Review

Green conversion of municipal solid wastes into fuels and chemicals

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Abstract

Presently, the society is facing a serious challenge for the effective management of the increasing amount of produced municipal solid wastes. The accumulated waste has caused a series of environmental problems such as uncontrolled release of greenhouse gases. Moreover, the increasing amount of wastes has resulted in a shortage of areas available for waste disposal, resulting in a nonsustainable waste management. These problems led to serious public concerns, which in turn resulted in political actions aiming to reduce the amount of wastes reaching the environment. These actions aim to promote sustainable waste management solutions. The main objective of these policies is to promote the recycling of municipal solid waste and the conversion of waste to energy and valuable chemicals. These conversions can be performed using either biological (e.g., anaerobic digestion) or thermochemical processes (e.g., pyrolysis). Research efforts during the last years have been fruitful, and many publications demonstrated the effective conversation of municipal solid waste to energy and chemicals. These processes are discussed in the current review article together with the change of the waste policy that was implemented in the EU during the last years.

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1. Introduction

The rising environmental problems, involving greenhouse gases (GHGs) and air and water pollution, together with the energy crisis and resource scarcity will become more imminent in the coming decades, necessitating the need to take actions toward a more sustainable society. Energy and chemicals are mainly produced from...
fossil resources, and this causes the release of CO₂ in the atmosphere together with other toxic compounds (such as volatile organic compounds and nitrogen oxides). It is estimated that 90% of the global emission of CO₂ (which reached approximately 34 billion tons of GHGs in 2011) has been derived from the combustion of fossil fuels [1]. Moreover, as these raw materials are finite, processes utilizing them as feedstock are not sustainable, and thus, the security of supply will be an important issue for humanity.

Another important challenge is the rising accumulation of wastes in the environment. The waste accumulation in the environment has raised the public awareness because of the problems caused by the amount of wastes disposed into the environment. However, the huge volumes that are produced globally alongside the diversity that these wastes present makes them ideal candidates to be used for high-value applications [2].

Conventional methods that are widely used for the treatment and management of municipal solid waste (MSW) including landfilling, incineration, and composting, present some disadvantages. Waste disposal through landfills causes severe environmental issues such as uncontrolled release of methane into the atmosphere, a gas that has 20 to 23 times higher GHG potential than CO₂, production of leachate that contaminates the soil and the ground water, unpleasant odors, and spread of pathogenic microorganisms [3,4]. For example, more than 95% of food waste (FW; estimated to be between 25% and 70% of MSW) end up in landfills, which has a catastrophic impact on the climate because of the release of methane and other GHGs (calculated to be 125 m³ of gas per ton of landfilled FW) [5,6]. In some places, waste is incinerated for the production of heat and energy. Although it is a valuable method, especially to more remote areas, it could result in air pollution [as dioxins and similar persistent organic pollutants (POPs) can be produced], and the chance to extract valuable chemicals from the waste is lost [6,7]. Moreover, incineration presents high capital and operating cost [8], and special care has to be taken for the safe disposal of the produced fly ash during the process. Composting is the process where organic materials are stabilized using indigenous microorganisms and can be used as an environmentally friendly fertilizer. However, the process of composting should be carried out properly; otherwise composting could result in problems such as strong odors and possible generation of GHGs [6]. Nevertheless, the potential of valorizing the wastes to produce valuable fuels and chemicals is an attractive alternative solution that has gained the interest of both scientific and public opinion. Our previous research has showed that refuse-derived fuels based on MSW showed improved fuel properties and lower emissions of POPs during combustion when MSW from areas with extensive separation of FW in the households was used [9,10].

Although MSW could be an excellent substrate for upgrading to valuable products and energy, especially considering its availability, their handling presents some challenges. For example, MSW presents a high variability in both regional and seasonal composition and volumes, which may, for instance, affect the emissions generated during incineration [11]. Another challenge is the high water content, which makes them prompt to microbial contaminations. This could also potentially result in public health issues as pathogens can also contaminate MSW. The high moisture content also results in increased volumes and weight of MSW, making drying an important step to reduce the cost of transportation. Drying and transportation are energy and cost demanding and in turn impact the total process cost. The fact that the generation of MSW is present in virtually every residual area can offer a solution to avoid both drying and long-distance transportation. A decentralized system can be introduced where low-volume facilities locally use MSW [12].

### 2. Municipal waste in Europe

The amount of MSW produced worldwide is estimated to be 2 billion tons per year with a projected increase to 9.5 billion tons per year by 2050 [5]. In Europe, according to Eurostat, the amount of MSW produced in 2014 was 475 kg/capita on average, which is a reduction compared to that in 2000 (523 kg/capita) [13]. The highest production of municipal waste is observed in Denmark (759 kg/capita) and Cyprus (626 kg/capita) and the lowest in Poland and Romania (272 kg/capita). The amount of waste produced in Sweden at that time was 438 kg/capita.

In 2001, the European Council adopted the first EU Sustainable Development Strategy (SDS) following the commitments taken during the Earth Summit in Rio de Janeiro (Brazil) in 1992 [14]. The aim of SDS was to support actions that will improve the quality of life of current and future generations [14]. It is well established in the union that environmental issues, especially effective waste management and resource efficiency, are the key priorities of European Commission, as demonstrated in the Roadmap to resource efficiency in Europe [15] and the 7th Environmental Action Programme [16]. In the field of MSW management, EU has implemented different policies setting member states targets to fulfill concerning recycling and deflection MSW from ending in landfill sites, with a target of recycling of 50% household waste by 2020 [17,18]. The main policy of EU concerning the waste management is demonstrated in Fig. 1 as established in the Waste Framework Directive 2008/98/EC [15,16]. According to this scheme, which reflects the policy followed by the member states of EU, the highest priority is the prevention of the production of new wastes followed by their reuse and recycling. Practices such as landfilling should be restricted to only those that are absolutely necessary.

According to Eurostat [20], during the period 2000–2014, it was observed that there was a decline (from 523 to 475 kg/capita) in the generated municipal wastes in EU27 (Fig. 2). What is more interesting about the data collected by the Eurostat is the change over time in the distribution of the different management practices of MSW. For example, the problematic practice of landfill significantly decreased from 288 to 131 kg/capita, which is equal to a 54.5% reduction over a period of 14 years. However, incineration of MSW increased by approximately 60%, recycling by 59%, and composting and digestion by 53%. Over these years, landfilling of MSW dropped from 55% to 27.6% of the total waste and from a dominant practice became the second most used, after recycling (27.8% of the total municipal wastes), European Environmental Agency reported an increase in the number of countries that recycle (including material recycling, compost, and anaerobic digestion) more than 25% of the total municipal waste, from 11 countries to 16 from 2001 to 2010, and a decrease in the number of countries that landfill more that 75% of municipal waste, from 17 countries to 11 for the same period [19].

According to another report from the same agency, in Austria, Denmark, Norway, the Netherlands, Belgium, Sweden, and Germany,
virtually no MSW is ending in landfills, which is very promising for the future of waste management in Europe [21]. As a result of the implemented MSW management policies by EU, the net emissions of CO₂ reduced from 67 Mt in 2001 to 29 Mt in 2010 [19]. Although the results are very promising, there is a significant variation between the results of different countries, with some countries performing very well and others underperforming or even reducing the amount of wastes recycled [19]. For example, in 2010, 5 countries were recycling more than 50% of their total wastes, whereas 7 countries were recycling less than 10%.

Sweden has a long history in environmental protection, which covers a wide range of actions, taking special care on the sustainable management of waste. For this reason, a number of legislations have been imposed, covering a wide range of waste management topics during the last two decades [22]. The two main waste legislations according to the same webpage are the Chapter 15 of the Environmental Act (1998:808) and the Waste Ordinance (2001:1063). The Swedish Environmental Protection Agency is responsible for guiding and supervising the authorities responsible for the inspection and enforcement, and then the municipalities are responsible for implementing the waste legislation. Finally, county administration boards are responsible for the major waste treatment plants [22].

In Sweden, according to the report of the European Environment Agency, recycling and incineration of municipal waste account for 49% each of the total amount, whereas only 1% of the total municipal wastes end in landfill [23]. According to the same report, the landfill tax that was imposed on January 1, 2000, and was raised in 2002, 2003 and 2006 (overall increase of 74%) played a vital role in the reduction of the amount of the wastes ending in landfills. Two more important milestones in the reduction of the amount landfilled were the landfill ban on sorted combustible waste in 2002, which in 2005 was expanded to include all the organic waste with minor exceptions—Förordning (2001:512) om deponering av avfall [23, 24].

All the actions that were taken in Sweden resulted in the gradual decrease of GHG emissions during the period 1990 to 2013, with the lowest level presented in 2013, although the emissions created in other countries as a result of Swedish consumption increased at the same time [25]. It can also be noted that from 1995, prior to the implementation of the EU legislation about waste management, landfills in Sweden accounted for 35.2% of the wastes, whereas the main practice for waste management was incineration (38.3%) (Fig. 3, data extracted from Eurostat [20]). It is also worth noticing that after 2009, the amount of waste ending in landfill was very low, accounting for less than 6 kg/capita. Finally, over the period of 1995–2014, the proportion of recycling materials in the total municipal waste increased from 20.2% to 33.3% and the proportion of compost and digestion increased from 6.2% to 16.4%.

3. Biotechnological process

Biotechnological conversion of MSW involves the use of microorganisms to convert the organic fraction of the MSW to different molecules. The most common processes of microbial conversion of MSW include the production of liquid fuels (ethanol) and gaseous fuels (methane and hydrogen). The composition of MSW varies according to the source of the waste, and this has a great impact on the yield of the subsequent processes as well. Generally, high composition of food and vegetable waste is more desirable as these wastes are easily degradable and often result in high yields compared to other wastes such as papers and cardboards. The effective decomposition of complex polymeric molecules (such as cellulose and proteins) to simple molecules (such as sugars and amino acids) is often considered a rate-limiting factor of the process. To improve the solubilization of the organic materials in the MSW, different research groups have evaluated a range of pretreatment processes such as thermo-chemical [26], hydrothermal [27], and enzymatic hydrolysis [28] and combinations of chemical, thermal, and enzymatic treatments [29]. Enzymatic hydrolysis (or saccharification) can involve a wide range of enzymes targeting different molecules, e.g., cellulases and hemicellulases for lignocellulose; α-amyloses, β-amyloses, and glucoamylases for the hydrolysis of starch; lipases for fats and oils; and proteases for proteins. The enzymes or their mixtures that will be used depend on the nature of the raw material, the targeted compound, and the ability of the used microorganisms to hydrolyze these compounds.

3.1. Ethanol

Ethanol is considered as one of the most important liquid biofuel and has been used as a vehicle fuel since 1896 when Henry Ford designed his first car that ran on pure ethanol [30]. Ethanol can be used in vehicles after blending with gasoline at different ratios from 5% (E5) to 100% (E100 or pure ethanol). An advantage of using ethanol as vehicle fuel is that it can be directly used in conventional cars with blends of up to E10, whereas when the proportion of ethanol increases, some modification (such as fuel pump) are required, with blends higher than E25 requiring engine modifications [31]. Other benefits of using ethanol as a fuel are the increase of the octane number in the blends...
(even small amounts cause disproportionately large increase in the octane number) and the higher oxygen content, which improves the efficiency of combustion [30,32]. Most importantly, the use of ethanol as fuel facilitates the reduction of the emission of carbon monoxide, sulfur oxides, volatile organic compounds, fine particulate matter, benzene, and hydrocarbons [33]. On the contrary, the disadvantages of using ethanol as fuel are the increase in the emissions of nitrogen oxides, acetaldehyde, formaldehyde, and acrolein [32]. Moreover, ethanol has lower energy output than gasoline, equal to 66% of the energy content of gasoline [34].

MSW is a promising raw material for the production of ethanol. During ethanol fermentation, the carbohydrate fraction of MSW (e.g., glucose, fructose, starch, and cellulose) can be converted to ethanol, whereas the proteins and minerals present in MSW are necessary for the growth of the fermenting microorganism.

There are many reports in the literature that used different sources of MSW. For example, Matsakas et al. [35] used household FW (HFW), which was dried in situ. More specifically, a two-stage process was applied, where the dried HFW was initially fermented to ethanol after an enzymatic saccharification/liquefaction, producing up to 43 g/L ethanol with a volumetric productivity of 2.85 g/L·h (Table 1). The remaining solids at the end of the fermentation were further utilized for the production of ethanol after the application of microwave-assisted hydrothermal pretreatment. During the second stage, an additional 16 g/L of ethanol was produced, resulting in an ethanol yield of 107.6 g/kg dry material. Moreover, FW from a university cafeteria in Seoul was used Kim et al. [36]. The authors evaluated a variety of commercial enzyme solutions for the conversion of the FW to glucose, with the most efficient combination being glucoamylase (from Aspergillus niger) or carbohydrate (from Aspergillus aculeatus) supplemented with protease (from Bacillus licheniformis). In the fermentation stage, the separate hydrolysis and fermentation (SHF) process was more effective than the simultaneous saccharification and fermentation (SSF), resulting in an ethanol yield of 0.43 g/g total solids (TS) in comparison to 0.31 g/g TS with SSF. The SHF process was more beneficial probably because the enzymes can act under their optimal conditions prior to fermentation (normally they present higher optimal temperatures than the temperature at which fermentation takes place). Same results of the advantage of SHF over SSF were also demonstrated in other works using various lignocellulosic materials such as sweet sorghum [37,38] and wheat straw [39].

FW from a university cafeteria was used by Moon et al. [40], who also examined the effect of the sodium chloride concentration on ethanol fermentation. They used an enzyme mixture of amyloglucoside and carbohydrase, which resulted in a glucose yield of 0.46 g/g FW after 3 h of treatment. This yield was higher than the yields obtained using single enzymes, underpinning the synergistic effect of these two enzyme solutions. At a subsequent fermentation, 29.1 g/L of ethanol was produced, resulting in an ethanol yield of 107.6 g/kg dry material. Moreover, FW from a university cafeteria in Seoul was used Kim et al. [36]. The authors evaluated a variety of commercial enzyme solutions for the conversion of the FW to glucose, with the most efficient combination being glucoamylase (from Aspergillus niger) or carbohydrate (from Aspergillus aculeatus) supplemented with protease (from Bacillus licheniformis). In the fermentation stage, the separate hydrolysis and fermentation (SHF) process was more effective than the simultaneous saccharification and fermentation (SSF), resulting in an ethanol yield of 0.43 g/g total solids (TS) in comparison to 0.31 g/g TS with SSF. The SHF process was more beneficial probably because the enzymes can act under their optimal conditions prior to fermentation (normally they present higher optimal temperatures than the temperature at which fermentation takes place). Same results of the advantage of SHF over SSF were also demonstrated in other works using various lignocellulosic materials such as sweet sorghum [37,38] and wheat straw [39].

### Table 1

<table>
<thead>
<tr>
<th>Source of raw material</th>
<th>Pretreatment</th>
<th>Enzymes</th>
<th>Ethanol yield parameters</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Concentration (g/L)</td>
<td>Productivity (g/L·h)</td>
</tr>
<tr>
<td>Household food wastes</td>
<td>–</td>
<td>Cellulases</td>
<td>42.8</td>
<td>2.85</td>
</tr>
<tr>
<td>Food waste from cafeteria</td>
<td>–</td>
<td>Glucoamylase and carbohydrate</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
<tr>
<td>Food waste from dinner center</td>
<td>–</td>
<td>Amyloglucoside and carbohydrate</td>
<td>28.1</td>
<td>1.94</td>
</tr>
<tr>
<td>Food waste from cafeteria and households</td>
<td>–</td>
<td>α-Amylases and glucoamylases</td>
<td>8</td>
<td>n.a.</td>
</tr>
<tr>
<td>Food waste from cafeteria</td>
<td>–</td>
<td>α-Amylases, amyloglucosidase, cellulase, and β-glucosidase</td>
<td>32.2</td>
<td>0.55</td>
</tr>
<tr>
<td>Food waste from cafeteria</td>
<td>–</td>
<td>Glucoamylases and β-glucanase</td>
<td>48.6</td>
<td>2.03</td>
</tr>
<tr>
<td>Food waste from retail store</td>
<td>–</td>
<td>α-Amylase, glucoamylase, and protease</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
<tr>
<td>Food waste from dinner center</td>
<td>–</td>
<td>α-Amylase and glucoamylase</td>
<td>87.9</td>
<td>1.83</td>
</tr>
<tr>
<td>Food waste from cafeteria</td>
<td>–</td>
<td>Enzyme solution produced in situ by A. awamori</td>
<td>58</td>
<td>1.81</td>
</tr>
<tr>
<td>Leachate from food waste resource recovery plant</td>
<td>–</td>
<td>–</td>
<td>24.2</td>
<td>0.61$^*$</td>
</tr>
<tr>
<td>Model organic fraction of municipal solid waste</td>
<td>85°C for 1 h</td>
<td>Mixture of cellulase, amylase, protease, hemicellulose, lipase, and pectate lyase</td>
<td>42.8</td>
<td>2.14</td>
</tr>
</tbody>
</table>

n.a.: not available.

$^*$ The productivity was calculated by dividing the ethanol concentration with 40 h, which was mentioned in the materials and methods as the period that the fermentation lasted.
was produced, with an ethanol yield of 0.23 g/g FW. It was also demonstrated that the addition of NaCl up to 3% w/v did not have any negative impact on the fermentation, whereas for concentrations higher than 4% w/v, they observed an inhibition in cell growth and substrate uptake, with the ethanol yield slightly decreasing as well.

Starchy FW from a university dinner center were used by Walker et al. [41], composed of corn, pasta, and potatoes. Prior to fermentation, the FW were saccharified with the use of α-amylases and glucoamylases, and ethanol production was up to 8 g/L. A combination of kitchen FW from both university cafeteria and households were used by Uncu and Cekmeceglioglu [42]. The authors used a combination of enzymes to saccharify the FW 6 h prior to fermentation. Fermentation was optimized with the experimental design, and under optimal conditions, 32.2 g/L of ethanol was obtained, with a volumetric productivity of 0.55 g/L·h. FW with high starch content and starch-targeting hydrolytic enzymes were also used by other researchers resulting in ethanol production between 23.3 and 81.5 g/L [43,44,45]. Other approaches to improve the ethanol production were the co-cultivation of different fermenting organisms (Saccharomyces cerevisae and Pichia stipites) [46] and the application of continuous cultivation, which resulted in a productivity of up to 24 g/L·h [47].

High ethanol concentration could result in the inhibition of the process. To overcome this problem, Huang et al. [48] proposed the application of vacuum for controlling ethanol under 100 g/L. The result of this process was the increase in ethanol yield from 0.327 to 0.358 g/g waste. Other methods such as cell immobilization were also examined [49] to increase the ethanol production. More specifically, they used cellulose-treated corn stock to immobilize Saccharomyces cerevisae cells, resulting in 87.9 g/L of ethanol, which was 6.5% higher than that of free cells during batch fermentation. When a continuous fermentation was applied with a hydraulic retention time (HRT) of 3.1 h, the ethanol production increased to 84.9 g/L, whereas an ethanol productivity as high as 43.5 g/L·h was achieved when the HRT was reduced to 1.55 h. Finally, Uçkun Kiran and Liu [50] used a process configuration where the enzymes necessary to hydrolyze the FW were produced by cultivating Aspergillus awamori on a waste cake collected from a catering unit. The produced enzymes were a mixture with different enzymatic activities, with the main activity against starch being glucoamylase activity, and the subsequent fermentation resulted in 58 g/L of ethanol when the FW were saccharified for 24 h. Other sources of FW have also been used by different research groups, such as FW leachate from FW resource recovery plant, where after process optimization, the ethanol production reached 24.2 g/L [51]. Finally, Nwobi et al. [52] performed a compositional analysis of household wastes collected by a collection company over a period of 8 months. The main fraction of the waste was FWs, accounting for the 74% of the total waste, followed by paper (11%). The authors prepared a model waste according to this composition, which was mildly treated (85°C for 1 h) and presaccharified with a mixture of commercial enzymes for different durations. In the following SSF process, ethanol productivity was as high as 2.14 g/L·h.

3.2. Methane

Biogas (methane) is a gaseous biofuel that is produced through the digestion of organic materials in the absence of oxygen and consists mainly of methane and CO2. Other compounds that are produced during the digestion include sulfur compounds (hydrogen sulfide and alkylthiols), ammonia, alcohols, carbonyl compounds (including aldehydes and ketones), carboxylic acids (such as formic acid and acetic acid), terpenes, and aromatic compounds [53]. The process of anaerobic digestion is a complex procedure that involves different stages, each one catalyzed by different consortia of microorganisms. These steps involve the hydrolysis of complex molecules to monomers, which is followed by the steps of acidogenesis, acetogenesis, and methanogenesis [54,55].

The applications of biogas involve its use as vehicle fuel (after enriching its composition in methane) and for the production of heat and electricity through burning in a special equipment called combined heat and power. The use of methane as a vehicle fuel presents some benefits as it does not require extensive modification of the vehicle, and it is a technology that has already been proven in practice [56]. Compared to other fuels such as ethanol, the production of methane is more efficient, resulting in a higher ratio of output to input energy, which reaches up to 28 [57,58]. For the production of combined heat and power, different apparatus are used, such as internal combustion engines, microgas turbines, and solid oxide fuel cells (SOFCs) [59] with varied efficiencies. For example, the use of traditional internal combustion engines result in electrical efficiencies in the range of 30–35% (with the power ranging between 1 and 500 kW), whereas novel technologies such as SOFC systems can reach efficiency of 65–70% [60].

MSW has been widely used as raw material for anaerobic digestion because it presents a favorable composition as they are normally rich in carbohydrates, proteins, and minerals. In addition to the source of MSW, other factors that affect the digestibility of MSW are the carbon to nitrogen (C:N) ratio, the particle size (wet vs. dry digestion), and temperature (thermophilic vs. mesophilic vs. thermophilic) of the digestion and the organic load that is fed in the digester. Presence of a pretreatment or conditioning step prior to digestion could have a positive impact on the digestion as it could result in easier decomposition of more recalcitrant compounds. Use of anaerobic digestion for MSW treatment instead of other processes, such as incineration and gasification, requires significantly less investment costs and has a lower gate fee [61], underpinning the importance of anaerobic digestion as a MSW treatment method.

Generally, FW results in higher methane yields than that of MSW that are composed of mainly other organic materials (such as papers and cardboards). For example, Zhang et al. [62] reported a methane yield of up to 435 mL CH4/g volatile solids (VS) from FW collected from different sources (restaurants, food markets, hotels, and businesses (Table 2). To increase the composition in FW and remove the rest of the organic materials (e.g., wood) and inorganic contaminants (e.g., plastic), the original waste went through a screening process in a waste management company. Davidsson et al. [63] evaluated different organic frictions of MSW (OFMSWs) for their methane production potential at both lab and pilot scale. The OFMSW differ from each other with regard to their origin (single family houses or apartment blocks), the wrappings and sack type in refuse bin (if any), and the pretreatment method used (screw press device, disc screen, shredder + magnetic separation, piston press device, or food–waste-disposer-system). The methane yields during the lab-scale digestion varied between 300 and 570 mL CH4/g VS, and the authors did not observe any systematic variations that were caused by the difference in origin or treatment. The corresponding values for pilot-scale digestion varied between 275 and 450 mL CH4/g VS.

The use of the organic fraction of MSW, which is rich in paper waste, can result in poor methane yields, such as the results reported by Macías-Corral et al. [64] where the methane yield was 37 mL CH4/g VS using OFMSW containing 62% of paper. A strategy proposed by the authors to improve this yield was codigestion with cow manure, which resulted in an improvement to 172 mL CH4/g VS. Codigestion can improve the nutrient deficiencies of the waste digested. For example, nitrogen-poor waste can be improved by the addition of nitrogen-rich waste resulting in a better C:N ratio. This was verified by Rivard et al. [65], who supplemented the digestion of MSW with either yeast extract and minerals or proteanerobically digested municipal sewage sludge; both acted as nutrient supplementation. The same positive impact of the codigestion of OFMSW with primary sludge and thickened excess activated sludge was also demonstrated by Sosnowski et al. [66] when they conducted the digestion in a two-stage quasi-continuous mode. Under these conditions, the biogas
yield improved from 419 to 532 mL/g VS (with a methane content of >60% in all cases). The concept of codigestion was also employed by Elango et al. [67] where MSW was codigested with domestic sewage at different organic feeding rates. Under the optimal rate of 2.9 g VS/mL/d, the methane yield reached a value of 380 mL CH₄/g VS.

Finally, Martín-González et al. [68] evaluated the codigestion of OFMSW: organic fraction of municipal solid waste; FOG: fat, oil, and grease waste.

<table>
<thead>
<tr>
<th>Source of raw material</th>
<th>Treatment/other operational conditions</th>
<th>Yield (mL CH₄/g VS)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Food waste from different sources</td>
<td>Screening and grinding to remove impurities</td>
<td>435</td>
<td>[62]</td>
</tr>
<tr>
<td>OFMSW from houses or apartments</td>
<td>Different mechanical treatments</td>
<td>300–570</td>
<td>[63]</td>
</tr>
<tr>
<td>OFMSW rich in paper waste</td>
<td>–</td>
<td>37</td>
<td>[64]</td>
</tr>
<tr>
<td>OFMSW rich in paper waste</td>
<td>Codigestion with cow manure</td>
<td>172</td>
<td>[64]</td>
</tr>
<tr>
<td>MSW</td>
<td>Supplemented with yeast extract and minerals</td>
<td>336</td>
<td>[65]</td>
</tr>
<tr>
<td>MSW</td>
<td>Supplemented with predigested municipal solid sludge</td>
<td>307</td>
<td>[65]</td>
</tr>
<tr>
<td>OFMSW</td>
<td>Operation in two-stage quasi-continuous mode</td>
<td>419*</td>
<td>[66]</td>
</tr>
<tr>
<td>OFMSW</td>
<td>Codigestion with primary sludge and thickened excess activated sludge in two-stage quasi-continuous mode</td>
<td>532*</td>
<td>[66]</td>
</tr>
<tr>
<td>MSW from yard</td>
<td>Codigestion with domestic sewage</td>
<td>360</td>
<td>[67]</td>
</tr>
<tr>
<td>OFMSW</td>
<td>–</td>
<td>240</td>
<td>[68]</td>
</tr>
<tr>
<td>OFMSW</td>
<td>Codigestion with FOG waste at a ratio of 7:1 (MSW:FOG)</td>
<td>350</td>
<td>[68]</td>
</tr>
<tr>
<td>Source-separated OFMSW</td>
<td>Postdigestion treatment at hyperthermic conditions with recycling of the treated particles to the digestor</td>
<td>640–790*</td>
<td>[74]</td>
</tr>
<tr>
<td>OFMSW from households</td>
<td>–</td>
<td>180</td>
<td>[75]</td>
</tr>
<tr>
<td>OFMSW from households</td>
<td>Bacterial hydrolysis in combination with thermal and alkaline treatment</td>
<td>400</td>
<td>[75]</td>
</tr>
<tr>
<td>MSW</td>
<td>–</td>
<td>247</td>
<td>[76]</td>
</tr>
<tr>
<td>MSW</td>
<td>Two-stage digestion, with the remaining solids after first stage to get pretreated with steam explosion and digested</td>
<td>355</td>
<td>[76]</td>
</tr>
<tr>
<td>MSW</td>
<td>As before, with the remaining solids of secondary digestion to be pretreated with steam explosion and digested</td>
<td>381</td>
<td>[76]</td>
</tr>
<tr>
<td>Industrial kitchen waste</td>
<td>Pretreatment with pressurize-depressurize</td>
<td>520*</td>
<td>[77]</td>
</tr>
</tbody>
</table>

OFMSW: organic fraction of municipal solid waste; FOG: fat, oil and grease waste.

a Results are presented as mL biogas per g volatile solids.

b Results are presented as mL biogas per g chemical oxygen demand.

Another process configuration that has been evaluated is multi-stage digestion. This strategy has the benefit that it could result in improved digestion of more recalcitrant substrates, as Hartman and Ahring [74] proposed in their work. More specifically, they applied a postdigestion treatment at hyperthermic conditions (68°C) when using source-separated OFMSW to convert the most recalcitrant particles to volatile fatty acids (VFAs), which then were recycled back to the digestor and converted to biogas. At the same time, higher temperatures facilitated the stripping of ammonium, which could be used as fertilizer. The use of the two-stage system resulted in 7% increase of VS reduction compared to that by the control (reaching 78–89%), with the biogas yield reaching 640–790 mL/g VS. The authors mentioned that there was no difference in the methane composition of biogas in between the two-stage and one-stage digestion.

Finally, another strategy to improve the biogas yield from MSW is the application of a pretreatment step prior to digestion. Pretreatment can result in the better hydrolysis of complex molecules and especially more recalcitrant molecules such as cellulose, which in turn improves their digestibility. Different pretreatment techniques can be applied alone or in combination. For example, Del Borghi et al. [75] evaluated the effect of bacterial prehydrolysis on biogas yield, alone or in different combinations with heat treatment (121°C, 20 min) and chemical treatment (4 g/L NaOH). Optimal hydrolysis of the OFMSW was obtained with the combination of all these three together, with the biogas yield increasing from 360 mL/g VS (180 mL CH₄/g VS) with the untreated to 870 mL/g VS (400 mL CH₄/g VS) with the treated MSW. Another pretreatment concept applied by Liu et al. [76] was to pretreat the undigested solids containing more recalcitrant compounds with steam explosion (240°C, 5 min) and further digest them in a secondary digestion. This system with the two digestions resulted in an increase in the methane yield by 43.3% from 247 to 355 mL CH₄/g VS, whereas application of another steam explosion pretreatment to the remaining solids from the second digestion resulted in a further increase of the methane yield to 381 mL CH₄/g VS (54.2% higher than the first digestion). Ma et al. [77] examined the effect of a variety of pretreatment methods on biogas yield from industrial kitchen wastes. More specifically, they evaluated the effect of acid pretreatment (HCl, pH 2, 18°C, 5 min), thermal (120°C, 30 min, with 30 min heating and cooling each), combined thermal and acid, pressure–depressurize (10 bar with CO₂ and depressurize), and freeze–thaw (from –80°C to 55°C) methods. From all the tested methods, pressure–depressurize resulted in the highest biogas yields (520 mL/g chemical oxygen demand), with the freeze–thaw and thermal treatment showing a small improvement over the control and the combined acid-thermal and acid treatment showing a negative impact.
3.3. Hydrogen

Hydrogen (H₂) is a gaseous fuel that is recognized as another promising alternative to the traditional fuels. Hydrogen is an environmentally friendly form of energy as it only produces water instead of GHGs during combustion and can also be directly used for the production of electricity through hydrogen fuel cells or other types of fuel cells such as SOFC [78, 79]. It has a high energy yield (122 kJ/g, which is 2.75 times higher than that of hydrocarbons) and is mostly produced from fossil-derived materials (approximately 95% globally) [78, 80, 81]. To minimize the dependence on fossil sources, it is important to switch the production to microbial conversion of renewable resources. Biological production of H₂ can be classified as fermentation (photofermentation or dark fermentation) or photosynthetic (direct biophotolysis of water by algae and cyanobacteria or bioelectrohydrogenesis in microbial fuel cells) processes [81, 82]. Because of the nature of the fermentative process, where an organic compound is required, it is considered more advantageous as it can utilize different wastes as raw materials. Moreover, production of H₂ through dark fermentation is estimated to have 340 times lower process costs than that of photosynthetic processes [83]. Fermentation can take place by using either pure cultures (such as Clostridium sp.) or mixed cultures [78]. When mixed cultures are used, the produced H₂ can potentially be utilized by hydrogenotrophic bacteria, and for this reason, heat treatment of the sludge is widely used to suppress this side pathway [7].

The use of MSW for the production of H₂ is another alternative for the conversion of this material to a high-value fuel. For example, Alzate-Gaviria et al. [84] digested OFMSW derived from a cafeteria (containing FW, recycled paper, and cardboards) in a packed bed reactor, resulting in 99 mL H₂/g VS (maximum hydrogen yield of 23%) at a mass retention time of 50 d (Table 3). The nature and composition of the MSW used greatly affect the hydrogen yields, which was shown by Dong et al. [78] in studies using different sources of MSW with varying composition. Materials rich in more simple forms of carbohydrates achieved higher H₂ yields, whereas oil and lignocellulosic materials resulted in very poor yields (Table 3). When fat was used as raw material, no H₂ was detected. The authors also observed that with protein substrate (lean meat), only a few mL of gas was produced, and no hydrogen was detected during incubation with carbon dioxide. A similar study evaluating different MSW materials [85] demonstrated similar trends, with the carbohydrate-rich material resulting in higher yields, whereas protein-rich material and fats resulting in significantly lower yields (Table 3). Another study evaluating the effect of the source of the material on hydrogen yield was performed by Kobayashi et al. [86], in which more complex waste was utilized. More specifically, they used separated domestic waste that were classified as 20 different waste fractions, ranging from animal and vegetable kitchen waste to newspaper waste and used paper. They demonstrated that the hydrogen yield varied significantly between the different waste fractions, and after a statistical analysis of the relationship between the composition of the different fractions and the hydrogen yield by PCA, they concluded that carbohydrate-rich feedstocks result in higher hydrogen yield ranges than protein-, fat-, and cellulose-rich feedstocks.

A process to improve the poor hydrogen yields from lipid-rich waste (more specifically lard) was later proposed by Kim et al. [80]. They mentioned that presence of CO₂ can result in the synthesis of succinate and formate from CO₂, pyruvate, and NADH, whereas CO₂ removal will allow the NADH to be reoxidized to NAD⁺ with simultaneous production of H₂. They evaluated the effect of CO₂ removal on the hydrogen yields by stirring and/or CO₂ scavenging with KOH. Stirring alone resulted in an increase of hydrogen yield from 4.5 to 40.3 mL H₂/g VS. However, the use of a KOH trap for CO₂ scavenging together with the stirring further improved the yield to 185.8 mL H₂/g VS. This system had an important impact on the concentration of VFAs, which were reduced from 522.2 to 278.8 mg/L, with the main impact of this reduction observed on the content of propionic acid, valeric acid, and n-butyric acid.

The hydrolysis of the organic particles present in the MSW is often considered a crucial part and rate-limiting factor of the process. One strategy to resolve this and improve the hydrolysis rates is the addition of surfactants such as Tween 80 and polyethylene glycol (e.g., PEG 6000).

### Table 3

Results of hydrogen production from different sources of municipal solid waste.

<table>
<thead>
<tr>
<th>Source of raw material</th>
<th>Treatment/other operational conditions</th>
<th>Hydrogen yield (mL H₂/g VS)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>OFMSW from cafeteria</td>
<td></td>
<td>99</td>
<td>[84]</td>
</tr>
<tr>
<td>Rice</td>
<td></td>
<td>134</td>
<td>[78]</td>
</tr>
<tr>
<td>Potato</td>
<td></td>
<td>106</td>
<td>[78]</td>
</tr>
<tr>
<td>Lettuce</td>
<td></td>
<td>50</td>
<td>[78]</td>
</tr>
<tr>
<td>Oil</td>
<td></td>
<td>6.3</td>
<td>[78]</td>
</tr>
<tr>
<td>Banyan leaves</td>
<td></td>
<td>1.8</td>
<td>[78]</td>
</tr>
<tr>
<td>Cabbage</td>
<td></td>
<td>23.6–61.7</td>
<td>[85]</td>
</tr>
<tr>
<td>Carrot</td>
<td></td>
<td>44.8–70.7</td>
<td>[85]</td>
</tr>
<tr>
<td>Rice</td>
<td></td>
<td>19.3–96</td>
<td>[85]</td>
</tr>
<tr>
<td>Lean meat</td>
<td></td>
<td>2.5–7.7</td>
<td>[85]</td>
</tr>
<tr>
<td>Chicken skin</td>
<td></td>
<td>3.6–10.2</td>
<td>[85]</td>
</tr>
<tr>
<td>Egg</td>
<td></td>
<td>2.6–7.1</td>
<td>[85]</td>
</tr>
<tr>
<td>Fats</td>
<td></td>
<td>4.4–11.1</td>
<td>[85]</td>
</tr>
<tr>
<td>Lard</td>
<td></td>
<td>4.5</td>
<td>[80]</td>
</tr>
<tr>
<td>Lard</td>
<td>Fermentation was under stirring</td>
<td>40.3</td>
<td>[80]</td>
</tr>
<tr>
<td>Lard</td>
<td>Fermentation was under CO₂ scavenging</td>
<td>116.7</td>
<td>[80]</td>
</tr>
<tr>
<td>Lard</td>
<td>Fermentation was under stirring and CO₂ scavenging</td>
<td>185.8</td>
<td>[80]</td>
</tr>
<tr>
<td>Restaurant wastes</td>
<td></td>
<td>87.4⁴</td>
<td>[87]</td>
</tr>
<tr>
<td>Restaurant wastes</td>
<td>Addition of 2.8 v/v Tween 80</td>
<td>109.9⁴</td>
<td>[87]</td>
</tr>
<tr>
<td>Restaurant wastes</td>
<td>Addition of 16.7 g/L PEG 6000</td>
<td>113.8⁴</td>
<td>[87]</td>
</tr>
<tr>
<td>Restaurant wastes</td>
<td>Addition of 2.8% v/v Tween 80 and 1.7 g/L PEG 6000</td>
<td>116.7⁴</td>
<td>[87]</td>
</tr>
<tr>
<td>Kitchen waste</td>
<td>Inoculum was heat treated at 100°C for 30 min prior to digestion</td>
<td>72</td>
<td>[88]</td>
</tr>
<tr>
<td>Kitchen waste</td>
<td>Digestion performed with isolated C. acetobutylicum</td>
<td>185.9⁴</td>
<td>[89]</td>
</tr>
<tr>
<td>Kitchen waste</td>
<td>Digestion performed with isolated S. marcescens</td>
<td>171.2⁴</td>
<td>[89]</td>
</tr>
<tr>
<td>Food waste from dining room</td>
<td></td>
<td>91.5</td>
<td>[90]</td>
</tr>
<tr>
<td>Pulp from facility processing municipal organic waste</td>
<td></td>
<td>80</td>
<td>[91]</td>
</tr>
<tr>
<td>Pulp from facility processing municipal organic waste</td>
<td>Pretreatment with ultrasonication for 30 min with 2-s sonication pulses</td>
<td>141</td>
<td>[91]</td>
</tr>
<tr>
<td>Food waste from cafeteria</td>
<td>Pretreatment with ultrasonication for 12 min with 2-s sonication pulses</td>
<td>149</td>
<td>[92]</td>
</tr>
</tbody>
</table>

⁴ Results are presented as mL H₂/g TS.

Results are presented as mL H₂/kg TS/d.
a strategy that was proposed by Elsamadony et al. [87]. More specifically, the use of Tween 80 (2.8% v/v) yielded 109.9 mL H₂/gCarbs, and the use of PEG 6000 (16.7 g/L) resulted in 113.8 mL H₂/gCarbs, both being higher than the yield of the control (87.4 mL H₂/gCarbs). A combination of both (2.8% v/v Tween 80 and 1.7 g/L PEG 6000) further improved the production of hydrogen to 116.7 mL H₂/gCarbs.

Generally, the MSW originating from kitchens (containing from FW to papers) is considered a very good substrate for hydrogen production. Jayalakshmi et al. [88] used kitchen wastes from a hostel, which mainly consisted of FW and vegetable waste (66% and 27% respectively), followed by packing material (1.4%), egg shells (1.1%), and tea waste (1%). After the initial stabilization of the hydrogen-producing system, which lasted 21 d, the hydrogen yield obtained was 72 mL H₂/g VS. In another study, the same group used a slightly different approach for the conversion of kitchen waste to hydrogen, where they isolated hydrogen-producing organisms from the biogas plant sludge [89]. The most efficient hydrogen-producing bacterium isolated was Clostridium acetobutylicum, which produced 185.9 mL H₂/kg TS/d, followed by Serratia marcescens with a production of 171.2 mL H₂/kg TS/d.

Other authors have also used FW from different sources, such as dining halls, for the production of hydrogen [90], achieving high hydrogen yields (91.5 mL H₂/g VS), thus underpinning the importance of the FW fraction in the MSW for the biohydrogen process.

Finally, other research groups have evaluated the effect of ultrasonication pretreatment on the digestibility of FW. Elbeshbishy et al. [91] examined the effect of ultrasonication time by keeping the TS constant at 6.5%, and at the optimal conditions, the hydrogen yield was 141 mL/g VS, with a productivity of 2.5 mL/h and a specific energy input of 23,000 kJ/kg TS. In a later work, Gadhe et al. [92] optimized both the ultrasonication time and the TS content of the treatment, and despite the fact that under optimal conditions (8% TS and 12 min ultrasonication) the hydrogen yield was similar (149 mL/g VS), the hydrogen productivity was higher (5.2 mL/h) and the energy inputs were significantly reduced to 13,500 kJ/kg TS.

3.4. Other biological products

In addition to the three main products described before, MSW has also been used for the production of other bioproducts. For example, the bacterium Clostridium beijerinckii P260 was used for the production of butanol through ABE (acetone, butanol, and ethanol) fermentation [93]. The substrate used in this work was FW from a local retail store, and the amount of ABE produced reached 18.9 g/L, with the butanol reaching 12.3 g/L. In two other studies, succinic acid was produced from waste bread and bakery waste [94,95]. In both studies, Actinobacillus succinogenes was used as the fermenting microorganism, and prior to fermentation the waste was hydrolyzed by enzymes produced by A. awamori and Aspergillus oryzae to release glucose and free amino nitrogen. When bread waste was used, 47.3 g/L of succinic acid was produced [94], whereas succinic acid production reached 24.8 g/L for cake hydrolysates and 31.7 g/L for pastry hydrolysate [95].

In another work, Zhang et al. [96] used FW from a dining room to produce biopesticide from the bacterium Bacillus thuringiensis. During a semi-solid fermentation with a water content of 75%, the amount of α-endotoxin produced in the media reached 862 μg/mL. After adjusting the pH and product inhibition, the authors observed a toxin production of up to 2478 μg/mL after four fermentation loops. FW from a canteen has also been used for the cultivation of microalgae (Schizochytrium mangrovei and Chlorella pyrenoidosa) after hydrolysis of the waste with A. awanori and A. oryzae [97]. When S. mangrovei was used, the biomass concentration reached 14 g/L with an oil content of 16% (of which docosahexaenoic acid (DHA) reached 40 mg/g biomass). The biomass concentration of C. pyrenoidosa reached 20 g/L with an oil content of 20% (of which α-linolenic acid accounted for 30 mg/g biomass).

Finally, another category of microbial products that have been produced from MSW are different categories of enzymes. This involves the production of Amylosis from FW by A. oryzae [98] and from bread waste by A. oryzae [99]. Other authors have reported the production of different carbohydrases from FW [4] or kitchen waste [100]. Pectinolytic enzymes have also been reported to be produced by a variety of different fruit wastes and proteases from a wide range of FWs such as shrimp waste and waste bread [8,99,101]. Finally, another category of enzymes produced were lipases where waste such as waste cooking oil have been used to cultivate microorganisms such as Yarrowia lipolytica [102] or different Aspergillus and Penicillium strains [103].

4. Thermochemical processes

Thermochemical conversion technologies for the sustainable integration of MSW mainly include gasification, pyrolysis, and torrefaction. These processes are generally characterized by elevated temperatures and fast conversion rates in comparison with biochemical treatment processes. Gasification, pyrolysis, and torrefaction are all performed in the absence of oxygen or with significantly less oxygen than what is required for complete combustion [104]. The operating conditions (e.g., temperature, heating rate, and oxygen supply) and the yield of products (gas, oil/condensables, and char) vary between these three processes. The fast heating rates and moderate temperatures of pyrolysis favor the generation of liquid products. The low temperatures and long residence times of torrefaction primarily yield chars, and the high temperatures and heating rates of gasification mainly generate gas products (condensable and noncondensable gases). Gasification, pyrolysis, and torrefaction cannot be defined as completely separated processes because, for instance, pyrolysis can be considered as an incomplete gasification process and torrefaction an initial stage of gasification and pyrolysis. Combustion is naturally also a thermochemical conversion process, however, with heat and/or power as the main output, and is therefore not included in the scope of this review. In Fig. 4, the major differences between combustion, gasification, pyrolysis, and torrefaction are illustrated in terms of operating conditions and conversion products.

The advantages of thermochemical conversion of MSW over traditional MSW incineration are mainly related to the increased energy efficiency, generation of value-added products, and improved pollution control [106]. The intermediate products from thermochemical conversion may be suitable for a wide range of applications, from high-quality fuels to fine chemicals. The low operating temperatures compared to those in MSW incineration can also potentially reduce the risk of alkali volatilization, fouling, slagging, and bed agglomeration [107]. Furthermore, thermochemical conversion systems for gasification and pyrolysis are commonly equipped with product cooling and collection units, which may enable improved control of emissions of organic and inorganic pollutants [108].

Despite the advantages in energy and material recovery, thermochemical conversion of MSW remains a subject of debate because of the potential negative environmental impact. Similar to combustion-based processes, trace amounts of inorganic and organic pollutants (e.g., heavy metals and dioxins) could be formed and emitted into the air, soil, and water bodies. The characteristics and distribution of these pollutants are highly dependent on the operating conditions and technologies used, which will be discussed in each subsection.

Currently there are more than 100 commercial-scale plants in continuous operation worldwide for MSW thermal treatment, with capacity ranging from 10 to 250 kton/year [109]. However, compared to conventional MSW incineration, thermal treatment at moderate temperatures (i.e., gasification and pyrolysis) involves more complex processes and is still at the stage of technical development. MSW is generally a complex mixture of various materials that largely differ in physical and chemical characteristics. An integrated waste management
system involving different types of pretreatment is often required, including mechanical treatments, mechanical biological treatments, and mechanical heat treatments [110]. The aim of such preprocessing is to improve the combustibility of the waste and recover as many recyclable materials as possible. In addition to pretreatment strategies that involve mechanical sorting, torrefaction (conducted at moderate temperature and in oxygen-deficient conditions) can also be applied to reduce the moisture content and to generate a MSW-based fuel for further thermochemical conversion [110].

Table 4 summarizes the typical processing parameters of different thermal conversion technologies and their influence on product yields and chemical compositions. The types of input MSW, operating conditions, and the types of reactors are highlighted because of their relevance on the physical and chemical properties of the conversion products. The studies listed in Table 4 include experiments ranging from lab-scale to up-scaled pilot and commercial plants.

4.1. Gasification

Gasiﬁcation is a partial oxidation with lower oxygen supply than that required for complete stoichiometric combustion [104]. The operating temperature is generally within the range of 800–1200°C, depending on the type of reactor and the feedstock composition. The process is largely exothermic, but heat is sometimes required to initialize and sustain the gasification process. Partial oxidation can be performed using air, oxygen, steam, carbon dioxide, or a mixture of these as gasiﬁer agents. The gas product (commonly referred to as syngas in literature) is a mixture of carbon monoxide, hydrogen, carbon dioxide, methane, and other low-molecular-weight hydrocarbons. It also contains a number of undesired components such as particulate matter, tar, alkali metals, chlorine, and sulfide [111].

Gasiﬁcation of MSW is advantageous over MSW incineration primarily because of the possibility of producing syngas, which can be used as clean fuel gas in a conventional burner or coupled to a boiler or a steam turbine. The possibility to combine different operating conditions with a speciﬁc reactor enables the adjustment of the syngas composition for different applications. However, the MSW gasiﬁcation technology is still in the development stage, and the number of plants commercially available worldwide is limited [107]. Flue gases from gasiﬁcation contain particulate matter, acidic gases (e.g., nitrogen oxides and hydrogen chloride), and organic pollutants such as dioxins. In addition, the ﬁnal process residues with potential leachability of heavy metals and organic pollutants represent a major environmental concern. The emissions of these pollutants are nowadays controlled by end-of-ﬁlter technologies such as electrostatic precipitators, bag ﬁlters, and the addition of slaked lime [107]. The costs required for syngas conditioning and cleaning in gasiﬁcation-based MSW treatment is higher than that for MSW incineration.

Various gasiﬁcation reactors have been used in practice, including entrained ﬂow gasiﬁers, ﬂuidized bed gasiﬁers, cyclone gasiﬁers, and packed-bed gasiﬁers [106]. The entrained ﬂow gasiﬁers in commercial operation generally have large capacities with installed plant sizes of up to a few thousand tons per day [112]. Fluidized bed reactors have the advantage of sufﬁcient mixing and high heat transfer, resulting in uniform and efﬁcient reactions. For most types of reactors, the feeding materials must be properly granulated. Sample preprocessing is often required, in particular for heterogeneous materials such as MSW, to obtain feeding materials with consistent physical and chemical characteristics. Such preprocessing methods include sorting/separation, shredding, grinding, blending, drying, and pelletization. Development and integration of various innovative technologies in thermochemical processes is thus desirable to reduce the need of pretreatment of the MSW [113].

A major challenge in MSW gasiﬁcation is the formation of tar substances, which can potentially lead to blocking, fouling, and corrosion. Tar is a complex mixture of condensable high-molecular-weight hydrocarbons. The differences in tar compositions are mainly a function of processing conditions. Tar removal can be achieved by different methods including physical (e.g., ﬁlters, scrubbers, and wet electrostatic precipitators) [122] and chemical processes (e.g., thermal and catalytic cracking) [114,123]. Steam gasiﬁcation has recently emerged as a promising technology for generating syngas with reduced tar formation and high yield of hydrogen [124]. In this process, steam is the only gasifying agent used, and almost no exothermic reaction is involved. Factors inﬂuencing the syngas yield are mainly MSW composition, particle size, temperature, and steam-to-feedstock ratio. Addition of catalysts such as calcined dolomite has been shown to increase carbon conversion efﬁciency and tar content. Hu et al. [125] proposed an in situ MSW gasiﬁcation technique with a downstream ﬁxed-bed reactor using CaO as catalyst and CO2 sorbent. They studied the effect of catalyst and reactor temperature on the yield and product composition and observed that complete tar decomposition can occur at elevated temperatures around 950°C when calcined dolomite is used as a catalyst.

Studies of MSW gasiﬁcation reported in literature have also been extensively focusing on the optimization of reaction conditions such as temperature, heating rate, and catalysts to improve the yield and quality of the syngas and simultaneously reduce the amount of undesired
by-products [114,115,126]. Panepinto et al. [127] studied the energy efficiency and environmental performance of MSW gasification and compared it with MSW incineration. They suggested that cofiring of syngas in large-scale power plants or the use of combined cycle gas turbines can improve energy conversion efficiency. A study by Consonni and Viganò [128] showed that gasification at pressures higher than atmospheric pressure can improve the energy conversion efficiency. The optimal temperature was about 700°C for obtaining syngas with high heating value. The yield of CO decreased as steam/feedstock ratio of polyethylene increased but no significant effect with bamboo.

An emerging technology involving thermal plasma gasification for MSW treatment has received increasing attention recently. The advantages are mainly related to improved energy recovery efficiency associated with the fast reaction times, low amount of oxidant, and high heat flux densities. Studies have shown that the high temperature of the plasma arc can reduce the formation of tar and other undesirable products in the syngas [129]. The solid residues are produced in the form of a vitrified slag, which can be utilized in construction. One such demonstration plant has been operating in Korea since 2010 [129]. An integrated furnace equipped with nontransferred thermal plasma torches was successfully applied for the direct treatment of MSW with a capacity for gasification of MSW at 10 ton/d. A comprehensive overview on the types of plasma working gases and various types of reactors has been given by Tang et al. [117].

### Table 4
Comparison of operating parameters and product yields in different thermochemical conversion technologies.

<table>
<thead>
<tr>
<th>Conversion technology</th>
<th>Feedstock</th>
<th>Key operating parameters</th>
<th>Type of reactor</th>
<th>Main findings (e.g., product yield, product properties)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gasification</td>
<td>Olive oil residues, meat and bone meal, dried sewage sludge</td>
<td>Temperature was in the range of 770–870°C. The air ratio varied from 0.23 to 0.43. Solid feeding flow rate ranged from 8 to 18 kg/h.</td>
<td>Pilot-scale bubbling fluidized bed</td>
<td>Gas yields ranged from 0.89 to 1.47 Nm³/kg (expressed as dry and nitrogen-free gas per kg of dry and ash-free feedstock). The gas yield increased with increasing stoichiometric ratio. Yield of CO decreased with increasing stoichiometric ratio. Yield of H₂ decreased from 5% to 0% when stoichiometric ratio decreased from 0.25 to 0.45 for meat and bone meal. High potassium content in the olive oil residue promoted sintering of the bed. Meat and bone meal yielded gas with lower heating value than that of other fuels. The yield of H₂ was 7.0–17.7% depending on the gasification temperature. Combustible gas components and heating value of syngas decreased as the equivalence ratio increased.</td>
<td>[114]</td>
</tr>
<tr>
<td>Pyrolysis</td>
<td>MSW collected from a waste treatment plant</td>
<td>300–700°C with a residence time of 1–5 h at a heating rate of 5°C/min</td>
<td>Lab scale muffle furnace</td>
<td>Char yields decreased from 65.6% to 27.8% as temperature increased from 300°C to 700°C. Increasing temperature increased aromatization and stability. Low temperatures resulted in higher carbon exchange capacity and available nutrients. Residence time influenced hydrophobicity and thermal stability. The optimal temperature was about 700°C for obtaining syngas with high heating value. The yield of CO decreased as steam/feedstock ratio of polyethylene increased but no significant effect with bamboo.</td>
<td>[115]</td>
</tr>
<tr>
<td>Pyrolysis</td>
<td>MSW</td>
<td>450–800°C with residence time of 15 min. CO₂ and N₂ were used as sweeping gas.</td>
<td>Lab-scale tubular electrical furnace</td>
<td>Char yields decreased from 60%, 52%, and 47% at pyrolysis temperatures of 300°C, 400°C, and 500°C, respectively. Organic carbon content and carbon exchange capacity of char products decreased with increased temperature, whereas surface area and organic carbon stabilities of char increased with increased temperature.</td>
<td>[116]</td>
</tr>
<tr>
<td>Pyrolysis/torrefaction</td>
<td>Poultry litter</td>
<td>300–600°C with reaction time varying from 130 to 372 min</td>
<td>Lab-scale muffle furnace</td>
<td>Char yields were 60%, 52%, and 47% at pyrolysis temperatures of 300°C, 400°C, and 500°C, respectively. Organic carbon content and carbon exchange capacity of char products decreased with increased temperature, whereas surface area and organic carbon stabilities of char increased with increased temperature.</td>
<td>[117]</td>
</tr>
<tr>
<td>Torrefaction</td>
<td>Synthetic MSW</td>
<td>250–450°C under N₂ atmosphere for 30 min.</td>
<td>Quartz tube in muffle furnace with N₂ purged.</td>
<td>Char yields increased from 58.4% to 86.8% when temperature decreased from 400°C to 250°C. Torrefaction at 300°C resulted in chars with calorific values comparable to those of standard coal. The chlorine content of the char (at 300°C) was 5% lower than that in the feedstock.</td>
<td>[118]</td>
</tr>
<tr>
<td>Hydrothermal treatment</td>
<td>Food waste and paper</td>
<td>Reactors were heated at 250°C for 20 h.</td>
<td>Stainless steel tubular reactor (160 mL)</td>
<td>Hydrochar yields were 43.8% and 29.2% for food waste and paper, respectively. 49–75% of the initially present carbon was retained within the chars.</td>
<td>[119]</td>
</tr>
<tr>
<td>Hydrothermal treatment</td>
<td>Chicken manure</td>
<td>Reactors were heated to temperatures of 140–220°C and was maintained for 25–60 min under constant agitation. The average heating rates were 11–14°C/min</td>
<td>Stainless steel reactor (200 mL) equipped with a cylindrical electric heater</td>
<td>Reduction of total solids in hydrochars ranged from 18% to 23% at a temperature of 220°C.</td>
<td>[120]</td>
</tr>
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4.2. Pyrolysis

Pyrolysis is a thermochemical decomposition process conducted under oxygen-deficient conditions and typically at temperatures ranging between 300°C and 650°C [130]. The major products of pyrolysis are char and condensable gases. Part of the condensable gases may be further decomposed into secondary products including CO, CO₂, H₂, and CH₄. Pyrolysis for the production of char as an energy carrier is not a new concept. It has been extensively used to produce charcoal and coke from biomass and coal [104,131]. For MSW pyrolysis, numerous studies have been conducted, with main focus on technology development and system design [132]. The pyrolytic liquid as a result of condensation of volatiles can be utilized as a fuel product (referred to as bio-oil) after further upgrading and/or as an intermediate for the synthesis of fine chemicals. The char may be used in a number of potential applications, including energy production, as soil amendment, and for long-term carbon sequestration.

The yields and chemical composition of the pyrolysis products depend on, for example, feedstock properties, pyrolysis temperature, and heating rate. On the basis of the heating rate, pyrolysis can be classified as slow or fast pyrolysis. In fast pyrolysis, the residence time for vapors is a few seconds and the primary products are bio-oil and gas. In slow pyrolysis, the residence time is longer (in minutes or more) and the primary product is char [104]. In addition, the so-called flash pyrolysis with high heating rate has recently been successfully applied at a demonstration scale for syngas production from solid-recovered fuel derived from MSW [133]. There are also new conceptual designs that integrate pyrolysis with microwave heating, commonly under vacuum conditions. The advantage of microwave-assisted pyrolysis includes shorter residence time, homogeneous heating, and higher heating value of the volatile products [105]. The efficiency of the microwave-assisted process greatly depends on the nature of the processed material in terms of its physical characteristics including structural arrangements, conductivity, and dielectric properties [134].

The reactors used for conventional pyrolysis of MSW are mainly rotary kilns and tubular reactors, in particular for up-scaled facilities, whereas fixed-bed and fluidized bed reactors have been frequently used for lab-scale studies [111]. N₂ flush is commonly used to provide an inert atmosphere. In addition, vacuum pyrolysis has been applied for recovery of animal-derived waste and printed circuit boards [135,136]. Pretreatments such as shredding and drying are often required, especially for heterogeneous MSW fractions. The currently available pyrolysis plants for MSW treatment at demonstration and commercial scales are generally operated in combination with gasification or combustion systems. Fully integrated plants at demonstration and industrial scales have been in operation in European countries such as Germany, Italy, and Sweden since the 1980s [137]. The MSW entering the gasifier is pyrolyzed directly, and the recirculated gas and/or chars are combusted to maintain the required temperature in the gasifier [132,137]. Recovery of value-added products (such as ferrous and nonferrous metals) from pyrolytic residues can be achieved by sorting or screening processes.

Operation of stand-alone pyrolysis is still under development for MSW treatment to produce liquid and char as end products. Application of pyrolysis using animal manure as feedstock has recently been demonstrated in a pilot-scale reactor [138]. Approximately 50% of the carbon in the feedstock was recovered in the char at a temperature of 620°C. The high P and K contents of the char suggest that it can be used as soil amendment to improve the soil fertility. The heating value of the char was comparable with medium-rank coal. That study also demonstrated the possibility to co-pyrolyze animal waste with pelletized plastic waste to improve energy efficiency.

The influence of pyrolysis temperature, heating rate, and residence time on the yields and composition of pyrolysis products have been discussed in the literature. Williams and Williams [139] conducted the pyrolysis of plastic waste (high- and low-density polyethylene, polypropylene, and PVC) using a fixed-bed reactor at temperatures between 500°C and 700°C. The study showed that increased temperature led to a dramatic increase in the yield of gas. It was also found that higher temperatures enhanced the yield of aromatic compounds in the liquid product. Chen et al. [140] described the influence of pyrolysis temperature on the adsorption capacity of organic molecules of the char by characterizing chars as being polarity selective (produced at 200–400°C) and porosity selective (500–600°C). This indicates that the polarity of the adsorbed compound is the most important factor for adsorption on low-temperature chars, whereas the size of the adsorbed compound is more crucial for adsorption on high-temperature chars [140]. Char produced at 700°C and conventional activated carbon were nonselective because of less amount of functionalities and larger pore size, and these chars also demonstrated the highest adsorption capacities [140]. It has also been reported that pyrolysis at high temperatures will remove volatiles in the thermoplastic phase, which increase the pore size, resulting in a nonselective type of char [141]. This type of char has properties similar to commercial activated carbon and has good adsorption capacity because of the large surface area.

The residence time for feeding MSW remaining in pyrolysis reactors can vary from a few seconds to 2 h [142]. It has been reported that increased residence time could lead to enhanced tar cracking and result in higher gas yields [142]. However, long residence times could reduce the processing efficiency in terms of the capacity of MSW treatment. Heating rates for MSW pyrolysis reported in literature varied from approximately 10°C/min in slow pyrolysis [143] to 600°C/s in flash pyrolysis [144]. It was commonly recognized that high heating rate could lead to a higher yield of volatile products and lower char yield [132]. In the case that volatiles are extracted immediately in the cooling trap, a higher yield of liquid products can be obtained. The effect of temperature on the stability, nutrient availability, and hydrophobicity of chars derived from MSW have been studied recently [116]. It was found that increasing the pyrolysis temperature increased the aromatization and stability of the char, whereas lowering the temperature (300–400°C) could improve the cation exchange capacity and nutrient availability of the produced chars.

Di Blasi [145] has reported on the influence of particle size on MSW pyrolysis and concluded that reduced particle size in general resulted in increasing heating rate and consequently higher yield of the liquid product. Another study, however, showed that the influence of particle size on the yield of the liquid product was minor when the temperature was sufficiently high [146]. Additionally, operating pressure is also an influencing factor. High-pressure pyrolysis increases the yield of char, although practically it may be difficult to operate [147].

The environmental impact of the formation of inorganic (i.e., HCl and heavy metals) and organic (i.e., polychlorinated dibenzo-p-dioxins and dibenzoofuran) contaminants in the pyrolysis of solid waste containing PVC, discarded tires, and demolition waste wood has been investigated [148,149,150,151]. Organic pollutants and heavy metals tended to largely remain in the liquid and char fractions, respectively. Studies also showed that the formation of some undesired inorganic by-products containing Cl, Br, and S could be reduced with the use of catalysts [152]. A study compared the behavior of heavy metals in MSW pyrolysis with that in incineration [153] and showed that the release of heavy metals in rapid-heating combustion generally exceeded that observed in pyrolysis. The volatilities of some heavy metals, e.g., Zn and Pb, were reduced in pyrolysis compared to those in combustion. It was concluded from that study that pyrolysis is a better choice for MSW treatment in terms of controlling heavy metal contamination. To control the emission of organic and inorganic pollutants associated with MSW pyrolysis, flue gas scrubbing is to date the most efficient method [132].
4.3. Torrefaction

Torrefaction is a mild and slow pyrolysis, conducted at temperatures ranging between 200°C and 350°C [154]. The process is generally operated at ambient pressure with an inert atmosphere to avoid oxidation and combustion of the feedstock [155]. The residence time can vary from a few minutes to several hours. The word torrefaction originates from the French word torréfaction, meaning roasting. Historically, it was typically used for the treatment of coffee beans, however, in the presence of oxygen [104]. The torrefaction process is initiated by moisture evaporation, followed by partial devolatilization. The char, which is the major product, has a substantially higher energy density than the feedstock. Depending on the processing temperature, torrefaction can be classified as light (below 240°C) and severe (above 270°C) torrefaction [156]. The advantages of torrefaction are the increase in energy density, improved grindability, reduced moisture content, and decreased susceptibility to microbial degradation. The char can be utilized as high-quality fuel in various applications including cofiring in power plants, entrained flow gasification, and small-scale combustion facilities [157]. The char can also be used as a water purification adsorbent and for in situ soil remediation purposes [104].

Published studies on torrefaction technologies for MSW treatment are relatively sparse compared with literature on gasification and pyrolysis. Research have mainly been conducted to investigate the physical and chemical properties of torrefied MSW [110,119,153,158]. The types of materials used as feedstock include FW, PVC plastic, discarded tires, and wood residues. It has been commonly recognized that the torrefaction temperature is one of the crucial factors and that the yield of the char decreases with increased temperatures. Song and Guo [118] studied the properties of chars obtained from thermal treatment of animal litter at different temperatures. The results showed that chars obtained under torrefaction conditions at 300°C showed improved adsorption capacity for nutrient substances because of the high surface functionalities and was thus recommended for use in agricultural purposes. Similar observations were made in another study using animal manure and crop residues as feedstock, showing that relatively low treatment temperature led to increased nutrient availability and reduced alkalinity [116].

The behavior of organic and inorganic pollutants in the torrefaction process when waste materials are used as feedstock has been investigated [147,153,159]. Generally, heavy metals with high boiling points (e.g., Pb and Zn) tended to be retained in the chars, whereas those with low boiling points such as Hg tended to enter the gas phase. Volatilization of heavy metals in torrefaction was suppressed at slow heating rates. However, organic pollutants such as dioxins and dioxin-like compounds have been reported to be mainly retained in the chars, with minor amounts found in the volatile fractions [159].

4.4. Hydrothermal carbonization

In both pyrolysis and torrefaction, the feedstock generally needs to be predried to remove moisture, which is energy demanding. For wet feedstocks, it is therefore a more feasible alternative to subject the material to a wet thermochemical conversion technique, such as hydrothermal carbonization (HTC). Similar to pyrolysis and torrefaction, HTC is a thermal technique that is performed in the absence of oxygen [160]. Unlike conventional pyrolysis, HTC is carried out in the presence of subcritical water. The process involves the heating of the feedstock together with water at a temperature of 180–250°C in a pressure vessel for several hours. The water contained in the feedstock is used as solvent to pressurize the reaction medium, and therefore, there is no need for pretreatment to remove water from the material. The transition from water to steam is avoided in HTC because of the high pressure. The energy consumed for heating the water is substantially lower than that required for water evaporation in pyrolytic treatment [160]. The formation of the HTC char (also known as hydrochar) is the result of a series of reactions including hydrolysis, condensation, decarboxylation, and dehydration. The resulting liquid product is mechanically easy to separate from the hydrochar.

HTC was initially conducted in the early 1900s by Bergius as a means to convert cellulose into coal-like materials [161]. To date, HTC has mainly been applied on lignocellulosic biomass to explore the potential to produce chars for soil amendments and as energy carriers. The feasibility to apply HTC to the treatment of waste has been investigated using different types of feedstocks including poultry manure, PVC, and food residues [120,121,162]. Compared to chars produced by conventional pyrolysis, hydrochars contain less aromatic carbon, although they have more surface functional groups containing hydrogen and oxygen, giving the char negative surface charge, which increases its cation exchange capacity [163]. This makes the hydrochar suitable for use as an adsorbent for organic pollutants in water purification applications, for instance. It has also been suggested that combining HTC with subsequent thermochemical treatment by pyrolysis or combustion is effective in practice for waste remediation and energy recovery [162].

The effects of processing temperature and treatment time on the physical and chemical properties of hydrochars have been investigated at different scales, from stainless steel tubular reactors [163,164,165], to commercial plants with a processing capacity of up to 1 ton of MSW [166]. The energy contents of the produced hydrochars were positively correlated to the treatment times and the heating values were comparable to that of low rank coals. It was also evident that at elevated temperature and pressure, water-insoluble organic chlorine was largely reduced in the hydrochars compared to that in feedstocks containing plastics [166]. This is probably due to the transformation of organic chlorine to water-soluble inorganic chlorine during the hydrothermal process. A comprehensive review by Zhao et al. [167] focuses on the recent development of HTC technology and the feasibility of HTC for the upgrading of waste materials.

5. Conclusions

The increasing amount of MSW presents a great challenge for their handling to minimize their environmental impact. Traditional methods of waste management such as landfills and burning have a negative environmental impact, and societies are trying to minimize their use. Novel approaches that turn waste to a valuable product or energy are gaining ground as methods for waste management. These methods involve both biological and thermochemical conversions, and the intense research that has been conducted in the last decade has resulted in improved yields of product or energy formation together with decreased environmental impact. Biological methods include the production of fuels (e.g., ethanol, biogas, hydrogen, and butanol), biopesticides, oils from microalgae, and enzymes (such as amylases, carbohydrases, pectinases, and lipases). Thermochemical methods of MSW utilization involve gasification, pyrolysis, torrefaction, and hydrothermal carbonization. Lot of research has been conducted in the last years on the use of these methods for the conversion of MSW, and this has resulted in very promising results, as discussed in the current review article.

Declaration of interest

All authors declare that there is no competing interest.

References


