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# PRODUCTION OF POLYMER-PRECURSOR CARBOXYLIC ACIDS FROM MUNICIPAL SOLID WASTE: FERMENTATION, CHAIN ELONGATION, AND DOWNSTREAM PROCESSING

SAFOORA MIRMOHAMADSADEGHI[1]* AND KEIKHOSRO KARIMI[2]

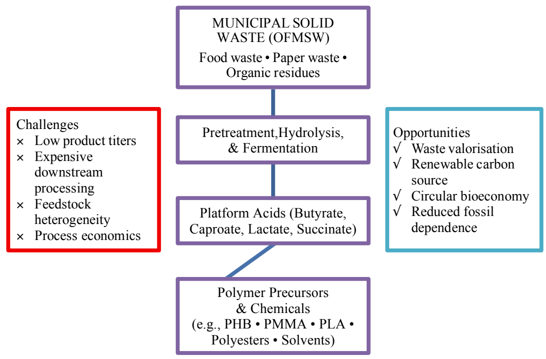
*[1]Department of Biotechnology, Faculty of Biological Science and Technology, University of Isfahan, Isfahan 81746-73441, Iran*
*[2]Department of Chemical Engineering, Vrije Universiteit Brussel, 1050 Brussels, Belgium*

**Corresponding author: s.mirmohamadsadeghi@bio.ui.ac.ir*

## HIGHLIGHTS

- MSW can be converted into polymer-precursor carboxylic acids.
- Butyrate, caproate, lactate, and succinate pathways are briefly reviewed.
- Lactate and butyrate appear to be more economically promising than succinate.
- Key challenges include contaminants, process integration, and separation.

## GRAPHICAL ABSTRACT

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## ABSTRACT

Municipal solid waste (MSW) represents an underutilised feedstock for the production of polymer-precursor carboxylic acids via the carboxylate platform and chain elongation. This preliminary review examines the production of four key building blocks from the organic fraction of MSW: Butyric acid (C4, carbon source for polyhydroxybutyrate production), caproic acid (C6, precursor to polyhydroxycaproate), lactic acid (C3, precursor to polylactic acid), and succinic acid (C4, precursor to polybutylene succinate). For each chemical, fermentation strategies, key microorganisms, and separation technologies are reviewed. Lactic acid achieves the highest yields and titres but suffers from optical purity issues from mixed MSW cultures. Butyric acid offers the best overall balance of yield, productivity, and separation feasibility. Caproic acid requires chain elongation with external electron donors, resulting in lower yields and titres, and limiting its economic viability. Succinic acid is the least mature, with low yields and high separation costs. Key knowledge gaps include contaminant impacts on chain-elongating consortia, process integration at pilot scale, and low-cost separation technologies compatible with MSW solids.

## Introduction

The accumulation of Municipal Solid Waste (MSW) presents one of the most pressing environmental challenges of the 21st century, with global annual generation exceeding 2 billion tonnes, of which less than 20% is effectively recycled or valorised (Kaza *et al.*, 2018). Simultaneously, the petrochemical industry's reliance on fossil resources for polymer production has driven interest in bio-based alternatives (Zhu *et al.*, 2016). This review bridges these two issues by examining the production of polymer precursor carboxylic acids from the Organic Fraction of MSW (OFMSW) via the carboxylate platform and chain elongation.

The most important chemicals in this context are short-chain volatile fatty acids (VFAs; C2–C5) and medium-chain carboxylates (MCCs; C6–C8), some of which act as direct monomers, while others serve as carbon sources for the biosynthesis of bioplastics and other bio-based polymers (Angenent *et al.*, 2016). Table 1 summarises the key chemicals, their properties, and polymer applications.

Table 1: Key polymer precursor carboxylic acids from MSW fermentation

| Chemical | Formula | Chain Length | Polymer Application | Polymer Precursor Role | References |
|---|---|---|---|---|---|
| Butyric acid | $C_4H_8O_2$ | C4 | Polyhydroxybutyrate (PHB) | Carbon source for PHB production | Vlaeminck *et al.* (2022) |
| Caproic acid | $C_6H_{12}O_2$ | C6 | Polyhydroxyalkanoates (PHAs) | Carbon source for the production of 3HHx-containing PHAs | Hahn *et al.* (2024) |
| Lactic acid | $C_3H_6O_3$ | C3 | Polylactic acid (PLA) | Direct monomer for PLA | Swetha *et al.* (2023) |
| Succinic acid | $C_4H_6O_4$ | C4 | Polybutylene succinate (PBS) | Direct monomer for PBS | Rajendran and Han (2023) |

While lactic and succinic acids are primarily produced via classical fermentation pathways (Beauprez *et al.*, 2010), caproic acid and, under certain conditions, butyric acid, can also be generated through chain elongation, a reverse β-oxidation process in which shorter-chain carboxylates (e.g., acetate) are elongated using electron donors such as ethanol or lactate (Angenent *et al.*, 2016). MSW provides an abundant, low-cost feedstock for these processes, but its heterogeneity, contaminants, and variable composition pose substantial challenges (Campuzano & González-Martínez, 2016). Figure 1 presents a conceptual overview of the major biological conversion routes leading to polymer precursor production from MSW. Accordingly, this review examines the production of each key polymer precursor from MSW, covering fermentation strategies, key microorganisms, and separation technologies, and concludes with a comparative analysis of technical readiness and economic viability.

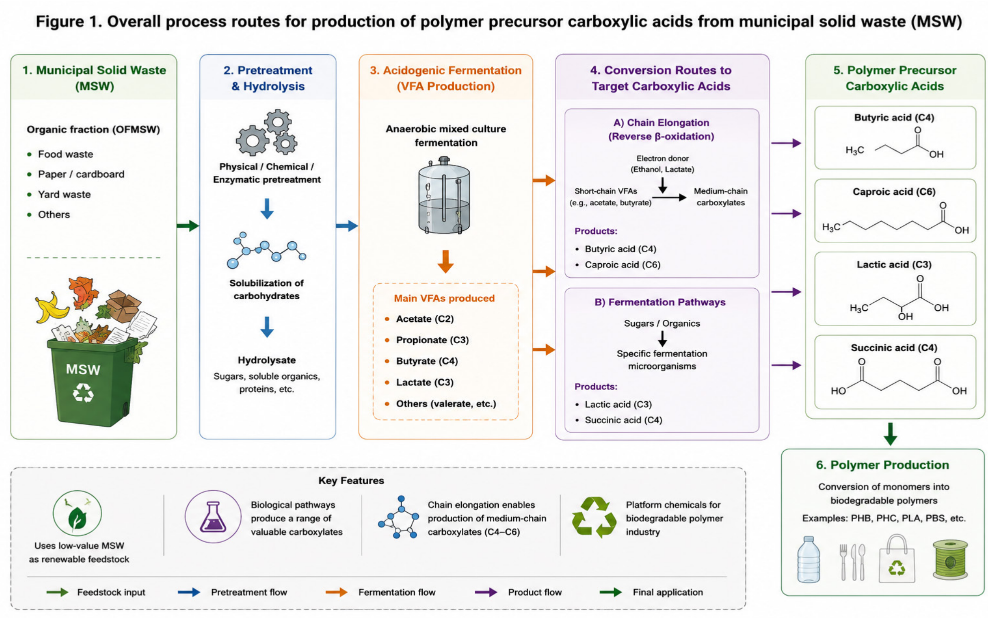


Figure 1: Overall process routes for production of polymer precursor carboxylic acids from MSW

### *Butyric Acid (C4) Production from MSW*

Butyric acid is a four-carbon saturated fatty acid that can serve as a carbon substrate for microbial polyhydroxybutyrate (PHB) biosynthesis, while PHB itself is a biodegradable thermoplastic composed of three-hydroxybutyrate monomer units and exhibits properties similar to polypropylene (Vlaeminck *et al.*, 2022).

### *Fermentation*

Butyric acid production from MSW typically employs anaerobic fermentation of the OFMSW (Strazzera *et al.*, 2018). Two main approaches exist: (i) Single-stage fermentation, where OFMSW is converted to butyric acid in a single stage; and (ii) Phase-separated systems in which hydrolysis and acidogenesis are operated in separate reactors to improve process control and butyric acid selectivity (Holl *et al.*, 2022).

Operational parameters strongly influence butyric acid production during the acidogenic fermentation of OFMSW. Previous studies have shown that mildly acidic conditions (approximately pH 5.5 to 6.5) favour the accumulation of butyric acid, while both mesophilic and thermophilic temperatures have been successfully applied. However, the optimal hydraulic retention time, organic loading rate, and butyric acid productivity vary considerably depending on feedstock characteristics, reactor configuration, and microbial community composition (Atasoy *et al.*, 2018; Strazzera *et al.*, 2018).

Temperature has also been shown to influence product selectivity in chain-elongating mixed cultures. Recent evidence suggests that decreasing the operating temperature may shift the fermentation profile from caproic acid toward butyric acid production by altering microbial community composition, with lower temperatures favouring the enrichment of butyrate-producing populations such as *Clostridium sensu stricto* while reducing the abundance of caproate-producing microorganisms (Sabbe *et al.*, 2025). A major challenge remains the concurrent production of competing metabolites, particularly acetate and propionate, which may reduce butyric acid selectivity in mixed-culture fermentations (Angenent *et al.*, 2016).

***Microorganisms***

The microbial communities responsible for butyric acid production during OFMSW fermentation are dominated by members of the phylum *Firmicutes*, particularly the class Clostridia (Vital *et al.*, 2014). Among them, species belonging to the genera *Clostridium* and *Megasphaera* have frequently been associated with butyric acid formation in mixed-culture anaerobic systems (Vital *et al.*, (2014); Atasoy *et al.*, (2018). Environmental factors, especially pH, play a critical role in shaping microbial community composition and metabolic pathways. Consequently, understanding the ecological interactions within mixed microbial consortia is essential for developing strategies to enhance butyric acid selectivity during OFMSW fermentation (Atasoy *et al.*, 2018; Strazzera *et al.*, 2018). The most important butyrate-producing microorganisms, substrate preferences, and representative yields are summarised in Table 2.

Table 2: Representative butyrate-producing microorganisms, substrate preferences, and reported yields

| Species | Substrate Preference | Notes | References |
|---|---|---|---|
| *Clostridium butyricum* | Glucose, starch | Most studied, robust | Fu *et al.* (2022) |
| *Clostridium acetobutylicum* | Multiple sugars | Also produces solvents | Jang *et al.* (2014) |
| *Megasphaera elsdenii* | Lactate, glucose | Lactate-utilising | Cabral and Weimer (2024) |
| *Butyrivibrio fibrisolvens* | Cellulose, hemicellulose | Degrades fibres | Asanuma *et al.* (2005) |

***Caproic Acid (C6) Production from MSW***

Caproic acid (hexanoic acid) is a six-carbon medium-chain carboxylate that has attracted increasing interest as a platform chemical because of its potential use as a carbon source for the biosynthesis of medium-chain-length polyhydroxyalkanoates (mcl-PHAs) in addition to its applications in lubricant formulations, antimicrobial agents, and flavour compounds (Hahn *et al.*, 2024; Wu *et al.*, 2024). Production of caproic acid from MSW typically relies on chain elongation, in which shorter-chain carboxylates such as acetate and butyrate are elongated using electron donors including ethanol and lactate (Wang *et al.*, 2023).

Chain elongation is a microbial process that transforms short-chain carboxylates into more valuable medium-chain carboxylates through the reverse β-oxidation pathway. During this process, electron donors provide reducing equivalents that drive the sequential elongation of carboxylate chains by two carbon atoms per cycle (Wang *et al.*, 2023). Among the products generated via reverse β-oxidation, caproic acid has received considerable attention because of its potential applications as a platform chemical and precursor for the synthesis of bio-based materials (Wu *et al.*, 2024). A simplified overview of the reverse β-oxidation pathway involved in caproate production is presented in Figure 2.

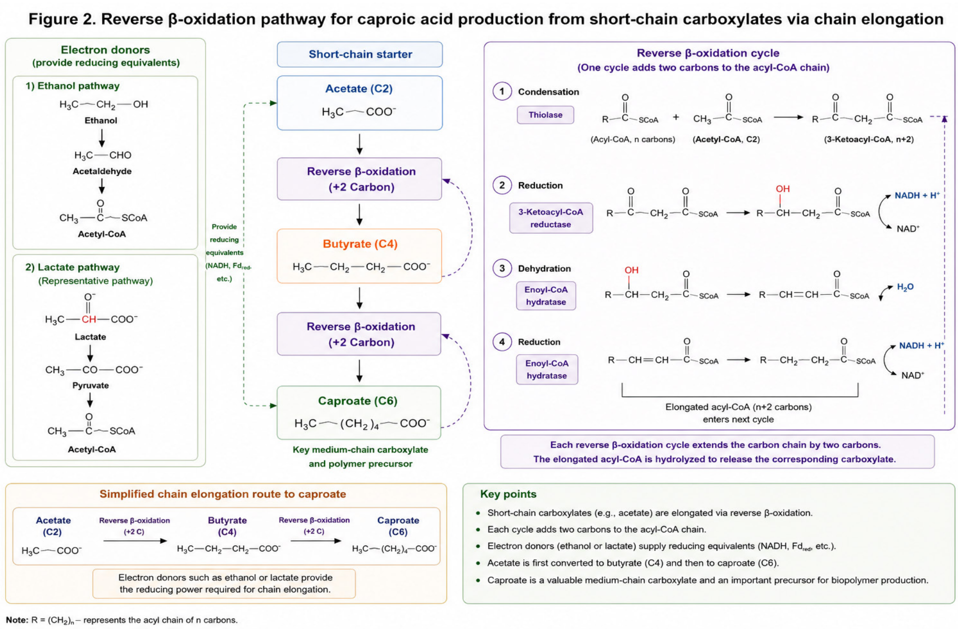


Figure 2: Reverse β-oxidation pathway for caproic acid production from short-chain carboxylates via chain elongation

### *Fermentation*

Caproate production from MSW primarily occurs through the reverse β-oxidation pathway, which constitutes the metabolic basis of microbial chain elongation. As illustrated in Figure 2, the reverse β-oxidation cycle involves the condensation of acetyl-CoA with an acyl-CoA intermediate, followed by reduction, dehydration, and a second reduction step. Through repeated cycles, short-chain carboxylates can be elongated by two carbon atoms per cycle, enabling the conversion of acetate to butyrate and subsequently to caproate. A simplified stoichiometric representation of caproate formation from acetate and ethanol is shown below:

$$C_2H_4O_2 \text{ (acetate)} + 2C_2H_5OH \text{ (ethanol)} \rightarrow C_6H_{12}O_2 \text{ (caproate)} + 2H_2O$$

In contrast to butyrate production, caproate synthesis through chain elongation is strongly influenced by electron donor availability and microbial competition. Reported caproate titres (5.4 g/L to 14.6 g/L) and productivities from OFMSW-derived substrates vary substantially depending on feedstock composition, reactor configuration, and operational conditions (Pu *et al.*, 2026).

The large-scale implementation of OFMSW-based caproate production is hindered by several interconnected challenges. The heterogeneous nature of food waste (FW) leads to unstable fermentation performance and frequent imbalances in pH and electron donor availability. In mixed microbial communities, competition from lactate producers, methanogens, and other fermentative microorganisms diverts carbon and reduces power away from chain elongation, thereby reducing caproate selectivity. Moreover, process efficiency is often constrained by product inhibition, difficulties in maintaining optimal operating conditions, and the presence of inhibitory compounds such as ammonium and salts. Addressing these limitations through improved process control, microbial management, and integrated product recovery strategies will be crucial for the development of economically viable caproate biorefineries based on food waste (Pu *et al.*, 2026).

***Microorganisms***

Caproate production is mediated by specialised chain-elongating bacteria (CEB), primarily from the phyla Firmicutes and Proteobacteria (Wang *et al.*, 2023). Among them, *Clostridium kluyveri* is the best-characterised caproate producer and represents an obligate chain elongator that relies on ethanol and short-chain carboxylates rather than sugars for growth (Fernández-Blanco *et al.*, 2024). In MSW consortia, *C. kluyveri* often coexists with *C. acetobutylicum* (which produces butyrate) *and Lactobacillus spp.* (which produce lactate) (Ulčar *et al.*, 2024).

A key recent discovery is lactate-mediated chain elongation, where lactate replaces ethanol as the electron donor, reducing external chemical addition costs (Wang *et al.*, 2022). However, maintaining stable lactate-driven chain elongation in mixed cultures remains challenging because of complex microbial interactions and competing metabolic pathways (Wu *et al.*, 2023).

Caproic acid recovery is more challenging than butyric acid due to its higher hydrophobicity and lower concentration in fermentation broth (Wang *et al.*, 2023).

Table 3: Representative chain-elongating bacteria for caproate production, electron donors, and reported yields

| Species | Electron Donor | C4 Intermediate | References |
|---|---|---|---|
| *Clostridium kluyveri* | Ethanol + acetate | Butyrate (trace) | Reddy *et al.* (2018) |
| *Megasphaera elsdenii* | Lactate + acetate | Butyrate (major) | Cabral and Weimer (2024) |
| *Eubacterium pyruvativorans* | Ethanol + acetate | Butyrate (minor) | Hernandez-Correa *et al.* (2023) |
| *Ruminococcaceae* bacterium CPB6 | Ethanol + acetate | Butyrate (intermediate) | Zhu *et al.* (2017) |

## Other Polymer Precursors from MSW

While butyric and caproic acids are the primary chain elongation products, MSW fermentation also produces other valuable polymer precursors, including lactic acid for polylactic acid (PLA) production (Song *et al.*, 2024) and succinic acid for polybutylene succinate (PBS) synthesis (Ioannidou *et al.*, 2023).

***Lactic Acid (C3) – Fermentation***

Lactic acid is mainly produced through the fermentation of carbohydrate-rich OFMSW by lactic acid bacteria, particularly species belonging to the genera *Lactobacillus* and *Weizmannia* (Song *et al.*, 2024). Process performance is strongly influenced by operational conditions such as pH and temperature, with mildly acidic conditions and mesophilic to moderately thermophilic temperatures generally favouring lactic acid accumulation (Aulitto *et al.*, 2024, Tang *et al.*, 2024).

A major challenge for PLA production is the requirement for high optical purity (i.e., a high proportion of the L-isomer), as mixed microbial cultures may produce both L- and D-lactic acid isomers (Swetha *et al.*, 2023). In this regard, *Weizmannia coagulans* (formerly *Bacillus coagulans*) has attracted increasing attention because of its thermophilic characteristics and ability to produce optically pure L-lactic acid under industrially relevant conditions (Aulitto *et al.*, 2024).

***Lactic Acid – Microorganisms***

Lactic acid production from MSW-derived substrates is commonly mediated by lactic acid bacteria, with the optical purity of the final product depending strongly on the microbial strain employed. Among the available producers, *Weizmannia coagulans* (formerly Bacillus coagulans) has received particular attention because of its thermophilic nature, which reduces contamination risks, and its ability to produce optically pure L-lactic acid (Aulitto et al., 2024). Other microorganisms commonly used for lactic acid production include *Lacticaseibacillus casei*, *Lactobacillus delbrueckii*, and *Lactiplantibacillus plantarum*, although their stereospecificity is often strain-dependent (Table 4).

Table 4: Representative lactic acid-producing microorganisms, optical isomer specificity, and reported yields

| Species | Isomer | References |
|---|---|---|
| *Lactobacillus casei* | L | Panesar *et al.* (2010) |
| *Lactobacillus delbrueckii* | D | Mukherjee *et al.* (2025) |
| *Weizmannia coagulans* (*Bacillus coagulans*) | L (> 99%) | Pamueangmun *et al.* (2023) |
| *Lactobacillus plantarum* | DL | Sudhakar and Dharani (2022) |

***Lactic Acid – Separation***

Downstream recovery of lactic acid remains a major economic challenge because of its high solubility in aqueous fermentation broths. Conventional separation strategies include precipitation, solvent extraction, electrodialysis, and membrane-based processes. Calcium lactate precipitation is still widely used because of its operational simplicity and technological maturity, whereas reactive extraction has emerged as a promising alternative for improving recovery efficiency and reducing downstream processing costs (Swetha *et al.*, 2023; Song *et al.*, 2024).

***Succinic Acid (C4) – Fermentation***

Succinic acid can be produced from OFMSW-derived hydrolysates through anaerobic fermentation by succinate-producing microorganisms (Yi *et al.*, 2013; Mitrea *et al.*, 2024). These processes are typically operated under near-neutral pH conditions and require $CO_2$ supplementation to support carboxylation reactions involved in succinate biosynthesis.

Reported succinic acid yields and final concentrations vary considerably depending on substrate characteristics, pretreatment methods, and microbial strains employed (Yang *et al.*, 2024). A major challenge associated with this process is the need to maintain strict anaerobic conditions together with adequate $CO_2$ availability, which can increase operational complexity and overall production costs.

***Succinic Acid – Microorganisms***

Among the microorganisms investigated for bio-based succinic acid production, *Actinobacillus succinogenes* has emerged as one of the most promising candidates because of its broad substrate utilisation spectrum, including both hexose and pentose sugars, as well as its high capacity for $CO_2$ fixation (Yang *et al.*, 2024). These characteristics make this organism particularly attractive for the valorisation of heterogeneous MSW-derived hydrolysates.

Table 5: Representative succinic acid-producing microorganisms, yields, and fermentation characteristics

| Species | Byproducts | Notes | References |
|---|---|---|---|
| *Actinobacillus succinogenes* | Acetate, formate | Most studied, high yield | Escanciano *et al.* (2024) |
| *Mannheimia succiniciproducens* | Acetate | $CO_2$-tolerant | Kim *et al.* (2025) |
| *Basfia succiniciproducens* | Acetate, lactate | Grows on glycerol | Rochón *et al.* (2024) |
| *Saccharomyces cerevisiae* (engineered) | Ethanol | Less robust | Malubhoy *et al.* (2022) |

***Succinic Acid – Separation***

Succinic acid recovery from MSW fermentation broths is highly complex due to its low baseline titres and the simultaneous presence of co-produced organic acids (e.g., acetic and formic acids) which possess overlapping chemical properties. Current separation technologies, including reactive extraction, electrodialysis, and crystallisation, suffer from severe membrane fouling and high chemical consumption caused by suspended MSW solids and colloidal impurities. Consequently, few currently available downstream methods appear economically viable for MSW-derived succinic acid at present titres, rendering this pathway the least technologically mature of the four examined precursors (Lithourgidis *et al.*, 2023).

**Critical Research Priorities**

Advancing MSW-to-polymer-precursor biorefineries requires bridging fundamental microbial ecology with applied process engineering:

1. Contaminant resilience: Systematic assessment of chain-elongation consortium stability under real MSW contaminant profiles (microplastics, heavy metals, xenobiotics) to enable non-sterile operation and cost reduction.
2. Microbiome engineering: Development of multi-omics-guided approaches for selective enrichment of target acidogens, including synthetic consortium design and non-sterile microbiome-management protocols.
3. Lactate-driven integration: Optimisation of lactate-mediated chain elongation directly coupled to homolactic fermentation from cellulosic MSW fractions, eliminating external electron donor costs.
4. Fouling-resistant separation: Innovation in downstream technologies (membrane systems, reactive extraction, electrochemical methods) robust to high-solids MSW broths and capable of in-situ product recovery.
5. Pilot-scale demonstration: Integrated demonstration systems combining hydrolysis, fermentation, and separation stages to validate economic performance and environmental metrics at pre-commercial scales.

**Conclusions**

Municipal solid waste represents a promising and underutilised feedstock for the sustainable production of polymer precursors. The technical feasibility of these pathways varies significantly by product. Lactic acid appears to be the most technologically mature option, delivering high yields and titres from OFMSW. However, the production of racemic DL-lactate from mixed MSW cultures remains a critical barrier for PLA synthesis, necessitating advanced strain engineering or the complex separation of L- and D-isomers. Meanwhile, butyric acid offers a favourable balance of yield and productivity. The integration of fermentation, chain elongation, and efficient product recovery could substantially improve the economic viability of MSW biorefineries and contribute to the transition toward a circular bioeconomy.

Chain elongation enables caproic acid production but introduces unique operational bottlenecks. Generating caproic acid from MSW requires external electron donors such as ethanol or lactate alongside longer hydraulic retention times, which ultimately results in lower yields and titres than those observed for butyric acid. While lactate-mediated chain elongation represents a promising recent development that can substantially reduce external chemical costs, its overall process stability remains inferior to conventional ethanol-based systems.

To advance MSW-to-polymer-precursor biorefineries, future research must bridge the gap between fundamental microbial ecology and process engineering. Key priorities include assessing the resilience of chain-elongation consortia against real-world MSW contaminants and developing non-sterile microbiome management strategies—potentially guided by multi-omics tools—to selectively enrich target acidogens. Furthermore, optimising self-sustaining, lactate-driven chain elongation from the cellulosic fraction of MSW remains critical to eliminate external electron donor costs. Finally, scaling up these technologies requires significant innovations in robust, fouling-resistant downstream separation systems capable of operating directly with high-solid MSW broths.

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**Conflict of Interest Statement**

The authors declare no conflict of interest.

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