosion of electrodes and reactors, especially under high temperatures and acid conditions, is normally inevitable and, in many cases, significant, directly leading to higher operational maintenance costs and reduced service lifetime.²³ For the non-ThPs, the processing efficiency and capacity are far from conventional industrial-scale satisfaction. Increasing discharge and/or handling volume generally sacrifices discharge uniformity,^{228,229} resulting in uneven physiochemical reactivity distribution and unsatisfactory reaction selectivity. Second, the lack of reliable and highly controllable power sources, which allow for a high-power input, low energy loss, and sufficient lifetime under different surrounding conditions, is a significant roadblock.¹⁶ Third, many industrial processes and reactions often require a pressurized environment, under which, however, the ignition and sustaining of plasmas, those stable and uniform ones, in particular, are difficult, limiting their applications. Furthermore, very less data is available on the cost estimates and economic analysis, and the results show the inferior performance of plasmas-based conversion. Although, as mentioned above, some successful demonstrations are capable of operating hundreds of tons of dry

feedstocks per day, the related ThPs capital expenditure is high, and the limitations, resulting from power outputs, electrode replacement, and so forth, again lead to a much-increased operating expenditure and shorter lifetime of the installation.^{23,53}

Issues concerning the basic physicochemical mechanisms, economic, and environmental impacts of plasma generation, plasma-feedstock interactions, product analysis, and mechanism studies for further process control and technology transformation still remain and should be carefully and thoroughly resolved in further developing and optimizing plasma-enabled up-carbonization technologies. The production of renewable energy, chemicals, and biofuels must be cost- and performance-competitive with petroleum-derived equivalents to be widely accepted by markets and society.²³⁰ Also, the plasma-based up-carbonization processes must compete with other well-developed and emerging techniques, not only based on technological and conceptual features but also on the product yield, quality, and selectivity, and more importantly, the overall energy efficiency/costs with different processing amounts and the viability of real-life transformation. Further advances in associated studies and technologies are required to make plasma up-carbonization more competitive.

Optimizations from designing more efficient reactors, discovering renewable solvents, introducing suitable catalysts, and improving the selectivity of chemical products are future directions for advancing plasma-enabled up-carbonization technologies. Water is a green and ideal solvent for different feedstock processing, the use of which avoids the costly predrying process and greatly enhances the economic benefits. Seeking suitable and handy plasma-based processes for feedstocks conversion in water is highly promising and awaits further study. Introducing suitable catalysts to further improve the yield and selectivity of chemical products is also of great importance, together with the in-depth insights into the complex physical and chemical processes during plasma-C-feedstocks interactions.

However, understanding both the physical and chemical mechanisms that underlie the plasma discharges and the plasma-feedstocks interactions is significant due to the lack of ideal physical and/or chemical characterization techniques for discharges involving other solid or liquid states complexity of plasma environments and thus-obtained products. The cooperations among different disciplines and strategies on the process and/or product simplification are vital. For example, for lignin depolymerization, to study the reaction mechanisms of plasma for the production of aromatics and organic acids, we can use simple raw materials, such as phenethoxybenzene,

guaiacylglycerol-beta-guaiacyl ester, and other commonly used lignin model compounds.

In addition, value-added products are obtained with solid carbon-feedstock or liquid derivatives being converted and/or depolymerized by discharge plasmas. Yet, to prove the real values of such products, we need to find suitable and ideal applications for them and validate their practicability or further improve their values. It is always a key prerequisite to output performance- and cost-attractive or competitive products, before a technique or process could stand out in practical applications, gain policy support, and industrial investment, and finally be accepted by the market. For example, although the H₂-rich gas can be obtained with competitive energy efficiency from ethanol using plasmas, we should also notice that the hydrogen contents obtained from this method are usually unsatisfactorily low, limiting the practical applications of the H₂. Improving the purity of thus-obtained H₂ also requires knowledge from different disciplines.

Although this paper mainly focuses on plasma up-carbonization of natural renewable carbon sources, it is worth emphasizing that plasma is also highly effective for transforming different low- or negative-value wastes into fine value-added products. Compared to other enabling techniques, the plasma-based waste-to-energy or chemicals is believed to have no adverse effects on the environment, while capable of achieving the high-efficient waste-to-profit purpose.²⁴ Taking plastic waste as an example, more than 400 million metric tons of plastic waste is generated annually, 55% of which ends up in landfills or the ocean, threatening both environment and human beings.²³¹ The increasing number of reports have proven that the plasma gasification and pyrolysis, especially when coupled with selected catalysts, can turn different plastics into hydrogen-rich gas, valuable chemicals such as the plastic monomers and BTX, and functional carbons such as carbon nanotubes, and can be developed as an important technological platform to a circular hydrogen economy.^{232,233}

Overall, the power-to-X conversion based on plasma technologies has proven valuable for carbon-rich feedstocks up-carbonization. However, fundamental studies of chemical and physical processes during the plasma or plasma-catalysis feedstocks up-carbonization are required, and technical advancement in the industrial scale-up, economic and environmental assessments, and engagement with stakeholders, including industry and policymakers, should also be furthered to realize its integration into other modern precursor upgrading processes.

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CONFLICTS OF INTEREST

The authors declare no conflicts of interest.

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