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Review of Biofuel Technologies in WtL and WtE

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Abstract

Processing of biomass feedstocks to produce energy, fuels, and chemicals via a combination of different applied technologies is considered a promising pathway to achieve sustainable waste management, with many environmental and economic benefits. In this chapter, we review the current state of the main processes associated with energy recovery and biofuel production under the concept of waste biorefineries. The reviewed technologies are classified into thermochemical, biological, and chemical, including combustion, gasification, steam explosion, pyrolysis, hydrothermal liquefaction, and torrefaction; anaerobic digestion, fermentation, enzymatic treatment, and microbial electrolysis; and hydrolysis, solvent extraction, transesterification, and supercritical conversion. Their brief history, current status, and future developments are discussed within a perspective of valorization and managing of current waste streams with no solution.

Keywords: biorefineries, biofuel production, energy recovery, waste-to-fuels, waste-to-energy, circular economy

1. Introduction

Waste can be defined as any substance or object that has no further use and is intended to be discarded [1]. In this sense, waste production is inevitable in a society based on consumption, making waste management a huge challenge taking into account the enormous quantities of residues that are produced globally. In fact, about 2.6 billion Mg of waste were produced in the European Union (EU) during 2014, from which 41% was discarded in landfills, 36% was recycled, 10% used in earthmoving operations, 7% treated in wastewater treatment plants, and 6% incinerated either for energy production or for destruction. Based on this, in recent decades, humanity is shifting their focus of traditional waste management from the concept of “collection and disposal” in favor of pyramid-based management of the waste hierarchy in order to increase sustainability [2]. However, even when environmentally-friendly practices such as recycling and reuse are accomplished, much of the operations are performed “downcycling,” meaning that the recycled product has an economic value below its original purpose. As such, the linear economy model based on the pyramidal hierarchy of wastes that we tend to use nowadays also has limitations. Actually, there are still opportunities for efficiency gains in many industrial processes, but these gains will probably be increasingly marginal and undifferentiated.

The future adoption of the concept of circular economy is, therefore, a necessary change of paradigm, in contrast to the current linear model. This new concept is increasingly viewed as a source of innovation in products, processes, and business models, opening excellent opportunities that should be seen by companies and organizations as competitive advantages in a dynamic and global market [3]. Specifically, with a circular flux in the consumption of resources, every waste generated is a potential raw material for another process, introducing novel ways of valorization and development of second and third generation products. The benefits are clear as few wastes would be generated and disposed of without treatment, potentially reducing environmental pollution.

Updated knowledge of current technologies is a crucial factor in determining the most suitable processes to valorize different types of wastes in future biorefineries. These waste biorefineries are facilities that integrate the necessary technologies in order to convert biomass feedstocks and other wastes into usable products, ensuring that circular economy transitions from theory to the real world. The available waste streams can either be transformed by technologies producing biofuels (waste-to-liquids, WtL) or energy (waste-to-energy, WtE) with both categories expected to be a key element in future waste management. Based on this, in this chapter, we briefly review the current state of main WtL and WtE technologies within a perspective of their use as tools for managing post-process residues and by-products. The review ends with a brief discussion on future developments regarding mentioned technological options.

2. WtL and WtE technologies: historical and technological overview

Biorefineries are a way to achieve sustainable waste management with many environmental and economic benefits. However, waste streams are often very selective in terms of the technological option most suitable for their valorization. As such, a complete understanding of each technology is a fundamental resource to determine if the different wastes available can be viewed as a raw material for valuable products. **Tables 1–3** summarize the different thermochemical, biological, and chemical processes discussed. A brief description of each technology follows.

2.1 Incineration/combustion

Combustion is the most common waste energy recovery technology used in the production of heat, steam, and electricity. Historically, this technology is considered one of the most “dirty” and polluting processes in waste management and disposal; however, advances in the treatment of emissions in the late 1980s and early 1990s, along with the development of command and control technologies and the pretreatment of waste, have led to combustion once again attracting the attention of researchers and investors around the world. In general, a modern incineration facility consists of pretreatment and/or sorting line from where the wastes are continuously and uniformly fed to a furnace (**Figure 1**). The furnace operates at very high temperatures to ensure complete combustion. The combustion parameters are continuously controlled, and emissions are treated in a set of filters to ensure the removal of the toxic pollutants. As a WtE technology, combustion is very mature with the most recent studies focused on the recovery of energy and ashes resulting from the co-combustion or co-incineration of different wastes in nonspecialized equipment [4]. In fact, this process is widely used for thermal energy recovery of waste forms with good calorific value [5]. In 2016, for example, 28% of municipal solid waste (MSW) generated in the EU-28 was incinerated [6]. Furthermore, about 13.1% of hazardous waste was incinerated with and without energy recovery [7].

Technology	Benefits	Limitations	Products and by-products	Applications	TRL/CRI/demonstration projects
Combustion/ incineration	Reduction of mass (70%) and volume (80%), fast and simple process, energy recovery	High capital cost, public opinion objection, toxic slag production, air pollution (dioxins)	Heat for boilers and furnaces. Potential metal recovery from slag	Heating, electricity	TRL9/CRI4
Gasification	Wide range of applications and feedstocks, high conversion efficiency	High capital cost, high sensibility processes, low flexibility, risk of mechanical failure, tars production	H ₂ , CO-rich syngas Biochar for soil remediation	Heating, electricity, transportation, fuels and high-value chemicals	TRL9/CRI3 Energos, Norway; Vaskiluodon Voima, Finland
Explosive decompression	Transformation of lignite, solubilization of hemicellulose	Production of toxic compounds, partial degradation	Sugars, digestible products	Heating, electricity, transportation, fuels, and high-value chemicals	TRL9/CRI2
Pyrolysis	High yield, reduced syngas treatment, reduction of waste volume (90%)	High capital, maintenance and operation costs, high bio-oil viscosity	Bio-oils, biochar, syngas	Additives, high-value chemicals, transportation, heating, and electricity	TRL8/CRI2 ABRITech, Canada; Ensyn Several, Canada; Metso, Finland; Rise, Sweden
Hydrothermal liquefaction	Higher LHV bio-oil and low moisture content	Low conversion efficiency (20–60%), higher pressure equipment and higher capital cost	Heavy oil, intermediate value chemicals	Additives, high-value chemicals, transportation, heating, and electricity	TRL7/CRI1 Steeper Energy, Denmark; PNNL, USA; Genifuel, USA; PilotABP, Spain; TERAX, New Zealand
Torrefaction	Homogeneous and stable products, easy pelletizing, high LHV, hydrophobic	Low-energy density, high ash quantity	Torrefied biomass	Heating, electricity	TRL7/CRI1 Torplant, Switzerland; ECN, Netherlands; Norris Thermal Technologies, Vega Biofuels, USA

TRL, technological readiness level; CRI, commercial readiness index.

Table 1.
 Comparative summary of different thermochemical conversion technologies [8–10].

Technology	Benefits	Limitations	Products	Applications	TRL/CRI/ demonstration projects
Anaerobic digestion	Solid waste reduction, high moisture content feedstock, methane- and carbon dioxide-rich biogas, low-cost organic fertilizer as by-product	Need to treat and clean the biogas; unstable system; large facilities are unattractive	Biogas, bio-digestate	Heating, electricity, transportation, fuels, and high-value chemicals	TRL9/CRI3
Fermentation	Does not contribute to increase of greenhouse gas emissions	Limited to sugar, starch, or cellulose-rich feedstocks	Liquids and CO ₂	Additives, high-value chemicals, transportation, heating, and electricity	TRL9/CRI2-3
Photofermentation	The photosynthetic bacteria can use a range of the electromagnetic spectrum	Low efficiency, inhibited in the presence of oxygen	Hydrogen, carbon dioxide, organic acids	Additives, high-value chemicals, transportation, heating, and electricity	TRL6/CRI1
Dark fermentation	Capable of converting a wide range of wastes, scalable technology, independent of light	Low theoretical limit, immature technology	Hydrogen, acetic acid	Additives, high-value chemicals, transportation, heating, and electricity	TRL5/CRI1 DiSAA Milan, Italy; LanzaTech, New Zealand
Enzyme treatment	Low power consumption, low by-product production, does not require toxic catalysts, can result in a reduced solvent	High cost of the enzymes, slow reactions, necessity of high purity, limited in temperature and pH range	Ethanol, amino acids	High-value chemicals, transportation, heating, and electricity	TRL9/CRI2 PROESA™, Italy; Kalundborg Bioethanol, Denmark
Microbial electrolysis	Hydrogen production, low-energy consumption, effluent degradation	High internal resistance, high capital cost, production greatly affected by substrate composition	Hydrogen, methane, acetate, formic acid	Wastewater treatment, high-value chemicals, transportation, heating, and electricity	TRL6/CRI1

TRL, technological readiness level; CRI, commercial readiness index.

Table 2.
Comparative summary of different biological conversion technologies [8–10].

Technology	Benefits	Limitations	Products	Applications	TRL/CRI/ demonstration projects
Hydrolysis	Less aggressive low-cost substances	Slow and inefficient, high alkalinity or acidity, formation of inhibitory salts	Cellulose, hemicellulose, and lignite	Additives, high-value chemicals	TRL9/CRI5
Solvent extraction	Moderate temperatures, reuse of solvents, high selectivity of solvents, pH control	Intermediate products, solvent saturation	Primary and secondary metabolites	Additives, high-value chemicals	TRL9/CRI3
Transesterification	No modification of equipment is necessary, reduction of air pollution, less toxic, easy to use, decrease in CO ₂ emissions	Weak supply chain, high viscosity, high cost, odor	FAME	Transportation, electricity	TRL9/CRI5
Super critical conversion	Uses cheap and abundant solvents; fast, lower thermal degradation; better purity of the compounds	High pressures required, supercritical state, difficult to maintain, complex maintenance and cleaning	Chemicals	Wastewater treatment, high-value chemicals, transportation, heating, and electricity	TRL7/CRI-1 Thar Technology, USA; Integrated Plantrose Complex, USA; New Oil Resources, USA

TRL, technological readiness level; CRI, commercial readiness index.

Table 3.
 Comparative summary of different chemical conversion technologies [8–10].

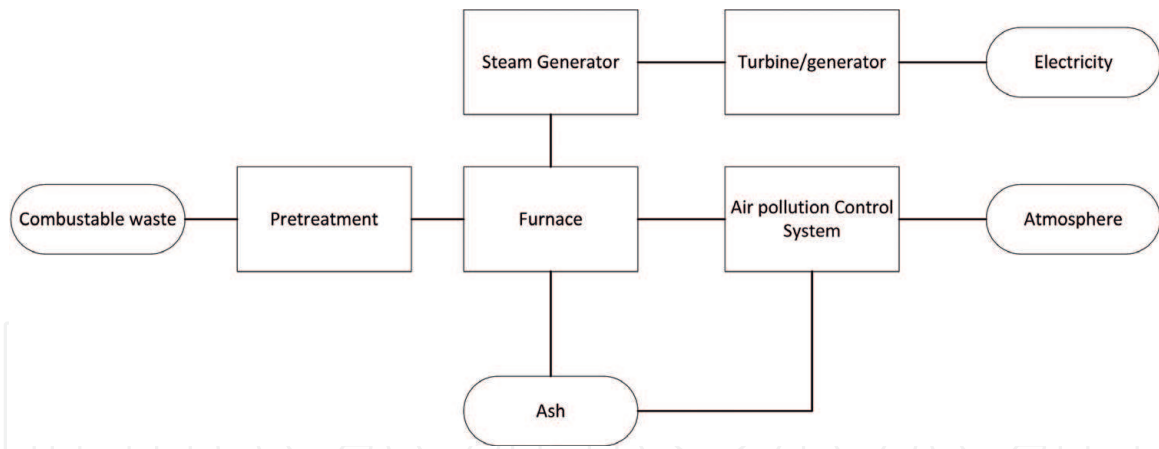


Figure 1.
Example scheme of incineration/combustion technology.

2.2 Gasification

Gasification is a thermochemical decomposition process which occurs without the presence of sufficient oxygen for a complete combustion and allows the transformation of waste feedstocks into a combustible gas known as syngas, a fuel with many potential applications (**Figure 2**). As a technology, gasification has a several-centuries-old history with progress made by advances and stalls. Widely used during industrial revolution in the 1850s to illuminate factories, streets, and houses, this technology fell into disuse during the twentieth century and only recently gained a continuous support for its development due to energy security threats and climate change.

Among WtE processes, gasification is one of the most promising with some specific barriers explaining its lack of penetration in the domestic and commercial sectors [11]. An extensive review on technology progress identified 50 companies offering “commercial” gasification plants in Europe, the USA, and Canada, mostly downdraft and fluidized bed systems (75 and 20%, respectively) [12]. Moreover, in 2013 there were more than 272 operating gasification plants worldwide with more under construction and planned until 2019 [13].

Supply chain development, waste pretreatment (drying/grinding/pelletization), and the potential need for treatment of syngas are usually pointed out as the main barriers to be overcome. Conventional drying systems are known to be expensive and energy intensive. In addition, complete drying of the biomass represents a decrease in

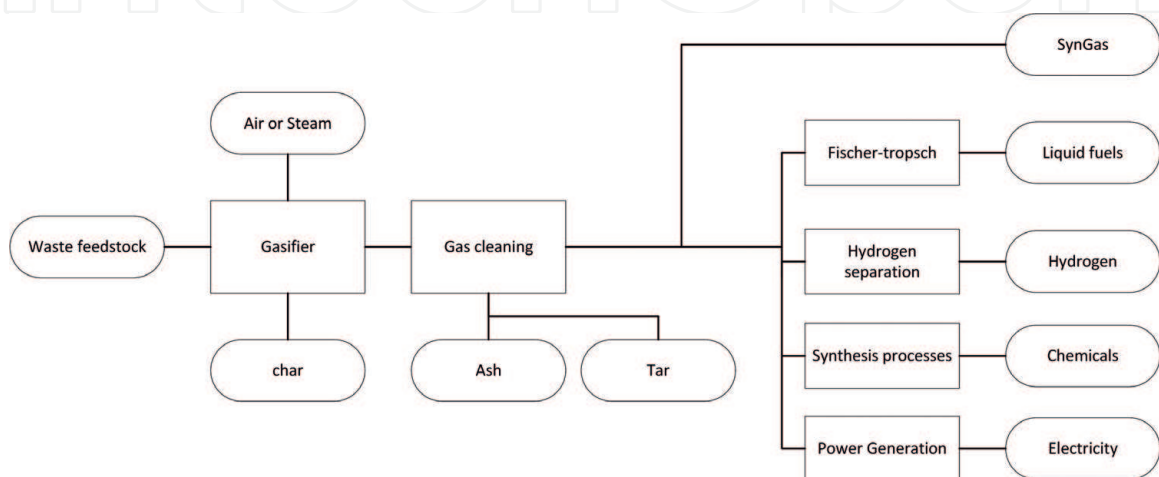


Figure 2.
Example scheme of gasification technology.

the amount of hydrogen that is potentially producible during gasification. Solar drying, though inefficient, is cheap and should be studied and viewed as an alternative. The potential presence of tars, particulate emissions, SO_x , NO_x , and NH_3 in the syngas also limits its range of use. Filtration of the syngas is important to obtain a syngas free of contaminants but requires constant cleaning of the filters as a way to prevent blockage and pressure drops. Tars are seen as the most complicated contaminant. In addition to filtration, it is also possible to resort to thermal decomposition and catalytic cracking as a form of treatment [14]. Thermal decomposition leads to melting of the ashes, which can also result in mechanical problems. Catalytic treatment is seen as the most effective for dealing with tars but ineffective against particles and other toxic gases. The combination of various forms of treatment is the best solution [15].

Pretreatment of the waste and biomass to be gasified, as well as reactor design and optimization of operational conditions, has been proven to be of great importance to maximize conversion efficiency, viability, and profitability [16]. In this regard, procedures such as sorting, grinding, and sifting are simple but essential. Fluidized bed reactors are considered the most suitable for a good and efficient process. Fluid bed material consisting of natural rocks such as dolomite and olivine is usually the best option due to reasonable prices. As for optimized conditions, mathematical models using 2D computational fluid dynamics (CFD) confirmed that gasification temperature has a key influence on the calorific value of the syngas produced [17]. Co-gasification of several wastes has been reported with promising results [18–20]. Inorganic additives such as calcium oxide (CaO) have been observed to decrease CO_2 and increase the quality of the syngas [21]. Integrating gasification and co-gasification into solid oxide fuel cells (SOFC) or internal combustion engine (ICE) cogeneration systems is a very promising option and is already considered economically viable [22–24].

2.3 Explosive steam decomposition

Explosive decomposition is a thermochemical pretreatment process which disrupts the rigid structure of lignocellulosic materials using steam and high pressures. Patented in 1931 by Mason [25], this process consists in heating the waste in hot steam at 285°C and at a pressure of 3.5 MPa for 2 min, before increasing the pressure once again, this time to 7 MPa for 5 s [26]. Naturally, time and temperature are a major influence in the disruption of the fibers composing the biomass, with the pretreatment process potentially resulting in just some grooves in the wood or in the total conversion into pulp. The main application of this technology is as pretreatment of lignocellulosic materials (**Figure 3**) which is essential for making the

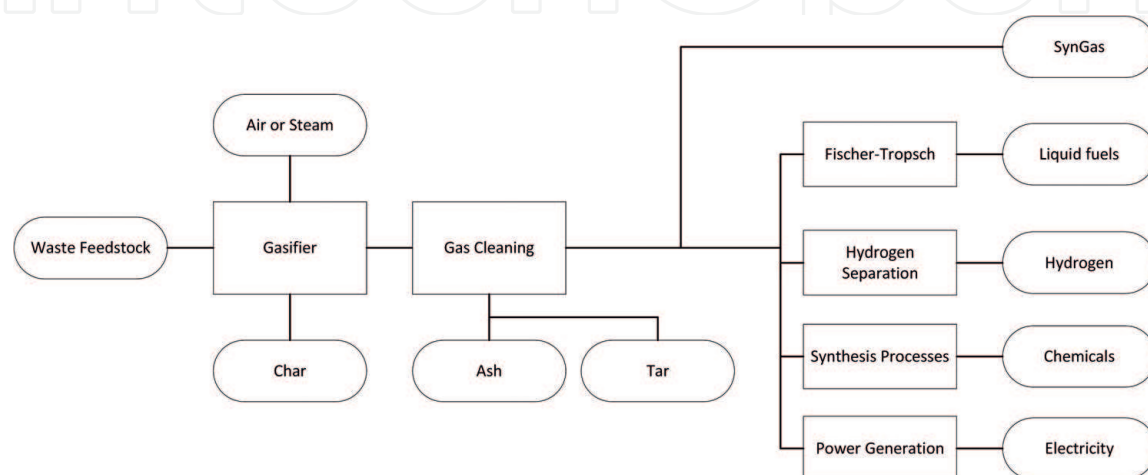


Figure 3.
Example scheme of explosive steam decomposition technology.

biopolymers accessible for further treatment via other processes such as fermentation, hydrolysis, anaerobic digestion, and densification. The production of biogas by anaerobic digestion using lignocellulosic wastes, for example, is considered a huge challenge due to its recalcitrant nature (non-biodegradability) [27]. In this regard, the use of explosive steam decomposition as a form of pretreatment has been proven to enhance the production of biogas. Moreover, ethanol production and syngas production using lignocellulosic feedstocks have also been reported to proceed with higher calorific value and lower temperatures, respectively, when precluded with steam explosion [28, 29]. A promising solution for continuous steam explosion has been presented by a research team from South China University of Technology [30] allowing for process scale-up and its potential integration in second-generation biorefineries.

2.4 Pyrolysis

Pyrolysis is a thermochemical decomposition process that occurs in the total absence of oxygen and at relatively low temperatures (500–800°C) when compared to gasification (800–1000°C). There are different types of pyrolysis, each favoring the production of three different products: pyrogas, pyrolysis oil, and char (**Figure 4**). The relative proportions of each product depend on the applied pyrolysis method, the type of feedstock, and temperature. Archeological evidence suggests that during the Middle Paleolithic, Neanderthals resorted to pyrolysis to produce a kind of tar which they would use as glue. The use of this process in the production of all types of products was widespread throughout the world until the beginning of the twentieth century. Nowadays, pyrolysis is once again being viewed as one interesting solution to produce energy, fuels, and chemicals using local wastes.

The major advantage of pyrolysis in waste recovery may be in being able to convert low-energy-density materials into high-energy-density products. As an example, pyrolysis has been adopted as an alternative to the treatment of plastic wastes to produce plastic-derived oil (PDO) [31] and pyrogas [32]. PDO has been reported to be similar to diesel (C_{13} – C_{20}) [33]; however, additional processing is needed to deal with aromatic compounds. The use of calcium carbonate ($CaCO_3$) in the pyrolysis of horse manure allows for lower temperatures due to the catalytic effects of $CaCO_3$ as a possible source of CO_2 [34]. Co-pyrolysis of different plastic mixtures [35], as well as the use of catalysts [36–39], has also yield interesting results concerning the productivity and quality of the PDO components.

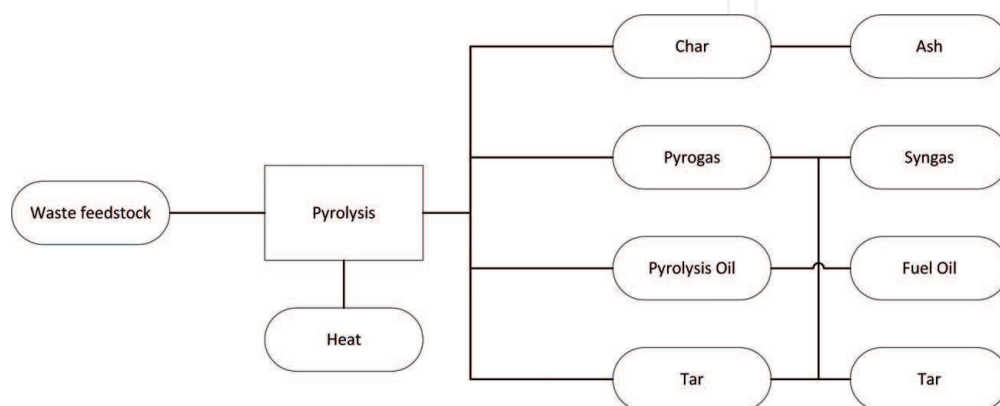


Figure 4.
Example scheme of pyrolysis technology.

2.5 Hydrothermal liquefaction (thermal depolymerization)

Hydrothermal liquefaction or thermal depolymerization is the thermochemical conversion of solid waste into a liquid using moderate temperatures (250–375°C) and high pressures (4–22 MPa). Similar to pyrolysis but occurring with the waste immersed in water at high pressures and temperatures, the process leads to the break of long carbon chains, resulting in a bio-oil with a good calorific value. As a technological option, the process does not need catalysts, but research has indicated that the use of alkaline catalysts allows the formation of high-value chemicals. Hydrothermal liquefaction is attractive because efficiencies greater than 80% are common when converting biomass into fuels and other high-value chemicals [40]. This technology has enormous potential, particularly to produce biofuels and raw materials for further chemical processing.

The concept of hydrothermal liquefaction was first explored in the 1920s and was further developed in the 1950s by H. Heinemann. However, only after the oil crisis in the 1970s did the first efforts to exploit this technology finally emerged, being the concept finally proved at pilot scale with the construction of Biomass Liquefaction Experimental Facility in Oregon, USA [41]. Recently, research regarding this technology has focused on finding new catalysts and developing novel ways of converting the produced bio-oils into high-value products. In practice, hydrothermal liquefaction is valued because it provides rapid conversion of waste biomass into bio-oil, avoiding the high energy cost of drying [42]. Most studies have shown that temperatures between 250 and 370°C are optimal for the production of bio-oil, with no general conclusion given about the effects of reaction time and moisture content [43]. Hydrothermal co-liquefaction is an interesting pathway and should be explored in future studies [44, 45]. Both the addition of potassium carbonate (K_2CO_3) [46] and the reuse of the liquid were reported to increase calorific value and productivity. The addition of solvents was also observed to enhance the process [47], while the addition of metallic catalysts led to deoxygenation and desulphurization of the bio-oil [48].

2.6 Torrefaction

Torrefaction is a form of thermal treatment which takes place between 200 and 500°C in the absence of oxygen. As temperature rises, moisture and superfluous volatiles are gradually released, and biopolymers such as hemicellulose, cellulose, and lignite are partially decomposed, depending on process conditions [49]. At mild temperatures (235–275°C), for example, the degradation of hemicellulose is accelerated, and the release of the volatiles is intensified, while cellulose is only consumed to some degree. On average, the process results in mass losses and decreases in calorific value (20% and 10%, respectively) but yields a more homogeneous waste composition and leads to higher energy densities. Some biomasses have characteristics that hinder their utilization as energy feedstocks; using this process as pretreatment allows the use of a broad spectrum of wastes in other WtE technologies. The main product of torrefaction is, therefore, a waste with improved characteristics regarding its energy use. More than 150 torrefaction installations worldwide with powers from 50 to 700 MWe have successfully tested the co-combustion of torrefied biomass, reducing greenhouse gas emissions and dependence on fossil fuels. It is expected that torrefied biomass could represent 5–10% of industrial applications in Europe [49]. However, the market for torrefied waste products is still very recent, and there is not enough data available about the real use of technology, its implementation, and its evolution.

Among researchers, torrefaction has been viewed as an excellent pretreatment for improving the energy recovery features of several wastes creating products with low oxygen to carbon ratios and high calorific values for co-gasification and co-combustion applications [50]. As an example, the torrefaction of several pomaces [51] and prunings [52] led to very promising results with calorific values increased to near lignite levels. Other interesting results have been reported by researchers [50] dealing with the very heterogeneous nature of MSW which along with high moisture contents make them challenging for application in WTE and WTL processes. Most studies reported a positive correlation between the calorific value and torrefaction temperature.

2.7 Anaerobic digestion

Anaerobic digestion (AD) consists in the conversion of biodegradable organic matter in the absence of oxygen in which a biogas rich in methane is produced [53]. Typically, the resulting biogas is composed of 50–75% CH₄, 25–50% CO₂, and 1–15% of other gases such as H₂O, NH₃, and H₂S. Another by-product of anaerobic digestion is the digestate, an excellent organic biofertilizer. Virtually all types of organic matter have the potential to be digested anaerobically to produce biogas. The most common organic wastes used in AD are agricultural, livestock industry, agroindustry, and municipal solid wastes and wastewater. Woody materials are less suitable because they contain a high proportion of lignite, making it very difficult to decompose biologically.

As a technology, AD is already mature and well developed. Since 2009, the number of biogas plants has greatly increased in Europe with biomethane production growing in line with sector development. In 2016 alone, energy production derived from biomethane increased by 4971 GWh (+40%) within the European countries reviewed [54]. The key to future research is thus the optimization of process parameters that affect efficiency. Temperature change, for example, is known to affect microbial activity and growth rates. Higher digestion temperatures, for instance in the thermophilic range, have been demonstrated to lead to higher biogas productivities, but thermophilic digestion represents a higher investment due to energy costs. On the other hand, digestion of simple substrates often results in a nutrient imbalance that affects the stability of the process. Thus, C/N ratio optimization by co-digestion has been widely tested with good results taking advantage of the synergies between different substrates. This strategy represents the most economical way to improve process productivity nowadays. The use of multiple steps in AD has also been observed to be an interesting solution for achieving the best use of different substrates [55–58].

The integration of anaerobic digestion with microalgae cultivation presents potential benefits [59, 60]. From an economic point of view, costs can be substantially reduced by using the digestate from AD as a source of nutrients for algae growth. However, several barriers will have to be overcome before the scale-up of the process. The main obstacle identified in the reviewed research was the need to find a robust microalga strain capable of binding with organic and inorganic carbon and tolerate extremes of pH.

2.8 Fermentation

Fermentation is an anaerobic metabolic process, in which microorganisms (bacteria, yeast) turn carbohydrates into fatty acids, alcohols, and gaseous products such as H₂ and CO₂ (**Figure 5**). The most common industrial products resulting from fermentation are ethanol, acetic acid, and citric acid (2-hydroxypropane-1,2,3-tricarboxylic

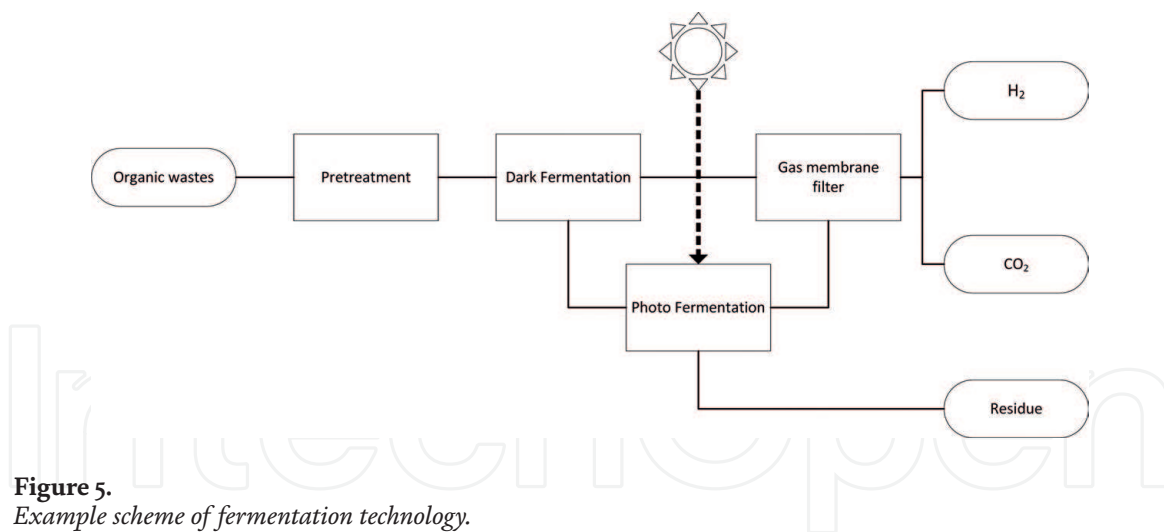


Figure 5.
Example scheme of fermentation technology.

acid). The conversion of sugars into ethanol is the most well-known form of fermentation, producing alcoholic beverages such as wine, beer, and cider. Interestingly, the same fermentation occurs in the production of bread, yogurt, and other foods fermented by the formation of lactic acid (2-hydroxypropanoic acid). In addition, there have been significant advances in the production of bioethanol, biobutanol (butan-1-ol), and bio-hydrogen (molecular hydrogen), among other high-valued chemicals.

Continuous fermentation of syngas using fixed-bed drip reactors for ethanol production has been proven as a valid concept with the highest ethanol concentration (13.2 g L^{-1}) obtained during co-current continuous syngas fermentation at a dilution rate of 0.012 h^{-1} [61]. However, despite being a promising technology, the process has encountered some difficulties in its development on an industrial scale. Besides fixed-bed bioreactors, other efforts related with reactor design have been focused on membranes combined with the formation of biofilms due to enhances in mass transfer. Studies on the production of bio-hydrogen have been focused on bio-photolysis of water using algae and cyanobacteria, photodecomposition of organic compounds by photosynthetic bacteria [62], and dark fermentation of organic compounds with anaerobes [63]. For dark fermentation, special attention has to be given to inhibitors such as the excess of substrate, micronutrients, macronutrients and metal ions, high temperatures, acidic pH levels, and competition from other microorganisms [63].

2.9 Enzyme treatment

Enzymes are macromolecular biological catalysts which accelerate chemical reactions. In 1897, Eduard Buchner resorted to enzymes extracted from yeasts grown in his lab to ferment ethanol, a seminal work for which he received the Nobel Prize for Chemistry in 1907. Industrially, their application lies either in converting substrates into greater value products or as pretreatment for energy recovery and biofuel production. Nowadays, nearly all types of commercially available enzymes are produced by fermentation, being part in virtually every aspect of our lives, from the pharmaceutical industry to laundry detergents. In 2016, an industrial unit including an enzymatic pretreatment started to operate within a perspective of energy recovery from MSW. Specifically, enzymes degrade a fraction of the organics present in MSW so that they can be easily digested anaerobically. The facility is located in Northwich, England, and produces 5 MWe consuming 15 Mg h^{-1} of MSW [64]. Another commercial application with good future perspective is enzymatic saccharification which can be used to produce bioethanol at a low cost. Some studies on bioethanol production from bamboo, for example, indicate that increasing the amount of the enzyme yields little improvement in the process highlighting

the need for optimization depending on the waste to be transformed [65]. Other experiments have focused on process enhancement via salt pretreatment. Addition of inorganic salts, for instance, has been reported to improve reducing sugar yields of sugarcane leaf wastes and mustard stalk and straw [66, 67].

2.10 Microbial electrolysis

Microbial electrolysis is a bioelectrochemical transformation where hydrogen or methane is produced from various wastes and wastewaters. Microbial electrolysis cells (MEC) use the metabolic activity of exoelectrogenic bacteria to catalyze redox reactions and promote the flow of electrons between the electrodes [68]. Specifically, the bacteria convert biodegradable substrates at the anode, releasing electrons and protons (**Figure 6**). The electrons are then transferred to the cathode (where hydrogen is produced) inducing an electrical current with electrical potential values (0.2–0.8 V) lower than in traditional electrolysis (1.8–3.5 V) [69]. Microbial electrolysis cells (MEC) have the potential to become one of the most important WtE technologies. However, electrode materials are still costly, and further developments are needed. In this regard, the use of biochar-based electrodes seems to compose an interesting research route [70–72]. Currently, coupling with other technologies for energy generation seems to be its leading application. The use of microbial electrolysis as a pretreatment for AD, for example, has been explored recently with interesting results. In a study focused on the valorization of highly concentrated FW [73], MEC was found to accelerate methane production rate and stabilization. As another example, post-processing of wastewater resulting from hydrothermal liquefaction for recovered hydrogen has also been demonstrated with effective results [74, 75]. As a technology, MEC are still in the early phase of development, and further progress is expected with the use of novel electrode materials and new reactor configurations.

2.11 Hydrolysis

Hydrolysis is probably the most prevalent chemical reaction in multiple WtE and WtL technologies. Hydrolysis is the chemical reaction where the addition of

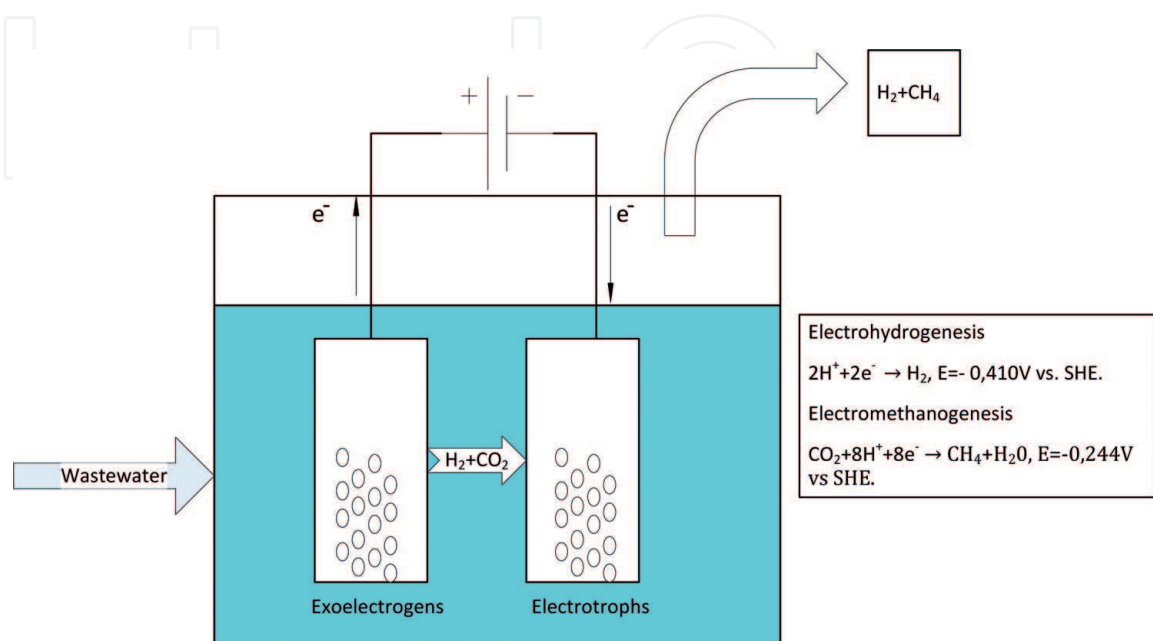


Figure 6.
 Example scheme of microbial electrolysis technology.

a water molecule breaks the chemical bond of another molecule and the resulting molecules bind to H^+ and OH^- ions. In 1819, Henri Braconnot discovered that he could produce sugars from cellulose through hydrolysis with sulfuric acid. This hydrolyzed sugar could then be processed and fermented to produce ethanol. The production of ethanol by hydrolysis began extensively at the beginning of the twentieth century, with maximum yields of 190 L Mg^{-1} of biomass. In the former USSR during the 1930s, the industrial growth at the time needed to develop processes of ethanol production that did not use food sources. In 1934, six pilot reactors were built with the objective of optimizing different hydrolysis technologies, not only to produce ethanol but also other products such as xylitol and furfural. After the First World War, this process was no longer economically viable against more conventional methods. With the advances of the last two decades, enzymatic hydrolysis seems to be the most promising application regarding hydrolysis techniques.

2.12 Solvent extraction

Solvent extraction is a relatively modern technology used in the extraction of products from its substrates (**Figure 7**). By choosing a solvent that best dissolves the wanted product, this process usually results in higher yields when compared with other methods. The separation is quick and efficient and most of the solvent can be reused. Extraction of oils via this technology is a common application in the industry, normally used after mechanical extraction. Hexane is the most used solvent, but ethanol and isopropanol have also been proposed as alternative options. The Soxhlet extractor is often the preferred method for lipid extraction due to the simplicity of operation, relative safety, and ease of replicating results on an industrial scale [76]. From research, organic solvents such as chloroform, ethanol, and hexane were found to produce the best results when performing lipid extraction from microalgae. Solvent mixtures were also observed to yield better results

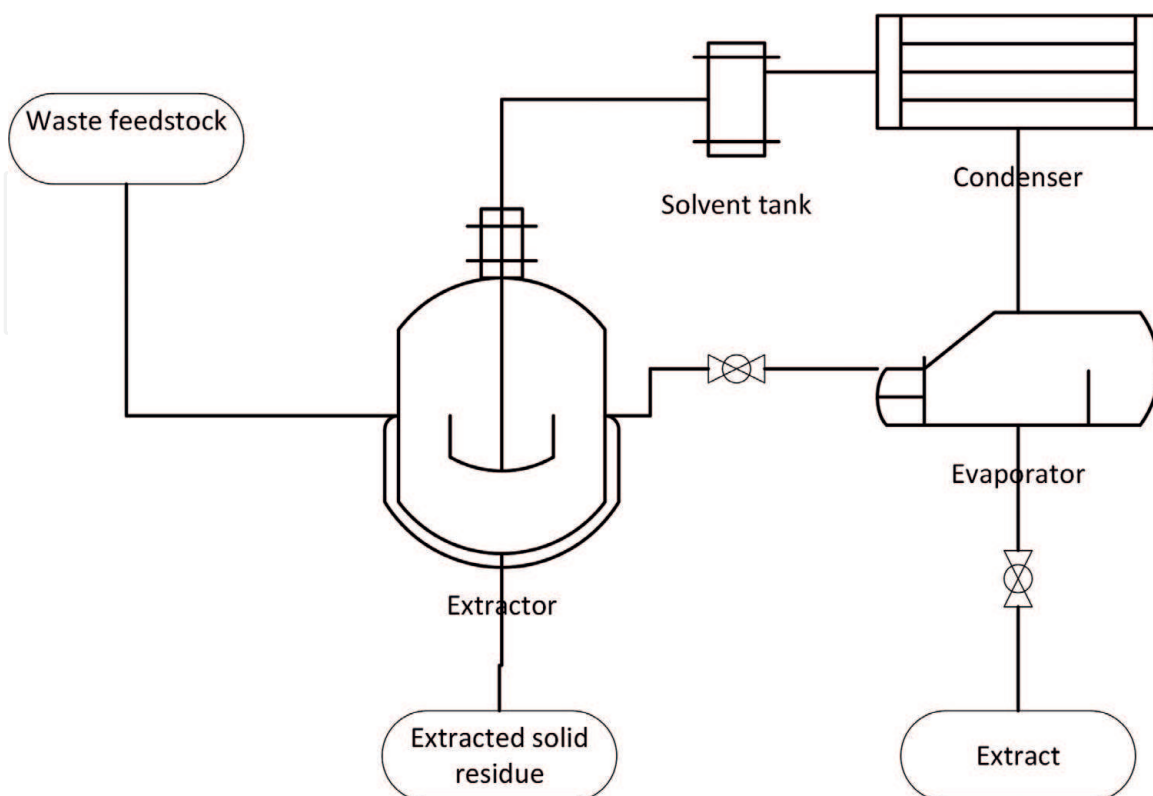


Figure 7.
Example scheme of solvent extraction technology.

than mono-solvent extractions, with a 50/50 mixture of chloroform and ethanol leading to 11.76% lipid extracts. As a mono-solvent, chloroform resulted in the highest quantity of lipids extracted at 10.78% with 3 h showing the best extraction efficiency [77]. Solvent extraction also has the potential to be integrated with other processes like supercritical extraction or pyrolysis in order to produce higher value chemicals from bio-oils [78, 79].

2.13 Transesterification

Transesterification is the main process used in the production of biodiesel in which vegetable oils are broken into methyl or ethyl esters by reacting with an alcohol and catalysts (acids, alkalis, and enzymes) with glycerol as the only by-product. Biodiesel production has increasingly been seen as a carbon mitigation tool, assuming increasing importance in promoting sustainability in European countries. Since January 1, 2010, for example, all commercial diesel fuel sold in Portugal has a 7% incorporation of biodiesel. Biodiesel production is a controversial issue due to the use, availability, and cost of raw materials, as well as greenhouse gases emission and food competition. In this context, the use of waste oils and nonfood crops seems to compose the best option for the widespread production of biodiesel in the future [80]. In Europe, it is estimated that about 4 million Mg of waste cooking oil are to be collected annually, seven times more than the current collected amount [81]. This underdeveloped collection chain led to record level imports in the first 8 months of 2018 with more than 235,000 Mg of waste cooking oil entering the EU from China. Biodiesel market thus does not show signs of slowing down [82]. Although already mature and well established commercially, biodiesel still needs a lot of research and development to achieve significant improvements in its production [83, 84]. In this regard, continued interest in the use of biodiesel as an alternative fuel has led to increased efforts to develop a new generation of biofuels. Heterogeneous catalysts have been increasingly tested since they offer process improvements over homogeneous catalyzed commercial production employing liquid bases. In more detail, the use of solid catalyst facilitates post-process separation and fuel purification, along with the continuous synthesis of biodiesel. The increasing use of low-grade waste cooking oil remains a challenge for existing heterogeneous catalysts since the high concentration of impurities (acid, moisture, and heavy metals) induces rapid deactivation in flow and requires purification. The development of more robust catalyst formulations tolerant to such components is, therefore, a necessity [85]. Cement was recently tested in the transesterification of *Pongamia pinnata* and sunflower oil with somewhat low conversion rates (76%), but research should continue in upcoming years [86]. In terms of process coupling, the blend of biodiesel with pyrolysis oil derived from lignocellulosic wastes is an attractive route as an alternative to diesel fuel [87]. Microalgae are also considered an attractive feedstock alternative to reduce costs in the extraction and conversion of this renewable fuel.

2.14 Supercritical conversion

Supercritical conversion is a new technique that uses high temperature and high-pressure fluids, above their critical point, to achieve the transformation of waste. Compared with conventional WtE and WtL technologies, this method may ignore drying or dehydration pretreatments, reduce reaction temperature, shorten reaction times, and increase product yield. In recent decades, supercritical conversion has gained interest not only for chemical extraction, but also in chemical conversion by replicating processes such as transesterification, gasification, hydrolysis, and others (**Figure 8**). Studies with real biomasses and at larger scales are lacking, but

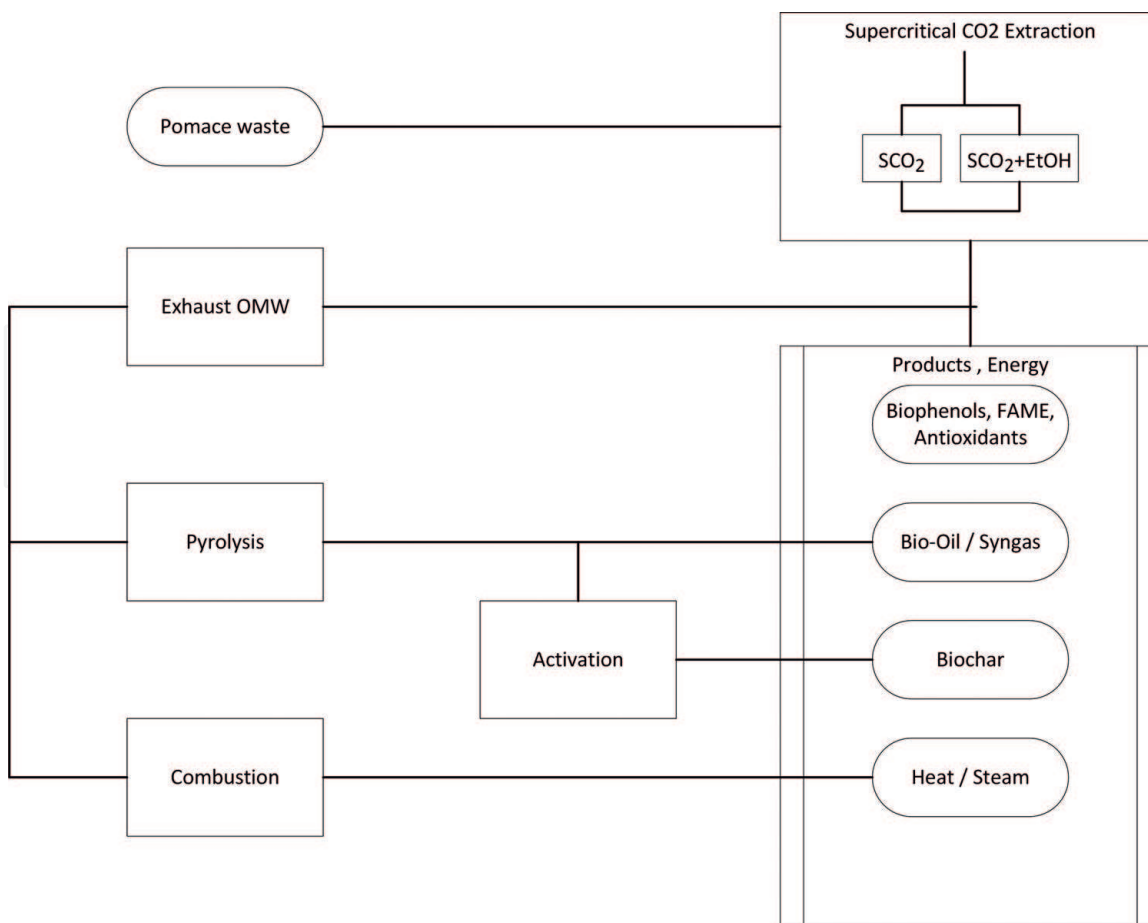


Figure 8.
 Example scheme of supercritical conversion technology.

the reviewed research generally suggests that, for example, supercritical gasification in both biorefineries and cogeneration has enormous potential. Supercritical water gasification of olive oil mill wastewater, for example, has been investigated recently with different alkali catalyst types [88]. The tests proved that an increment in catalyst concentration would improve hydrogen yield to a maximum of 76.73 mol $\text{H}_2 \text{ kg}^{-1}$ in specific conditions. Extraction with supercritical carbon dioxide for biodiesel production is another process investigated [89]. In the example study reviewed, the best productivity was 0.312 kg of oil per kg of seed⁻¹ at a pressure of 500 bar and 40°C. Fatty acid content was observed to decrease with increasing pressure. In fact, the extraction of fatty acids and transesterification in a single step are considered one of the greatest potentials for this technology [90].

3. Economics of WtE

The most apparent barrier for the implementation of WtE technologies is capital cost, specifically the upfront expense of building and installing the energy generation system. While not enabling a detailed view of project economics, an assessment of capital costs offers simple and clear information which can be used to evaluate the status of different commercial technologies. **Figure 9** shows estimates of capital cost for a range of WtE power generation technologies. Capital costs are low for mature technologies such as cocombustion and anaerobic digestion integrated with ICE or gas turbine (GT). For early-stage technologies, the capital costs are extremely uncertain, and as such many were not included in the analysis. Pyrolysis, plasma arc gasification, and refused-derived fuel (RDF) direct combustion, for

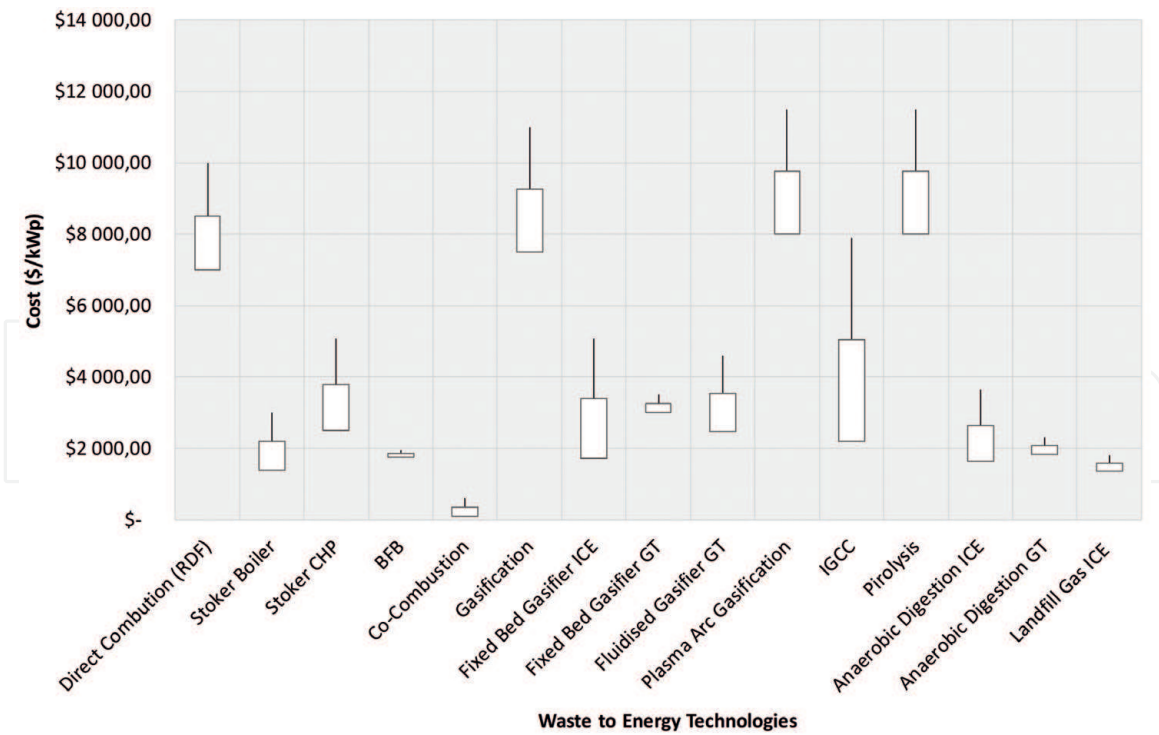


Figure 9. Capital cost (in \$/kW) for selected WtE power generation technologies [91–95].

example, have higher capital costs due to technical hurdles and novelty status. As for integrated gasification combined cycle (IGCC), the costs vary widely as the process is still not established with significant cost reductions expected. The size of cost decline, however, is likely to be very dependent on geographical location and in line to the support given by global policy-makers and national frameworks regarding each technology [91].

4. Conclusions

This chapter explored the possibility of using postprocess residues as abundant biorenewable and low-cost resources in future waste biorefineries. Available waste streams have a complex and varied composition according to its source, requiring new logistic platforms of assortment and valorization. With the exhaustion of the “collection and disposal” linear economy, new waste handling methods are unavoidable in the long term. As such, waste biorefineries that produce green energy and make virtually zero-waste high-value products in a “closed loop” and “up-cycling” approach are the “landfills” of the future. They are expected to be crucial in taking sustainable waste management into the real world allowing game-changing economic growth under the concept of circular economy. However, from the reviewed technologies, it can be concluded that single WtL and WtE processes are almost always limited in their scope, producing many times unwanted products. In this regard, the technology with more potential and scope in single applications is by far gasification; nonetheless, even this process has drawbacks such as reactor design, feeding system, and tar production that require costly posttreatment and/or further technological developments. Conversely, combining multiple WtE and WtL processes in an integrated waste biorefinery will allow the mitigation and elimination of each single process drawbacks. In gasification, for example, some of the unwanted substances generated may be utilized and valued by subsequent chemical processing, and even syngas can be upgraded. This novel waste valuation pyramid will create opportunities

for niche technologies such as explosive decompression and torrefaction to make it into practical application by enhancing other technologies that are already well established when used in an integrated approach. Future research should primarily focus on the establishment of a hierarchy of processes to produce the highest value products and then progress gradually to low-cost products and energy production. For this vision to be a reality, however, an increased effort on the part of the researchers will be required with a combined continuous and sustained support from all potential stakeholders. More demonstration projects at pilot or semipilot scale should materialize in the upcoming years, focusing on aspects such as energy balance and cost-benefit analysis guaranteeing the viability of the proposed solutions.

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