

Solid Waste Management through the Application of Thermal Methods

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1. Introduction

Human life in modern societies is inevitably related to waste generation. Around 255 million tones of municipal solid waste were generated in the 27 Member-States of the European Union in 2006, an increase of 13% in comparison to 1995. This represented an average of 517 kg of municipal waste per capita, an increase of 9% over 1995. Therefore, it is not strange that waste management has become a crucial subject with increasing interest for scientists, local authorities, companies and simple citizens.

The effective management of solid waste involves the application of various treatment methods, technologies and practices. All applied technologies and systems must ensure the protection of the public health and the environment. Apart from sanitary landfill, mechanical recycling and common recycling routes for different target materials, the technologies that are applied for the management of domestic solid waste include biological treatment (composting, anaerobic digestion) and thermal treatment technologies (incineration, pyrolysis, gasification, plasma technology).

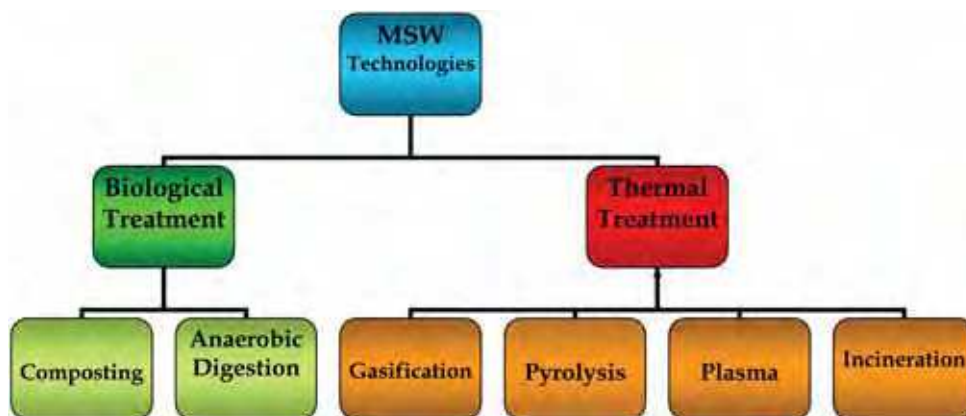


Fig. 1. Different biological and thermal methods for solid waste management

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This chapter focuses on the description of the alternative thermal practices for municipal solid waste management. Thermal methods for waste management aim at the reduction of the waste volume, the conversion of waste into harmless materials and the utilization of the energy that is hidden within waste as heat, steam, electrical energy or combustible material. They include all processes converting the waste content into gas, liquid and solid products with simultaneous or consequent release of thermal energy.

According to the New Waste Framework Directive 2008/98/EC, the waste treatment methods are categorized as "Disposal" or "Recovery" and the thermal management practices that are accompanied by significant energy recovery are included in the "Recovery" category. In addition, the pyramid of the priorities in the waste management sector shows that energy recovery is more desired option in relation to the final disposal.

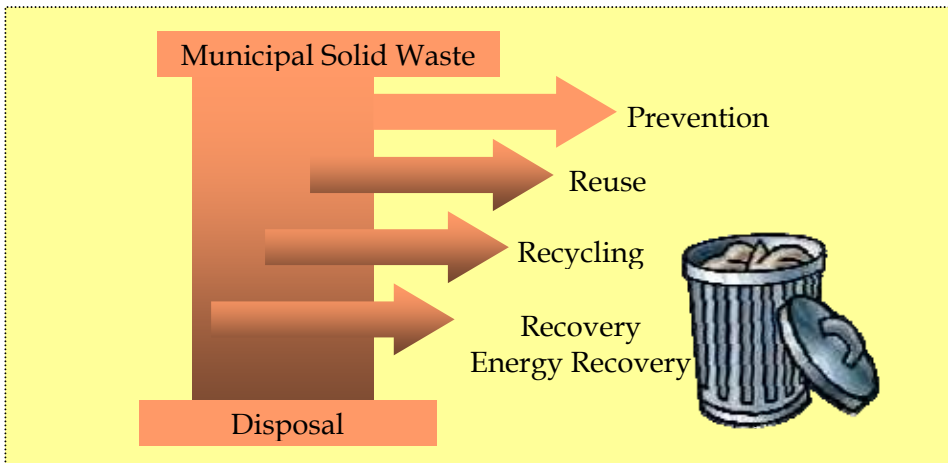


Fig. 2. Pyramid of the priorities in the waste management sector

That is why more and more countries around the world develop and apply Waste-to-Energy technologies in order to handle the constantly increasing generated municipal waste. Technologically advanced countries in the domain of waste management are characterized by increased recycling rates and, at the same time, operation of a high number of Waste-to-Energy facilities (around 420 in the 27 European Member-States). More specifically, on the basis of Eurostat data the percentages of municipal waste treated with thermal methods for the year 2007 in Denmark, Sweden, Luxembourg, Netherlands, France (Autret et al., 2007), Germany, Belgium and Austria were 53%, 47%, 47%, 38%, 36%, 35%, 34% and 28% respectively. On the other hand, there are still Member-States that do not apply thermal techniques in order to handle the generated municipal waste, especially in the southern Europe and the Baltic Sea. Such countries include Bulgaria, Estonia, Iceland, Cyprus, Latvia, Lithuania, Slovenia, Malta, Poland, Romania and Greece.

General information about the use of thermal technologies for solid waste management around Europe and worldwide is provided. Data referring to incineration – mass burn combustion, pyrolysis, gasification and plasma technology is presented. The different aspects of each technology, the indicative respective reactions, as well as the products of each thermal process, are described. The issue of air emissions and solid residues is addressed, while the requirements for cleaning systems are also discussed for each case.

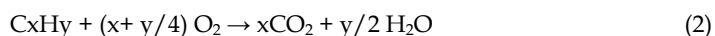
Finally, the first attempt to treat municipal waste in Greece with the use of gasification / vitrification process is presented.

2. Incineration

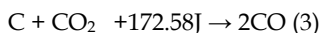
2.1 General

The incineration (combustion) of carbon-based materials in an oxygen-rich environment (greater than stoichiometric), typically at temperatures higher than 850°, produces a waste gas composed primarily of carbon dioxide (CO₂) and water (H₂O). Other air emissions are nitrogen oxides, sulphur dioxide, etc. The inorganic content of the waste is converted to ash. This is the most common and well-proven thermal process using a wide variety of fuels.

During the full combustion there is oxygen in excess and, consequently, the stoichiometric coefficient of oxygen in the combustion reaction is higher than the value "1". In theory, if the coefficient is equal to "1", no carbon monoxide (CO) is produced and the average gas temperature is 1,200°C. The reactions that are then taking place are:



In the case of lack of oxygen, the reactions are characterized as incomplete combustion ones, where the produced CO₂ reacts with C that has not been consumed yet and is converted to CO at higher temperatures.



The object of this thermal treatment method is the reduction of the volume of the treated waste with simultaneous utilization of the contained energy. The recovered energy could be used for:

- heating
- steam production
- electric energy production

The typical amount of net energy that can be produced per ton of domestic waste is about 0.7 MWh of electricity and 2 MWh of district heating. Thus, incinerating about 600 tones of waste per day, about 17 MW of electrical power and 1,200 MWh district heating could be produced each day.

The method could be applied for the treatment of mixed solid waste as well as for the treatment of pre-selected waste. It can reduce the volume of the municipal solid waste by 90% and its weight by 75%. The incineration technology is viable for the thermal treatment of high quantities of solid waste (more than 100,000 tones per year).

A number of preconditions have to be satisfied so that the complete combustion of the treated solid waste takes place:

- adequate fuel material and oxidation means at the combustion heart
- achievable ignition temperature
- suitable mixture proportion
- continuous removal of the gases that are produced during combustion
- continuous removal of the combustion residues
- maintenance of suitable temperature within the furnace
- turbulent flow of gases
- adequate residence time of waste at the combustion area (Gidarakos, 2006).

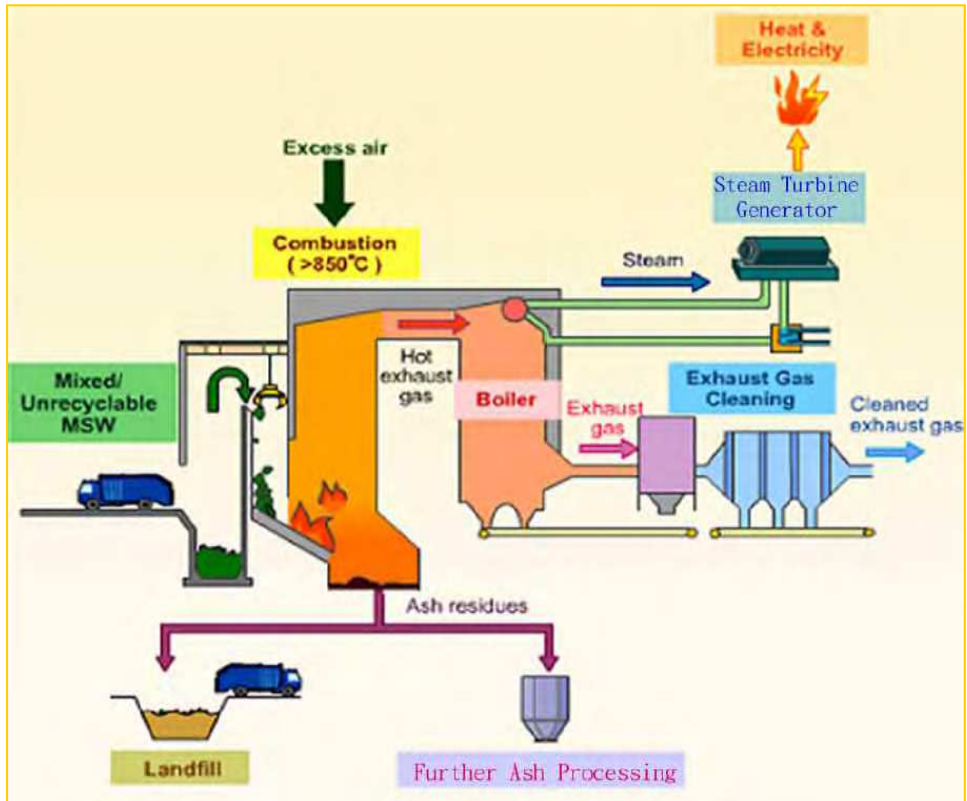


Fig. 3. A schematic diagram of incineration process

The existing European legislative framework via the Directive 2000/76/EC prevents and limits as far as practicable negative effects on the environment, in particular pollution by emissions into air, soil, surface water and groundwater, and the resulting risks to human health, from the incineration and co-incineration of waste (European Commission, 2000).



Photo 1. MSW incineration plants in Amsterdam, Brescia & Vienna respectively

2.2 Typical Incineration plant

A typical incineration plant includes:

Weighing System

The system for weighing solid waste aims at the control and recording of the incoming loads and it has to be practical so as to minimize the time that vehicles remain at this point.

Reception Site

Due to the fact that waste does not arrive on continuous basis (contrary to the feeding of the facility), the existence of waste reception and temporary storage site is considered necessary. The design of the site is made in a way that the following are ensured:

- the unloading time is as little as possible
- all transferred waste is received
- the homogeneity of the waste that will be used as feeding material is achieved
- the smooth feeding of the facility is ensured

Moreover, the design of the reception site should be based on the minimization of the environmental consequences. For instance, the solid waste should remain for maximum two days so as to avoid odours, while the bottom of the site has to be characterised by weathering to allow the leachates and washing wastewater to go away.

Feeding System

The feeding system has to be adapted to the rate and feeding velocity of the installation.

Combustion Hearths

The ignition of solid waste at incineration facilities is achieved through the use of specific burner, which operates with secondary fuel. Basic parameters for the appropriate operation of the combustion hearths are:

- achievement of the minimum desired temperature
- adequate combustion time
- achievement of turbulence conditions / homogenous waste incineration

Boiler

The boiler is the system with which the energy content of the fuel material (hot off-gases) can be utilized in a suitable way through steam production (e.g. at neighbouring industrial facilities or for the heating of urban areas. Pressure, temperature and steam production rate are basic parameters for the effective operation of the boiler.

System for the removal of residues

Residues represent 20 - 40% of the weight of the initial waste and are categorized into:

- Residues that go out of the grates: 20 - 35%
- Residues that go through the grates: 1 - 2%

The residues are collected at hoppers where they are transferred with specific system for cooling.

Emission control system

The role of the emission system control focuses on particles, HCl, HF, SO₂, dioxins and heavy metals and is discussed below (Niessen, 2002).

2.3 Typical emissions from incinerations

The emissions derived from the operation of typical incinerations plants include:

1. Air emissions

The generated air emissions contain the typical combustion products (CO , CO_2 , NO_x , SO_2), excess of oxygen, dust particles as well as other compounds. The presence and the concentration of other compounds, such as HCl , HF , suspended particles which contain heavy metals, dioxins and furans, depend on the composition of the waste that is subjected to incineration. During incineration, a quantity of 4,000 - 5,000 m^3 of air emissions is generated per ton of waste.

Air emissions must be controlled by applying appropriate anti-pollution systems, such as:

- Bagfilters
- Electrostatic filters
- Cyclones
- Wet cleaning systems, e.g. scrubbers, wet cleaning towers, rotate sprayers, etc.

Dioxin or furan refers to molecules or compounds composed of carbon and oxygen. These compounds when reacting with halogens, such as chlorine or bromine, acquire toxic properties. Most research on halogenated dioxin and furan has been concerned with chlorinated species. It is generally accepted that dioxin and furan are by-products of combustion processes including domestic and medical waste combustion or incineration processes. In combustion processes, hydrocarbon precursors react with chlorinated compounds or molecules to form furans or/and dioxins. They may also be generated in a post-combustion flue gas cooling system due to the presence of precursor compounds, free chlorine, or unburned carbon and copper species in the fly ash particles.

The toxic influence of dioxins and furans had not been made clear until the end of the decade of 80. The application of the MACT Regulations led to the drastic reduction of the TEQ-Toxic equivalent of the dioxin emissions. As a result, the dioxin emissions have been limited to one thousandth in relation to the year 1987, reaching values lower than 10 gr TEQ per year (Fig. 4). It should also be noted that on the basis of data provided by the US EPA the uncontrolled burning of waste is considered as the main source of dioxins, producing around 600 gr annually.

Dioxins and furans are produced in almost all combustion processes, in the gas phase, while the exact mechanism for their formation is not known. It is known that their formation temperature is 300C° , temperatures where two reactions are possible, formation and decomposition. The existence of chlorinated organic substances in waste and the increase of their content in oxygen encourage their formation. Consequently, the operating conditions of incinerators influence the dioxin formation at higher degree than the waste composition and PVC quantity included in it.

There are indications for the contribution of dioxins and furans to human cancers, fact that makes necessary to take basic and secondary measures so as to limit such emissions.

In order to remove the suspended particles and the gas pollutants, different cleaning systems can be applied. Indicatively, deposition chambers, where 40% of suspended solids is removed, cyclones (removal efficiency 60-80%), wet cleaning towers (removal efficiency 80-95%), electrostatic precipitators (removal efficiency 99-99.5%) and bagfilters (removal efficiency 99.9%) are referred. Apart from the removal of suspended solids, it is often necessary to remove other gas pollutants in the case that they exceed the limit values (like HCl generated during the combustion of PVC and oxides of nitrogen, sulphur and phosphorus. Next, the main cleaning systems that are used for the treatment of the gas products during incineration are briefly described.

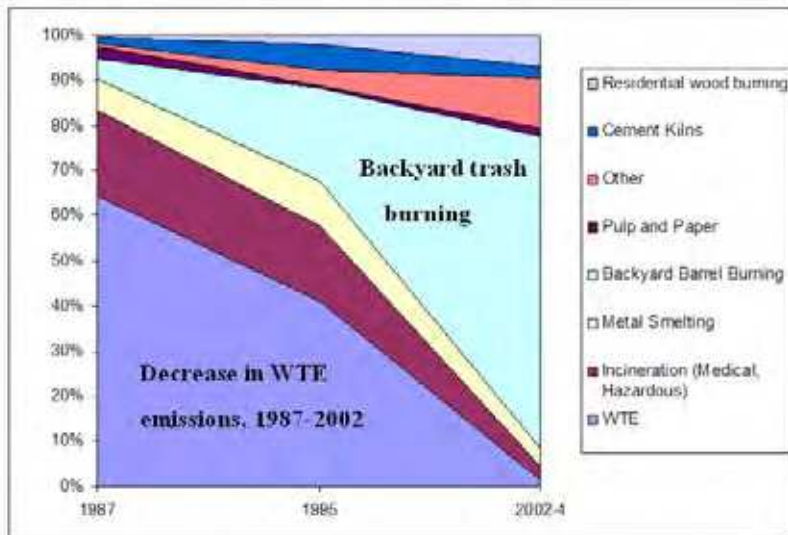


Fig. 4. Dioxins emission in the USA (Deriziotis, 2004).

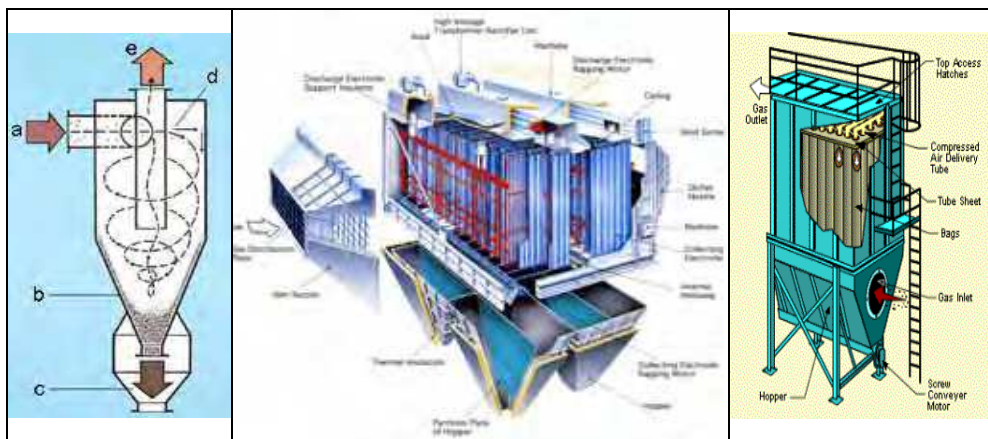


Fig. 5. Cyclones (left), electrostatic precipitators (middle) & bagfilters (right)

Bagfilters: The gases go through porous materials, where the suspended particles are detained. Depending on the requirements, the material of the filters is from natural fibres, plastic ones, glass, minerals, etc. Dust that is collected at the filter cells is removed by vibration or knocks or contrary air provision.

Electrostatic Precipitators (Electro filters): They are consisted of the cathode that can be a simple thin wire and the anode. Another configuration includes a system of parallel tablets, with potential difference between them. Voltage with values between 30-80 KV is developed between the anode and the cathode. When the particles enter the cathode field, they are charged and the negative ones are moving to the positive pole (anode). The velocity of the particles depends on the weight and the Coulomb forces that are developed.

Cyclones: They are based on the development of centrifugal force at the entry of gases at a symmetrical area. The particles due to the centrifugal force and the rotary flow are led towards the walls and then moved downward. Cyclones are often applied together with electrostatic precipitators (Allsopp et al., 2001).

2. Wastewater

Wastewater is generated by the use of water during the incineration process and in particular:

- extinguishing of ash (0.1 m³ of water/tn of waste)
- cooling of air gasses (2 m³ of water/tn of waste)
- wet absorbance towers (2 m³ of water/tn of waste)
- electrostatic filters (precipitators)

The wastewater stream contains suspended solids as well as dissolved organic and inorganic substances. It is characterized as hazardous wastewater and specific treatment is required prior to its final disposal.

3. Solid residues

The secondary solid residues that are generated during incineration can be categorized as follows:

- Fly ash: It is the lightest fraction of the generated solid residues and is collected by the appropriate filters (bagfilters or electrostatic filters). The fly ash contains high concentrations of heavy metals and is characterized as hazardous waste stream.
- Bottom ash: It is the residue of the incineration process (inorganic matter) and is collected at the bottom of the incinerator
- Boiler ash
- Filter dust
- Other solid residues generated during the air emissions cleaning

The solid residues stream must be treated prior to their final disposal, while a main portion of their quantities could be recycled by applying specific processes.

2.4 Types of incinerators

There are various types of incinerators, such as moving grate, fixed grate, rotary-kiln, fluidized bed, etc (Fig. 6).

Moving grate

The typical incineration plant for domestic solid waste is a moving grate incinerator. The moving grate enables the movement of waste through the combustion chamber to be optimized to allow more efficient and complete combustion. A single moving grate boiler can handle up to 35 tones of waste per hour, and can operate 8,000 hours per year with only one scheduled stop for inspection and maintenance of about one month's duration. Moving grate incinerators are sometimes referred to as Municipal Solid Waste Incinerators.

The waste is introduced by a waste crane through the "throat" at one end of the grate, from where it moves down over the descending grate to the ash pit in the other end. Here the ash is removed through a water lock.

Part of the combustion air (primary combustion air) is supplied through the grate from below. This air flow also has the purpose of cooling the grate itself. Cooling is important for the mechanical strength of the grate, and many moving grates are also water cooled internally.

Secondary combustion air is supplied into the boiler at high speed through nozzles over the grate. It facilitates complete combustion of the flue gases by introducing turbulence for better mixing and by ensuring a surplus of oxygen. In multiple/stepped hearth incinerators, the secondary combustion air is introduced in a separate chamber downstream the primary combustion chamber.

According to the European Waste Incineration Directive, incineration plants must be designed to ensure that the flue gases reach a temperature of at least 850 °C for 2 seconds in order to ensure proper breakdown of organic toxins. In order to comply with this at all times, it is required to install backup auxiliary burners (often fueled by oil), which are fired into the boiler in case the heating value of the waste becomes too low to reach this temperature alone.

The flue gases are then cooled in the superheaters, where the heat is transferred to steam, heating the steam to typically 400 °C at a pressure of 40 bar for the electricity generation in the turbine. At this point, the flue gas has a temperature of around 200 °C, and is passed to the flue gas cleaning system.

Often incineration plants consist of several separate 'boiler lines' (boilers and flue gas treatment plants), so that waste receipt can continue at one boiler line, while the others are subject to revision.

Fixed grate

The older and simpler type of incinerator was a brick-lined cell with a fixed metal grate over a lower ash pit, with one opening in the top or side for loading and another opening in the side for removing incombustible solids called clinkers.

Rotary-kiln

The rotary kiln incinerator is applied by municipalities and by large industrial plants. This type of incinerator has two chambers, a primary chamber and secondary chamber. The primary chamber consists of an inclined refractory lined cylindrical tube. Movement of the cylinder on its axis facilitates movement of waste. In the primary chamber, there is conversion of solid fraction to gases, through volatilization, destructive distillation and partial combustion reactions. The secondary chamber is necessary to complete gas phase combustion reactions.

The clinkers spill out at the end of the cylinder. A tall flue gas stack, fan, or steam jet supplies the needed draft. Ash drops through the grate, but many particles are carried along with the hot gases. The particles and any combustible gases may be combusted in an "afterburner".

Fluidized bed

According to the technology that is applied for this type of incinerator, a strong airflow is forced through a sand bed. The air seeps through the sand until a point is reached where the sand particles separate to let the air through and mixing and churning occurs, thus a fluidized bed is created and fuel and waste can now be introduced (European Commission, 2006).

3. Gasification

3.1 General

Gasification is the thermal process that converts carbon-containing materials, such as coal, petcoke, biomass, sludge, domestic solid waste to syngas which can then be used to produce electric power, valuable products, such as chemicals, fertilizers, substitute natural gas,

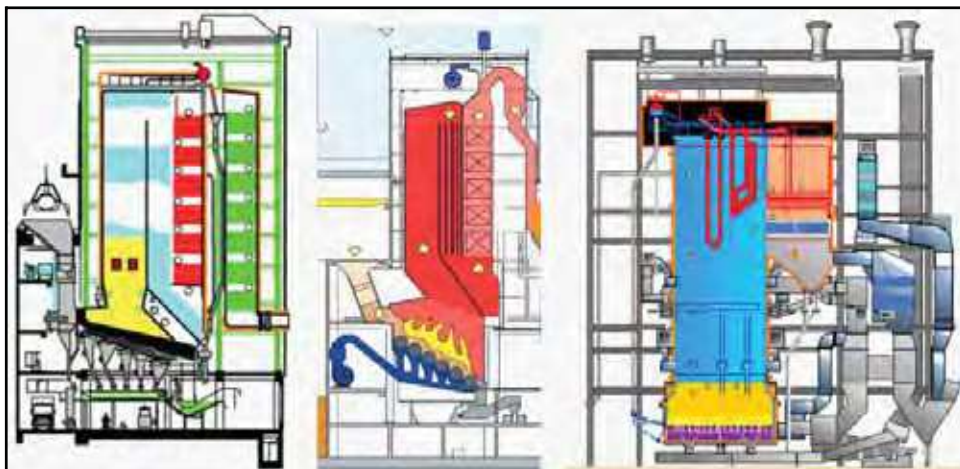
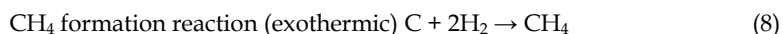
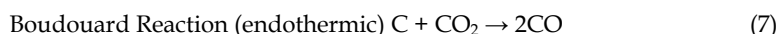
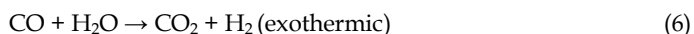
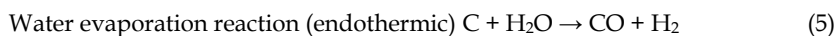
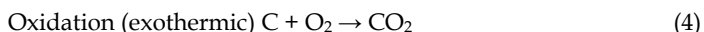


Fig. 6. three types of incinerators: (a) fixed grate, (b) rotary kiln, (c) fluidized bed

hydrogen, steam and transportation fuels. Gasification is defined as a thermal reaction with insufficient oxygen present for reaction of all hydrocarbons (compounds of carbon, hydrogen and oxygen molecules) to CO_2 and H_2O . This is a partial oxidation process which produces a composite gas (syngas) comprised primarily of hydrogen (H_2) and carbon monoxide (CO).

The major benefit of gasification of biowaste is that the product gas can be used directly, after significant cleaning, to fuel a gas turbine generator which itself will form part of a Combined Heat and Power (CHP) or Combined-Cycle Gas Turbine system, thus theoretically improving the overall thermal efficiency of the plant. The main disadvantage is that there can be more items of large equipment and the capital investment is correspondingly higher (Yassin et al., 2009).

The main reactions taking place during gasification are:



3.2 Typical gasification plant

A typical gasification plant includes:

A) Feedstock

Gasification enables the capture – in an environmentally beneficial manner – of the remaining “value” present in a variety of low-grade hydrocarbon materials (“feedstocks”) that would otherwise have minimal or even negative economic value. Gasifiers can be designed to run on a single material or a blend of feedstocks:



Fig. 7. A schematic diagram of gasification process

- Solids: All types of coal and petroleum coke (a low value byproduct of refining) and biomass, such as wood waste, agricultural waste and household waste
- Liquids: Liquid refinery residuals (including asphalts, bitumen, and other oil sands residues) and liquid waste from chemical plants and refineries
- Gas: Natural gas or refinery/chemical off-gas.

B) Gasifier

The core of the gasification system is the gasifier, a pressurized vessel where the feed material reacts with oxygen (or air) and steam at high temperatures. There are several basic gasifier designs, distinguished by the use of wet or dry feed, the use of air or oxygen, the reactor's flow direction (up-flow, downflow, or circulating), and the gas cooling process. Currently, gasifiers are capable of handling up to 3,000 tons/day of feedstock throughput and this will increase in the near future. After being ground into very small particles – or fed directly (in the case of gas or liquid) – the feedstock is injected into the gasifier, along with a controlled amount of air or oxygen and steam. Temperatures in a gasifier range from 1,400-2,800 degrees Fahrenheit. The heat and pressure inside the gasifier break apart the chemical bonds of the feedstock, forming syngas. The syngas consists primarily of H_2 and CO and, depending upon the specific gasification technology, smaller quantities of CH_4 , CO_2 , H_2S , and water vapour. Syngas can be combusted to produce electric power and steam

or used as a building block for a variety of chemicals and fuels. Syngas generally has a heating value of 250-300 Btu/scf, compared to natural gas at approximately 1,000 BTU/scf. Typically, 70-85% of the carbon in the feedstock is converted into the syngas. The ratio of carbon monoxide to hydrogen depends in part upon the hydrogen and carbon content of the feedstock and the type of gasifier used.

C) Oxygen plant

Most gasification systems use almost pure oxygen (as opposed to air) to help facilitate the reaction in the gasifier. This oxygen (95-99% purity) is generated in a plant using proven cryogenic technology. The oxygen is then fed into the gasifier through separate co-feed ports in the feed injector.

D) Gas Clean-Up

The raw syngas produced in the gasifier contains trace levels of impurities that must be removed prior to its ultimate use. After the gas is cooled, the trace minerals, particulates, sulphur, mercury, and unconverted carbon are removed at high degree using commercially proven cleaning processes common to the chemical and refining industries.

For feeds (such as coal) containing mercury, more than 95% of the mercury can be removed from the syngas using relatively small and commercially available activated carbon beds.

E) By-products

Most solid and liquid feed gasifiers produce a glass-like by-product called slag, which is non-hazardous and can be used in roadbed construction or as roofing material. Also, in most gasification plants, more than 99% of the sulphur is removed and recovered either as elemental sulphur or sulphuric acid.

Hydrogen and carbon monoxide, the major components of syngas, are the basic building blocks of a number of other products, such as chemicals and fertilizers. In addition, a gasification plant can be designed to produce more than one product at a time (co-production or "polygeneration"), such as the production of electricity, steam, and chemicals (e.g. methanol or ammonia). This polygeneration flexibility allows a facility to increase its efficiency and improve the economics of its operations.

3.3 Types of gasifiers

The basic types of the gasifiers are:

- Vertical steady bed
- Horizontal steady bed
- Fluidized bed (Groi et al., 2008)
- Multiple hearths
- Rotary kiln

Among the total five types of installations, the development of vertical and horizontal steady bed facilities, as well as fluidized bed ones is more common.

The facilities of vertical steady bed have advantages, such as the fact that they are simple and have low capital cost, but they are influenced directly by the variations in the composition of the incoming waste (it has to be homogenous, e.g. RDF in condensed form - pellets).

On the basis of the results of pilot applications for units that were operating at temperatures from 650 to 820°C, it was proved that:

- The produced solid residue has high absorption ability and can be used in facilities for the tertiary treatment of water and wastewater.
- The gas product can be used as fuel in oil combustion engines in a proportion 4:1, with the engine performance reaching 76% of the performance in the case that only oil was used (Belgiorno et al., 2003).



Photo 2. MSW gasification plant in Chiba (Japan)

Summarizing, gasification is not an incineration or combustion process. If gasification was compared with incineration, it could be supported that gasification is a conversion process that produces more valuable and useful products from carbonaceous material. Both gasification and combustion processes convert carbonaceous material to gases. Gasification processes operate in the absence of oxygen or with a limited amount of oxygen, while combustion processes operate with excess oxygen.

The objectives of combustion are to thermally destruct the feed material and to generate heat. In contrast, the objective of gasification is to convert the feed material into more valuable, environmentally friendly intermediate products that can be used for a variety of purposes including chemical, fuel, and energy production. Elements generally found in a carbonaceous material such as C, H, N, O, S, and Cl are converted to a syngas consisting of CO, H₂, H₂O, CO₂, NH₃, N₂, CH₄, H₂S, HCl, COS, HCN, elemental carbon, and traces of heavier hydrocarbon gases. The products of combustion processes are CO₂, H₂O, SO₂, NO, NO₂ and HCl.

From an environmental standpoint, gasification offers several advantages over the combustion of solids, heavy oils, and carbonaceous industrial and domestic waste. First, emission of sulphur and nitrogen oxides precursors to acid rain, as well as particulates from gasification are reduced significantly due to the cleanup of syngas. Sulphur in the gasifier feed is converted to H₂S, while nitrogen in the feed is converted to diatomic nitrogen (N₂) and NH₃. Both H₂S and NH₃ are removed in downstream processes, producing a clean syngas. Therefore, if the resulting clean syngas is combusted in a gas turbine to generate electricity or in a boiler to produce steam or hot water, the production of sulphur and nitrogen oxides are reduced significantly. If the clean syngas is used as an intermediate product for manufacture of chemicals, these acid-rain precursors are not formed.

The particulates in the raw syngas are also significantly reduced due to multiple gas cleanup systems used to meet gas turbine manufacturers' specifications. Particulate removal takes place in primary cyclones, scrubbers, or dry filters and then in gas cooling and acid gas removal systems.

A second major advantage is that furan and dioxin compounds are not formed during gasification. Combustion of organic matter is a major source of these highly toxic and carcinogenic pollutants. The reasons why furans and dioxins are not formed in gasification are:

1. The lack of oxygen in the reducing environment of the gasifier prevents formation of free chlorine from HCl and limits chlorination of any precursor compounds in the gasifier
2. High temperature of gasification processes effectively destroys any furan or dioxin precursors in the feed

Furthermore, if the syngas is combusted in a gas turbine where excess oxygen is present, the high combustion temperature does not favor formation of free chlorine. In addition, post-combustion formation of dioxin or furan is not expected to occur because very little of the particulates that are required for post-combustion formation of these compounds are present in the flue gas.

Limited data is available on the concentration of volatile organic compounds, semi-volatile organic compounds (SVOCs), and polycyclic aromatic hydrocarbons (PAHs) from gasification processes. The data that is available indicate that VOCs, SVOCs, and PAHs are either non-detectable in flue gas streams from IGCC process or, in some cases where they were detected, they are at extremely low levels (on the order of parts per billion and lower). The analysis of syngas also indicates greater than 99.99 percent chlorobenzene and hexachlorobenzene destruction and removal efficiencies and part per billion or less concentration of selected PAHs and VOCs (Rezaiyan & Cheremisinoff, 2005; Klein, 2002; Radian International LLC, 2000).

4. Pyrolysis

Pyrolysis is the thermal degradation of carbon-based materials through the use of an indirect, external source of heat, typically at temperatures of 450 to 750°C, in the absence or almost complete absence of free oxygen. This drives off the volatile portions of the organic materials, resulting in a syngas composed primarily of H₂, CO, CO₂, CH₄ and complex hydrocarbons. The syngas can be utilized in boilers, gas turbines or internal combustion engines to generate electricity. The balance of the organic materials that are not volatile are left as char material. Inorganic materials form bottom ash that requires disposal, although some pyrolysis ash can be used for manufacturing brick materials. Pyrolysis involves the thermal degradation of organic waste in the absence of free oxygen to produce a carbonaceous char, oils and combustible gases.

Although pyrolysis is an age-old technology, its application to biomass and waste materials is a relatively recent development. An alternative term for pyrolysis is thermolysis, which is technically more accurate for biomass energy processes because these systems are usually starved-air rather than the total absence of oxygen. Although all the products of pyrolysis may be useful, the main fuel for power generation is the pyrolysis oil. Depending on the process, this oil may be used as liquid fuel for burning in a boiler or as a substitute for diesel fuel in reciprocating engines, although this normally requires further processing (Institution of Mechanical Engineers, 2007).

The reactions taking place initially are decomposition ones, where organic components of low volatility are converted into other more volatile ones:



Moreover, at the early stages of pyrolysis process, reactions occurring include condensation, hydrogen removal and ring formation reactions that lead to the formation of solid residue from organic substances of low volatility:



In the case of existence of oxygen, CO and CO₂ are produced or the interaction with water is possible. The produced coke can be vaporized into O₂ and CO₂.

The pyrolysis products can be liquid, solid and gaseous. The majority of the organic substances in waste are subjected to pyrolysis by 75 - 90 % into volatile substances and by 10 - 25 % to solid residue (coke). However, due to the existence of humidity and inorganic substances, the quantity of volatile substances varies from 60 to 70% and the coke between 30 and 40%.

In order to achieve the successful operation of a pyrolysis facility, continuous control is required due to the complex processes taking place during the method development. Moreover, solid waste with no major composition variation that does not include metals and glass has to be fed on continuous basis (use of waste after successful implementation of separation at source or mechanical separation). In addition, special care is needed about

Solid	Carbon that is incorporated into several inert products	-
Gas	Dust particles, CO, CO ₂ , CH ₄ , H ₂	700 m ³ off-gases / tone of waste
Liquid	CH ₃ COOH, CH ₃ COCH ₃ , CH ₃ OH, complex oxygenised H/C	

Table 1. Brief description of the solid, liquid and gas products from the operation of a pyrolysis unit

% v/v gas composition	Pyrolysis temperature (°C)			
	500	650	815	926
CO	33.6	30.5	34.1	35.3
CO ₂	44.8	31.8	20.6	18.3
H ₂	5.6	16.5	28.6	32.4
CH ₄	12.5	15.9	28.6	32.4
C ₂ H ₆	3.0	3.1	0.8	1.1
C ₂ H ₄	0.5	2.2	2.2	2.4
Calorific Value (btu/St/t)	312	403	392	385

Table 2. Composition of the produced gas at different pyrolysis temperatures

whether the liquid products satisfy the specifications of commercial fuel (mainly due to the humidity within these products).

The product proportions depend on the waste nature, the temperature conditions and the treatment time.

The products produced from pyrolysing materials are a solid residue and a synthetic gas (syngas), while some of the volatile components form tars and oils can be removed and reused. The solid residue (sometimes described as a char) is a combination of non-combustible materials and carbon. The syngas is a mixture of gases (combustible constituents include carbon monoxide, hydrogen, methane and a broad range of other VOCs). A proportion of these can be condensed to produce oils, waxes and tars. The syngas typically has a net calorific value of between 10 and 20 MJ/Nm³. If required, the condensable fraction can be collected by cooling the syngas, potentially for use as liquid fuel (Gidarakos 2006).

Typical Pyrolysis Facility

In a typical pyrolysis facility the following are taking place:

- Drying of solid waste (100-200°C)
- Initial decomposition of substances, initiation of the decomposition of H₂S and CO₂ (250°C)
- Break of the bonds of aliphatic substances – Start of the separation of CH₄ and other aliphatic substances (340°C).
- Enrichment of the produced material in carbon (380°C)
- Break of the bonds C – O and C – N (400°C).
- Conversion of coal tar materials into fuel material and tar (400 - 600°C).
- Decomposition to materials resistant to heat – Formation of aromatic substances (600°C).
- Production of aromatic substances, processes for hydrogen removal from organics like butadiene, etc. (>600°C).

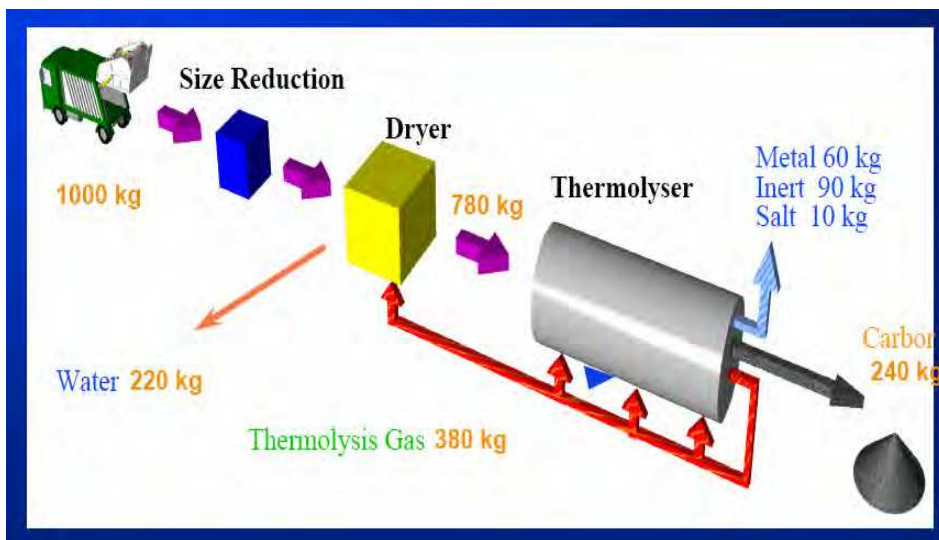


Fig. 8. A schematic diagram of gasification process

The main advantages of pyrolysis in comparison to incineration are:

- The decomposition temperature is lower than the incineration temperature, so the thermal distress of the whole facility is less intense than in incineration.
- The decomposition takes place in reducing atmosphere and not in oxidizing like in incineration. The demand for less oxygen is also the reason for less air emissions in the case of pyrolysis.
- The ash content in carbon is much higher than in the case of incineration.
- The metals that are included in waste are not oxidized during pyrolysis and have higher commercial value.
- The produced gas is at different hearth and probably other site from the pyrolytic reactor.
- No ash is produced from the combustion of the pyrolysis gas and the cleaning of the off-gas is a simpler process.
- The initial waste volume is reduced at higher level in comparison with the incineration.

The main disadvantages of pyrolysis include:

- The big problem of this technique is that pre-treatment is required including cutting and separation of waste prior to pyrolysis which can increase the cost for the installation and operation of such units substantially.
- The pyrolysis products cannot be disposed without further treatment.
- The facilities for cleaning the gases and wastewater require extremely high cost.
- At present, the application of the method at large scale is limited. Nevertheless, the prospects for reactors of average temperature with the form of rotary drum or fluidized bed seem to be better.

5. Plasma technology

5.1 General

Plasma refers to every gas of which at least a percentage of its atoms or molecules is partially or totally ionized. In a plasma state of matter, the free electrons occur at reasonably high concentrations and the charges of electrons are balanced by positive ions. As a result, plasma is quasi-neutral. It is generated from electric discharges, e.g. from the passage of current (continuous, alternate or high frequency) through the gas and from the use of the dissipation of resistive energy in order to make the gas sufficiently hot. Plasma is characterized as the fourth state of matter and differs from the ideal gases, because it is characterized by 'collective phenomena'. 'Collective phenomena' originate from the wide range of Coulomb forces. As a result, the charged particles do not interact only with neighbouring particles through collisions, but they also bear the influence of an average electromagnetic field, which is generated by the rest charges. In a large number of phenomena, collisions do not play important role, as 'collective phenomena' take place much faster than the characteristic collision time (Blahos, 2000).

Plasma technology can be used as a tool for green chemistry and waste management (Mollah et al., 2000). Thermal plasmas have the potential to play an important role in a variety of chemical processes. They are characterized by high electron density and low electron energy. Compared to most gases even at elevated temperatures and pressures, the chemical reactivity and quenching rates that are characteristic of these plasmas is far greater. Plasma technology is very drastic due to the presence of highly reactive atomic and ionic species and the achievement of higher temperatures in comparison with other thermal

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