CHAPTER

5

Technological advancements in biofuel, bioproducts, and bioenergy production from fast pyrolysis of lignocellulosic biomass

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5.1 Introduction

Lignocellulosic biomass is a largely abundant, sustainable and renewable resource that holds great potential for production of biofuels, bioproducts and bioenergy on a global scale. It is estimated that over 1 billion dry tons of lignocellulosic biomass is generated annually worldwide from agricultural and forest residues as well as dedicated energy crops (Zadeh et al., 2020). With depleting fossil fuel reserves and growing concerns over climate change impacts of greenhouse gas emissions, transitioning to a bio-based economy utilizing lignocellulosic biomass feedstocks is gaining significant attention worldwide.

Several thermochemical, biochemical and physicochemical routes have been investigated for converting lignocellulose to biofuels and bioproducts. Among these, pyrolysis has emerged as a promising pretreatment technology due to its ability to convert the heterogeneous

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lignocellulosic biomass structure into more energy-dense and homogeneous intermediate products (Fardhyanti, 2022; Makepa et al., 2023a). Pyrolysis involves thermal decomposition of biomass in an inert atmosphere to produce liquid (bio-oil), solid (biochar), and gaseous (syngas) fractions that can serve as fuels, chemicals or additional feedstock for downstream processing. Depending on the heating rate and residence time employed, pyrolysis occurs via three main regimes—slow, intermediate, and fast pyrolysis (Fig. 5.1).

Fast pyrolysis in particular has attracted significant research focus due to its ability to generate high liquid bio-oil yields of around 75 wt. % from the biomass feed (Alvarez et al., 2019). However, the chemical complexity and reactive nature of raw bio-oil poses challenges for its direct utilization as fuel. Thus, efforts have focused on advanced fast pyrolysis technologies coupled with catalytic upgrading of bio-oil and integrated utilization of all pyrolysis products (Makepa et al., 2023b).

Globally, the United States, European Union, Brazil, and China are pioneers in developing commercial fast pyrolysis technologies targeting renewable heat, power and fuels applications from lignocellulosic feedstocks. For instance, the U.S. Department of Energy has set a strategic goal of making cellulosic biofuels cost-competitive with petroleum through targeted research. Several industrial-scale fast pyrolysis (>10 MW) producing renewable heat, power and transportation fuels from woody biomass are operational or under construction across North America and Europe (Oasmaa et al., 2015). In Asia, countries like India, Japan, and South Korea are actively supporting development of

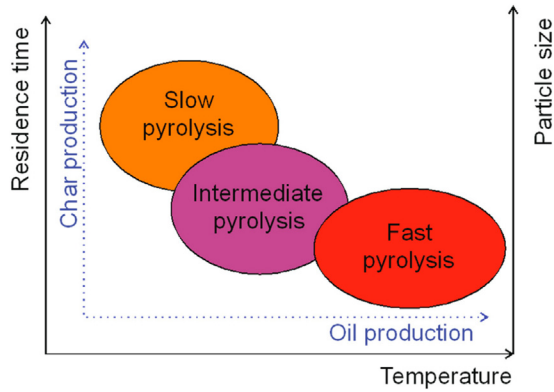

FIGURE 5.1 The three main pyrolysis regimes. *Source: From Slezak, R., Unyay, H., Szufa, S., & Ledakowicz, S. (2023). An Extensive review and comparison of modern biomass reactors torrefaction vs. biomass pyrolizers—Part 2.* Energies, 16(5). https://doi.org/10.3390/en16052212, 02212 g004.

fast pyrolysis technologies to diversify their energy mix and enhance energy security.

This chapter provides a comprehensive review of the latest technological advancements in fast pyrolysis of lignocellulosic biomass followed by upgrading of bio-oil and utilization of all pyrolysis products into fuels, chemicals and energy on both lab and commercial scales. Key developments in fast pyrolysis technologies, catalytic bio-oil upgrading techniques, process integration strategies, and the current prospects and challenges will be discussed based on an extensive evaluation of published literature. The global perspectives and significance of these emerging bio-refinery concepts are also highlighted.

5.2 Biomass pyrolysis

Biomass pyrolysis is a thermochemical degradation process that can occur in the presence or absence of oxidizing agents, as illustrated in Fig. 5.2. It primarily consists of two stages. In the initial primary pyrolysis stage, biomass is heated to induce the evolution of volatile compounds at lower temperatures. This is followed by secondary pyrolysis reactions involving further cracking of volatiles into smaller molecules and the charring of solid residues at higher temperatures (Liu et al., 2023).

The principal products generated through pyrolysis are gas, liquid, and solid fractions. The gas consists mainly of syngas components like carbon monoxide, carbon dioxide, hydrogen, and methane. Other gaseous byproducts include water vapor. The liquid fraction is commonly

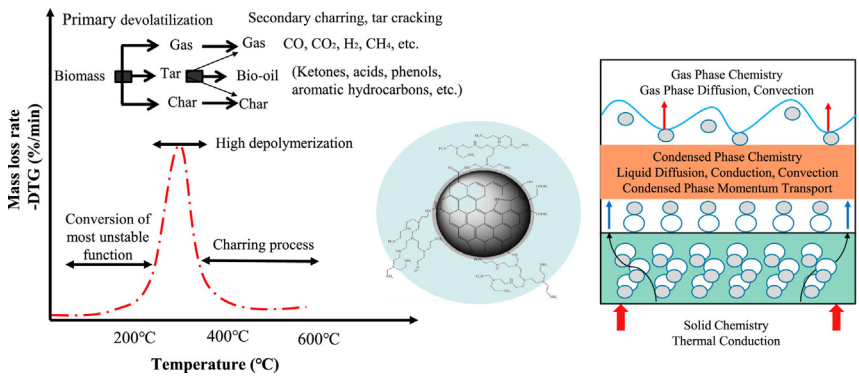

FIGURE 5.2 Stages of biomass pyrolysis. *Source: From L., Juping, C., Xu, C., Wei, X., Mingwei, C., Yingquan, C., Hanping, Z., Kuo, & Yang, H. (2023). Biomass pyrolysis mechanism for carbon-based high-value products.* Proceedings of the Combustion Institute, 39*(3), 3157–3181. https://doi.org/10.1016/j.proci.2022.09.063, https://ars.els-cdn.com/content/image/1-s2.0-S1540748922004722-f05-01-9780443292545_lrg.jpg.*

known as bio-oil or pyrolysis oil (Makepa et al., 2023a). Solids remaining after volatilization are termed char.

The underlying processes occurring during biomass pyrolysis are highly complex, as they entail numerous chemical reactions and transformation pathways. Over a hundred individual compounds may form as biomass decomposes into its pyrolytic byproducts (Yogalakshmi, 2022). Within a pyrolysis reactor system, these reactions take place in multiphase conditions involving solid-phase chemistry on char/biomass surfaces, liquid diffusion through evolving bio-oil, gas-phase molecular interactions, and coupled heat and mass transfer throughout. Effective reactor design requires an integrated understanding of these interlinked pyrolytic transformations and transport phenomena (Brennan Pecha et al., 2019).

Several process parameters play a critical role in influencing the product yields and characteristics obtained through biomass pyrolysis. These include the temperature, pressure, and heating rate of the reaction system (Mutsengerere et al., 2019).

Pyrolysis can be classified into different categories based on the temperature, heating rate applied, and target product fractions favored. Slow pyrolysis occurs at relatively low heating rates of 0.1°C−2°C/s and is characterized by long residence times and temperatures below 400°C (Makepa et al., 2023a). This process, also called carbonization, typically produces around 50% solid char and is commonly used for charcoal manufacturing.

Fast pyrolysis utilizes higher heating rates of 10°C−200°C/s and medium temperatures in the 500°C−600°C range. It features reduced residence times under 2 s and yields 50%−70% bio-oil. Flash pyrolysis applies an even faster heating rate of 103°C−104°C/s and extremely short residence times less than 0.5 s, capable of attaining high bio-oil yields of 75%−80% (Makepa et al., 2023a). Both fast and flash pyrolysis methods aim to optimize liquid bio-oil production.

For maximum gas generation, higher temperatures from 800°C to 1000°C are preferred. Regarding integrated multiproduct systems, the optimum condition reported is 600°C−900°C using a relatively slow heating rate of 10°C/min, which balances yields of combustible gas, bio-oil, and solid char (Tokmurzin et al., 2022). The pyrolysis classification depends on adjusting process variables to control residence times and temperatures for prioritizing the favored product fraction between gases, bio-oil, and char.

5.3 Properties of pyrolysis products

5.3.1 Bio-oil

Bio-oil is a dark brown, free-flowing liquid with a smoky odor. It has high viscosity, thermal instability, acidity, and is corrosive

(Makepa et al., 2023a). Bio-oil shares some characteristics with petroleum but contains oxygen in the form of hydroxyl and carboxyl groups (Michailof et al., 2016). It has potential applications as fuel for turbines, boilers, and engines, or as a feedstock for production of chemicals and transport fuels via upgrading methods. These include catalytic hydrodeoxygenation (HDO), emulsification with diesel, and steam reforming.

Compositionally, bio-oil consists of water and organic compounds separated into an oil phase and aqueous phase. The aqueous phase contains organic acids, alcohols, and ketones while the oil phase comprises phenols, aldehydes, sugars, and other oxygenates. Over 200 individual compounds may be present. Bio-oil composition depends strongly on feedstock characteristics and pyrolysis conditions used (Staš et al., 2017).

Key physicochemical properties include: carbon (10–75 wt.%), oxygen (15–70 wt.%), hydrogen (6–9 wt.%), nitrogen (0.2–0.8 wt.%), sulfur (0.01–0.10 wt.%), density (0.86–1.26 g/cm^3), viscosity (2–116 cSt), pH (2–4.5), higher heating value (5–40 MJ/kg), water content (11–40 wt.%), and ash (0.02–6.5 wt.%) (Toscano Miranda et al., 2021). Characterization methods like NMR, GC–MS, and thermal analysis help determine structure and composition.

Due to undesirable properties, upgrading is usually required before fuel use. Methods address issues like water content (distillation, dehydration), oxygen content (HDO, hydrogenation), and thermal stability. HDO produces hydrocarbons at high pressures and complex equipment while hydrogenation is inexpensive but generates coke and low quality fuels (Toscano Miranda et al., 2021). Other emerging techniques include catalytic cracking (Lahijani et al., 2022), emulsification (Farooq et al., 2020), and transesterification (Makepa et al., 2023b). Pyrolysis converts waste biomass into a complex bio-oil that has fuel potential upgraded, though properties depend strongly on feedstock and process conditions used.

5.3.2 Biochar

Biochar, also called char or charcoal, is a solid product generated through pyrolysis of biomass. Slow pyrolysis typically yields the highest amounts of biochar, while fast pyrolysis produces the lowest. Biochar is primarily composed of carbon (65%–90%) along with oxygenated functional groups and aromatic compounds (Tan et al., 2021). This chemical composition makes it highly resistant to biological degradation. Potential applications of biochar include use as a natural soil amendment to improve fertility as well as a solid fuel source for process heat generation. It can also be activated into an adsorbent for gas/liquid treatment or utilized in chemical/pharmaceutical industries due to properties like low sulfur and phosphorus content (Miranda et al., 2023).

Char production predominantly occurs between 250°C and 600°C via exothermic and endothermic reactions. This includes biomass dehydration, thermal decomposition of sugars at low temperatures, removal of volatile matter through volatilization, and char oxidation. Feedstocks higher in fixed carbon and ash tend to yield more char (Das et al., 2021). In addition, characteristics vary depending on the biomass type due to differences in physicochemical properties. Biochar is a carbon-rich coproduct of pyrolysis with diverse application potentials, though its formation is influenced by operating conditions and biomass composition.

The physicochemical properties of biochar produced from lignocellulosic biomass pyrolysis has been studies extensively. Biochar from lignocellulosic biomass contain 68%–85% carbon and show high heating values ranging from 23 to 29 MJ/kg. Oxygen content varies between 10% and 28% while nitrogen levels are low at 0.5%–1.3%. Proximate analyses indicate volatile matter levels of 15%–57% and fixed carbon of 36%–85%. Biochar ash content is moderate at 3.6%–22.7% (Miranda et al., 2023; Toscano Miranda et al., 2021). Moisture content is reported between 1.98% and 7.7% in some studies (Carrier et al., 2012; Parthasarathy & Narayanan, 2015). Pyrolysis conditions influence biochar properties, with higher temperature/lower heating rate processes yielding biochar higher in carbon and heating value as well as lower in volatile matter, oxygen, and ash content. Lignocellulosic biomass is demonstrated to be a suitable feedstock for producing biochar with characteristics that could make it useful for various applications.

5.3.3 Gas

In addition to bio-oil and biochar, pyrolysis also produces noncondensable gases. Gas yield is typically the lowest of the three products. Gases consist of components that do not condense into bio-oil, such as hydrogen, methane, carbon dioxide, carbon monoxide, and light hydrocarbons (C1–C5) (Shumeiko et al., 2021). Heating values range from 6 to 10 MJ/kg (Miranda et al., 2023).

Secondary pyrolysis mainly forms gases through steam reforming reactions that break down oxygenated compounds into smaller molecules. Gas composition depends on the biomass components and their decomposition pathways. For example, sugarcane bagasse, carbon dioxide is the dominant gas due to decarboxylation of carboxyl/acetic groups and cellulose rings (Miranda et al., 2023). Carbon monoxide is produced through cracking of carbonyl/carboxyl groups in cellulose and lignin. Hydrogen and methane result from breaking aromatic rings and methoxyl groups in lignin, primarily in secondary pyrolysis (Lu & Gu, 2022).

In-situ gasification and steam reforming can further increase hydrogen and carbon monoxide yields. Analytical tools such as gas chromatography

with thermal conductivity or mass spectrometry detectors can identify and quantify individual gas species and monitor gas streams online. Pyrolysis gases provide useful energy sources but represent the smallest product fraction versus bio-oil and biochar. Their makeup links closely to the biomass composition.

5.4 Advances in bio-oil upgrading techniques

5.4.1 Catalytic pyrolysis

Catalytic pyrolysis involves adding catalysts directly to the pyrolysis reactor to promote specific cracking and reforming reactions, generating improved bio-oil quality during initial production (Abou Rjeily et al., 2021). Early works used zeolites (Liang et al., 2021), metal oxides (Zhang et al., 2019) and other solid acids but faced challenges with coke formation (Ochoa et al., 2020). Recent advances involved custom designing catalyst formulations for optimal pore size/acid strength to minimize coking while enhancing aromatics/olefins yields (Ahmad et al., 2021). Researchers are developing novel catalyst architectures with hierarchical pore networks to enhance mass transfer properties and increase structural stability. Conventional catalysts possess uniform microporosity, limiting both internal diffusion, and heat dissipation. Newly designed hierarchical catalysts integrate micropores with additional mesoporosity to overcome these limitations. The bimodal pore structure provides dual benefits (Tian et al., 2020). Finer micropores (<2 nm) maintain high surface area for reactive sites. Larger mesopores (2−50 nm) then facilitate intracrystalline transport of reactants, products, and heat through interconnected channels. This hierarchical design mitigates potential internal diffusion restrictions compared to microporous analogs (Weissenberger et al., 2021). Moreover, the introduction of mesopores generates a more robust framework owing to reduced walls thicknesses and improved defect accommodation. The stabilized structure exhibits greater mechanical strength and thermal shock resistance and is consequently more refractory to degradation under reactive conditions.

Shape-selective cracking of volatiles into target fractions is achievable through micro/mesoporous materials due to their inherent control over mass transport and reaction pathways. Contemporary catalyst designs, encompassing mixed oxides, metallocenes, and carbides/nitrides, unlock novel C−O/C−C transformation routes by leveraging their unique structural and electronic properties. Furthermore, the incorporation of bifunctional facets, integrating both acid, and base catalytic sites, enables streamlined multistep reactions within a single catalytic framework (Aralekallu et al., 2024).

Advanced characterization techniques, including transmission electron microscopy/scanning electron microscopy for nanoscale imaging, X-ray photoelectron spectroscopy/Fourier-transform infrared spectroscopy for surface analysis, and spectroscopic methods, contributed to fundamental insights into catalyst deactivation/regeneration mechanisms, enabling the rational design of robust catalyst formulations. This structure−performance correlation facilitated the targeted improvement of catalyst performance.

Continuous catalytic pyrolysis with integrated product separation was demonstrated as a promising approach for online bio-oil upgrading (Yung et al., 2023). This approach combined pyrolysis and separation in a single unit, enhancing efficiency and product quality. Specifically, reactive distillation intensified desired reactions through selective condensation, while membrane separation facilitated the identification of optimal operating windows for efficient product recovery (Barrientos et al., 2023). Process modeling and simulation supported the scale-up of the technology (Fakhroleslam & Sadrameli, 2019), while techno-economic analysis identified key areas for cost reduction (Makepa et al., 2023c). Further integration with downstream hydroprocessing enabled the production of fungible fuels with reduced oxygen content, enhancing economic viability.

5.4.2 Hydroprocessing

Hydroprocessing involves using hydrogen gas at elevated temperatures and pressures in the presence of a catalyst to remove oxygen, stabilize and upgrade bio-oil (Zacher et al., 2019). Early studies utilized batch reactors and conventional hydrotreating catalysts to reduce oxygen by HDO (Zacher et al., 2019). However, bio-oil's complexity posed challenges like catalyst deactivation. Advances in continuous-flow reactor design improved contact between gaseous hydrogen and liquid bio-oil (Oh et al., 2020). Tubular and fixed-bed reactors operating in the 300°C−450°C, 150−350 bar range can accelerate HDO kinetics (Asiedu & Kumar, 2019). Introducing recycle loops can also help increase hydrogen partial pressure. New catalytic formulations enhanced stability against coking, decarbonylation, and cracking reactions.

Specialized catalysts utilizing additional functionalization beyond hydrotreating showed promise for selective upgrading. Supported metal carbide, boride and nitride catalysts facilitated C−O cleavage and C=C hydrogenation. Bifunctional catalysts combined acid/base and hydrogenation sites to guide reaction pathways. Microreactor technology provided precise control over short residence times (<5 s). Uniform heating/mixing optimized selectivity toward fuels over light gases.

Membrane reactors integrated hydrogen delivery directly into the reaction zones (Wunsch et al., 2018).

Online product analysis using GC × GC−Ms, GC−TOF−MS, and 2D-NMR allowed rapid catalyst screening and reaction pathway elucidation. Offline analysis using pyrolysis-GC/MS linked catalyst performance to changes in chemical composition. Process modeling and simulation aided reactor and catalyst design (Elnashaie & Elshishini, 2022). Techno-economic analyses indicated some configurations were economical compared to conventional refining or pyrolysis alone. Intensified separation via extractive units, membranes or reactive distillation reduced cost of product purification (Errico et al., 2020). Progress in integrated hydroprocessing-upgrading systems brought the technology closer to full industrial deployment for stable, fungible biofuels and chemicals production from biomass.

5.4.3 Supercritical fluids

Supercritical fluids such as water have properties that make them well suited for upgrading pyrolysis bio-oil. Their unique balance of solvent power like dissolution capabilities combined with their low viscosity at supercritical conditions enables many of the desired reactions to take place for upgrading bio-oil (Rashid et al., 2021). Early research focused on using supercritical water for complete homogenization and upgrading of bio-oil (Fardhyanti, 2022) however challenges remained around corrosion of equipment from the harsh conditions and difficulty separating upgraded products.

More recent approaches have focused on using subcritical water or water mixed with cosolvents which operate at milder conditions and have shown potential for selectively upgrading specific problematic compounds in bio-oil such as acids, aldehydes, ketones, and sugars (Yadav et al., 2021). Continuous-flow reactor designs that allow precise control over temperature, pressure and residence time through the use of tubular and fixed-bed reactors coupled with integrated heat exchanger sections have enabled optimization of reaction conditions for supercritical upgrading (Asiedu & Kumar, 2019).

The application of microreactor technology for supercritical upgrading reactions has provided benefits such as rapid and uniform heating within the system improving kinetic control and selectivity for reactions. Adding catalysts such as transition metal sulfides, metal oxides and zeolites provides both thermal and catalytic effects aiding important reactions like deoxygenation, decarboxylation/decarbonylation, and cracking that reduce the oxygen content and upgrade bio-oil (Zhao et al., 2023).

The use of cosolvents in conjunction with supercritical water has also shown promise for tuning solvent properties to better solubilize both reactants and products to improve upgrading efficiency. Alcohols, ethers, ketones, and glycols have all been studied as potential cosolvent additives (Shahbeik et al., 2024). Advanced analytical techniques such as comprehensive two-dimensional gas chromatography, Fourier-transform ion cyclotron resonance mass spectrometry and nuclear magnetic resonance spectroscopy give deeper insight into reaction pathways and products distributions from supercritical upgrading. Life cycle and techno-economic analyses help evaluate the feasibility and optimization of different supercritical upgrading systems at various scales of operation (Zheng et al., 2023). Ongoing research aims to further improve catalytic performance, develop continuous process integration, reduce capital, and operating costs as well as couple supercritical upgrading with fractionation steps to produce targeted fuels and chemicals.

5.4.4 Esterification

Esterification involves reacting organic acids in bio-oil with alcohols to form esters, reducing acidity and corrosion potential. Early works employed batch reactors with homogeneous acid catalysts like H_2SO_4 (Mei et al., 2020). However, product separation was challenging and corrosivity remained high. Advances utilized heterogeneous catalysts like ion-exchange resins, acidic inorganic oxides and solid acid catalysts in continuous-flow fixed/fluidized bed reactors (Rezayan et al., 2023). This facilitates easy catalyst recovery and reuse. Intensified mixing and controlled residence times accelerated esterification kinetics while limiting side reactions. Novel ordered mesoporous catalysts with tunable acidity/functionality achieved high conversion with minimal coking/leaching. Bifunctional catalysts integrated acid/base sites for one-pot esterification/transesterification with simultaneous alcohol upgrading (Mulyatun et al., 2022). Microchannel reactors utilized millisecond contact times for shape-selective esterification (Boffito & Fernandez Rivas, 2020). Membrane reactors coupled separation with reaction, driving equilibrium. Reactive distillation directly removed esters, facilitating pseudo-homogeneous esterification.

Advanced analysis using 2D-NMR, HPLC, IR, and mass spectrometry unlocked reaction mechanisms and byproduct formations, aiding catalyst optimization. Online product analysis linked performance to composition changes. Process modeling aided design of optimal reactor configurations. Techno-economic studies identified priority areas for cost reductions in separation/purification. Integration with downstream treatments further upgraded bio-oil quality/stability. Collectively, these

intensified process and material developments have greatly enhanced the catalytic activity, selectivity, and feasibility of esterification as a bio-oil upgrading strategy (Mei et al., 2020).

5.4.5 Molecular distillation

Molecular distillation utilizes low pressures and temperatures just above the boiling points of substances to fractionate bio-oil based on molecular weights (Chan et al., 2020). Early systems used simple batch distillation columns but lacked process control and yielded inconsistent fractions. Advances incorporated continuous short-path distillation units with intricate internal designs like falling/wiped film configurations (Sagili, 2023). Mechanical wiped film molecular distillation systems offer rapid heat transfer and enhanced separation efficiency of thermolabile compounds. Controlled thermal/pressure profiles carefully separate heavy oligomeric fractions without further decomposition. Intelligent automation precisely regulates intricate process parameters like vacuum levels, reflux ratios, and stripper conditions using online feedback loops (Sagili, 2023).

Advanced materials selection addressed corrosion challenges—sophisticated alloys and inert coatings withstand acidic/aqueous pyrolysis vapors under vacuum. Specialized designs integrate membrane separators for azeotropic/hybrid distillation (Zhong et al., 2023). Advanced online analytical systems like mass spectrometers, densitometers and refractometers allow real-time optimization of molecular weight cut-off points and end-points. Offline NMR/Ms profiling tracks molecular changes. Process modeling and hybrid simulation techniques aid complex molecular distillation design/scale-up decisions by predicting separation sequences, energy requirements, and equipment sizing (Idárraga-Vélez et al., 2023). Integrated molecular distillation with product fraction stabilization (esterification, hydrotreating etc.) boosts yields of stable biofuels/chemicals by careful selection and upgrading of individual molecular cuts obtained (Julie Chandra et al., 2023). Collectively these process intensification efforts have propelled molecular distillation toward industrial viability for high-value bio-oil fractionation refineries.

5.4.6 Electrochemical or electrocatalytic upgrading of bio-oil

Early electrochemical upgrading research focused on using undivided electrolytic cells with bio-oil as the electrolyte and inert electrodes (Li et al., 2012). However, this lacked selectivity and produced complex product mixtures. Advances incorporated divided flow cells with improved mass transfer and dimensionally stable anodes. Novel electrode materials like carbon-based, metal oxide, and metal catalysts were

developed for selective reactions like dehydrogenation, deoxygenation and decarboxylation. Carbon-based electrodes enabled shape-selective cracking of heavy compounds to lighter fractions through controlled surface flaws and pore sizes. Metal/metal oxide catalysts facilitated targeted C−O/C−C bond cleavage. Bifunctional electrodes combining metal/metal oxide catalyst sites with carbon support achieved one-pot upgrading via complementary HDO and electrocatalytic reactions (Page et al., 2023).

Membrane electrode assemblies integrated proton exchange membranes for intensified upgrading within an electrochemical double layer (Mirshekari et al., 2021). Microfluidic cells optimized mass transport at micro/nanoscales for kinetic selectivity. Solar/wind-coupled designs explored renewable energy integration. Online product analysis via GC−MS, NMR, and electroanalytical methods provided reaction optimization. Computational modeling aided catalyst design. Techno-economic analysis identified economically feasible designs like flow-through packed bed reactors for industrial viability. Process integration with downstream stabilization enhanced product yields (Trevisan et al., 2021). Rational electrode/cell designs coupled with intensified processing provide clean electrochemical route for upgrading bio-oil to fuels/chemicals.

5.5 Advancements in the utilization of bio-oil

Significant progress has been made in utilizing bio-oil produced from fast pyrolysis in various applications (Fig. 5.3). In biofuels production, improved processing techniques such as catalytic upgrading, esterification and HDO have enabled higher blending levels of bio-oil in petroleum-derived fuels with less corrosion and stability issues (Valle et al., 2019). Advancements in catalytic cracking and coprocessing with vacuum gas oil have also paved the way for bio-oil utilization in conventional oil refineries. Meanwhile, targeted bio-lubricant production via selective esterification of fatty acid fractions is being commercialized (Barbera et al., 2022). There have also been strides in producing valuable biochemicals like aromatics and phenolics by optimizing catalytic pyrolysis conditions. Enhancements in bio-oil stabilization and fractionation methods coupled with downstream intensification are expanding the potential of bio-oil as a source of renewable fuels, lubricants and chemicals.

5.5.1 Biofuels production

Bio-oil, a complex mixture of organic liquids derived from biomass pyrolysis, holds immense potential as a renewable feedstock for biofuels. However, its direct use in existing infrastructure is hindered by several

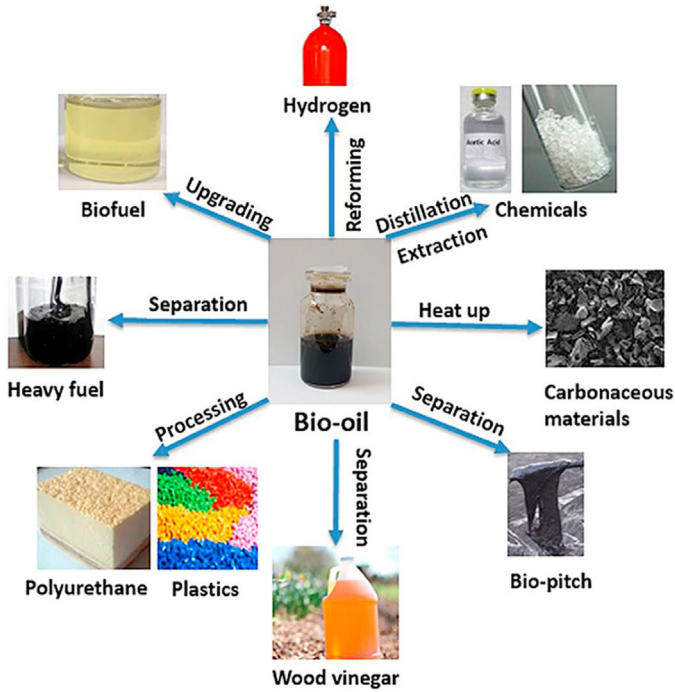

FIGURE 5.3 Utilization of bio-oil in various applications. *Source: From Hu, X., & Gholizadeh, M. (2020). Progress of the applications of bio-oil.* Renewable and Sustainable Energy Reviews, 134. *https://doi.org/10.1016/j.rser.2020.110124*, *https://ars.els-cdn.com/content/image/1-s2.0-S1364032120304159-fx1_lrg.jpg*.

limitations, including high oxygen content, instability, and immiscibility with conventional fuels (Makepa et al., 2023b). Recent advancements in pretreatment and upgrading technologies are tackling these challenges, paving the way for a more efficient and sustainable biofuel production process.

5.5.1.1 Pretreatment

Pretreatment of bio-oil is important to address properties like high oxygen content, water content, and acidity prior to downstream processing (Kumar et al., 2020). Careful control of moisture levels through various dehydration techniques can optimize downstream conversions. Hydration techniques under investigation aim to either remove excess water or tailor water concentrations. Promising options showing technical success include microwave-assisted drying and membrane filtration systems. Microwave irradiation directly heats water molecules for faster drying kinetics (Rattanadecho & Makul, 2016). Membranes with specialized pore sizes allow selective phase separation.

Catalytic deoxygenation focuses on reducing the oxygenated functional groups through targeted reactions. HDO over heterogeneous catalysts facilitates cleavage of C-O bonds via hydrogenation pathways (Shi, 2019). Active areas of research involve engineering supported noble and transition metal nanoparticle catalysts with optimized acid-base properties and metal-support interactions for high activity and stability.

Decarboxylation is another pathway pursued for low-cost oxygen removal (Pattanaik & Misra, 2017). Acid catalysts such as zeolites promote selective carboxylic acid decarboxylation. Supercritical fluids present a non-catalytic route leveraging solvent effects to facilitate decarboxylation through ionic intermediates under carefully controlled subcritical conditions (Rashid et al., 2021). Computational modeling aids reaction mechanistic understanding. Collectively, optimized pretreatment schemes address deleterious oxygen functionality through customized catalytic and non-catalytic routes to yield bio-oil intermediates better compatible with existing fuel infrastructure.

5.5.1.2 *Upgrading reactors*

One of the key focus areas in upgrading bio-oil is the development of efficient reactor systems. For catalytic upgrading of bio-oil into hydrocarbon-like fuels, various heterogeneous catalysts have been investigated in fixed-bed, slurry, and moving-bed reactor designs. These promote upgrading reactions like cracking, isomerization, and alkylation to modify molecular structures. Zeolite catalysts, supported metal oxides, and multifunctional nanoparticle formulations are being tailored for specific reaction pathways through parameters like acid-base properties, pore size, and metal dispersions (Zhang & Medlin, 2018). Another important reactor application involves esterification of bio-oil with an alcohol like methanol to produce biodiesel. Areas of improvement include developing solid acid catalysts as more sustainable alternatives to conventional mineral acids in batch and continuous reactors. Enzymatic reactors also show potential via selective esterification routes. Furthermore, reactive distillation offers an intensified process where reactions and separations are coupled within distillation columns. Novel structured and divided wall column designs along with in-column catalytic packs are optimizing this hybrid process for efficient bio-oil fractionation and simultaneous upgrading. Continued research on reactor engineering and catalyst design will be pivotal for techno-economically viable bio-oil upgrading on an industrial scale.

5.5.1.3 *Separation/Fractionation*

Separation and fractionation of upgraded bio-oil components into valuable products is important. Advanced distillation remains a core technology, with recent improvements in column internals and structured

packings enhancing mass transfer for more effective separations based on boiling point differences under tailored vacuum conditions (Kiss, 2013). Membrane separation offers energy efficient alternatives through selective permeability barriers. Membrane modules with specific pore sizes or surface chemistries facilitate separations driven by pressure or concentration gradients. This area remains an active area of study as membranes capable of withstanding the chemical environment of upgraded bio-oil streams are developed.

Solvent extraction is another useful technique, where target analytes preferentially partition between a bio-oil and immiscible solvent phase. Rational solvent selection based on solubility parameters can highly purify recovered products. Recent innovations involve reactive extraction combining chemical transformations within single extraction-reaction-separation units (Nutrizio et al., 2022).

Combined fractionation schemes coupling two or more technologies also show promise. For example, distillation followed by solvent extraction or membrane separation provides multidimensional purification. Process modeling and life cycle analysis aid optimization. Advanced separation options address the heterogeneous, reactive nature of bio-oil intermediates to provide high-value fractions for fuels or other biomaterial conversion platforms.

5.5.1.4 Refinery processing

One strategy pursued is coprocessing bio-oil components with conventional petroleum refinery inputs. Liquid fractions upgraded from bio-oil through stabilization and fractionation can be directly blended with conventional feeds like vacuum gas oil (Chan et al., 2020). This allows for synergy between existing refinery processes and renewable inputs, facilitating drop-in biofuel compatibility.

Pilot tests have demonstrated that coprocessing selected bio-oil fractions results in fuel blendstocks with properties suitable for existing refinery hydrotreating units. Hydrotreating employs hydrogen gas in the presence of conventional solid catalyst formulations at elevated pressures and temperatures (Zacher et al., 2019). This final refining step efficiently removes oxygen, nitrogen, sulfur, and other impurities from coprocessed feeds through hydrocracking and hydrodesulfurization reactions.

Continuous research optimizes bio-oil fraction composition and catalyst design. Online analyzers coupled to demo units provide compositional data to guide fraction selection and hydrotreating conditions ensuring output fuels meet regulatory product specifications. Techno-economic modeling aids commercial assessment of coprocessing into existing refinery infrastructure networks. Coprocessing and hydrotreating represent promising routes for cost-effectively producing drop-in renewable fuels utilizing current refinery assets and logistics.

5.5.2 Biolubricants production

Pyrolysis oil, comprised primarily of oxygenated organic compounds, has attracted research interest as a potential renewable substitute for fossil-based fuels and chemicals (Makepa et al., 2023b). While initial work explored direct utilization of this oxygenate-rich bio-crude, the chemical complexity, and reactivity of its constituent compounds necessitated upgrading treatments. More recent investigations now demonstrate the promise of harnessing pyrolysis oil derivatives toward lubricating applications as well. Through appropriately designed catalytic treatments and separation protocols, targeted fractions rich in high molecular weight esters, fatty acids, and neutral lipids can be isolated with stability and physical properties approaching industrial lubricant specifications. For example, esterification of carboxylic acids leveraging solid acid catalysts produces methyl esters exhibiting enhanced oxidative stability relative to native pyrolysis oil (Mei et al., 2020). Multistep fractionation schemes combining distillation, solvent extraction and membrane separations can further enrich specific components aligned with lubrication performance benchmarks. Continued exploration of optimized catalytic pathways and intensified product purification holds potential to yield pyrolysis oil-derived lubricant bases capable of partial or full substitution of petroleum-derived lubricants. This presents new opportunities for higher added value realization from biomass pyrolysis while establishing economically viable routes for securing sustainable lubricant supply to satisfy growing demand.

Esterification plays an important role in transforming bio-oil into a lubricant base stock (Mei et al., 2020). During this reaction, fatty acids present in bio-oil are transformed into esters through the addition of an alcohol such as methanol. Esters are highly desirable for lubricant applications as their molecular structure provides excellent lubricating properties. Esterification essentially takes the bulky, oxygen-rich fatty acid molecules, and streamlines them into more lightweight esters that can readily flow and reduce friction between moving surfaces (Hu, 2019).

Catalytic upgrading utilizes specialized catalysts to enhance bio-oil refining by selectively guiding reactions like removing unwanted oxygen and sulfur. Think of these tailor-made catalysts as tiny molecular assistants, expertly escorting bio-oil molecules through different conversions that purify and stabilize the composition. Their precise guidance helps transform bio-oil into a cleaner burning formulation with improved thermal properties suitable for engines.

Hydrotreating builds upon esterification and catalytic upgrading by further purifying the bio-oil blend through the addition of hydrogen. Taking place over complex catalyst formulations, hydrotreating tweaks and tunes the bio-oil composition by stripping away residual impurities

to precisely match viscosity targets and other performance traits needed for smooth, efficient lubrication of engines, and machinery. It provides the final polish to bio-oil derived lubricants, akin to fine-tuning an engine for optimal performance (Zacher et al., 2019).

5.5.3 Biochemicals production

Recent advancements have demonstrated pyrolysis oil to be a far more versatile intermediate capable of serving as a platform for multiple bio-based commodity chemicals. Through appropriately designed catalytic upgrading and separation protocols, various high-value molecules can be selectively targeted from the complex mixture of oxygenated hydrocarbons comprising pyrolysis oil. These include aromatic compounds such as phenols and furfurals suitable for polymeric materials, aliphatic intermediates compatible with green solvent formulations, and carboxylic acids amenable to biomanufacturing routes (Berg & Guzmn, 2023). When integrated with catalytic transformations and process intensification techniques, this diverse array of oxygenate functionality embedded within pyrolysis oil has the potential to displace petrochemicals across a multitude of applications. The ability to produce an assortment of vital bulk and specialty chemicals through biomass pyrolysis oil intermediaries holds broad implications for transitioning to a bio-based economy. Ongoing research optimizing catalytic pathways and separation protocols will be instrumental to bringing this vision to commercial fruition on an industrial scale. These developments signal pyrolysis oil is far more than just a biofuel—it can function as a widely versatile carbon platform to enable sustainable chemical manufacturing.

Catalytic upgrading plays a vital role in transforming bio-oil's composition. Specialized catalysts act as molecular matchmakers, selectively facilitating reactions to convert bio-oil's myriad oxygenated molecules into targeted high-value building blocks. Like deft chemical engineers, these nanoscale catalysts efficiently guide reactions to churn out customized intermediaries tailored for downstream processing (Ahmad et al., 2021).

An arsenal of separation techniques then meticulously sorts through these transformed bio-oil streams. Advanced distillation columns and membranes act as sophisticated filters, fractionating components by physical properties to ensure pure streams of molecules (Kiss, 2013). Chromatographic methods further refine separations, almost surgically extracting precise constituents. Through separation, bio-oil's complex molecules are splendidly refined into sorted supplies of specialized building blocks.

Microbial fermentation then introduces nature's own alchemists—microbes worked with by scientists to synthesize new materials.

When provided bio-oil intermediates as a carbon source, microbes diligently metabolize specific components, transforming them into high-value biochemicals through metabolic pathways (Rangabhashiyam et al., 2022). Under carefully controlled conditions, these microscopic factories churn out customized organic molecules with astounding precision. Together, catalytic upgrading, separation science, and fermentation open new possibilities for sustainably crafting chemicals, unlocking keys from bio-oil's treasured locks through man and nature's cleverest technologies.

5.6 Advancements in the utilization of biochar

Biochar has a wide range of uses beyond soil amendment due to its carbon-rich porous structure and associated chemical and physical properties. Significant research is exploring applications of biochar in various technological fields such as catalysis, bioenergy production, adsorption, and energy storage (Fig. 5.4). This section discusses some of the most promising new and developing utilization pathways for biochar, focusing on its roles in biofuel and bioproduct synthesis, power generation through combustion and gasification, production of activated carbon, and integration with technologies like fuel cells, anaerobic digestion and electrochemical energy storage systems. Harnessing biochar's beneficial characteristics in these application areas holds potential to enhance process efficiencies, lower costs, and promote more sustainable product and energy solutions from renewable lignocellulosic feedstocks.

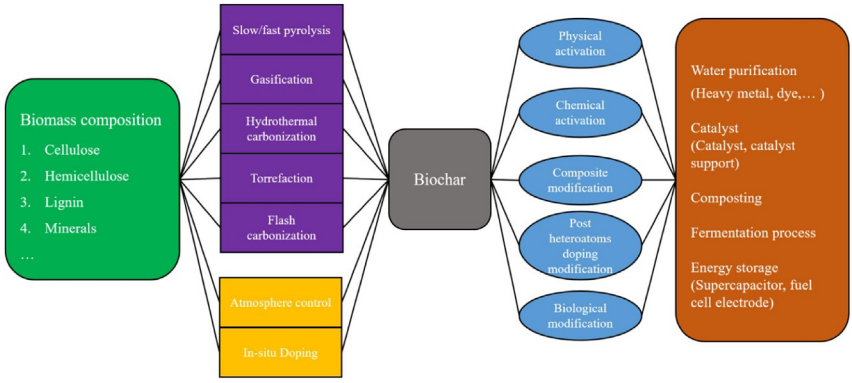

FIGURE 5.4 Production and application pathways for biochar. *Source: From L., Yunchao, X., Bo, D., Yan, H., Xinhong, & Wang, S. (2020). A critical review of the production and advanced utilization of biochar via selective pyrolysis of lignocellulosic biomass.* Bioresource Technology, 312. *https://doi.org/10.1016/j.biortech.2020.123614, https://ars.els-cdn.com/content/image/1-s2.0-S0960852420308865-f05-01-9780443292545_lrg.jpg*.

5.6.1 As catalysts in biofuel production

Biochar has shown promise as an effective and sustainable catalyst for various biofuel production processes. One area that has seen progress is using biochar to accelerate reactions involved in producing biodiesel. Biodiesel is produced through a process called transesterification, where triglycerides such as vegetable oils or animal fats react with methanol to form fatty acid methyl esters (biodiesel) and glycerol. Biochar has been explored as a heterogeneous catalyst for this transesterification reaction (Niju et al., 2023).

Research has found that biochar produced from various feedstocks like wood, agricultural waste and animal manure can effectively catalyze the transesterification of triglycerides with methanol. The porous carbon structure and functional groups on the biochar surface provide sites that can adsorb reactants and lower the activation energy of the reaction (Yang et al., 2020). Studies have shown biochar catalysts can achieve biodiesel yields comparable to or higher than commonly used homogeneous catalysts like sodium hydroxide and sulfuric acid within a shorter reaction time (Balajii & Niju, 2019). This makes biochar a potentially more sustainable alternative to traditional chemical catalysts that require additional purification and waste treatment steps.

Beyond biodiesel, biochar is also being investigated for its potential to catalyze other biofuel production processes. For example, biochar combined with alkali hydroxides has demonstrated abilities to accelerate the processing of lignocellulosic biomass into fermentable sugars through pretreatments (Zhao et al., 2022). This could aid in making cellulosic ethanol production more economical. Research is also ongoing into developing biochar catalysts for thermochemical processes like pyrolysis that can generate liquid bio-oils from biomass that can then be upgraded into drop-in biofuels.

5.6.2 Bioenergy production

In addition to its use in agriculture and environmental applications, biochar is increasingly being investigated for its potential role in bioenergy systems. One way biochar contributes to bioenergy is through pyrolysis, the thermochemical decomposition process used to produce biochar. During pyrolysis, the biomass feedstock is heated in a low-oxygen environment, yielding biochar, syngas, and liquid bio-oil (Mutsengerere et al., 2019). The syngas and bio-oil produced during pyrolysis can be burned directly for heat and power generation or upgraded into transportation fuels (Makepa et al., 2023a). Pyrolysis has been demonstrated as an effective way to densify low-density biomass into an energy-dense solid fuel in the form of biochar. The heat content

of biochar makes it a valuable solid fuel suitable for combustion in stoves, furnaces, boilers, or gasification systems to produce renewable energy.

In integrated bioenergy systems, biochar may be used onsite as fuel to provide heat and power to support pyrolysis operations (Mutsengerere et al., 2019). Any excess biochar can then be sold or land applied for its carbon sequestration benefits (Cha et al., 2016). Some research is focused on co-firing biochar with coal in conventional power plants to extend fuel resources and reduce emissions compared to coal alone (Dang et al., 2015). New technologies are also exploring the use of biochar in gasification and pyrolysis processes to maximize energy capture from biomass. Gasification converts biomass and biochar into syngas, while pyrolysis liquefaction aims to optimize liquid biofuel production. Such systems could combine bioenergy production with biochar recycling, creating full biomass-to-bioenergy-to-biochar cycles for enhanced sustainability. Biochar offers opportunities to boost the efficiency, economics and environmental profile of bioenergy facilities.

5.6.3 Production of activated carbon

Activated carbon is a highly porous carbon material with a large internal surface area, making it an effective adsorbent. Activated carbon finds wide use in applications such as water treatment, air purification and filtration. Traditionally, activated carbon has been produced from carbon-rich sources like coal, coconut shells and lignite through physical or chemical activation processes (Adeniyi et al., 2023).

In recent years, biochar has emerged as a promising feedstock for activated carbon production. Biochar offers advantages over conventional feedstocks, including renewability and the potential for lower costs from waste biomass sources. Research has shown that biochar produced from various agricultural and forest residues through pyrolysis can be further activated to create highly porous carbon structures suitable for adsorption applications (Zhu et al., 2021).

Common activation methods explored for biochar include physical activation using steam or carbon dioxide and chemical activation employing acids or bases like zinc chloride (Panwar & Pawar, 2020). These activation processes increase the biochar's surface area and introduce additional oxygen-containing functional groups on the carbon surface. Studies have found biochar-derived activated carbons to perform comparably or even better than commercial activated carbons in applications like water purification and gas separation/storage when optimized (Othmani et al., 2021). Converting biochar to activated carbon offers a higher-value use of this carbon-negative product. It also provides an outlet to utilize biochars that may not be suitable for soil

application due to high ash or nutrient content. Ongoing research aims to reduce the energy inputs required for biochar activation and to maximize the production of higher surface area activated carbons for industrial use. The activated carbon market provides an important opportunity for biochar utilization.

5.6.4 In fuel cells

Fuel cells are electrochemical devices that efficiently convert chemical energy from a fuel into electricity through oxidation reactions. They have potential as alternatives to combustion engines, especially for transportation and small-scale distributed power generation applications. Research shows biochar may offer useful properties when utilized as an electrode material or catalyst support in various types of fuel cells (Mahurede et al., 2023). Biochar is being investigated as a cost-effective electrode for microbial fuel cells, which generate electricity from the metabolic activity of microbes. Biochar electrodes have demonstrated better power generation than conventional graphite electrodes, likely due to their porous structure and surface functional groups enhancing microbial attachment and electron transfer (Mahurede et al., 2023).

Biochar is also a candidate material for carbon-based metal−air batteries and fuel cells that oxidize fuels like methanol or hydrogen (Liu et al., 2019). Studies found biochar-based cathode catalyst layers improved power generation from zinc−air and aluminum−air batteries compared to conventional activated carbon. This is attributed to biochar's functional oxygen groups promoting oxygen reduction reactions. When used as a support material, biochar can enhance the performance of precious metal catalysts commonly used in hydrogen fuel cells and direct methanol fuel cells. Its porous carbon structure helps disperse catalyst nanoparticles while functional surface oxygen enhances catalyst utilization (Chen et al., 2021). Researchers are optimizing biochar supports to enable more efficient, lower cost catalyst formulations for renewable fuel cell technologies.

5.6.5 Sustainable adsorbents

Due to its high surface area, porosity and functional groups, biochar has excellent adsorption properties and shows potential as a low-cost and renewable alternative to commercial activated carbon adsorbents. Research explores utilizing biochar for removing heavy metals, dyes, organic pollutants, and other contaminants from wastewater (Huang et al., 2019).

Studies found biochar effectively removes heavy metals like lead, cadmium, nickel, and arsenic from water through mechanisms like

electrostatic interactions, coordination, and surface complexation. Biochar adsorbs metal ions with efficiency comparable to activated carbon and resin adsorbents (Zhang et al., 2020). Biochar also demonstrates strong affinity for adsorbing organic pollutants. It can uptake over 90% of some common industrial dyes from water in a single treatment. This is attributed to $\pi-\pi$ interactions between aromatic rings in dyes and biochar. Biochar has been shown to remove pharmaceuticals, pesticides and petroleum hydrocarbons from contaminated sources (Antunes et al., 2021).

In addition to wastewater treatment, biochar shows potential as an odor-controlling adsorbent. It can capture volatile organic malodorous compounds emitted from livestock facilities, landfills and wastewater treatment plants (O'Neill et al., 2022). Research optimizations including surface modification are enhancing biochar's adsorption capacity and selectivity. Combining biochar with other materials also expands its pollutant removal abilities. Biochar's low-cost, renewability, and comparable or potentially superior adsorption performance to commercial products positions it as a promising sustainable adsorbent for various environmental remediation applications.

5.6.6 Electrochemical energy storage devices

With the increasing incorporation of renewable but intermittent energy sources like solar and wind, there is growing demand for efficient and low-cost electrochemical energy storage technologies. Biochar shows potential as an electrode material to enhance the performance of batteries, supercapacitors, and other electrochemical storage devices (Senthil & Lee, 2021). Research has explored using biochar as the anode material in lithium-ion batteries. Biochar anodes demonstrate high reversible capacity, good rate capability, and cycling stability. This is attributed to biochar's interconnected porosity facilitating ion/electron transport, and structural stability during charge/discharge processes (Xia et al., 2021). Biochar has also been investigated as an electrode in sodium-ion and magnesium-ion batteries as safer alternatives to lithium batteries. Preliminary studies show biochar electrodes can support reversible sodium and magnesium storage/removal through pseudocapacitive surface reactions.

When used to modify electrodes, biochar increases the surface area and introduces functional groups that boost the capacitive performance of supercapacitors. As an electrode material, biochar supercapacitors exhibit high power density, decent energy density, and superior cycling life compared to activated carbon devices. Other emerging storage technologies leveraging biochar include lithium–sulfur batteries and flow

batteries. Biochar's low cost, sustainability, and tunable properties make it a promising candidate for developing next-generation energy storage systems. Optimization of biochar-based electrodes could enable greener electrochemical energy solutions.

5.6.7 In anaerobic digestion for biofuel production

Anaerobic digestion is the process by which microorganisms break down biodegradable material in the absence of oxygen to produce biogas, a renewable energy source composed primarily of methane and carbon dioxide (Kunatsa & Xia, 2022). Adding biochar to anaerobic digesters has been shown to improve their efficiency and stability for enhanced biogas and biofuel production.

Research finds biochar helps optimize digestion conditions by buffering pH levels, adsorbing toxins, and providing a microhabitat for methanogenic microbes. Its large surface area also increases biomass retention times in digesters (Johnravindar et al., 2021). Biochar has been used successfully in wet and dry fermentation systems digesting various feedstocks like manure, food waste and energy crops. As little as 1%–5% biochar addition appears sufficient to realize benefits. Co-digesting biochar with feedstocks may offer a sustainable solution for digestate management too (Kumar et al., 2021). Pilot and full-scale agricultural digesters incorporating biochar are showing prolonged stable operation with higher resistance to process imbalances. The scrubbed biogas can then be upgraded to renewable natural gas or transportation fuels. Ongoing research optimizes biochar properties and dosage rates for different digester configurations and substrates. Efforts are also evaluating integrating anaerobic digestion with pyrolysis to realize synergies between biogas and biochar production.

5.7 Advancements in the utilization of pyrolysis syngas

5.7.1 As an alternative fuel source in thermal conversion systems

The syngas produced from pyrolysis contains combustible gases like carbon monoxide, hydrogen, and small hydrocarbons that can be collected and used as a fuel source (Makepa et al., 2023a). Research has investigated utilizing pyrolysis syngas in boilers, heaters, and heat exchangers traditionally powered by natural gas or fuel oil. Pyrolysis syngas has a heating value of 4–6 MJ/Nm^3, comparable to low-Btu fuels (Nwokolo, Mukumba, & Obileke, 2020). Pyrolysis syngas can be combusted effectively in steam boilers for process heat and electricity

generation on-site. Integrating pyrolysis with existing steam and heating systems permits renewable fuel switching. The syngas replaces or supplements conventional fuels, reducing reliance on imported fuels. This allows facilities to extract further economic and carbon benefits from biomass resources.

Some pilot studies have directly substituted pyrolysis syngas for natural gas in commercial boilers with no reported issues (Kiedrzyńska et al., 2020). Other systems use syngas in combustion engines or turbines coupled to generators to produce clean power from biomass. The corrosion potential of syngas contaminants like tars poses a challenge but can be mitigated with conditioning systems (La Villetta et al., 2018). Ongoing optimization work focuses on cleaning and upgrading syngas to achieve stable, efficient combustion performance. However, utilizing pyrolysis syngas captures renewable thermal energy from biomass that would otherwise be wasted. This enhances the viability of integrated pyrolysis systems while displacing fossil fuels in thermal applications.

5.7.2 Production of bio-based hydrogen

Pyrolysis syngas contains hydrogen produced during biomass thermal decomposition. Researchers are investigating technologies to isolate and concentrate this hydrogen into a pure stream for fuel cell and industrial applications. One method being explored is catalytic steam reforming of pyrolysis syngas. This involves adding steam and using nickel catalysts at high temperatures to shift chemical equilibrium toward hydrogen. Studies show yields up to 60% can be achieved from syngas derived from various biomass feedstocks (Akubo et al., 2019).

Integrating pyrolysis with water electrolysis is another approach. Noncombustible gases from syngas like carbon monoxide and methane are fed to an electrolyzer, using catalysts to split them into hydrogen and carbon dioxide. The hydrogen can then be purified for fuel cell or hydrogenation reactions. Thermochemical processes leveraging syngas like the sulfur–iodine cycle are in research stages with the aim of more efficiently producing hydrogen from biomass at commercial scales. Producing bio-based hydrogen from pyrolysis syngas offers a renewable alternative to fossil fuel-derived hydrogen (Onwuemezie et al., 2023). Further technology innovations integrating pyrolysis with syngas conditioning and hydrogen extraction steps could enable decentralized production of green hydrogen to fuel both stationary and mobile zero-emission applications. This improves the economics and environmental profile of biomass pyrolysis.

5.7.3 Fischer–Tropsch synthesis

Fischer–Tropsch synthesis is a catalyzed chemical process used to convert syngas (a mixture of carbon monoxide and hydrogen) into liquid hydrocarbons (Mehariya et al., 2019). This process has traditionally relied on syngas from natural gas or coal gasification. Researchers are now exploring the use of syngas derived from biomass pyrolysis. Pyrolysis syngas with its carbon monoxide and hydrogen content is well-suited as a feedstock for Fischer–Tropsch synthesis (Konarova et al., 2021). Studies have shown pyrolysis syngas can be converted efficiently using conventional iron-based Fischer–Tropsch catalysts to produce a range of desirable fuel molecules (Chun et al., 2020). Typical products include linear hydrocarbons in the gasoline, kerosene, and diesel fuel ranges that can serve as direct replacements for conventional transportation fuels. Greener plant-derived waxes and olefins are also synthesized for producing renewable carbon materials.

By integrating pyrolysis with Fischer–Tropsch processing, the gaseous, liquid, and solid outputs of biomass thermal decomposition can be optimally leveraged (Fan et al., 2015). This allows for the sustainable production of drop-in biofuels that require no engine modification, helping facilitate renewable fuel adoption. Ongoing research focuses on developing improved hybrid catalysts optimized for pyrolysis syngas composition. Efforts are also underway to improve process efficiency and economics through techniques such as tar reforming, combined heat and power integration, and upgrades to gasoline/diesel fuel blending. Fischer–Tropsch processing opens new possibilities for fuel production from pyrolytic biomass streams.

5.7.4 Bioethanol production

In addition to producing fuels directly via Fischer–Tropsch synthesis, pyrolysis syngas can also serve as a feedstock for the microbial production of bioethanol (Monir et al., 2019). The hydrogen and carbon monoxide in syngas provide a source of reducing power and carbon that can be utilized by fermentative microorganisms. Research has explored integrating pyrolysis with gas fermentation technologies (Soltan et al., 2019). In this process, syngas is exposed to anaerobic bacteria or yeast capable of fixed carbon gas assimilation. Common strains used include *Clostridium* and *Ralstonia* species. During gas fermentation, microbes metabolize syngas components into ethanol and other alcohols. Studies demonstrate yields averaging 50–80 gallons of ethanol per ton of biomass processed can be achieved depending on pyrolysis conditions and fermentation optimization (Bengelsdorf et al., 2013).

Compared to fermentation of lignocellulosic hydrolysates, gas fermentation allows utilization of both the solid and gaseous biomass fractions for alcohol production. It also avoids many of the challenges associated with pretreating and hydrolyzing recalcitrant lignocellulose. Ongoing efforts focus on developing more tolerant and efficient gas-fermenting microbial strains. Pilot demonstrations are proving out scale-up feasibility. Coupling pyrolysis and gas fermentation expands options for converting various biomass resources into biofuels like cellulosic ethanol.

5.8 Prospects and challenges

Fast pyrolysis of lignocellulosic biomass shows promising prospects for the commercial production of biofuels, bioproducts and bioenergy. The abundance and low cost of biomass feedstocks provide a sustainable and renewable source of energy and materials. Fast pyrolysis has emerged as a versatile thermochemical platform to convert biomass into valuable bio-oil, biochar and syngas intermediates. Significant technological advancements have been achieved in the various process steps of fast pyrolysis as well as in upgrading bio-oil and utilizing all three pyrolysis products. Upgrading bio-oil through catalytic pyrolysis, hydroprocessing, supercritical fluids processing, and other techniques makes it possible to utilize this intermediate in conventional refinery infrastructure and as transport biofuels. Utilization of biochar as catalysts, adsorbents, and in energy storage applications enhances the overall economics and feasibility of fast pyrolysis systems.

However, for large-scale commercial deployment, fast pyrolysis technology still faces several technical and economic challenges. The low energy density and instability of raw bio-oil limits its direct utilization and requires upgrading via additional treatment steps that increase capital and operating costs. Scaling-up fast pyrolysis reactors along with integrating the entire process from feedstock handling to product separation poses significant technical challenges. The high oxygen content and corrosive nature of bio-oil also creates materials compatibility issues during transportation, storage and upgrading. There is a lack of standardized quality specifications and testing protocols that restrict market acceptance of bio-oil and upgraded products. High capital expenditures and operational costs associated with fast pyrolysis plants, bio-oil upgrading facilities and downstream processing hampers competitive commercial deployment against conventional fuels. Limited availability of long-term performance data on different process components poses technical and economic risks.

5.9 Conclusions

Significant advancements have been achieved over the past decade in the various process steps involved as well as upgrading and utilization of the pyrolysis products. Fast pyrolysis followed by catalytic upgrading of bio-oil has the potential to produce drop-in biofuels that can supplement or substitute petroleum-based transportation fuels. The ability to produce valuable biochar and syngas coproducts further enhances the economic viability and sustainability of fast pyrolysis systems. However, large-scale commercial deployment of fast pyrolysis still faces technical and economic challenges that need to be addressed, particularly in stabilizing and improving the energy density of bio-oil for transportation applications. Challenges also remain in scaling-up reactor designs and integrated process configurations to reduce capital and operating costs. Standardization of bio-oil quality assessment methods is required to facilitate market acceptance.

AI disclosure

During the preparation of this work the author(s) used Claude in order to the AI was used as a tool to assist the authors in refining the language and readability of the manuscript. The authors carefully reviewed and revised the manuscript to ensure its accuracy, appropriateness, and alignment with the original content and scientific integrity. After using this tool/service, the author(s) reviewed and edited the content as needed and take(s) full responsibility for the content of the publication.

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