

ADVANCED THERMAL TREATMENT OF WASTES

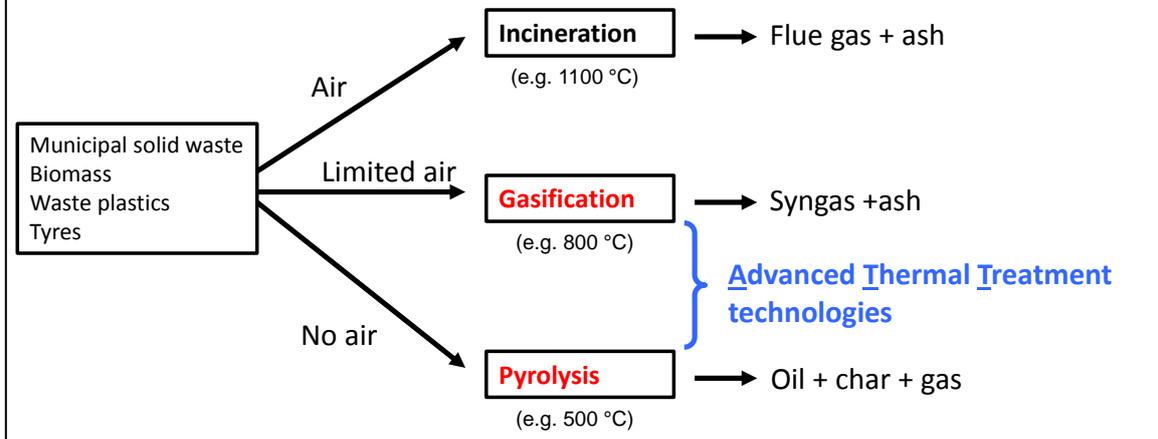
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What is Advanced Thermal Treatment?

Advanced thermal treatment means second generation treatment options, mainly pyrolysis and gasification. Incineration is a mature technology and well established and would not be considered as an advanced thermal treatment. The regulation of waste incineration, pyrolysis or gasification facilities is regulated under the EC Industrial Emissions Directive (2010).

The difference between pyrolysis, gasification and incineration of wastes, including waste plastics relates to the conditions of the process (Figure 1). The key difference is the amount of oxygen (usually in the form of air) supplied to the thermal reactor and the operation temperature. For pyrolysis there is an absence of oxygen, for gasification a limited supply of oxygen, such that complete combustion does not take place, instead producing combustible gases, carbon monoxide and hydrogen. Incineration, involves the complete oxidation of the waste in an excess supply of oxygen to produce carbon dioxide, water and ash, plus some other products such as metals, trace hydrocarbons, acid gases etc. The temperatures involved are typically, 500 °C for pyrolysis, 700-800 °C for gasification and more than 1000 °C for incineration.

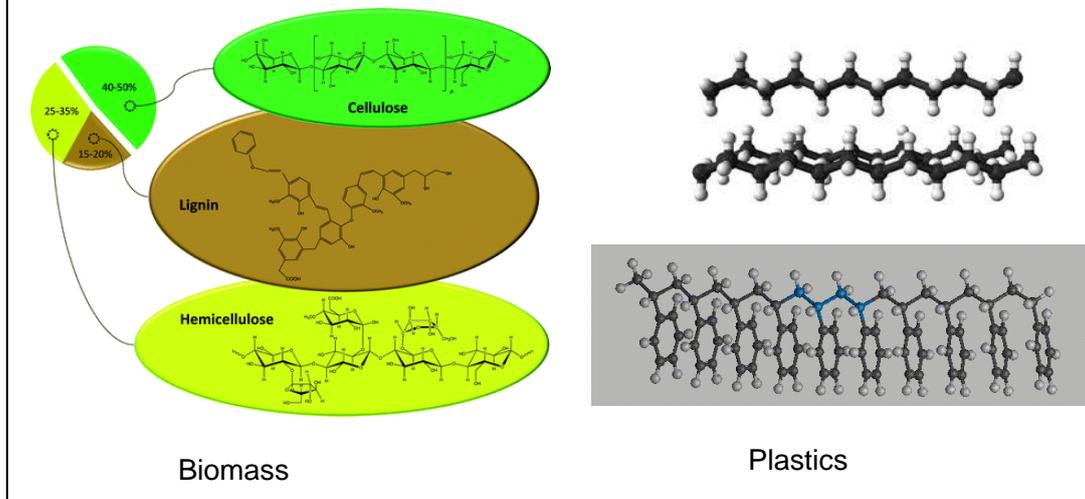
Fig. 1. Thermal conversion technologies



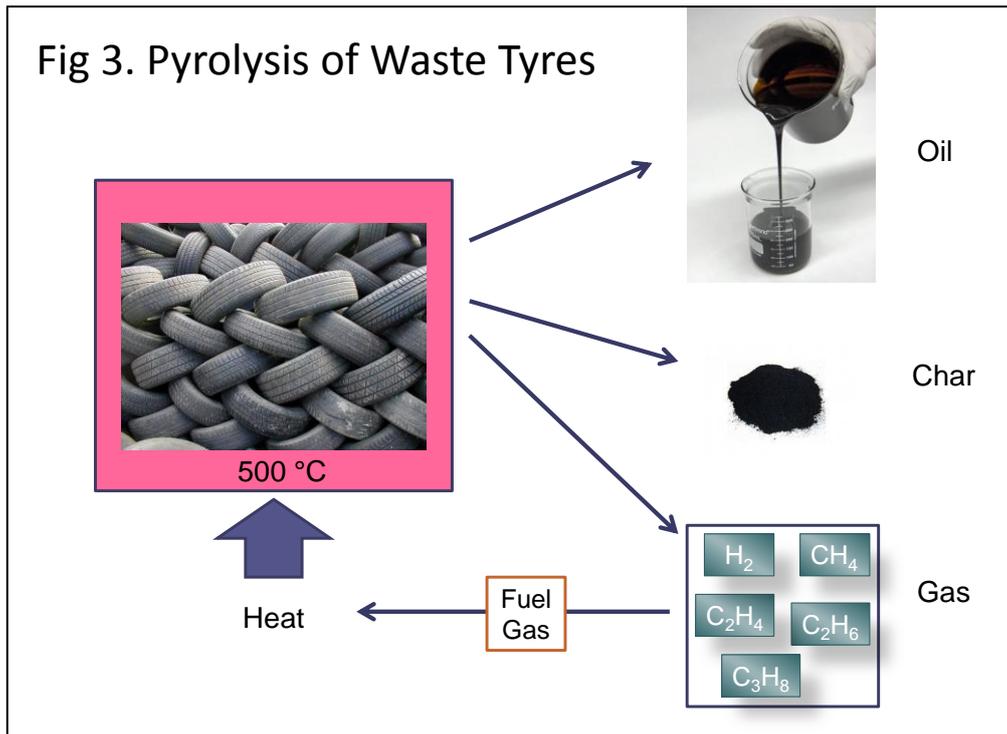
What is Pyrolysis?

Waste materials are composed of complex chemical compounds, for example municipal solid waste contains paper and cardboard which are composed of large, complex polymeric, organic molecular chains such as cellulose, hemicellulose and lignin (Figure 2). Similarly, wastes such as forestry wastes and biomass are also mainly composed of cellulose, hemicellulose and lignin polymeric molecules. Plastics are also composed of large polymer chains. The process of thermal degradation or pyrolysis of such materials, in the absence of oxygen, results in the long polymer chains breaking to produce shorter molecular weight chains and molecules. These shorter molecules result in the formation of the oils and gases characteristic of pyrolysis of waste.

Fig. 2. Typical polymers found in wastes



Pyrolysis therefore produces **an oil, a char and gas product**. Relatively low temperatures are used in the case of pyrolysis, typically around 500 °C. The production of oils from the pyrolysis of waste has been investigated with the aim of using the oils directly in fuel applications or with upgrading to produce refined fuels. The pyrolysis oils derived from a variety of wastes have also been shown to be complex in composition and contain a wide variety of chemicals which may be used as chemical feedstock. The oil has a higher energy density, that is, a higher energy content per unit weight, than the raw waste. The solid char can be used as a solid fuel or as a char-oil, char-water slurry for fuel, alternatively the char can be used as carbon black or upgraded to activated carbon. The gases generated have medium to high calorific values and may contain sufficient energy to supply the energy requirements of a pyrolysis plant.



The process conditions are altered to produce the desired char, gas or oil end-product, with pyrolysis temperature and heating rate having the most influence on the product distribution (Table 1). The heat is supplied by indirect heating such as the combustion of the gases or oil or directly by hot gas transfer. Pyrolysis has the advantage that the gases or oil product derived from the waste can be used to provide the fuel for the pyrolysis process itself.

Table 1. Pyrolysis: Technologies

Technology	Residence time	Heating rate	Temp (°C)	Major products
Slow pyrolysis	Hours - days	Very low	300 - 500	Charcoal
Conventional pyrolysis	5 – 30 min	Medium	400 - 600	Char, liquids, syngas
	5 – 30 min	Medium	700 - 900	Char, syngas
Fast pyrolysis	0.1 – 2 sec	High	400 - 650	Liquids
	< 1 sec	High	650 - 900	Liquids, syngas
	< 1 sec	Very high	1000 - 3000	Syngas

Very slow heating rates coupled with a low final maximum temperature maximises the yield of char, for example, the production of char from wood in the form of charcoal involves a very slow heating rate to moderate temperatures. The process of carbonisation of waste results in reduced concentrations of oil/tar and gas product and are regarded as by-products of the main charcoal forming process. Moderate heating rates in the range of about 20 °C/min to 100 °C/min and maximum temperatures of 600 °C gives an approximate equal distribution of oils, char and gases. This is referred to as conventional pyrolysis or slow pyrolysis. Because of the slow heating rates and generally slow removal of the products of pyrolysis from the hot pyrolysis reactor, secondary reactions of the products can take place. Generally, a more complex product slate is found. Very high heating rates of about 100 °C/s to 1000 °C/s at temperatures below 650°C and with rapid quenching lead to the formation of a mainly liquid product, referred to as fast or flash pyrolysis. Liquid yields up to 70% have been reported for biomass feedstocks using flash pyrolysis. In addition, the carbonaceous char and gas production are minimised. The primary liquid products of pyrolysis are rapidly quenched and therefore prevents breakdown of the products to gases in the hot reactor. The high reaction rates also cause char forming reactions from the oil products to be minimised. At high heating rates and high temperatures the oil products quickly breakdown to yield a mainly gas product.

Pyrolysis oils

The oils derived from the pyrolysis of waste materials tend to be chemically very complex due to the polymeric nature of the wastes and the range of potential primary and secondary reactions. Municipal solid waste pyrolysis oils contain hundreds of different chemical compounds, including organic acids, phenols,

alcohols, aldehydes, ketones, furans, etc. These are derived from the biomass fraction of municipal solid waste such as waste paper, cardboard and wood. The municipal solid waste would also contain plastics, which would produce additional products in the oil. For example, polyethylene, which is the main plastic in municipal solid waste, will produce mainly alkane and alkene compounds. The product oils derived from pyrolysis of plastic waste produce end-products which are based on the original polymer structure. For example, the oils produced from the pyrolysis of the polyalkene plastics, such as polyethylene and polypropylene, produce an almost exclusively aliphatic oil consisting of alkanes and alkenes. Pyrolysis of polystyrene produces an oil very high in concentration of the monomer, styrene and also other aromatic compounds.

Tyres manufactured for motor vehicles typically contain several different rubber polymers; for example, styrene-butadiene rubber, natural rubber (polyisoprene), nitrile rubber, chloroprene rubber and polybutadiene rubber. The pyrolysis of tyres produces a wide variety of products in the oil and compounds identified in significant concentrations have included isoprene and dipentene, benzene, toluene, xylene, styrene, limonene, indane, indene, polycyclic aromatic hydrocarbons, such as naphthalene, fluorene and phenanthrene, vinylalkenes, alkanes and alkenes.

The oil may be used directly as a fuel, added to petroleum refinery stocks, upgraded using catalysts to a premium grade fuel or used as a chemical feedstock. The composition of the oil is dependent on the chemical composition of the feedstock and the processing conditions. For example, oils derived from biomass have a high oxygen content, of the order of 35% by weight due to the content of cellulose, hemicellulose and lignin in the biomass, these are large polymeric structures containing mainly carbon, hydrogen and oxygen. Similarly, oils derived from municipal solid waste have a high oxygen content due to the

presence of cellulosic components in the waste such as paper, cardboard and wood. The pyrolysis oils from pyrolysis of various waste materials have been analysed in terms of their fuel properties (Table 2). The oils have significant calorific values ranging from 24 MJ kg⁻¹ for oils derived from municipal solid waste to 42 MJ kg⁻¹ for oils derived from scrap tyres and oils derived from plastics at >50 MJ kg⁻¹. The calorific values may be compared to typical petroleum-derived fuel oils at between 44.0 and 46.6 MJ kg⁻¹

Table 2 Fuel properties of waste-derived pyrolysis oils

Property	Polyethylene Pyrolysis Oil	Tyre Pyrolysis Oil	MSW Pyrolysis Oil	Biomass Pyrolysis Oil
Flash point (°C)	33.6	24	56	110-120
Pour point (°C)	2.7	-	-	-
Density (kg m ⁻¹)	0.86	0.91	1.3	1.2
Viscosity cSt (at 50 °C)	2.19	3.50 ^a	-	-
Carbon (wt%)	-	87.0	57.5	50 - 67
Hydrogen (wt%)	-	10.0	7.6	7-8
Nitrogen (wt%)	-	0.4	0.9	0.8-1
Sulphur (wt%)	0.01	1.5	0.1-0.3	<0.01
Oxygen (wt.%)	-	-	33.4	15-25
Initial B.Pt. (°C)	-	80	-	<100
10% B.Pt (°C)	-	140	-	-
50% B.Pt. (°C)	-	230	-	25-280
90% B.Pt (°C)	-	340	-	-
Calorific value (MJ kg ⁻¹)	52.3	42.0	24.4	-

Pyrolysis chars

Pyrolysis of waste materials also produces a char product, the percentage production depending on process conditions. Pyrolysis of municipal solid waste produces a char product between 33 and 50 wt.%, depending on process conditions, with a high ash content of up to 37 wt.%. Tyre pyrolysis under slow heating rate conditions produces a char of 40 - 50 wt.% with an ash content of about 10 wt.%. Pyrolysis of biomass and biomass wastes produces a char which can be used as a solid fuel with a calorific vale of about 30 - 35 MJ kg⁻¹ and a low ash content of about 1 - 3 wt%.

Pyrolysis Gases

The gases produced from the pyrolysis of wastes reflect the thermal degradation reactions of the waste constituents as they break down and also the secondary cracking reactions of the primary products produced during pyrolysis of the wastes. Therefore, higher gas yields are found where the products of pyrolysis have a long residence time in the hot zone of the reactor. In addition, if the temperature of pyrolysis is high, for example above 750 °C, the primary products of pyrolysis are thermally degraded or ‘cracked’ to produce lower molecular weight compounds, i.e. gases.

Biomass wastes and municipal solid waste have high oxygen contents within such oxygenated structures as cellulose, hemicellulose and lignin. Therefore, the main pyrolysis gases are carbon dioxide and carbon monoxide produced from the thermal degradation of the oxygenated constituents. Other pyrolysis gases produced from biomass wastes and municipal solid waste are hydrogen, methane and lower concentrations of other hydrocarbon gases. The pyrolysis of scrap tyre and mixed plastics waste produces higher concentrations of hydrogen, methane and other hydrocarbons gases, since the waste material is high in carbon and hydrogen compounds in these less-oxygenated compounds.

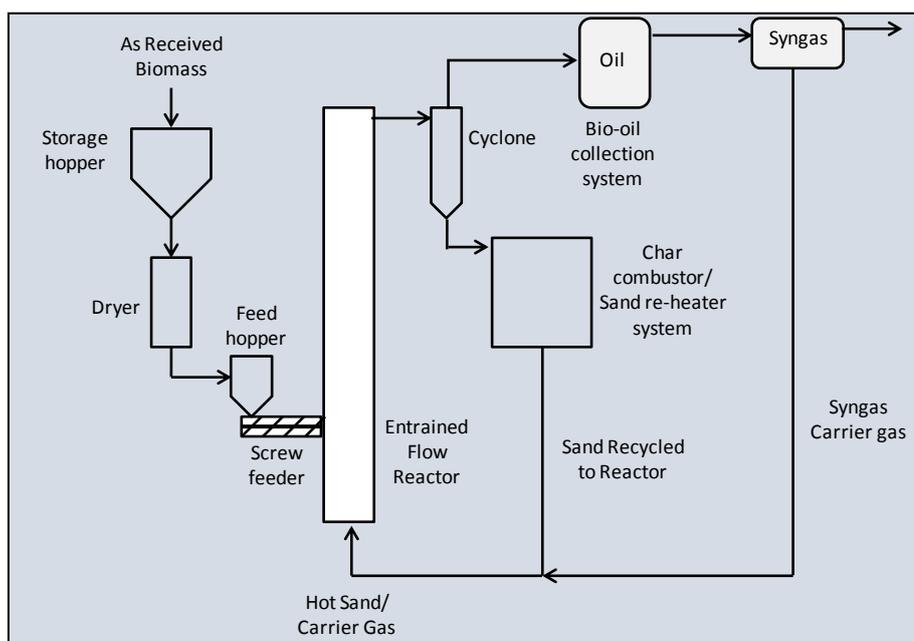
The polyalkene plastics, polyethylene and polypropylene, produce similar gas compositions, where the main gases formed are alkenes, mainly ethene and propene, and also alkanes such as methane, ethane and propane derived from the thermal degradation of their similar polyalkene chemical structures.

The gases have a significant calorific value, and typically the gas has been used to provide the energy for the pyrolysis process. The gas produced from the conventional pyrolysis of municipal solid waste has a calorific value of the order of 18 MJ Nm⁻³ (cubic meters under normal temperature, 25°C, and atmosphere

pressure) and wood waste produces a gas of calorific value 16 MJ Nm^{-3} .¹ Tyre pyrolysis produces a gas of much higher calorific value, of about 40 MJ Nm^{-3} , depending on the process conditions.¹⁷ The high calorific value is due to the high concentrations of hydrogen and other hydrocarbons. By comparison, the calorific value of natural gas is about 37 MJ Nm^{-3} .

Example of commercial waste pyrolysis

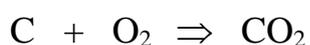
The Ensyn (Canada) entrained flow process has been developed for the processing of biomass and agricultural wastes. The Ensyn pyrolysis system is a rapid-heating, fast-pyrolysis system designed to produce an oil product. The feedstock is introduced as received (wet) biomass waste and dried using heat generated from combustion of the product char. The dried biomass is fed to a hopper where metered amounts of the feedstock are fed to the main entrained flow reactor. The system utilises a solid heat carrier of sand, with a carrier gas comprised of the product pyrolysis syngas to carry heat into a turbulent vertical entrained flow reactor. The sand material used to transfer heat to the feedstock is heated by combustion of the product char in the combustor/sand re-heater system. Very rapid interaction occurs with the waste feedstock to produce fast pyrolysis primary products which are then rapidly quenched to produce a liquid oil product. Temperature ranges possible are from 400 to 950 °C and residence times from 50 to 1500 milliseconds. Feedstock throughputs are in the range of 100 tonne day⁻¹. High liquid yields up to 75 wt.% of the original dry feedstock have been recorded. The products from the pyrolysis are quenched with water. The solid char and sand is removed via a cyclone and passed to a char combustion system which re-heats the gas and also provides heat for the biowaste drying process. The hot sand is recycled back to the reactor. The pyrolysis gases pass from the cyclone to the oil condensation collection system where the main targeted product of bio-oil is collected and stored. The non-condensable gases are partially used to provide the carrier gas for the entrained flow reactor to lift the sand, but also excess syngas is exported for use.



What is Gasification?

Gasification is a process that converts hydrocarbon materials into a gas product (often referred to as syngas), ash and a tar product in the presence of limited, sub-stoichiometric oxygen in the form of air, steam, CO₂ or pure oxygen at high temperature, typically 800 °C. The main purpose of the gasification process is to produce combustible gases that can be used for generation of heat and electricity through combustion. Gasification differs from pyrolysis in that oxygen in the form of air, steam or pure oxygen is reacted at high temperature with the available carbon in the waste to produce a gas product, ash and a tar product. Partial combustion occurs to produce heat and the reaction proceeds exothermically to produce a low to medium calorific value fuel gas. The operating temperatures are relatively high compared to pyrolysis, at 800 - 1100 °C with air gasification and 1000 - 1400 °C with oxygen. Calorific values of the product gas are low for air gasification, in the region of 4 - 6 MJ/m³ and medium, about 10 - 15 MJ/m³ for oxygen gasification.

The principle reactions occurring during gasification of waste in air are;



Oxidation - Exothermic



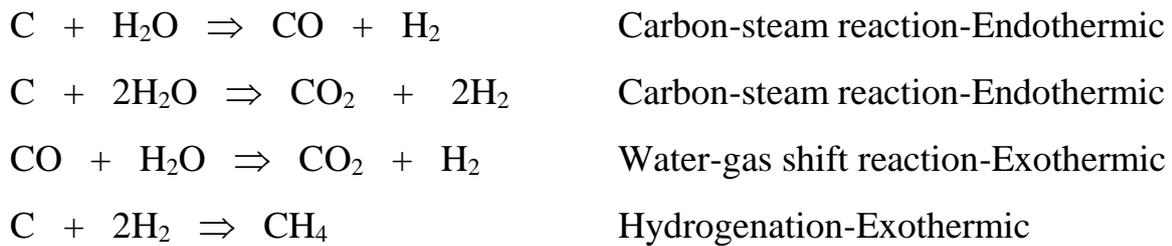
Boudouard Reaction - Endothermic

Overall ;

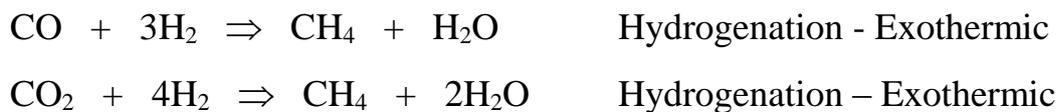


Exothermic

Steam gasification;



For high pressure steam gasification, additional reactions include;



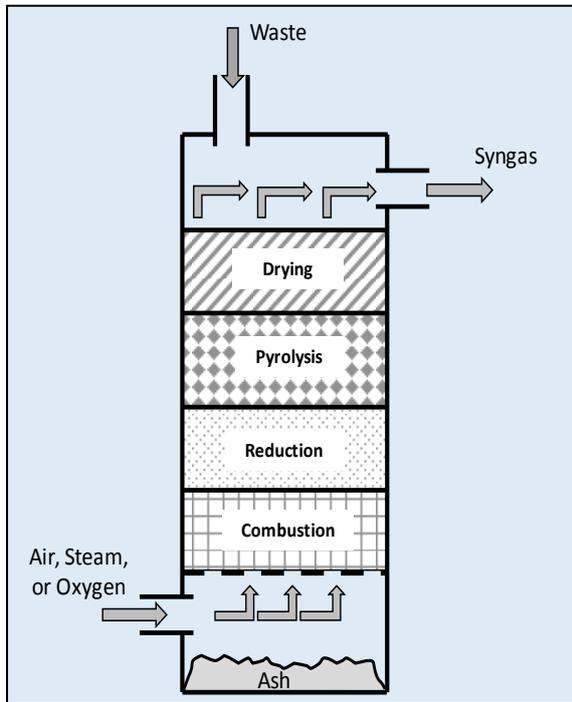
In practice there is usually some moisture present with the air which produces some hydrogen. In addition, the heating of the waste produces pyrolytic reactions and methane and higher molecular weight hydrocarbons or tar are formed. When air is used the non-combustible nitrogen in the air inevitably reduces the calorific value of the product gas by dilution. Therefore, the major components of the product gas from waste gasification are carbon monoxide, carbon dioxide, hydrogen and methane and where air gasification is used, nitrogen will also occur as a major component.

Table 3. Products from the gasification of different wastes

Raw material	MSW	Sawdust	Wood	Biomass	Pine wood
Gasification agent	Steam	Steam	Air	Air	Steam/oxygen
Reactor bed	Fixed	Fluidised	Fluidised	Fluidised	Fluidised
Temperature (°C)	900	780	860	780 - 830	785 - 830
Gas yield (Nm ³ kg ⁻¹) ^b	0.68	1.2	2.99	1.25-2.45	0.86 - 1.14
Gas composition (Vol.%)					
CO	55.6	22.1	9.3	9.9 - 22.4	42.5 - 52.0
H ₂	32.6	49.5	9.3	5.0 - 16.3	13.8 - 31.7
CO ₂	10.9	19.1	13.3	9.0 - 19.4	14.4 - 36.3
CH ₄	0.6	6.5	4.2	2.2 - 6.2	6.0 - 7.5
N ₂	-	-	62.8	41.6-61.6	-
LHV (MJ/Nm ³)	10.8	12.1	5.0	3.7 - 8.4	10.3 - 13.5

Typical gasification systems

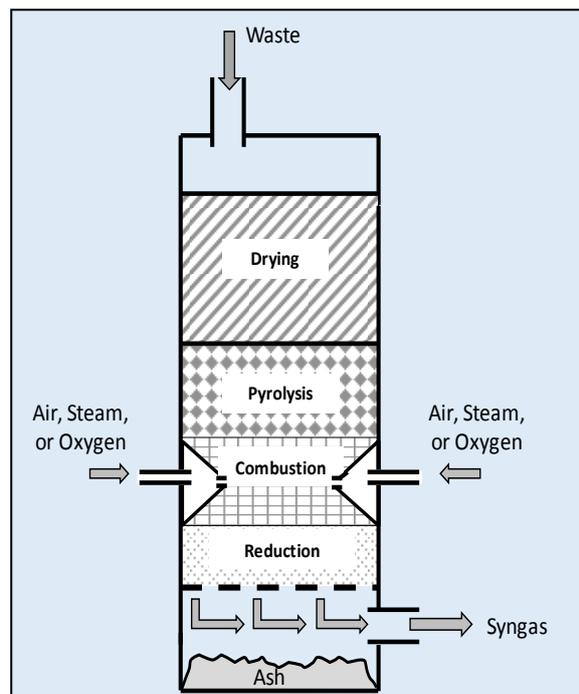
Updraft Gasification



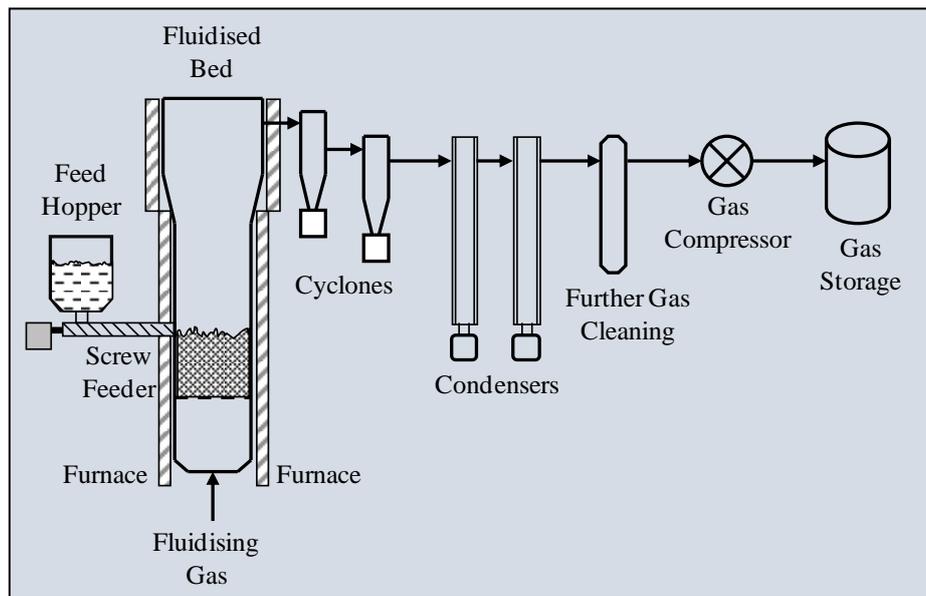
In an up-draft gasifier the feed is introduced at the top; it then flows down slowly through drying, pyrolysis, reduction and oxidation zones. In the pyrolysis zone, raw materials are converted into volatile gases and solid char, which are further converted into carbon monoxide and hydrogen as they pass through the reduction zone. The product gas moves upwards and leaves the reactor. Volatile compounds are released quickly in the pyrolysis zone and partly leave the gasifier with the product gas, without the opportunity to pass through the combustion zone. This results in a high tar content in the gas products for the up-draft gasifier.

Downdraft Gasification

Downdraft gasification is a fixed bed system where the air and the waste flow co-currently down the reactor. Gasification takes place in a slowly moving 'fixed' bed. There is an increased level of thermal breakdown of the tars and heavy hydrocarbons as they are drawn through the high temperature oxidation zone, producing increased concentrations of hydrogen and light hydrocarbons. The air/steam or oxygen is introduced just above a 'throat' or narrow section in the reactor influences the degree of tar cracking.



Fluidised Bed Gasification



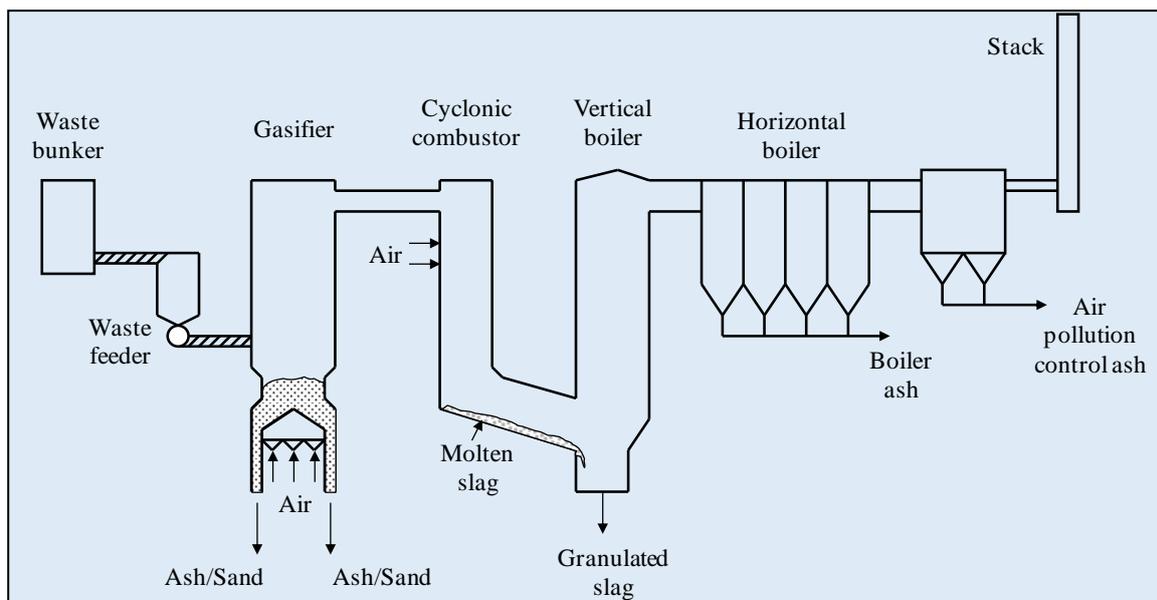
Waste is fed into the fluidised bed at high temperature. The fluidised bed may be a bubbling bed where the solids are retained in the bed through the gasification process. Alternatively, circulating beds may be used with high fluidising velocities, the solids are elutriated, separated and recycled to the reactor in a high solids/gas ratio resulting in increased reaction. Twin fluidised bed reactors may be used where the first bed is used to gasify the waste and the char is passed to a separation unit and then to a second fluidised bed where combustion of the char occurs to provide heat for the gasifier reactor.

Example of commercial waste gasification

An example of a large-scale commercial gasifier is the Ebara, TwinRec gasifier in Kawaguchi, Japan, which processes 125,000 tonnes per annum of municipal solid waste and has been operational since 2002.

The Ebara TwinRec gasification system

The TwinRec gasifier system requires a particle size for feeding of 300 mm. Waste is gasified in an air-blown, internally-circulating fluidised-bed gasifier operated at temperatures between 500 and 600 °C. The design of the distributor within the fluidised bed provides more turbulence and improved combustion efficiency though at lower fluidising velocity than a circulating fluidised bed. The somewhat low gasification temperature results in a slower, more easily controllable process. The synthesis gas and entrained carbonaceous char are passed to a cyclonic combustor where combustion takes place with added secondary air at temperatures between 1350 and 1450 °C. The high temperatures of the cyclonic combustor melts the fly ash to form a molten slag, which is then quenched to produce non-leachable granulates. Energy is recovered as steam for either electricity generation or district heating. Bottom ash from waste gasification is recovered from the base of the fluidised bed where recovery of metals such as iron, copper and aluminium takes place. The technology produces a reduced mass-flow of the flue gas, allowing for a reduction in the size of the steam boiler and the emissions control system that is located after the combustor. There are more than ten Ebara TwinRec systems operating in Japan, using mixed wastes and MSW with capacities ranging from 19,000 to 165,000 tonnes per annum.



Useful publications

[1] Advanced Thermal Treatment of Municipal Solid Waste, UK Government, Department of Environment, Food and Rural Affairs, 2013

https://www.gov.uk/government/uploads/system/uploads/attachment_data/file/221035/pb13888-thermal-treatment-waste.pdf

[2] The EC Industrial Emissions Directive;

<http://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX:32010L0075>

[3] Ebara. Ebara Twin-Rec gasification. Available:

<http://www.ebara.co.jp/en/index.html>

[4] UNEP, *United Nations Environmental Programme: Converting Waste Plastics into a Resources*, International Environmental Technology Centre, Osaka, Japan, 2009.