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An Overview of the Technological Applicability of Plasma Gasification Process

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Abstract

Recent increased environmental and political pressures, the unstable perspective of the fuel prices, and the fossil-resource-based energy have risen the industrial interest into the energy that can be produced from waste and have enhanced the technological findings in waste-to-energy sector. Sustainable waste treatment is an essential element in efforts to improve sustainability. Plasma gasification is considered an alternative for the abatement of municipal waste and has been demonstrated for the treatment of various wastes more in Japan, Canada, and the USA than in Europe. The goal of this mini-review is to brief the plasma-based gasification technology. This study includes a technological overview of the PG process, a survey of existing PG facilities, a comparison with other thermal techniques, and an identification of its environmental impacts.

Keywords

 $Plasma\ gasification \cdot Waste\ management \cdot Sustainability \cdot Green\ energy \cdot Thermal\ technology$

Highlights

- We summed up the plasma gasification technology.
- Survey of waste treatment facilities worldwide using plasma gasification.
- Technical and environmental comparison with other thermal technologies.
- Barriers on the plasma gasification application are addressed.

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15.1 Introduction

Recent increased environmental and political pressures, the unstable perspective of the fuel prices, and the fossil-resource-based energy have raised the industrial interest into the energy that can be produced from waste and have enhanced the technological findings in waste-to-energy sector (Tendler et al. 2005; Vaish et al. 2016, 2019). The disposal of waste remains a crucial issue, as stockpiling or landfilling of garbage has a negative impact. The European countries have to improve their waste management policy according to the Waste Directive Framework (Directive 2008/98/EC) for sustainable development, but the lack of project investments is apparent, and the problem persists.

Plasma gasification (PG) is a thermochemical process whereby wastes (produced or currently being landfilled) are converted into valuable energy in the form of gaseous fuel (syngas) that can be used for heat, power, or biofuel production. PG technology aims to the destruction of waste using high temperature (Fauchais 2007). Several companies through their representative solutions have facilities in various stages of permitting, constructing, or planning worldwide that could potentially destruct different wastes. However, PG facilities globally are currently operating under stringent regulations with different wastes, and it is expected that the facilities equipped with the most advanced air pollution control systems will be able to meet or exceed the regulatory restrictions in Europe.

The goal of this review is to provide a technical overview of the potency of the PG application. This assessment includes a technological analysis of the PG process, a survey of existing PG facilities, an assessment of the environmental aspects of PG technology, a characterization of useful end products, and a generic approach of PG economics incorporating operating costs and revenue potential from PG operations.

15.2 Plasma Gasification Technology

15.2.1 Feedstock

In a typical plasma gasifier, the feedstock enters from the top to the bottom of the furnace. It was found that PG technology has considerably expanded in the areas of municipal solid waste (MSW), fly ash, and hazardous and industrial waste (Leal-Quirós 2004; Serbin and Matveev 2010). Although the demonstration of PG to hazardous feedstocks is limited worldwide, no significant technical barriers to the application of this technology in processing hazardous seem to exist. This is particularly evident in the significant expansion of PG use, including feedstocks that are more heterogeneous than MSW, automotive shredder residue (ASR), tires, and mixed waste (An'Shakov et al. 2007; Dave and Joshi 2010).

15.2.2 Thermochemical Reactions

Gasification process includes various chemical reactions that are strongly dependent on the reactor conditions (temperature, gasification agent, etc.). While gasification processes vary considerably, typical gasifiers operate at temperatures between 700 and 800 °C (Basu 2010). The intrinsic gasification reactions are given in Eqs. 15.1, 15.2, 15.3, 15.4, 15.5, 15.6, 15.7, and 15.8 (Higman and Van Der Burgt 2008):

$$C + CO_2 = 2CO$$
 $\Delta Ho = +172 \, kJ$ (15.1)

$$C + H_2O(g) = CO + H_2$$
 $\Delta Ho = +130 \text{ kJ}$ (15.2)

$$C + 2H_2O(g) = CO2 + 2H_2 \quad \Delta Ho = +88 \,\text{kJ}$$
 (15.3)

$$C + 2H_2 = CH_4 \qquad \Delta Ho = -71 \, kJ \qquad (15.4)$$

$$CO + H_2O(g) = CO_2 + H_2 \quad \Delta Ho = -42 \text{ kJ}$$
 (15.5)

$$CO + 3H_2 = CH_4 + H_2O(g) \quad \Delta Ho = -205 \, kJ$$
 (15.6)

 $C + 1/2O_2 = CO$ $\Delta Ho = -109 \, kJ$ (15.7)

$$C + O_2 = CO_2 \quad \Delta Ho = -309 \, \text{kJ} \tag{15.8}$$

It is notable that synthesis gases for liquid fuels and chemicals are composed of gaseous mixtures of CO_2 and hydrogen. The carbon monoxide–hydrogen ratio is varied under process conditions and is typically related to the range of products. In contrast, pyrolysis does not include a reactive step, and its gaseous yield is lower and cannot be used for direct fuel or chemical synthesis without further processing (De Souza-Santos 2008).

PG operates at elevated temperatures to break the feedstock to molecules (Higman and Van Der Burgt 2008). Plasma is generated by heating a gas to very high temperatures where the molecules and atoms are ionized and toxic compounds such as dioxins are completely decomposed to harmless chemical elements.

15.2.3 Plasma Gasification Unit

A PG facility includes a preprocessing unit (i.e., shredder), a feeding system, an equipment to process the by-product (slag) derived from the plasma furnace, a syngas treatment system, and a monitoring and control system. The main device of a PG facility is the plasma-based furnace and specifically the plasma torches (Bratsev et al. 2006a, b).

15.2.3.1 Plasma Gasification Vessel

The gasification vessel is the main design component in the PG plant. The choice of reactor type and torch configuration relies on the process conditions and the feed-stock type (Bratsev et al. 2006a, b; Hrabovsky et al. 2006). Plasma gasification reactor (PGR) is a vertical furnace that is similar to that used in the foundry facilities for the melting of metallic materials. PGR can afford high internal temperatures and corrosive environment. The gasification reactions will convert the organic substance of the MSW feedstock into a syngas which exits the PGR, while the inorganic fraction will be transformed into a molten slag that exits the bottom. The PGR operates at elevated temperature in the lower part of the chamber, and oxygen and/or steam are injected into the process.

Two configurations of plasma gasifier (Fig. 15.1) are commonly used in industrial scale and are related to the placement location of the plasma torches. The typical configuration of a PG furnace is that the processed waste feedstock is fed into the furnace from the top. The electrodes which are responsible for the arc generation with the help of current extend into the lower part of the furnace, the so-called melting chamber. Gas enters the furnace through the torches and is ionized due to the high-temperature (up to 6000 °C) plasma jets applied. Various gases (O₂, air, N₂, CO₂, H₂O_(g)) can be used with air to be the most cost-effective. Additional gas (most common air or stream) is introduced through the nozzles to control the gasification reactions. An alternative plasma gasification technique used in industrial scale combines the plasma technology and the common gasification. This technique is not considered exactly as a thermal PG technology but as a thermal plasma treatment of gases leaving the reactor. In this case, the plasma arc destructs the tars, toxins, and furans included in the syngas at the exit of the plasma gasifier (Fourcault et al. 2010).

The combined process is able to produce a clean synthetic gas (main components H_2 and CO) that can be used to generate electricity in combined heat power (CHP) gas engines or can substitute natural gas. The multistage process unit combines gasification and plasma conditioning. A main component of the process is the thermal aftertreatment of the syngas by means of generated plasma. It is necessary for

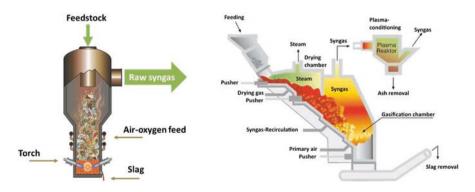


Fig. 15.1 Plasma-assisted gasifier from Alter NRG (left) and combined plasma gasifier from Europlasma (right) (Alter NRG; CHO-Power)

cracking and transformation of macromolecular hydrocarbons. Plasma torches are only used for the thermal cracking of the syngas and for slag vitrification.

15.2.3.2 Post-Processing Unit

The gaseous product exits the furnace that can be used for energy and fuel production. The thermal energy resulting from the syngas can be exploited in a variety of ways. These include the steam generation for further electricity and heat production. The design of the posttreatment equipment used to clean the effluent gases is crucial for the viable operation of a PG plant. Advanced emission control systems are required to meet regulatory standards. Typical process equipment for the treatment of exhaust gases consists of particulate filters, wet scrubbers, or electrostatic precipitators. Syngas is cleaned in a multistage process, the number of stages being dependent on how clean the syngas needs to be for the particular utilization and conversion process specified in each specific project. These multistage elements can add considerably to the capital costs and incur significant operating costs for the disposal of secondary residues. They can also reduce the overall plant operational availability and, in some circumstances, lower revenues from energy sales.

15.3 Survey of PG Facilities Worldwide

A literature-based identification of existing PG facilities was conducted, and their basic characteristics are given in Table 15.1. Alter NRG is a company with extensive experience and has built several commercial installations in Japan, China, the United Kingdom, and India. PEAT International, SRL Plasma, and InEnTec have also constructed facilities with a capacity up to 10 tpd using industrial, medical, and hazardous wastes. The pending PG projects were not identified in the analysis.

15.4 Products of PG Facility

The most crucial product from alternative conversion processes is the gaseous product so-called synthetics gas or syngas (Fig. 15.2). The syngas is a valuable gas with the main components CO and hydrogen. This synthetic gas can be used for fuel production, heat, or energy (Ducharme and Themelis 2010). The commercial applications of synthesis gas are split between chemical production, fuel production, and energy (heat/power) production. The percentage of PG facilities producing electrical power and utilizing post-combustion products has risen significantly due to demand and deregulation of electricity markets as well as accumulation of wastes.

Other potential products of PG processes include chemicals and fuels which can be stored and sold when the market price is higher. Inorganic materials in the feedstock are melted into slag, which is nonhazardous and can be used in a variety of applications, such as road construction and roofing materials. Marketing feasibility depends on the cleanliness, quantity, and packaging of the slag. Metal sources are also generated from the plasma gasification process. The metals produced can be

| Table 15.1 Plants | for waste trea | tment by plasma tecl | hnique currently in operat | ion around th | Table 15.1 Plants for waste treatment by plasma technique currently in operation around the world and plant projects for the next years | years | |
|---------------------------------------|-------------------|-----------------------------|-------------------------------------|---------------|---|------------------|------------|
| Technology | | | (| Capacity | | (| |
| supplier | Country | City, province | Owner | (tpd) | Feedstock | Output | Commission |
| Alter NRG | Japan | Utashinai, Hokkaido | Hitachi Metals | 220 | MSW, ASR | Power | 2003 |
| Alter NRG | Japan | Mihama-Mikata | Hitachi Metals, Hitachi | 24 | MSW, WW sludge | Heat | 2002 |
| Alter NRG ^a | Japan | Yoshi | Hitachi Metals, Hitachi | 151 | MSW | | 1999 |
| Alter NRG | India | Nagpur | SMS Envocare | 68 | Hazardous waste | Power | 2008 |
| Alter NRG | India | Pune | SMS Envocare | 68 | Hazardous waste | Power | 2009 |
| Alter NRG | China | Wuhan, Hubei | Wuhan Kaidi | 150 | Biomass | Biofuel | 2012 |
| Alter NRG | China | Shanghai | GTS Energy | 30 | Medical waste, incinerator fly ash | Slag | 2014 |
| Alter NRG ^a | USA | Madison, Pennsylvania | Alter NRG | 48 | Over 100 tested | Syngas | 1990 |
| Advanced Plasma Power | United Kingdom | Wiltshire | NG, Stonehouse, PR, CNG Services | 300 | Waste, biomass | Syngas, power | 2008 |
| Advanced Plasma Power ^a | United Kingdom | Swindon, Wiltshire | NG, Advanced Plasma Power, PE | 22 | RDF | bioSNG | 2017 |
| Advanced Plasma Power | United Kingdom | Energy Park Peterborough | | | Mixed waste | Power | 2014 |
| CHO-Power | France | Morcenx | | 200 | Cardboard, wood, paper, tissues | Power, heat | 2012 |
| Bellwether RG | Romania | Brasov | Dunarea SA | 240 | Calorific waste | Power, heat | 2008 |
| InEnTec | Japan | Iizuka | Fuji Kaihatsu Ltd. | 10 | Industrial wastes | Power | 2002 |
| InEnTec ^a | Japan | Okinawa | Kawasaki | | PCB oil and PCB-contaminated materials | | 2003 |

| InEnTec ^a | USA | Kapolei | Asia Pacific Environmental | | Medical waste | Power | 2001 |
|---|-----------|----------------------|---|---------|---|---------------|-------------|
| InEnTec ^a | Taiwan | Kuan Yin (Taipei) | Global Plasma Technology Limited | 4 | Medical waste, batteries, solvents, lab packs, mercury vapor lamps | | |
| InEnTec | USA | Arlington | InEnTec Columbia Ridge LLC | | MSM | Syngas, H_2 | |
| InEnTec° | USA | Richland | InEnTec LLC | 4 | Hazardous waste | | 1996 |
| InEnTec | USA | Richland | InEnTec LLC | | Hazardous and nuclear waste; TSCA and PCB waste | | 1999 |
| InEnTec | USA | Richland | Allied Technology Group, Inc. | | Mixed hazardous and radioactive wastes | | 1999 |
| InEnTec | Malaysia | Kuala Lumpur | Boeing Company/ BioPure Systems | | | | |
| InEnTec | Japan | Harima | Kawasaki Plant Systems | | Asbestos | | |
| InEnTec | USA | Midland, Michigan | Dow Corning Corp. | | Industrial by-products | | |
| PyroGenesis ^b | Canada | Montreal | PyroGenesis | 0.5-2.5 | Mixed waste | | 2002 |
| PyroGenesis | USA | US Navy | US Navy | 7 | Shipboard wastes | | 2004 |
| PyroGenesis | USA | Hurlburt Field | Air Force Special Operations Command | 10.5 | MSW, hazardous wastes | | 2011 |
| Plasco Energy Group ^a | Canada | Ottawa | | 85 | MSW | Power | 2007 |
| SRL Plasma – PLASCON ^a | Australia | | Nufarm Limited | 0.8 | Chlorophenols, phenoxies, toluene, dioxins/furans | | 1995 |
| | | | | | | | (continued) |

| Technology | | | | Capacity | | | |
|----------------------------|-----------|------------------|---------------------|----------|-------------------------------------|--------|------------|
| supplier | Country | City, province | Owner | (tpd) | Feedstock | Output | Commission |
| SRL | Australia | | BCD Technologies | 1 | Concentrated polychlorinated | | 1997 |
| Plasma – | | | | | biphenyl (PCB) waste | | |
| PLASCON^a | | | | | | | |
| PEAT | China | Shanghai | Abada Plasma | 1.2 | Medical waste, oil refinery sludge | | 2013 |
| International ^b | | | Technology Holdings | | | | |
| PEAT | Taiwan | Tainan | | 4 | Waste and toxic waste such as | | 2005 |
| International ^a | | | | | incinerator fly ash, medical waste, | | |
| | | | | | inorganic sludges | | |
| PEAT | USA | Lorton, Virginia | | 7 | Defense department waste, medical | | |
| International ^a | | | | | waste | | |

Alter NRG, CHO-Power, PEAT, InEnTec, PyroGenesis Canada, Tetronics International, Advanced Plasma Power, Plasma Arc Technologies, Plasco Energy Group, Westinghouse Plasma, Europlama ^aDemonstration ^bPilot cTest facility

Table 15.1 (continued)

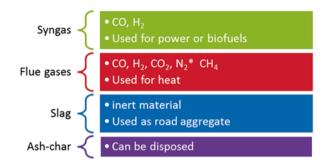


Fig. 15.2 Product range from plasma gasification operation

collected in molten form from subsequent processing in smelters. If the volume of metals is large enough to warrant separation, then the plant is configured to recapture metals. It is reported that slag derived from the vitrification of inorganic waste fraction has shown acceptable leachability limit and can be regarded as inert waste and therefore can be used as building components or disposed to a landfill.

15.5 Air Emissions from Plasma Gasification Operations

PG process is regarded as a promising technique to break down hazardous waste (i.e., medical waste) (Nema and Ganeshprasad 2002). It also displays lower environmental impacts in terms of air emissions and slag leachate toxicity as compared to other waste-to-energy processes, such as incineration (Hlína et al. 2006; Chang et al. 1996). However, empirical data on the environmental impacts of PG facilities are limited and depend on the local air permits and exhaust aftertreatment systems utilized at each facility. PG process has some emission advantages compared to conventional thermal treatment processes since it produces emissions far below the most stringent regulatory requirements. PG decomposes various types of wastes including low-strength radioactive waste to their elemental form. PG offers considerable environmental benefits with negative carbon footprint in comparison with other thermal energy technologies and has the highest landfill diversion rate of any available technology, making it very attractive to local authorities (Murphy et al. 2002). When compared to operations that utilize combustion of waste tires, it is generally accepted that PG technology will yield lower environmental risks and impacts in most areas. However, the information available is limited, due to the secrecy of full-scale PG facilities. Additionally, some older information on PG facilities may not be relevant due to recent advances in emission controls.

Air emissions may be the greatest environmental concern in PG operations. The output gases of plasma gasifiers contain a variety of air pollutants that must be eliminated prior to their release into the atmosphere. There are many strategies available for controlling emissions from PG process. The PG process differs in a number of key ways from common thermal processes, as the former generate intermediate gaseous products that can be converted into fuels or chemicals with almost no direct emissions. Information regarding output products of plasma gasification and problems that may be encountered is difficult to obtain as performance data from plasma gasification operations are often proprietary.

15.6 Market Potential of PG Technology

The profitability of any individual facility appears to depend on a number of other factors, including economic considerations, facility costs, feedstock availability, products range, and the permitting process (Artemov et al. 2012). There are several factors that affect the cost and ultimately the profitability of PG waste-to-energy conversion operations, and these are shown in Fig. 15.3.

The sensitivity of the estimated cost and expected revenues from the sale of syngas and heat coproduced by the conversion of waste depends on the world markets and prices for energy and industrial materials. At present, little data is available for currently operating facilities and how these facilities would be affected by market changes. The value of PG process is attributed to the combination of the avoided cost of conventional disposal and the expected revenue stream from coproduction (Popov et al. 2011). Table 15.2 summarizes information for different thermal technologies. Information was collected from (1) refereed technical literature and (2) commercial literature and/or referenced websites (Table 15.3).

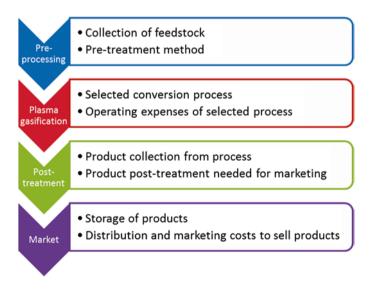


Fig. 15.3 Factors that influence the economic assessment of a plasma gasification facility

| | | USERPA | EC 2000/76 | | | |
|--------------------|------------|----------|------------|-------------------|-------------------|-------------------|
| Emission | Unit | standard | standard | Unit ^a | Unit ^b | Unit ^c |
| PM | mg/ Nm3 | 20 | 14 | 3.3 | <3.3 | 12.8 |
| HCL | mg/ Nm3 | 40.6 | 14 | 6.6 | 2.7 | 3.1 |
| NOx | mg/ Nm3 | 308 | 281 | 74 | 162 | 150 |
| SOx | mg/ Nm3 | 85.7 | 70 | - | - | 26 |
| Hg | mg/ Nm3 | 50 | 14 | 0.0002 | 0.00067 | 0.0002 |
| Dioxins/ furans | ng/ Nm3 | 13 | 0.14 | 0.000013 | 0.0067 | 0.009245 |

Table 15.2 Emissions from thermal plasma treatment facilities (Bowyer and Fernholz)

^aEPA Environmental Technology Verification Testing (2000) of InEnTec Plasma Arc Gasification of 10 tpd of Circuit Boards, Richland, Washington

^bEPA Environmental Technology Verification Testing (2000) of InEnTec Plasma Arc Gasification of 10 tpd of Medical Waste, Richland, Washington

^cResults of Third-Party Demonstration Source Tests (2008–2009) of Plasco Energy Plasma Arc Gasification of 110 tpd of MSW, Ottawa, Canada

| Property | Pyrolysis | Incineration | Conventional gasification | Plasma gasification |
|------------------------|--|---|---|---|
| Process temperature | 500–800 °C | 850–1200 °C | 400–900 °C | 1500–4000 °C |
| Atmosphere (agent) | Inert/nitrogen | Air | O ₂ , H ₂ O | O_2 , H_2O Plasma gas: O_2 , N_2 , Ar |
| Feedstock | Biomass and MSW Low flexibility | Mixed MSW High flexibility | MSW, RDF, sludge, medical waste Medium flexibility | MSW, RDF, medical and hazardous waste High flexibility |
| Produced gases | CO, H ₂ , CH ₄ , other hydrocarbons, N ₂ | CO ₂ , H ₂ O, O ₂ , N ₂ , NOx, SOx, HCl, VOCs | CO, H ₂ , CO ₂ ,H ₂ O, CH ₄ , N ₂ * | CO, H ₂ , CO ₂ , N ₂ *, CH ₄ |
| Solid phase | Ash, coke (biochar) | Ash (approx. 30% of initial volume) | Ash, char | Ash, char, inert slag (12% of initial volume) |
| Liquid phase | Pyrolysis oil and water | None | None | None |
| Emissions | N.A. | Far greater than (plasma) gasification | Less than incineration | Less than gasification and incineration |

 Table 15.3
 Characteristics of different thermal technologies

(continued)

| Property | Pyrolysis | Incineration | Conventional gasification | Plasma gasification |
|-----------------------------------|--|---|---|---|
| Gas cleaning | Intermediate cleaning before gas utilization | Intermediate cleaning before gas utilization | Intermediate cleaning before gas utilization | Cleaner gas is produced after the plasma arc |
| Pollutants | N.A. | PM , NO_X , SO_X , fly ash, ash, | PM, tars, NO _x , SO _x , dioxins, furans, hydrocarbons, CO, char | Low levels of CO, NO _x , tars, other pollutants vitrified in slag |
| Energy recovery | N.A. | Lower resulting from excess air leading to more waste heat | Higher from less heat loss (not all chars are broken down) | Higher gross energy recovery |
| Energy use | N.A. | Heat to electricity (steam boiler) | Heat to electricity Syngas for electricity Other commercial uses | Heat to electricity Syngas for electricity Other commercial uses |
| Input energy requirements | N.A. | None | Autothermal, partial oxidation | Very high (1200–1500 MJ/ tonne of waste) |
| Power to grid (kWh/ton MSW) | N.A. | 544 | 685 | 816 |

| Table 15.3 | (continued) |
|------------|-------------|
|------------|-------------|

Basu (2006, 2010), Higman and Van Der Burgt (2008), De Souza-Santos (2008), Annamalai and Puri (2006), Rezaiyan and Cheremisinoff (2005), Luche et al. (2012), Hrabovsky (2009), Kalinenko et al. (1993), Ghofur et al. (2018), Arazo et al. (2017), Huang et al. (2016), Moustakas et al. (2005, 2008), Mountouris et al. (2006, 2008), Achinas and Kapetanios (2012, 2013) and Bratsev et al. (2009) *NA* not available

15.7 Barriers

Three cardinal issues must be addressed for any of PG technology to be implemented successfully: legislative/regulatory, involvement of market and agreements, and social aspect. Regulatory facet is the most essential obstacle for this alteration facility. The local authority must also play the dominant role in the management of solid waste, water, and air. The planned facility that comprises premises, classification, water supply, usableness, site design reconsideration, and air emissions must be audited by the local planning agency. It is obligatory for a PG facility to obtain permission hence to start its construction activities.

Safe agreements to obtain a feedstock availability are required for the profitability of PG projects. The amount of feedstock must be more or less stable through the project's life. A thorough estimation of advantageous and disadvantageous consequences concerning ecosystem, society, and profit must be acquired before a facility passes to the stage of building. If markets are not developed for recycled products from the presorting process, revenue that otherwise would have been generated is lost. Furthermore, if no market share exists and clients are not found for the gas products, the facility will be forced to close due to a lack of revenue. The operating costs of these facilities will depend on (1) costs and quantities of labor used, (2) cost and quantities of utilities and expendable supplies needed to operate the facility, and (3) the capital costs for construction of the facility (Clark and Rogoff 2010).

Disadvantages exist for PG plants, especially in relation to feedstock size, electricity requirements, and cost issues (Loghin 2008; Yang et al. 2011). It is important to note that pretreatment is a key issue with respect to thermochemical processing. In some cases, further research in this area will be required in order to make the technology viable for specific wastes. A large portion of electricity generated is necessary for the operation of the plasma torches. This leads to a net reduction in electricity generation from the facility. It can vary significantly and depends largely on the throughput (Yang et al. 2011).

Moreover, the public's negative association with thermal treatment waste facilities is another barrier that needs to be overcome. In addition, smell, noise, and visual aesthetic complaints are fairly common from affected community members after waste management facilities have been installed.

15.8 Conclusion

The utilization of PG technology may be expanded in the future with continuing improvements in the technology. It is important to obtain a better understanding of this technology and its potential impacts on the environment, the economy, and existing markets. Besides, evaluations show that syngas production through PG is advantageous over other thermochemical techniques because PG is energy-efficient and environmentally friendly technology. Moreover, current research activities aim to improve PG control and therefore the performance of the process, which indicates the growing economic potential of plasma gasification in the coming decades over yet established thermochemical techniques.

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