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Innovative Solutions for a Circular Economy: a Review on Waste To Chemicals Valorization Plants

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Global concerns over fossil fuel dependence drive biomass use for fuel and chemical production. The goal is to develop conversion methodologies that make bio-based products competitive with petroleum-based ones. This review examines recent advances in biomass conversion processes, including both thermochemical and biochemical techniques. The selection of the most suitable conversion technique depends on biomass availability and the end goal. Currently, the focus is on developing catalysts and optimizing process parameters to make conversion technologies more efficient. Although some technologies are already commercialized, methods to process lignocellulosic and marine biomasses are still under development. In addition, significant resources are being devoted to optimizing processes to extract basic chemicals from biomass, consolidating the biorefinery concept. This review illustrates the main developments in these directions.

1. Introduction

Amid growing environmental challenges and resource constraints, the transition to a circular economy emerges as a key strategy for sustainability and waste reduction. (Trinca et al., 2022). Awareness of rising greenhouse gas emissions and declining fossil fuel reserves boosts interest in renewable and sustainable energy systems, utilizing naturally replenishing energy sources. Central to this paradigm shift is the concept of valorizing waste streams, transforming them from mere disposal challenges into valuable resources. Even in contemporary times, landfill disposal continues to be a dominant waste management approach. However, it is often considered the least favorable approach for handling waste, both economically and environmentally. Biomass utilization has an advantage over other renewables as it's less location and climate-dependent, and easily storable and transportable. Using biomass waste for fuel and chemicals isn't new but is inefficient. Technologies, including mechanical, chemical, thermochemical, and biochemical methods, upgrade biomass. Thermochemical methods like pyrolysis and hydrothermal liquefaction (HTL) transform biomass into bio-oil, while gasification produces synthetic gas, useful for fuels and chemicals. Research focuses on catalysts to improve product quality and address issues like tar formation. Biochemical methods, like anaerobic digestion (AD) and fermentation, offer targeted chemical production. Anaerobic digestion involves the breakdown of organic materials by microbial consortia in an oxygen-depleted environment, leading to the generation of biogas comprising methane and carbon dioxide. The methane generated can be integrated into the existing infrastructure of European gas pipelines, provided that the specifications of the network are adhered to (Colelli et al., 2024). Fermentation, another vital biochemical process, employs microbial enzymes or organisms to convert biomass sugars into biofuels, such as ethanol, or other biochemicals. Concurrently, chemical processes encompass traditional chemical transformations facilitated by catalysts or specific reaction conditions to modify the molecular structure of biomass or waste, enabling the synthesis of target molecules. These advanced technologies provide varied pathways for sustainable waste and biomass conversion, reducing environmental impact.

This article delves into the growing landscape of Waste to Chemicals (WtC) facilities, providing a comprehensive review of their operational principles, technological innovations, and potential implications for a more sustainable industrial ecosystem. This review aims to reveal the transformative potential of innovative solutions by exploring synergies between waste management and chemical production, shaping a circular, resource-efficient future.

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2. Thermochemical approach

Thermochemical conversion technologies play a pivotal role in transforming biomass and waste into valuable resources, offering sustainable alternatives to conventional energy sources. The main technologies are pyrolysis, hydrothermal liquefaction, and gasification.

Pyrolysis is a process that thermally breaks down biomass in conditions with minimal or no oxygen. The main products are in bio-oil, biochar, and gaseous components rich in light hydrocarbons, carbon dioxide, and carbon monoxide (Trinca, Segneri, et al., 2023). The success of this method depends largely on optimizing the production of the desired product, so, for example, if bio-oil is to be obtained, techniques such as fast pyrolysis will be used, whereas if biochar is to be produced, slow pyrolysis will be employed. However, the direct output from pyrolysis tends to have drawbacks such as a high moisture content (15–30 wt%) and a notable presence of oxygenated substances like acids, ketones, and alcohols (45–50 wt%). To enhance its quality, catalytic pyrolysis methods have been developed. These methods employ techniques like hydrodeoxygenation (HDO), hydrocracking, and specific condensation reactions such as esterification and aldol condensation. Beyond energy applications, bio-oil can be further refined to generate valuable substances like benzene, toluene, assorted carboxylic acids, and furans. The stability of the bio-oil is severely affected by the polymerization reaction of tar components at ambient conditions. Tar can be converted into gases through catalytic cracking, making it a major area of research in biomass pyrolysis and gasification technologies. In recent years, numerous tar catalysts have been studied, and current advancements in catalyst preparation and utilization have been reviewed in various publications, with a focus on both synthetic metal catalysts and natural ore-based catalysts (Trinca, Segneri, et al., 2023). Pyrolysis represents the optimal choice for converting plastic waste and boasts economic advantages in operation (Anuar Sharuddin et al., 2016). This process demonstrates applicability to complex materials such as tires. Through pyrolysis, the organic volatile compounds within tires, primarily rubber polymers, are broken down into low molecular weight liquids or gases. The non-volatile carbon black and inorganic components remain relatively unchanged as char. The gaseous fraction produced from tire pyrolysis can serve as a fuel source for powering the pyrolysis plant. The resulting liquid product is more manageable, storable, and transportable, suitable for various applications. Additionally, the residual char can be utilized as combustible material or as adsorbents, either with or without an activation process (Labaki & Jeguirim, 2017). This method presents numerous benefits, including improvements to waste management systems, decreased reliance on fossil fuels, expansion of energy sources, and prevention of environmental contamination.

Hydrothermal liquefaction converts biomass into liquid fuels via hot, pressurized water, breaking down the solid structure into mainly liquid components. HTL is an effective method for converting waste into valuable products, particularly bio-oil. Unlike pyrolysis, HTL has the capability to utilize wet biomass, resulting in a bio-oil with approximately twice the density of pyrolysis oil. Despite pyrolysis yielding relatively high quantities, the bio-oil produced through HTL exhibits more favorable characteristics in terms of its oxygen and water contents. The HTL process generates diverse products depending on the origin of the biomass. By lowering the activation energy of the reaction, catalysts provide various benefits, including enhancing bio-oil yield and improving biomass conversion efficiency. The HTL methodology has harnessed both homogeneous (acids and alkalis) and heterogeneous catalysts (transition metal oxides, supported metal catalysts, molecular sieves, and rare metals). Researchers have unveiled a collaborative interplay between homogeneous (NaOH) and heterogeneous (CuO) catalysts during corn straw HTL at distinct operational temperatures (Chen et al., 2019). Their findings underscored that aromatic compound percentages in bio-oil escalate at elevated temperatures, achieving an 89.84% aromatic compound yield at 230°C. L. Feng et al. (2021) investigated HTL of lignin across varying temperatures (250–310 °C) and reaction durations, utilizing different solvents (water, methanol, and ethanol) alongside various metals supported on MCM-41 mesoporous catalysts. With ethanol as the solvent, the highest bio-oil yield of 56.2 wt% was achieved using Ni-Al/MCM-41. Conversely, using water as the solvent resulted in a bio-oil yield of 44.3 wt%, while methanol significantly improved the yield to 48.1 wt%. Alcoholic solvents promote lignin decomposition, and water, especially with a catalyst, notably enhances lignin degradation. Researchers have reported directional microwave-assisted liquefaction employing sulfuric acid as a catalyst and subsequent phased extraction to generate premium platform chemicals, including aromatics and monosaccharides (J. Feng et al., 2017). Diverse organic solvents, including methanol, ethanol, 1-propanol, and acetone, have been integrated as co-solvents to amplify bio-oil yields. Recent studies have embarked on HTL of varied lignocellulosic biomasses using 1,4-dioxane–ethanol–formic acid co-solvents, demonstrating promising recycling potential and yielding minimal residues (Wu et al., 2021). Enhanced bio-oil yield and quality parameters such as H/C and HHV have been documented with glycerol co-solvents (Cao et al., 2016). Deep-eutectic solvents (DESs) have emerged as both catalysts and co-solvents, displaying enhanced bio-oil selectivity (Alhassan et al., 2016). Gasification transforms solid biomass into a gaseous form, producing synthesis gas or syngas, a key material for various chemicals and fuels (Segneri et al., 2022). Through the Fischer-Tropsch process, this syngas can be further refined into paraffin-like hydrocarbons, essentially a form of synthetic crude, for sustainable fuels (Colelli et al., 2023). The process efficiently converts biomass into both gas and char, scalable for broader applications. Current research is dedicated to refining different gasifier designs and operations. Challenges arise from tar formation within the gasifier; however, methods like physical separation, thermal cracking, and catalytic conversion have been explored to address this issue. Catalysts, including dolomite, olivine, Ni-doped materials, and others, play crucial roles in these processes (Trinca, Segneri, et al., 2023). One of the key considerations is managing the high levels of greenhouse gases like CH_4 and CO_2 in the syngas. To refine this, techniques like catalytic steam reforming are adopted, converting CH_4 into more usable forms like H_2 and CO. Advanced methods, especially with specific catalysts, combining gasification and catalytic reforming show promise in enhancing efficiency. A recent research study indicated that employing olivine and NiO/olivine as tar destruction catalysts within a decoupled triple-bed gasification system enhanced tar removal and increased H_2 production during the steam gasification of biomass (Tursun et al., 2019).

3. Biochemical conversion

Biochemical processes for biomass conversion encompass a variety of methods, prominently featuring fermentation and anaerobic digestion, which play pivotal roles in transforming organic materials into valuable products. Anaerobic digestion proves effective for processing diverse materials such as municipal, agricultural, and industrial wastes, along with plant residues. It is recognized as a viable technology for effectively treating organic waste while concurrently generating renewable energy. The products of anaerobic digestion typically include biogas, which is a mixture of methane and carbon dioxide, along with digestate, a nutrient-rich residue that can be used as fertilizer. Several techniques have been devised to extract CO_2 from gas streams, such as adsorption, absorption, cryogenics, and membrane processes, to upgrade biogas in biomethane. Due to progress in nanotechnology, adsorption is emerging as a potent method for directly capturing CO_2 using nanomaterials (Segneri et al., 2023). Rosa et al. (2023) studied a method to adsorb CO_2 using biomass waste functionalized by Nanoparticles. The study led to the synthesis of a new material formed by iron oxide nanoparticles supported on a lignocellulosic matrix with an adsorbent high capacity: CO_2 adsorbed 25 mg/g. Multi-stage systems, building upon the feasibility of a single stage, can be employed to maximize substrate utilization, such as producing H_2 followed by CH_4. Conducting H_2 production before CH_4 production not only generates energy but also acts as a substrate pretreatment method, enhancing the startup of CH_4 digestion without depleting biomass. Researchers have highlighted peak biogas production at a C/N ratio of 25, whereas the most efficient digestate performance was observed at a C/N ratio of 35 (Ning et al., 2019). Combining various substrates with inoculum can boost biogas production effectively. Utilizing multiple substrates aids in maintaining the appropriate C/N ratio and nutrient balance in anaerobic digestion processes. Pre-treatment methods can enhance the biodegradability and solubilization of biomass, leading to improved process efficiency and increased biogas production. Fermentation processes can yield ethanol from any material containing sugar. Various raw materials in ethanol production are categorized into sugars, starches, and cellulose for fermentation. Various pretreatment techniques exist, including mechanical, chemical (such as alkaline, wet oxidation, and acid treatments), and physicochemical methods like steam explosion, liquid hot water, ammonia fibre explosion, ammonia recycle percolation, and supercritical fluid (Hassan et al., 2018). Effective pretreatment remains a significant challenge, with research focusing on methods that yield digestible solids, enhance sugar extraction, minimize degradation, reduce inhibitor formation, and increase lignin recovery. Recent approaches have utilized olive tree biomass for second-generation bioethanol (Martínez-Patiño et al., 2017). Sequential acid/alkaline oxidative pretreatment was employed to produce 15 g ethanol/100 g olive tree biomass. Emerging techniques like microwave irradiation and ultrasound are also being explored for their potential in pretreatment. For instance, microwave-assisted alkali pretreatment has proven effective, significantly boosting sugar yields from brewer's spent grain. The expense of enzymes is recognized as one of the foremost factors influencing the ultimate product cost in the processes of lignocellulose hydrolysis and fermentation. Enzyme immobilization and recycling represent effective strategies for cost reduction (Sóti et al., 2018). Through current process efficiencies and prevailing commercial enzyme prices, enzyme immobilization can potentially lead to approximately a 60% decrease in costs compared to using free enzymes. However, if enzyme prices decrease, the percentage of savings related to immobilization may also decrease, but overall enzyme expenses will still witness significant reductions.

4. Chemical Conversion

Ongoing research explores new biomass building blocks and catalytic systems to boost efficiency in established block production. This highlights the versatility and potential of carbohydrate-based resources in biotechnology and chemical synthesis. Through this process, many platform biochemicals can be derived from carbohydrates.

3-Hydroxypropionic Acid (3-HP) has been designated as one of the 20 fundamental biomass-derived building blocks chosen by the U.S. Department of Energy. In recent developments, the production of 3-Hydroxypropionic Acid (3-HP) derived from glycerol or 1,3-propanediol has demonstrated greater efficiency, yielding a final concentration of 67 g/L, surpassing the glucose-based process. Since glycerol is abundantly generated during biodiesel production, it presents a sustainable alternative raw material for 3-HP production, obviating the need for glucose. Furthermore, a recent advancement in the recovery process involves a reactive extraction method utilizing HFMC, achieving a recovery yield exceeding 90% (László et al., 2018). Succinic acid (SUA), a dicarboxylic acid containing four carbons, is recognized for its versatility as a fundamental C4 chemical. It promises to substitute the maleic anhydride platform, mirroring the concept of fumaric or maleic acid. Recent research has demonstrated the conversion of various lignocellulosic fractions into succinic acid using natural SUA producer strains. These studies have shown final titers ranging from 15 to 70 g/L, yields ranging from 0.05 to 1.24 g/g, and productivities ranging from 0.02 to 3.3 g/L/h (Akhtar et al., 2014). 2,5-Furandicarboxylic Acid (FDCA) is considered an excellent eco-friendly substitute for terephthalate, a prominent monomer in the polymer industry. The most efficient route for FDCA production from biomass or its sugar derivatives involves chemical catalysis. Enzyme catalysts offer significant potential for developing efficient processes with notable savings in both atomic and energy resources, especially in future biorefineries (Drault et al., 2020). Despite their versatility, enzymatic carboxylation of cyclic compounds is in its early stages, posing several challenges. This requires advancements in biological catalysts, materials, reactors, and innovative processes for effective integration.

5. Evaluation of Techno-economic Viability and Commercialization

Table 1: Examples of industrial plants for biomass conversion

Owner	Location	Technology	Raw Material	Product	TRL
Pyrocell	Sweden	Fast Pyrolysis	Saw dust (85,000 t/y)	Pyrolysis oil (24,000 t/y)	7
BEST	Austria	Gasification with FT-synthesis	Biogenic residues and waste (1 MW)	FT liquids (44 t/y) and syngas	6-7
Eni	Italy	Hydro-treatment	Oilcrops, oils and fats	SAF (10,000 t/y)	9
Versalis/Eni	Italy	Fermentation	Several biomasses	Ethanol (25,000 t/y)	9
BIOGAS VIENNA - SIMMERING	Austria	Anaerobic Digestion	Food waste (22,000 t/y)	Biogas (1.5 Mm^3/y)	9

Biomass and waste conversion is already an industrial reality (Table 1). However, to advance and commercialize technologies that convert biomass, it's crucial to conduct techno-economic evaluations, primarily focusing on production costs. Expenses vary between 65 to 158 €/MWh (17-44 €/GJ) for biomass-derived production and 48 to 104 €/MWh (13-29 €/GJ) for waste-derived production, indicating the cost benefits associated with utilizing waste feedstocks (Figure 1). By contrast, recent fossil fuel prices range from 30-50 €/MWh (8–14 €/GJ) (Advanced Biofuels –Potential for Cost Reduction, 2020). The initial capital required for gasification processes is usually higher than for pyrolysis or biochemical methods, the operational costs can be more favourable, resulting in a lower overall production cost. Research by Zhao et al. (2015) identified fast pyrolysis with hydroprocessing as the most economically favourable route for producing biofuels, despite not being profitable at projected energy prices. A study comparing pyrolysis, gasification, and combustion routes found that gasification, especially when producing methanol and capturing carbon dioxide simultaneously, had a higher Net Present Value than other methods (Brigagão et al., n.d.). Dimitriou et al. (2018) highlighted the potential of Biomass-to-Liquid (BTL) technologies based on circulating fluidized bed gasification and Fischer-Tropsch synthesis for commercial scalability. The overall energy efficiency and production costs of the BTL projects evaluated range from 17.88 to 25.41 € per GJ of fuel produced. Deterministic estimates of the production costs of this project indicate that the BTL process is not yet competitive with conventional refineries, as the production costs of biofuels are around 8% higher than current market prices. Trinca, Bassano, et al. (2023) examined the technical and economic viability of incorporating methanol-to-gasoline processes into BTL facilities, integrating Carbon Capture and Storage (CCS), and utilizing green hydrogen, underlining a gasoline production cost of 99$/bbl when CCS is implemented. Currently, none of these BTL technologies can rival conventional fossil fuels in terms of cost-efficiency, primarily due to the latter's established infrastructure and economies of scale. While many biofuels and biochemicals are not cost-competitive with fossil fuels at present, avenues for commercialization could open through strategies like using more cost-effective second-generation feedstocks, enhancing conversion efficiency, and reducing downstream processing costs.

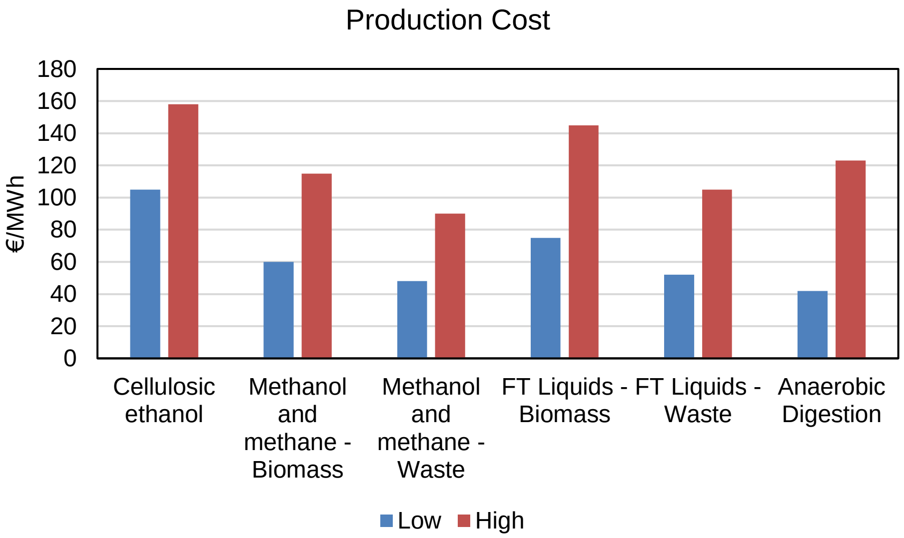

Figure 1: Current cost ranges of advanced biofuels (Advanced Biofuels –Potential for Cost Reduction, 2020).

6. Conclusion

The conversion of biomass offers a pathway to sustainable energy and eco-friendly chemicals. Utilizing low-cost biomass resources like agricultural residues and waste materials is crucial. Sustainability hinges on maximizing the value of each biomass component while maintaining product diversity. Thermochemical and biochemical approaches are used, with the former being simpler but energy-intensive, and the latter offering specificity but facing challenges like high pretreatment costs and enzyme expenses. Current research focuses on improving catalysts and refining processes to increase yield and specificity while reducing costs and enhancing energy efficiency. Collaboration and ongoing efforts are key to realizing the potential of biomass conversion for a sustainable energy and environmental future.

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