

Advanced Thermal Treatment of Wastes for Fuels, Chemicals and Materials Recovery

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ABSTRACT

The advanced thermal technologies of pyrolysis and gasification provide important economic and environmental options to convert waste materials into useful and high-value materials, fuels and chemicals. In this chapter, pyrolysis is described in terms of the production of oils, char and gas, with examples of various reaction systems. Gasification is also reviewed in terms of example process systems, influences of gasification temperature and the presence of catalysts. Commercial examples of both technologies are also described.

1 Introduction

The thermal treatment options of pyrolysis, gasification and combined pyrolysis/gasification systems are generating increasing interest as viable alternative environmental and economic options for waste processing. These options have a number of advantages over conventional incineration or land-filling of waste. Depending on the technology, the waste can be processed to produce gas or oil products for use as fuels or petrochemical feedstocks and/or a carbonaceous char for use in applications such as effluent treatment or for gasification feedstock. The production of storable end-products such as a gas,

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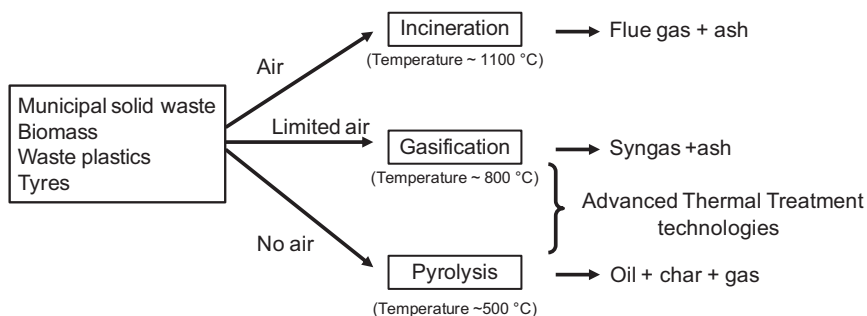


Figure 1 Thermal treatment technologies for waste.

oil or char enables the possibility of de-coupling the end-use of that product, be that for energy production or petrochemical use, from the waste treatment process.

Figure 1 shows the main operational differences between pyrolysis, gasification and incineration. The key difference is the amount of oxygen supplied to the thermal reactor. 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 such as carbon monoxide and hydrogen. The oxygen for gasification is supplied in the form of air, steam or pure oxygen. 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.*

In this chapter, the advanced thermal technologies of pyrolysis and gasification are described in terms of process systems, product yield and composition, and the influence of process conditions. Examples of commercial systems are also described.

2 Pyrolysis

Pyrolysis is the thermal degradation of organic waste in the absence of oxygen to produce a carbonaceous char, oil and combustible gases.¹ Waste materials are composed of complex chemical compounds: for example, municipal solid waste (MSW) contains paper and cardboard which are composed of large, complex polymeric, organic molecular chains such as cellulose, hemicellulose and lignin. Similarly, wastes such as forestry wastes and urban waste wood 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 chains and lower molecular weight molecules. These smaller molecules constitute the oils and gases characteristic of pyrolysis of waste.

The advantage of producing an oil product from waste is that the oil can be transported away from the pyrolysis process plant and therefore de-couples the

processing of the waste from the product utilisation. 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 pyrolysis oils derived from a variety of wastes have also been shown to be complex in composition and contain a wide variety of chemicals that may be used as chemical feedstock. For example, oils derived from biomass wastes have 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 high oxygen content due to the presence of cellulosic components in the waste, such as paper, cardboard and wood. Biomass and municipal solid waste pyrolysis oils derived from flash pyrolysis processes tend to have a high viscosity and consist of a single water/oil phase. The oils are therefore high in water that markedly reduces the calorific value of the oils. Oils derived from scrap tyre pyrolysis and plastics, on the other hand, are composed of mainly carbon and hydrogen.

The oil has a higher energy density, *i.e.* 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. Figure 2 shows some of the potential uses of the pyrolysis product gases, oils and char.

Pyrolysis may be divided into different types according to the operating conditions: slow pyrolysis, fast pyrolysis and flash pyrolysis. The terms “slow pyrolysis”, “fast pyrolysis” and “flash pyrolysis” are somewhat arbitrary and have no precise definition of the times or heating rates for each process. “Fast pyrolysis” and “flash pyrolysis” are sometimes both characterised as “fast pyrolysis”. The main ranges of the operation parameters for each type of pyrolysis are presented in Table 1.²⁻⁴ Slow pyrolysis is associated with the production of charcoal at low temperature with a long vapour-residence time. The process of carbonisation of waste results in reduced concentrations

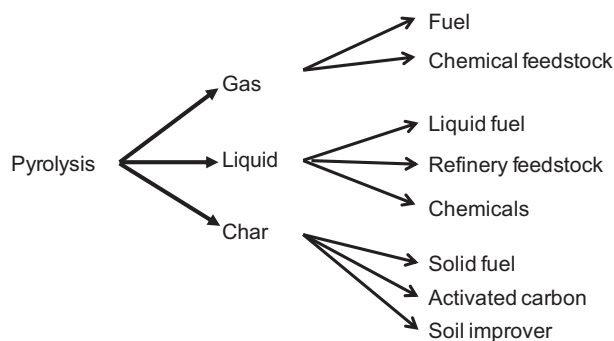


Figure 2 Potential uses of pyrolysis products.

Table 1 Range of main reaction parameters for different types of pyrolysis processes.²⁻⁴

<i>Pyrolysis type</i>	<i>Residence time</i>	<i>Heating rate</i>	<i>Temperature (°C)</i>	<i>Major products</i>
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
	0.1–2 s	High	400–650	Liquids
Fast pyrolysis	<1 s	High	650–900	Liquids, syngas
	<1 s	Very high	1000–3000	Syngas

of oil/tar and gas product that are regarded as by-products of the main charcoal-forming process. Conventional pyrolysis involves moderate heating rates in the range of about 20 to 100 °C min⁻¹ and a maximum temperature of 600 °C, giving an approximately equal distribution of oils, char and gases. Because of the relatively 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 and, generally, a more complex product mixture is found. Fast pyrolysis involves high heating rates of about 100 °C s⁻¹ at moderate temperatures of *ca.* 600 °C and with rapid quenching leads to the formation of a mainly liquid product.³⁻⁵ 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, which prevents breakdown of the oil products to gases in the hot reactor. Fast pyrolysis at higher temperatures of around 1000 °C gives mostly gaseous products since the high temperature thermally degrades the oil products to gas.

Several basic phenomena have been proposed during the pyrolysis process.^{6,7}

- i. Temperature increases inside the raw materials by heat transfer from the heat source;
- ii. Initial degradation of raw materials due to increasing temperature, resulting in the release of moisture, volatiles and the formation of tar;
- iii. Outflow of volatiles with heat transfer between the hot volatiles and cooler unpyrolysed raw material;
- iv. Heavy tar condensation on the surface of char; and
- v. Secondary pyrolysis reactions (*i.e.* cracking or polymerisation) of volatiles, resulting in production of heavy tar and gases such as H₂, CO and CH₄.

Pyrolysis systems for municipal solid waste, tyres, plastics, sewage sludge and biomass have been investigated.^{3,8-11} There has been particular interest in the pyrolysis of biomass as a source of bio-oil for use as boiler fuel or, *via* upgrading, to produce premium grade fuels.^{12,13} There is also recent interest in the

Table 2 Product yield from the pyrolysis of wastes.

<i>Waste</i>	<i>Reactor</i>	<i>Pyrolysis type</i>	<i>Temp.</i> (°C)	<i>Char</i> (wt%)	<i>Oil</i> (wt%)	<i>Gas</i> (wt%)	<i>Ref.</i>
Tyres	Fixed bed	Conventional	600	39.2	54.0	6.8	17
Tyres	Fluidised bed	Fast	600	40.0	51.0	9.0	18
Plastic mixture	Fixed bed	Conventional	700 ^a	2.9	75.1	9.6 ^b	19
Plastic mixture	Vacuum	Fast	520	1.3	91.8	6.3	20
MSW plastics	Fluidised bed	Fast	787	25.4	26.4	43.6	21
MSW plastics	Fixed bed	Conventional	430	16.0	59.0	25.0	22
Refuse-derived fuel	Fixed bed	Conventional	500	41.0	40.0	19.0	23
Biomass (wood)	Fixed Bed	Conventional	600	22.6	50.4	27.0	1
Biomass (wood)	Fluidised bed	Fast	550	17.3	67.0	14.9	1

^aFinal temperature.^bGas includes HCl.

production of bio-char from pyrolysis of biomass as a soil improver and as a means of sequestering and storing carbon.^{14,15} The range of biomass feedstocks investigated is extensive, but more recently has concentrated on second-generation biomass as biomass residues/wastes rather than using food crops for bio-oil production. Such biomass wastes include, for example, urban wood waste, rice husks, sugar cane bagasse, olive husks, coconut shells, forestry residues, *etc.*¹⁶ Table 2 shows examples of the product yield from a range of different wastes and biomass.

2.1 Bio-oil Production

There have been several recent reviews on the pyrolysis of biomass and biomass wastes to produce bio-oils and on the techniques used to upgrade the bio-oil.^{12,13,16} The production of bio-oil from biomass wastes involves fast pyrolysis which, with its high heating rates and moderate temperatures, favours the production of oils. To assist rapid heating, the biomass waste is processed to produce a fine-grained feedstock. This rapid heating is achieved in reactors such as fluidised beds, ablative reactors and entrained flow reactors.¹³

Bio-oil can be distinctly different when derived from different feedstocks and when using different pyrolysis conditions, such as heating rate and reaction temperature. The oils are chemically very complex, containing several hundred organic compounds, such as acids, alcohols, ketones, aldehydes, phenols, ethers, esters, sugars, furans, nitrogen compounds and multifunctional compounds.²⁴ In addition, the bio-oils contain fine-sized particulate material and ash. The complexity and quality of the crude bio-oil makes it incompatible with the existing petroleum refining infrastructure due to its high acidity, corrosiveness and low thermal stability. In addition, bio-oil is immiscible with other hydrocarbon liquids such as petroleum fuels.^{13,25} Bridgwater¹³ has extensively

reviewed the properties of bio-oils from fast pyrolysis of biomass and reports that the bio-oil has a calorific value of about 17 MJ kg^{-1} . The oils are highly oxygenated (typically 30–40 wt%), acidic due to the content of organic acids and contain significant amounts of water, ranging from 15 wt% up to 30–50 wt%, depending on feedstock and the process used. In addition, the bio-oil has poor stability over long periods of storage, *e.g.* the bio-oil is a single phase but can separate into two phases of water and oil over time; there may also be polymerisation of the oil over extended storage times.²⁶

Lu *et al.*²⁴ have reported on the fuel properties of biomass fast pyrolysis oils. They reported that bio-oils, because of the high water content, acidity and low calorific value, are of poor quality compared to petroleum fuels and that they have poor ignition and combustion properties. Spray combustion applications of bio-oil, which represent the most common routes for oil combustion applications, showed that rather than evaporation of the fuel to produce a vapour cloud and consequent uniform combustion, as would be the case with petroleum fuels, the combustion of bio-oil droplets involved initial evaporation, bubbling and disruption, swelling and collapsing, and consequently poor combustion characteristics. In addition, pyrolysis oils may contain solid microscopic char particles due to carry-over from the pyrolysis reactor. Consequently, their use in liquid spray or atomisation combustion systems such as diesel engines, furnaces and boilers may result in the spray or atomisation system becoming blocked and/or corroded. Table 3 shows the typical range of fuel properties of bio-oil.

The flash point of a liquid fuel is the temperature at which the oil begins to evolve vapours in sufficient quantity to form a flammable mixture with air. The viscosity of a fuel is an important property since it affects, for example, the flow of the fuel through pipes and other plant items, the atomisation of the fuel in spray combustion systems and the performance and wear of delivery pumps. The distillation range of the pyrolysis oils reflects the fact that the oils are unrefined and consequently would be expected to have a wide range of boiling

Table 3 Typical fuel properties of biomass pyrolysis oils.^{1,13,24}

Carbon residue (%)	0.1–3
Viscosity (cSt)	17 (at 100 °C) 90 (at 50 °C)
Density (kg m^{-3})	1.2
Flash point (°C)	110–120
Hydrogen (%)	7–8
Carbon (%)	50–67
Nitrogen (%)	0.8–10
Oxygen (%)	15–25
Initial boiling point (°C)	< 100
50% boiling point (°C)	250–280
Calorific value (MJ kg^{-1})	17.0–24.7
Sulfur (%)	< 0.01

Table 4 Fuel properties of petroleum-derived fuels.²⁷

Fuel Test	Kerosene	Gas Oil	LFO	HFO
Carbon residue (%)	<0.15	<0.35	-	-
Viscosity, 40 °C (cSt)	1.2	3.3	21	30
Water content (%)	-	0.05	0.1	-
Density (kg m ⁻³)	0.84	0.78	0.89	0.95
Ash content (%)	-	0.01	0.02	-
Flash point (°C)	40	75	79	110
Carbon (%)	-	87.1	85.5	-
Hydrogen (%)	13.6	12.8	12.4	11.8
Sulfur (%)	0.1	0.9	1.4	2.1
Initial b.pt. (°C)	140	180	200	252
10% b.pt. (°C)	-	-	-	-
50% b.pt. (°C)	200	300	347	-
90% b.pt. (°C)	315	-	-	-
Calorific Vale (MJ kg ⁻¹)	46.6	46.0	44.8	44.0

LFO = Light Fuel Oil, HFO = Heavy Fuel Oil.

points for the components of the oil. For bio-oils, the complete distillation in air is not possible because above around 280 °C, the oils begin to polymerise and form large carbonaceous molecules and result in a char residue of 35–50%. Table 4 shows the typical fuel properties of several petroleum-derived fuels for comparison.²⁷

2.1.1 Upgrading of Bio-oil. To overcome some of the problems of high oxygen content, high viscosity, acidity and polymerisation associated with the oils derived from biomass wastes, research has been undertaken to upgrade the oils. The research has concentrated on the use of processes to produce a premium quality fuel for liquid transport fuels or chemical feedstocks. Upgrading methods for bio-oils mainly involves catalytic cracking, catalytic esterification^{28–30} and catalytic hydroprocessing.^{31,32} The main process conditions from various upgrading technologies for bio-oil have been summarised in Table 5. Catalytic cracking requires comparatively high temperature (>450 °C), while esterification normally needs temperatures of less than 200 °C. In addition, model compounds such as acetic acid are usually used for the investigation of bio-oil upgrading.

Bio-oil is a complex mixture of oxygenated compounds^{4,33} and upgrading of bio-oil can be carried out on-line or off-line of the pyrolysis process. For an on-line upgrading process, the gaseous products derived from pyrolysis are introduced to a secondary catalytic cracking system. In some cases, particulates and other pollutants such as Cl and S are removed before the catalytic cracking stage. For an off-line upgrading process, bio-oils are initially collected through the pyrolysis of raw materials. The bio-oils are stored and then upgraded through a separate catalytic cracking process. Off-line upgrading of bio-oil requires transportation of liquid from scattered pyrolysis stations, while for on-line upgrading of bio-oil, transportation of low-density biomass to the pyrolysis plant would be needed which thereby increases the cost of production of

Table 5 Summary of processes for up-grading of bio-oil.

Process	Reactor	Raw material	Temp. (°C)	Time	Catalyst bed	Product yields (wt%)			Ref.
						Liquid	Char	Gas	
Catalytic cracking	fluidised bed	pine wood	450	5.9 s ^a	Sand	32.7	15.3	52.0	34
	fluidised bed	sawdust	450 500	- -	HZSM-5 H-ZSM-5	33.7 59.5 63.5	9.0 28.5 21.5	52.1 12.0 15.0	35
Esterification	autoclave	bio-oil and methanol	70 150	30 min ^b	Amberlyst-70 ^c	30 wt% acetic acid conversion 90 wt% acetic acid conversion			29
	two-neck flask	acetic acid and methanol	50	200 min ^b	SO ₃ Na-SBA-15 ^d	2 wt% acetic acid conversion			36
				1200 min ^b	SO ₃ H-SBA-15 ^e SO ₃ H-SBA-15	30 wt% acetic acid conversion 70 wt% acetic acid conversion			
Hydrodeoxygenation	autoclave	acetic acid and H ₂	200	120 min ^b	Mo-10Ni/Al ₂ O ₃ 10Ni/Al ₂ O ₃	33 wt% acetic acid conversion 8.4 wt% acetic acid conversion			37
	autoclave	phenol, dodecane and H ₂	250	10 h ^b	Co-Mo	96 wt% phenol acid conversion			38

^aVapour residence.^bReaction time.^cCommercial catalyst from Merck.^dSodium exchanged SO₃H-SBA-15.^eSulfonic acid functionalised mesoporous material.

high-quality bio-oil. A key issue with off-line upgrading is that the bio-oil is difficult to re-vaporise and, typically, as previously noted, only 35–50 wt% can typically be distilled because of the extensive secondary, tertiary and polymerisation reactions to produce a carbonaceous coke.

Catalytic cracking of bio-oil has attracted much attention as a means to upgrade the bio-oil by reducing the acidity and oxygen content of the oil.^{35,39} Through catalytic cracking, oxygen in the bio-oil will be removed in the form of water and carbon oxides using shape-selective catalysts. The products of catalytic cracking of the bio-oil are a two-phase liquid (aqueous and organic), gases (CO , H_2 , CO_2 , CH_4 , *etc.*) and coke (deposited on the surface of the catalyst). The main advantage of catalytic cracking of bio-oil is that there is no need for hydrogen and high pressure processing, which means that costs tend to be lower. Zeolites have frequently been applied as catalysts for catalytic cracking of bio-oil to produce a high quality liquid product (*e.g.* gasoline). ZSM-5 zeolites are the most used zeolites for the cracking of bio-oil,^{34,35,39,40} because of their optimised shape selectivity to produce $< \text{C}_{12}$ hydrocarbons, prohibition of coke deposition and their high thermal stability.⁴¹ For example, Chen *et al.* studied the catalytic cracking of carbohydrates with a fixed-bed reactor in the presence of ZSM-5 catalyst.⁴² They obtained a yield of aromatics of 18% of total carbon for an aqueous glucose feed. They also regarded the bio-oil (with an H : C ratio less than 1.0) as hydrogen-deficient, compared with the petroleum-derived feeds with H : C ratios higher than 1.0. Coke deposition on the surface of the catalyst in the catalytic cracking of the bio-oil will deactivate the catalyst. Coke deposition on the catalyst surface depends on the type of bio-oil, catalyst and cracking temperature, *etc.*^{41,43,44} Regeneration of the catalyst deposited with coke may be carried out through combustion in air.⁴¹

The reactive oxygenated compounds, especially organic acids, in the bio-oil are the key consideration for the upgrading of the bio-oil. Esterification is an important route to convert the reactive organic acids in bio-oil to more stable esters.^{29,30,36,45–47} Solid acid catalysts and alcohol are normally needed for the esterification of bio-oil, where the reactive aldehydes react with alcohol to produce much more stable acetals. Simultaneous catalytic esterification and acetalisation of a bio-oil, obtained from the pyrolysis of mallee woody biomass, with methanol using a commercial Amberlyst-70 catalyst has been carried out at temperatures between 70 and 170 °C.²⁹ The results showed that the conversion of light organic acids and aldehydes to esters and acetals increased significantly with the increase of catalytic temperature, reaction time and catalyst loading. Xu *et al.*³⁷ used a series of nickel-based catalysts for upgrading bio-oil derived from pyrolysis of pine sawdust. Results showed that the pH value of the bio-oil increased, water content increased, dynamic viscosity decreased and ester compounds were significantly increased, when the raw bio-oil was catalytically upgraded with a Mo-10Ni/ γ - Al_2O_3 catalyst.

Hydrodeoxygenation of bio-oil is a process to upgrade the bio-oil by deoxygenation with H_2 in the presence of catalysts. During hydroprocessing of bio-oil, the oxygenated compounds present in the oil react with H_2 to form water and saturated C–C bonds. However, it is suggested that hydrogenation of

aromatic compounds in the bio-oils should be avoided to prevent decrease of the octane number and increasing H_2 consumption.³³ Catalysts are one of the key factors for bio-oil hydroprocessing. Most studies of catalysts have focused on sulfided CoMo^{38,48,49} and NiMo-based catalysts^{50–52} since they have been commercially used for removal of oxygen from petrochemical feedstocks. Other catalysts such as zeolites^{53–55} and metals supported on zeolites³² have also been reported to be effective for upgrading bio-oil through hydrodeoxygenation.

2.2 Pyrolysis Oils from Other Wastes

Pyrolysis of non-biomass wastes to produce an oil which may be used as a fuel-oil or as a petrochemical feedstock have concentrated on particular niche wastes such as waste plastics and scrap tyres. These wastes have the advantage that they can be collected as a separate waste fraction and are rich in carbon and hydrogen. Table 6 shows typical fuel properties of pyrolysis oils derived from waste. 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 $> 50 \text{ MJ kg}^{-1}$. The calorific values may be compared to typical petroleum-derived fuel oils at between 44.0 and 46.6 MJ kg^{-1} (see Table 4). Although in some respects the product oils have similar properties to petroleum-produced oils, particularly those derived from plastics and tyres, the direct use of such fuels in combustion systems designed and optimised on fuels refined from petroleum may be difficult. For example, performance guarantees for the use of non-standard fuels in combustion systems may invalidate the manufacturers' warranties which would be based around standard, *i.e.* petroleum-refined, fuels. Emission limits from the combustion system, set at National and European level, would also have to be met irrespective of the fuel being used.

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. It is suggested that the thermal degradation of the polyethylene and polypropylene as the plastic is heated in the pyrolysis reactor occurs *via* random scission to yield a wide spectrum of hydrocarbon fragments which may contain any number of carbon atoms.⁵⁶ The C–C bond is the

Table 6 Fuel properties of waste-derived pyrolysis oils.

<i>Property</i>	<i>Polyethylene oil</i> ⁵⁶	<i>Polystyrene oil</i> ⁵⁶	<i>Mixed plastic polypropylene, polyethylene, nylon oil</i> ⁵⁶	<i>Polyester styrene copolymer oil</i> ⁵⁷	<i>Tyre oil</i> ¹⁷	<i>MSW oil</i> ¹
Flash point (°C)	33.6	26.1	26.0	26.0	24	56
Pour point (°C)	2.7	-67	-5	-	-	-
Density (kg m ⁻¹)	0.86	0.96	0.80	0.83	0.91	1.3
Viscosity cSt (at 50 °C)	2.19	1.4	1.49	3.9 ^a	3.50 ^a	-
Carbon (wt%)	-	-	-	86.1	87.0	57.5
Hydrogen (wt%)	-	-	-	7.2	10.0	7.6
Nitrogen (wt%)	-	-	-	0.4	0.4	0.9
Sulphur (wt%)	0.01	0.01	0.01	0.0	1.5	0.1–0.3
Initial b.pt. (°C)	-	-	-	75	80	-
10% b.pt. (°C)	-	-	-	93	140	-
50% b.pt. (°C)	-	-	-	189	230	-
90% b.pt. (°C)	-	-	-	354	340	-
Calorific value (MJ kg ⁻¹)	52.3	50.4	46.3	33.6	42.0	24.4

^aViscosity measured at 40 °C.

weakest in the polymer structure and leads to formation of straight-chain alkanes. In addition, during the degradation process, the stabilisation of the resultant radical after chain scission leads to the formation of carbon double bonds, C=C, in the structure. Therefore, the product oil will consist of mainly alkanes and alkenes.

Pyrolysis of polystyrene produces an oil very high in concentration of the monomer, styrene and also other aromatic compounds. For example, Kaminsky *et al.*²¹ used a fluidised bed reactor at 520 °C for the pyrolysis of polystyrene and reported a styrene concentration of 76.8 wt% of the original polymer. Other compounds present in significant concentrations are the styrene dimer and trimer. In addition, the pyrolysis oils contain a significant proportion of toluene, xylene and alkylated benzenes, indene and indane and naphthalene. The thermal degradation mechanism for polystyrene has been shown to be *via* first chain scission and then random scission, which results in the formation of the styrene monomer and also styrene dimer, trimer and tetramer.⁵⁶

The pyrolysis of polyvinyl chloride produces a highly aromatic oil in addition to hydrogen chloride yields of more than 50 wt%.^{20,58} The oil contains mainly aromatic compounds. Benzene has been identified as the main aromatic compound at 22.1 wt% in the oil from the fluidised bed pyrolysis of polyvinyl chloride. The thermal degradation mechanism of polyvinyl chloride is initiated by a dechlorination reaction, resulting in the formation of hydrogen chloride. The process of the elimination of a chlorine atom from the structure results in the formation of a carbon double bond in addition to hydrogen chloride. Further carbon double bonds are formed as more hydrogen chloride is evolved from the resultant chain. Eventually the chain undergoes cyclisation to yield aromatic and alkylaromatic compounds.⁵⁶

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 most commonly used tyre rubber is styrene–butadiene copolymer, containing around 25 wt% styrene. In addition to the rubber, tyres contain reinforcing textile cords, steel or fabric belts and steel-wire reinforcing beads. Other additives used in the manufacture of tyres include carbon black, which is used to strengthen the rubber and aid abrasion resistance, and extender oil, which is a mixture of aromatic hydrocarbons that serve to soften the rubber and improve workability. Sulfur is used to cross-link the polymer chains within the rubber and also to harden it and prevent excessive deformation at elevated temperatures. An accelerator is added, which is typically an organosulfur compound that acts as a catalyst for the vulcanisation process. Zinc oxide and stearic acid are added and act to control vulcanisation and enhance the physical properties of the tyre.

The thermal degradation 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.⁵⁹

The thermal degradation of the various rubbers used in tyres has been investigated. The pyrolysis of natural rubber produces the monomer, isoprene, and the dimer, dipentene, with other oligomers up to the hexamer in significant concentrations. It is suggested that the isoprene monomer is formed *via* a depropagating mechanism in the polymer chain and that the dipentene dimer is formed either by intramolecular cyclisation followed by scission, or by monomer recombination *via* a Diels–Alder reaction. The pyrolysis of polybutadiene rubber has been shown to be a two-stage process, products from the first stage being mainly butadiene and dipentene, formed as a result of depolymerisation. Material not undergoing depolymerisation is cyclised and cross-linked to form a residue which is degraded in the second stage. The product of pyrolysis from the second stage is a complex mixture of hydrocarbons. The pyrolysis of styrene–butadiene rubber produces butadiene and butadiene fragments at lower pyrolysis temperatures and styrene and/or benzene at higher temperatures. The thermal degradation of styrene–butadiene rubber starts with the butadiene elements of the co-polymer and higher temperatures are required to degrade the styrene elements of the polymer.⁵⁹

2.3 *Pyrolysis Chars*

Pyrolysis of biomass and biomass wastes produces a char which can be used as a solid fuel with a calorific value of about 30–35 MJ kg⁻¹ and a low ash content of about 1–3 wt%. Indeed, the production of char as charcoal from the pyrolysis of biomass has been known for centuries. However, char produced from biomass pyrolysis is increasingly being referred to as ‘biochar’, which may be used as a soil improver. The char can be produced from slow, fast or conventional pyrolysis of biomass wastes, however, slow pyrolysis enhances the yield. It is acknowledged that a lower heating rate of pyrolysis yields less volatile compounds compared with a higher heating rate of pyrolysis. A low heating rate of pyrolysis enables an extended residence time of the volatiles in the particles of the raw material, thus increasing the occurrence of repolymerisation of the volatiles. In addition, secondary reactions generate lighter compounds that have a lower C : H ratio, forming charcoal at the surface of the solid particles. Therefore, a high yield of charcoal is then obtained through slow pyrolysis.⁶⁰

Char obtained from pyrolysis of biomass contains nutrients (*e.g.* nitrogen, phosphorus) and can be utilised as a fertiliser supplement in agricultural systems. Furthermore, adding biochar to the soil has been reported to significantly improve the quality and productivity of soils and could contribute to carbon abatement.^{61,62} The biochar is very porous, which encourages retention of water in the soil and increases surface area, enabling more efficient interaction of the nutrients in the biochar, soil and fertiliser with the plants.^{14,15} In addition, the biochar is chemically and biologically very stable, therefore the carbon contained in the biochar is sequestered from the atmosphere into the soil, thereby acting as a carbon sink and mitigating the effects of climate change.

Char yield from biomass pyrolysis has been reported to be normally less than 30 wt% of the raw materials,⁶³ although yields higher than 40 wt% have also been reported by pyrolysis of cellulose, hemicelluloses and woody materials under high pressure.^{64,65} Most of the reports for char production from pyrolysis of biomass have been carried out at a constant heating rate or through simple isothermal treatment. Elyounssi *et al.*⁶⁶ investigated the influence of temperature on the thermal behaviour of the constituents of the biomass, and proposed the possibility of improving the fixed-carbon yield under atmospheric pressure by adjusting the temperature–time profile of the thermochemical conversion process. They reported a two-phase production of fixed-carbon. The first phase is decomposition of hemicelluloses and cellulose, where char formation was promoted by low temperatures. The yield of fixed-carbon was reduced at the beginning of the second phase of the low temperature isothermal pyrolysis. However, an immediate rise of temperature at the end of the first phase pyrolysis helped to preserve the maximum yield of the fixed-carbon.

Pyrolysis of other 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%.²³ Tyre pyrolysis under slow heating rate conditions produces a char of 40–50 wt% with an ash content of about 10 wt%. The significance of a high ash content in the chars means that the value of the char as a fuel is reduced. The chars may be used directly as fuels, *e.g.* briquetted to produce solid fuels. The calorific values of the chars are relatively high: for example, char derived from municipal solid waste has a calorific value of about 19 MJ kg⁻¹, tyre char about 29 MJ kg⁻¹, and wood waste produces a char of calorific value of about 33 MJ kg⁻¹.¹ These figures compare with a typical bituminous coal of calorific value of 30 MJ kg⁻¹.

2.4 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.⁶⁷ Pyrolysis of plastics which contain some oxygen, such as polyethylene terephthalate and polyester, would also produce some carbon dioxide and carbon monoxide in addition to alkane and alkene gases. Pyrolysis of polyvinyl chloride produces high concentrations of hydrogen chloride gas. Consequently, mixed plastic waste produced from municipal solid waste that contains polyethylene, polypropylene, polyethylene terephthalate, polystyrene and polyvinyl chloride produces a mixture of gases based on the constituent plastics. The major gases are hydrocarbons, with smaller amounts of carbon dioxide and hydrogen chloride. The major hydrocarbons produced are the alkene gases, ethene, propene and butene, and the alkane gases, methane, ethane, propane and butane.¹⁹

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} .

2.5 *Material Recovery from Wastes*

Several useful and sometimes high-value materials can be recovered from wastes using pyrolysis technology. Pyrolysis is a particularly advantageous technology when heterogeneous composite materials are involved. For example, the pyrolysis recycling of tyres produces a char, oil and gas product, but the steel reinforcement from the tyre can also be recovered and can be recycled into the steel industry,⁶⁸ the steel typically comprising about 10% of the weight of the tyre.

Chars produced from wastes may also be used as activated carbons.^{69,70} Activated carbons are used extensively in industrial purification, waste water treatment and chemical recovery operations. They are particularly advantageous because of their high internal surface areas and active surfaces. In general, higher surface areas result in higher adsorption capacities. The upgrading of waste-derived pyrolysis chars to activated carbon has been investigated extensively. Commercially used activated carbons have surface areas typically in the range of $500\text{--}2000 \text{ m}^2 \text{ g}^{-1}$ and pore sizes which can be manipulated by the process conditions or source feedstock to produce the desired pore size distribution for a particular application.

Activated carbons may be produced through either physical or chemical activation. Chemical activation involves impregnation with a chemical such as zinc chloride, phosphoric acid or potassium hydroxide, followed by carbonisation using the pyrolysis process. Physical activation involves pyrolysis of the source material to produce a char, followed by steam or carbon dioxide gasification. Such techniques have been applied to waste materials to enhance the properties of the derived char to produce an activated carbon with properties similar to those produced commercially.^{71,72} For example, char derived from tyres has an initial surface area of about $60 \text{ m}^2 \text{ g}^{-1}$, however, activation of the carbonaceous char with steam at temperatures above 800°C produces an activated carbon with a surface area of over $650 \text{ m}^2 \text{ g}^{-1}$.⁷² The action of the steam is to react with the carbon to produce carbon monoxide, carbon dioxide and hydrogen, opening up pores and increasing the surface area. Chemical activation of waste, where an absorbent waste such as biomass waste absorbs a reacting chemical such as zinc chloride or potassium hydroxide, followed by pyrolysis at 500°C , has produced very high surface area activated carbons of over $2000 \text{ m}^2 \text{ g}^{-1}$.⁷³ Pyrolysis of refuse-derived fuel produced from municipal solid waste produces a char with a surface area of $66 \text{ m}^2 \text{ g}^{-1}$, however, after steam activation at 800°C , the surface area increased to $500 \text{ m}^2 \text{ g}^{-1}$.⁷⁴ Man-made textile waste (acrylic) has been pyrolysed and produced a char with a low surface area of $2 \text{ m}^2 \text{ g}^{-1}$, but after steam activation the surface area reached more than $600 \text{ m}^2 \text{ g}^{-1}$.⁷⁵

Printed circuit boards derived from waste electrical and electronic equipment contain approximately 40 wt% metals, 30 wt% plastics/resin and 30 wt% of ceramic material.⁷⁶ The metals present include large amounts of copper, aluminium and iron, but also precious metals such as gold, silver and palladium. The yield of products from waste printed circuit boards depends on the original bulk composition of the materials present. Pyrolysis of printed circuit boards has been undertaken in a batch autoclave reactor at 500°C and produced 76.5 wt% solid residue, 16.2 wt% oil and 7.3 wt% gas.⁷⁷ The solid residue consisted of char, metals and ceramic materials, and the oil and gas was produced from pyrolysis of the plastic/resin of the circuit boards. Pyrolysis of printed circuit boards derived from waste computers, televisions and mobile telephones produced solid residues of 68.9 wt% residue, 60.0 wt% residue and 82.2 wt% residue, respectively.⁷⁸ The pyrolysis gases consisted mainly of CO_2 and CO and C_1 to C_4 gases; some inorganic bromine was also present, produced from the pyrolysis of the brominated flame-retardants often present in printed circuit boards. Williams⁷⁹ has reviewed the products of pyrolysis of printed circuit boards. After pyrolysis, the solid residue of printed circuit boards consists of a carbonaceous solid which is very friable and from which the metallic components and glass fibre reinforcement of the board can easily be separated. De Marco *et al.*⁷⁷ found that the main metals present in the solid residue from pyrolysis of an epoxy resin-based printed circuit board consisted of mainly copper, aluminium, tin, lead, zinc and nickel. In addition, high-value metals such as gold, silver and palladium were identified at concentrations of 0.03, 0.16 and 0.01 wt%, respectively.

Advanced composite materials used for manufacturing (for example, glass-reinforced polyester, sheet moulding compound and dough moulding compound, *etc.*) have been widely used in industry due to the advantages of their high strength, lightness and corrosion resistance. Composite materials are regarded as being very difficult to recycle and large amounts of waste fibre composites are disposed of to landfill.⁸⁰ Pyrolysis has been applied to recover the fibres from the solid residue from pyrolysis of such wastes while other products, such as oil and gases, are also generated as potential fuels and chemicals.^{80–84} The product distribution is dependent on the properties and original composition of the raw materials. Table 7 summarises the yields of char, oil and gas from the pyrolysis of various waste fibre composites. A large fraction of solid residue was obtained after pyrolysis of the waste fibre composites and contains char (formed during pyrolysis), inorganic compounds (*e.g.* CaCO₃), filler, fibres and organics.⁸⁵

Pyrolysis temperature has been investigated for its influence on the products from the pyrolysis of waste fibre composites. The results showed that there were only small differences in the product yield, compared with pyrolysis of waste plastics and biomass;^{80,85} this is suggested to be due to the high content of solid material.

The properties of the recycled fibres recovered from the pyrolysis of waste composite materials, such as tensile strength, flexural strength and flexural modulus, hardness, *etc.*, have been determined and compared with the properties of virgin fibres. For example, Marco *et al.* studied the pyrolysis of sheeting moulding compound and compared the recovered glass fibre with virgin fibres.⁸³ They reported that there were no significant differences between the mechanical properties of the recycled carbon fibres and those of virgin fibres. However, the mechanical properties have been reported to be affected by pyrolysis temperature. Pickering *et al.*⁸⁶ found that 450 °C was the optimal temperature to obtain high-strength glass fibres, while higher pyrolysis temperature significantly reduced the tensile strength. In addition, Akesson *et al.*⁸¹ investigated microwave pyrolysis of waste composite material from the blades of wind turbines. They reported that the strength of recycled glass fibre derived

Table 7 Products distribution from pyrolysis of waste-fibre composites.

Raw material	Polyester	Polybenzoxazine		Sheet moulding compound		
Fibre type and content	39 wt% glass fibre	58 wt% carbon fibre	58 wt% carbon fibre	25 wt% glass fibre	25 wt% glass fibre	25 wt% glass fibre
Pyrolysis temp. (°C)	450	450	700	500	700	400
Gas (wt%)	5.8	1.5	3.8	11.0	12.8	9.2
Liquid (wt%)	39.6	22.0	24.6	14.2	13.7	15.7
Solid (wt%)	45.2	74.4	70.0	74.9	72.6	75.2
Reference	82	80	80	85	85	83

from pyrolysis at 360 °C was 25% lower than that of the virgin fibres. Increasing pyrolysis temperature to 440 °C showed less difference in relation to the strength of recycled fibres; however, 600 °C was reported to generate very brittle fibres. Carbon fibre composite material in the form of carbon fibres in a polybenzoxazine resin was pyrolysed at a range of different temperatures to recover the high-value carbon fibres by Nahil and Williams.⁸⁰ They reported that solid residues of between 70 and 83.6 wt%, liquid yields of 14–24.6 wt% and gas yields of 0.7–3.8 wt% were obtained, depending on pyrolysis temperature. The carbon fibres recovered from the sample exhibited mechanical properties which were up to 90% of those of the original virgin carbon fibres. Cunliffe *et al.*⁸² made dough moulding compound test plaques, with different contents (20, 25 and 100 wt%) of recovered glass fibre obtained from pyrolysis, and compared these with plaques made without adding recycled glass fibre. They reported that 20 wt% replacement of virgin fibre with recycled glass fibre made a dough moulding compound with mechanical properties meeting manufacturers' quality limits, however, a marked deterioration of mechanical properties was reported when 100 wt% recovered fibres were used.

2.6 Reactors for Pyrolysis

A range of different reactors, such as fixed-bed/batch, screw kiln, rotary kiln and fluidised-bed reactors, have been used for pyrolysis of wastes. In the following section, various common reactors are summarised in relation to the pyrolysis process.

2.6.1 Fixed-bed/batch Pyrolysis. At the laboratory scale, pyrolysis is often carried out in a fixed-bed reaction system for research purposes.^{87–91} A typical reaction system can be seen in Figure 3. Typically, a few grams of raw material are placed into the reaction tube which is heated externally by an electrical furnace. The furnace controls the pyrolysis temperature, which is measured by a thermocouple connected to a temperature controller. Nitrogen or another inert gas is used as a carrier gas when pyrolysis is investigated at the laboratory scale. The decomposed products are carried by the carrier gas and are processed downstream, using systems such as a secondary reforming process or direct condensation.

At the commercial level, a fixed-bed, batch reactor has been used for the pyrolysis of waste tyres at loads of up to 1 tonne.⁹² The process involves loading the whole and shredded tyres, including the steel core, into a reactor vessel which is then placed inside a kiln. The reactor is purged with nitrogen to ensure oxygen-free conditions. Oil burners heat the kiln initially, but as the pyrolysis of the tyres proceeds the oil is replaced by the gas produced by the tyre pyrolysis. The pyrolysis time is of the order of 6–8 hours to ensure complete pyrolysis of the tyres. The evolved pyrolysis oil vapours and gases are passed through a heat exchanger to cool them and then into an oil-condensing tank; the non-condensed gases are then passed to a scrubbing unit to clean them before passing to the burner or to storage. The oil from the condensing

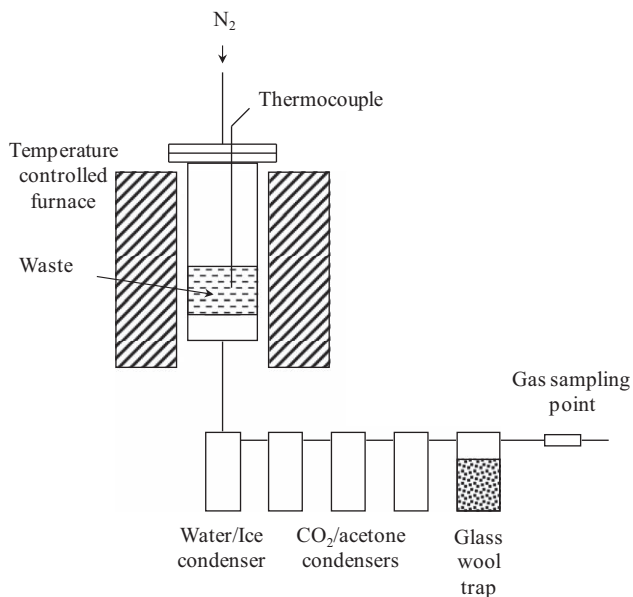


Figure 3 Schematic diagram of fixed-bed reaction system.

tank is pumped to storage or used to provide auxiliary fuel for the burners. The reported yield was 20.9 wt% oil, 40.7 wt% char and 23.9 wt% gas, with 12.9 wt% steel recovered from the tyres. Small-scale pyrolysis of waste plastics has been used as fixed-bed batch process to treat plastic wastes in quantities of about 1 tonne per day.⁹³ Several Japanese companies have developed the technology to process mixed plastic waste derived from municipal solid waste to produce oils which may be used directly as fuels or refined to produce higher grade fuels (see section 2.7.)

2.6.2 Screw Kiln Pyrolysis. Screw kiln pyrolysis has been used for continuous processing, which is regarded as a preferred reaction system for industrial commercialisation.^{94–96} The screw kiln reactor was suggested to have the potential to be used for the processing of waste plastics, which possess complex chemical and physical characteristics. Furthermore, the screw kiln reaction system might reduce the over-cracking of raw materials and generates a comparatively narrow oil product range that could be easily reformed in a downstream stage to produce hydrogen gas. A schematic diagram of screw kiln reaction system is shown in Figure 4.

In Figure 4, raw materials are loaded and continuously fed into the screw kiln reactor which is externally heated. Pyrolysis occurs inside the reactor and residues are collected by a char collection system. Derived gaseous products will be fed into downstream processes such as an oil condensation system or a higher temperature gasification system. Nitrogen is normally used as a carrier gas in the laboratory-scale reaction system.

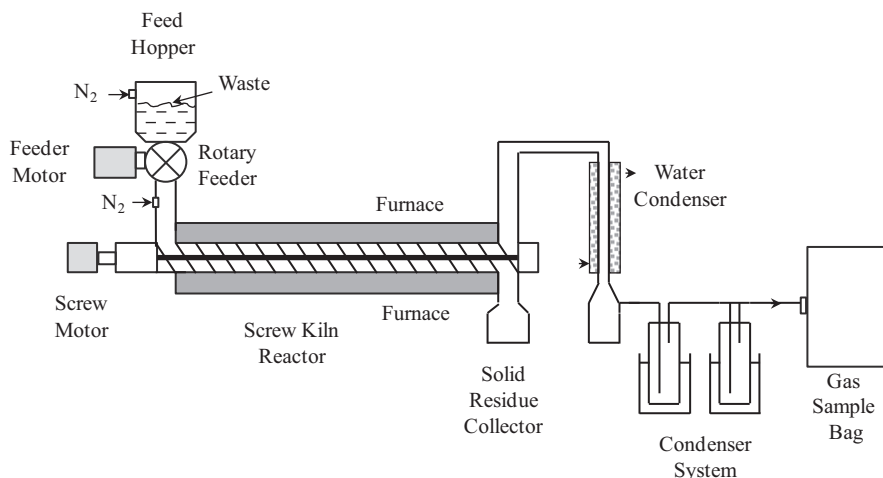


Figure 4 Schematic diagram of a screw kiln pyrolysis system.

A screw kiln pyrolysis system has been used for catalytic conversion of polyethylene-lubricating oil mixtures.⁹⁶ Thermal cracking and catalytic cracking were investigated at various mixing ratios of polyethylene and lubricating oil. The authors concluded that the experimental results demonstrated that the screw kiln reactor is an efficient system for the continuous processing of plastic-lubricant oil mixtures by thermal and catalytic treatment. Pyrolysis of automobile shredder residue has been researched using a laboratory-scale screw kiln reactor with a feed rate of about 100 g hr^{-1} at reaction temperatures between 500 and 750°C . The screw kiln reaction system was reported to be easy to operate and control; reaction temperature and sample residence time were found to be the main factors that influenced the distribution of the products (oil and gas).

2.6.3 Fluidised Bed Pyrolysis. The fluidised bed reactor has been extensively used for pyrolysis of biomass,⁹⁷ tyre,⁹⁸ plastic polymers,^{99,100} oil sludge¹⁰¹ and coal,¹⁰² since it provides excellent heat and material transfer rates and uniform temperature distribution. A schematic diagram of a typical fluidised bed pyrolysis system is presented in Figure 5. A fluidised bed consists of a bed of sand particles contained in a vertical refractory-lined chamber through which the primary combustion air is blown from below; the sand particles are fluidised by adjusting the air flow. The waste is fed *via* a screw directly into the fluidised bed and heated to the pyrolysis temperature, typically between 600 and 900°C . The derived pyrolysis gases pass through a cyclone to remove particulates and are cooled in a condensation system where oils are collected. The non-condensed gases may be further cleaned, pressurised and stored.

Many laboratory-scale or pilot-scale fluidised bed systems have been reported for both fast and slow pyrolysis. For example, a 3-inch diameter fluidised bed with a 2.5 kg hr^{-1} feedstock feeding rate was built at Eastern

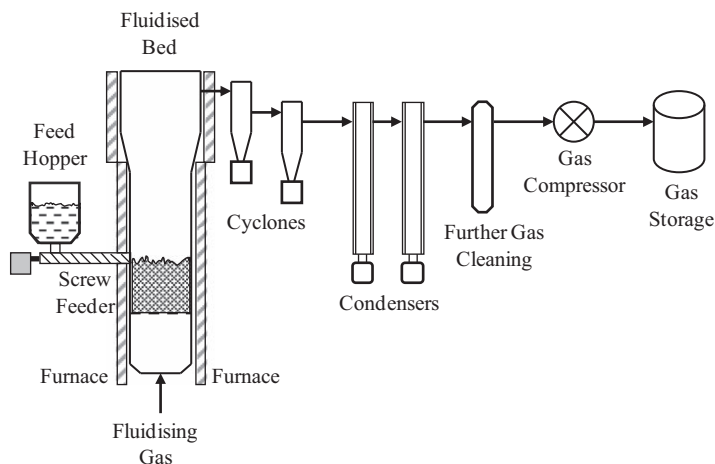


Figure 5 Schematic diagram of a typical fluidised bed for pyrolysis of wastes.

Regional Research Center, United States Department of Agriculture.¹⁰³ A pyrolysis fluidised bed with a capacity of 1 kg hr^{-1} was reported from the Mississippi State University.¹⁰³ Kaminsky *et al.*²¹ used a fluidised bed to pyrolyse a range of waste materials, including tyres, plastics and automotive shredder residues. Their fluidised bed is at the pilot scale, with a reactor diameter of 450 mm enabling high throughputs of $\sim 30 \text{ kg hr}^{-1}$ and temperatures typically between 500 and 780°C . The fluidised bed is heated indirectly *via* radiant heat tubes within the bed of quartz sand, in which the product pyrolysis gas is combusted to provide heat. The fluidising gas is also the product gas and is preheated to 400°C . A range of wastes and process conditions have been investigated that provide the flexibility to produce a range of products; for example, pyrolysis of plastics to produce waxes and oils for the petrochemical industry, or oils with high concentrations of benzene, xylenes and toluene.

2.7 Examples of Semi-commercial and Commercial Pyrolysis Systems

Table 8 shows examples of pyrolysis processes for waste at the semi-commercial and commercial scale. The list of processes is not meant to be exhaustive but gives an indication of the types of process reactor, outputs, throughputs, *etc.*

Figure 6 shows the Ensyn (Canada) entrained low process 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 for use as a chemical feedstock and/or fuel oil. 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

Table 8 Examples of commercial and semi-commercial pyrolysis systems.

<i>Company</i>	<i>Location</i>	<i>Reactor Type</i>	<i>Feedstock</i>	<i>Output</i>	<i>Capacity</i>
Ensyn	Renfrew, Ontario	entrained flow reactor	biomass	bio-oil	100 tonnes day ⁻¹
Dynamotive	West Lorne, Canada	fluidised bed	biomass	bio-oil	130 tonnes day ⁻¹
BTG-BTL	Netherlands	rotating cone reactor	biomass	bio-oil	5 tonnes hour ⁻¹
Pacific Pyrolysis	Sydney, Australia	rotary kiln	biomass and wastes	bio-char	ca. 10 tonnes day ⁻¹
Splainex Ltd	Netherlands	rotary kiln	tyres	tyre-oil and gas	ca. 20 tonnes day ⁻¹
Kouei Industries	Vancouver, Canada	fixed bed/batch	tyres	tyre-oil, char and gas	16 tonnes day ⁻¹
Toshiba	Sapporo, Japan	rotary kiln	mixed plastics	pyrolysis oil	14 000 tonnes year ⁻¹
MCC Ltd.	Yukaki, Japan	fixed bed/batch	mixed plastics	pyrolysis oil	1–2 tonnes day ⁻¹
Mogami-Kiko Co. Ltd.	Yamagata, Japan	fixed bed/batch	mixed plastics	pyrolysis oil	1–2 tonnes day ⁻¹

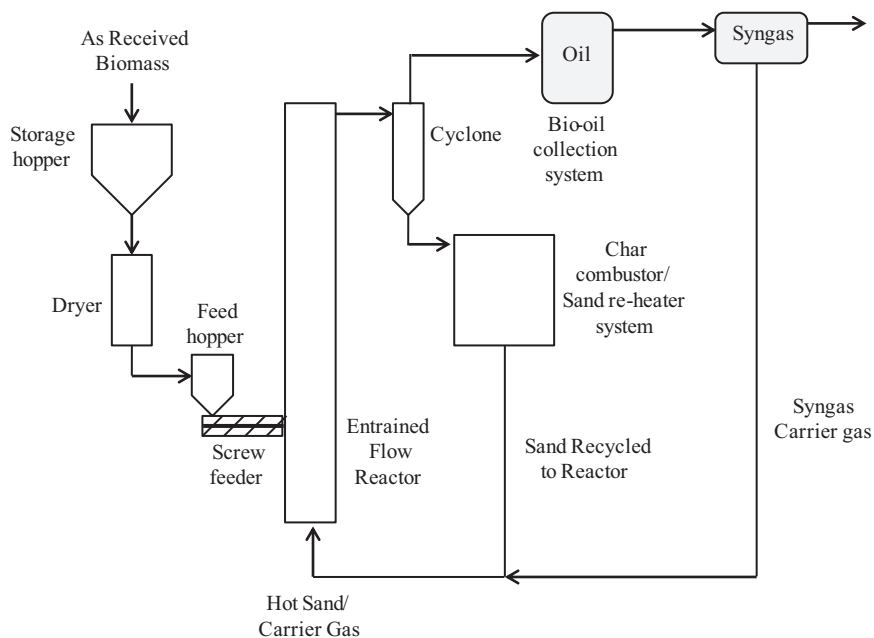


Figure 6 Schematic diagram of the Ensyn entrained flow pyrolysis reactor system.¹⁰⁴

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.

The Mogami-Kiko Co. Ltd plastics pyrolysis plant in Yamagata, Japan, is a fixed-bed, batch-pyrolysis system that is used to process mixed plastics collected from municipal solid waste. The unit operates as two pyrolysis lines. The main pyrolysis vessels would typically process one tonne per day of plastics. External heating of the vessel is *via* combustion of the product oil or gas. Initial heating

of the plastic wastes at *ca.* 400 °C produces a hydrogen chloride-rich off-gas due to decomposition of the polyvinyl chloride in the waste plastics. This low-temperature pyrolysis gas, containing hydrogen chloride and hydrocarbons, is combusted and then cooled and scrubbed, using an alkaline scrubbing solution to remove and collect the hydrogen chloride. After the primary de-chlorination process at lower temperature, the evolved pyrolysis gases are switched away from the de-chlorination system and the temperature of pyrolysis is raised to 500 °C. Pyrolysis of the main bulk of plastics then takes place over a period of 12–15 hours to produce a medium and light oil, and the non-condensed gases are flared. The product oil is used partially as fuel for the pyrolysis process.⁹³ Figure 7 shows a schematic diagram of the principle steps of the Mogami-Kiko process.

Larger-scale plastics pyrolysis is carried out at the Toshiba waste plastics plant (Japan), where ~14 000 tonnes of plastic are processed per year, representing 40 tonnes per day on a two-line continuous process.⁹³ The main pyrolysis reactor consists of a rotary kiln and the plant is able to process mixed plastic waste from municipal solid waste. The plastic waste is first shredded and pelletised for ease of feeding. Because the waste plastics contain polyvinyl chloride (PVC), a pre-treatment step is used, involving melting at lower temperature to drive off the chlorine as hydrogen chloride. The pyrolysis gases containing the hydrogen chloride are combusted and hydrochloric acid is recovered from the scrubber solution. The de-chlorinated molten plastic enters the rotary kiln where pyrolysis takes place and the condensed oil is collected in a drum. The oil is then distilled to produce three fractions: a heavy oil, a medium oil and a light oil, with the off-gases combusted to raise steam. Figure 8 shows a schematic diagram of the various process steps of the Toshiba waste plastics pyrolysis process.

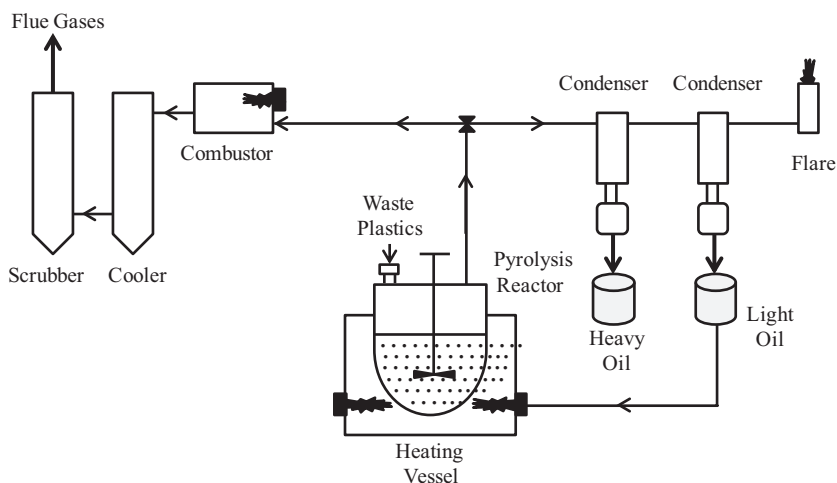


Figure 7 Schematic diagram of the Mogami-Kiko Co. Ltd plastics pyrolysis plant, Yamagata, Japan.⁹³

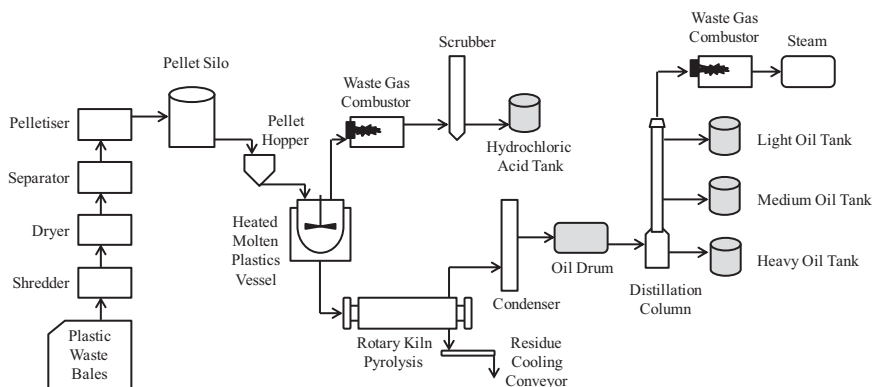


Figure 8 Schematic diagram of the Toshiba waste plastics pyrolysis process.⁹³

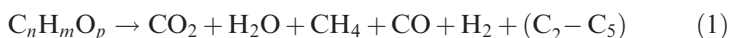
3 Gasification

3.1 Introduction to 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, CO_2 or pure oxygen at high temperature, typically 800°C . The purpose of the gasification process is to produce combustible gases that can be used for generation of heat and electricity through combustion, or for post-gasification hydrogen production, or for the production of transportation fuels and chemicals.¹⁰⁵ Gasification has been extensively used as a clean energy technology in the utilisation of biomass,^{106–109} coal,^{110–117} sewage sludge^{118–120} and municipal solid waste (MSW).^{121–124} Gasification of hydrocarbon materials, for heat and power generation through subsequent combustion of syngas, has some advantages compared with direct combustion of the raw feedstock. For example, syngas production from gasification of raw materials enables the removal of nitrogen- and sulfur-containing compounds, which result in emissions of SO_x and NO_x during combustion of the syngas. In addition, the net efficiency of the gasification–combustion process is also reported to be higher than the sole combustion of raw materials using a steam turbine for heat and power generation.^{125,126}

A number of stages have been suggested for the complex process of gasification as follows:

- i. **Drying stage:** where the moisture content of the raw materials is removed at temperatures around 150°C ;
- ii. **Pyrolysis stage:** where volatile species are produced from pyrolysis in the absence of oxygen. Reactions at this stage could be summarised as:



- iii. **Oxidation stage:** where carbonised contents of the raw materials are reacted with oxygen. Hydrogen also partially reacts with oxygen to generate water. A large amount of energy is released due to the exothermic reactions. Reactions occurring at this stage are as follows:



- iv. **Reduction stage:** where several endothermic reactions occur in the absence of oxygen at high temperature; they are characterised as follows:



Gasification can be classified according to the reaction agent used in the process: air gasification, oxygen gasification, steam gasification, CO_2 gasification and gasification with mixtures of the above agents. Process conditions and the main characteristics of the products are summarised in Table 9.

Gasification in the presence of air reduces the calorific value of the produced gases. For example, air gasification of biomass waste normally produces a gas with a calorific value between 4 and 7 MJ Nm^{-3} , whereas gasification with oxygen–steam generates high calorific value gases ($10\text{--}18 \text{ MJ Nm}^{-3}$).¹²⁷ However, air gasification has advantages of low energy input and low tar content in the gaseous stream. Oxygen gasification is not common due to the high cost of production of oxygen. Steam gasification has attracted increasing interest recently because it produces gases having a high content of H_2 . However, oxygen mixed with steam has been investigated and produces high calorific value gases.¹²⁸ Additionally, steam gasification also has the advantages of reducing the tar content of the syngas by tar-reforming reactions and prevention of coke deposition on the surface of any catalyst used in the gasification process.

Syngas generated from gasification of hydrocarbon materials such as biomass, coal and MSW has been extensively researched and applied for production of heat and electricity.¹³³ During biomass gasification for power generation, a large amount of waste heat is available. Therefore, combined heat and power (CHP) is gaining much attention and has been successfully applied to improve the overall process efficiency.^{134–136} More advanced technologies, such as solid oxide fuel cells (SOFC) combined with gasification, have been

Table 9 Summary of the gasification process with different reaction agents.

Reference	129	130	131	132	128
Gasification agent	steam	steam	air	air	steam–oxygen
Reactor bed	fixed	fluidised	fluidised	fluidised	fluidised
Raw material	MSW	sawdust	wood	biomass	pine wood
Temperature (°C)	900	780	860	780–830	785–830
Solid phase	dolomite	sand	sand	dolomite	sand
<i>Proximate analysis</i> (wt%)					
Moisture	-	8.5	10.4	7–15	10–14
Volatiles	82.3	77.4	70.4	-	74–76
Fixed carbon	11.8	12.9	17.9	-	12–13
Ash	5.9	1.2	1.3	-	0.5–1.2
<i>Process conditions</i>					
Sample feeding rate (kg hr ⁻¹)	0.3	3.46	-	7.6–11.4	5–20
ER ^a	-	-	-	0.18–0.45	0.24–0.51
Agent flow rate (kg h ⁻¹)	0.117	2.98	-	-	-
Agent : sample ratio (kg/kg)	0.39	0.87	2.3	-	0.48–1.11
Gas yield (Nm ³ kg ⁻¹) ^b	0.68	1.2	2.99	1.25–2.45	0.86–1.14
<i>Gas composition</i> (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

Equivalence Ratio (ER): ratio of the fuel-to-oxidiser to the stoichiometric fuel-to-oxidiser ratio, Nm³: cubic meters under normal temperature (25 °C) and atmosphere pressure.

examined, as the efficiency of the gasification–SOFC process is much higher than gasification–CHP.^{137–140} SOFC has the advantage of utilising carbon monoxide compared with other fuel cell technologies such as Proton exchange membrane fuel cells (PEMFC). However, tar content, fine particulates, pollutants such as SO_x, etc., are major challenges for the subsequent process after the gasification of hydrocarbon materials.¹⁴¹ These by-products generally cause erosion and corrosion of metals. The types of contaminants and problems caused for the downstream facilities are summarised in Table 10.^{142–145}

Many definitions have been reported for tar; for example, Milne *et al.*¹⁴⁶ defined tar as largely aromatic organics; Devi *et al.*¹⁴⁷ defined tar as a complex mixture of condensable hydrocarbons, including single-to-multiple ring aromatics; the International Energy Agency Bioenergy Gasification Task, the Directorate General for Energy of the European Commission and the US Department of Environment have all defined tar as hydrocarbons with

Table 10 Summary of the contaminants and problems for the gasification process.

<i>Unwanted contaminant</i>	<i>Presence</i>	<i>Problems</i>
Tar	A complex mixture of condensable hydrocarbons.	The formation of tar causes major operational and maintenance process problems, including tar blockages of pipework, plugging and corrosion in downstream fuel lines, filters, engine nozzles and turbines.
Particulates	Produced from ash and char bed materials if used for the fluidised bed reactor.	Causes blockage of downstream equipment, such as deposition on SOFC anodes, resulting in blocking of gas diffusion paths.
H ₂ S, SO _x and HCl	Derived from sulfur and chlorine in the original raw materials.	Causes corrosion of equipment.
Alkali metals	Derived from original raw samples.	Causes problems such as fouling, slagging and corrosion of components in the subsequent systems.

molecular weights higher than that of benzene.¹⁴⁸ Specifications of the tar content in the product syngas for downstream use is normally less than 100 mg Nm⁻³ for internal combustion engines and 5 mg Nm⁻³ for gas turbines.¹⁴⁶ However, the tar content in the product gas is generally much higher, for example, 10 g Nm⁻³ for air-blown fluidised bed gasifiers and 0.5–100 g Nm⁻³ for the other types of reactors.¹⁴⁹ Tar reduction methods can be divided into primary methods (inside the reactor) and secondary methods (outside the reactor).¹⁴⁹ Primary methods are to prevent tar formation inside the reactor, include optimum design of the reactor, adjusting reaction conditions and adding bed materials (*e.g.* catalyst).¹⁵⁰ Secondary methods, reducing tar content in a downstream facility, can be further divided into dry-gas cleaning equipment (including cyclones, electrostatic precipitators and bag/baffle/ceramic/fabric filters, *etc.*) and wet-gas cleaning, with equipment including spray towers, scrubbers, *etc.*¹⁴³

3.2 Influence of Gasification Conditions

3.2.1 Influence of Gasification Temperature.

Reaction temperature plays an important role in the gasification process and has been extensively investigated for various materials, such as biomass, coal, MSW, *etc.*^{151–154} Carbon conversion and gas production are normally increased with the increase of gasification temperature, since more secondary reactions occur at high temperature. However, energy costs will be increased at a high temperature, therefore, an optimal energy input is needed to obtain the desired products. Temperatures from 600 to 900 °C have been investigated for catalytic steam gasification of

biomass in a fixed-bed reactor in the presence of dolomite.¹⁵³ It was shown that raising the temperature resulted in increased gas production and this was suggested as being due to faster pyrolysis at higher temperature, improved gasification of char and secondary steam reforming of tars. The improved char gasification in Equation (2) resulted in higher concentrations of carbon dioxide in the gas stream (see Table 3). Hydrogen concentration was reported to increase from 25.2 vol% to 49.5 vol% with the increase of gasification temperature from 600 to 900 °C and might be due to the reaction of Equation (5). Carbon monoxide concentration was reduced from 37 vol% to 18.8 vol% with the increase of gasification temperature and it was suggested that this is due to the endothermic water–gas shift reaction shown in Equation (7).

Others have shown that gas yield was increased by the increase of gasification temperature from 650 to 800 °C, when various biomass materials were tested for steam gasification in a small pilot-scale fluidised-bed reactor.¹³⁰ He *et al.*¹²¹ studied the influence of temperature on the yields of products and gas compositions during catalytic steam gasification of MSW. They reported that char production was reduced from 21.7 to 8.12 wt% with the increase of gasification temperature from 700 to 950 °C, while the gas yield increased from 81.8 to 104.2 wt%. Hydrogen and methane concentrations were increased with the increase of temperature, consistent with the results from Table 10. However, carbon monoxide concentration was increased and carbon dioxide concentration was decreased when the gasification temperature was increased from 700 to 950 °C. The composition of the raw samples might contribute to the different results of changing carbon monoxide and carbon dioxide concentrations reported by Luo *et al.*¹⁵³ and He *et al.*¹²¹

3.2.2 Introduction of Catalyst in Gasification. Introduction of a catalyst into the gasification process is known to increase gas and hydrogen yield and to reduce the required gasification temperature. The presence of a catalyst has also been shown to reduce the tar content in the syngas stream during the gasification process. Catalysts can be introduced by two methods: mixing with the raw waste materials during gasification (primary catalytic) or placed in a secondary reactor for products reforming, including tar cracking (secondary catalytic). For the primary catalytic gasification process, since the catalyst is mixed with raw materials it is difficult to recycle and, therefore, low-cost materials are required for the catalyst selection. This type of catalyst normally includes natural minerals such as dolomite and olivine. Olivine and calcined dolomite have been tested for catalytic gasification of biomass in a fluidised-bed reactor. It has been reported that tar concentration was reduced in the presence of olivine or dolomite, compared to the gasification carried out in the presence of inert quartzite.¹⁵⁵ Andrés *et al.* investigated the behaviour of dolomite and olivine as primary catalysts in the air–steam gasification of sewage sludge by using a fluidised-bed reactor at around 800 °C.¹⁵⁶ They concluded that tar production was significantly reduced in the presence of dolomite, whereas olivine was less effective for tar reduction. Increasing gas and hydrogen production and reduction of tar yield in the presence of

dolomite or olivine during the primary catalytic gasification process has also been reported by other authors.^{157–159} Although dolomite has been reported to be an effective catalyst for primary catalytic gasification (higher catalytic effect than olivine), dolomite is not as hard as olivine and gives rise to a large production of fine particles which cause problems in the downstream facilities, such as pipe and valve blockages.^{149,159}

Extensive research has been carried out investigating the secondary catalytic reforming of tars derived from primary gasification. Catalytic reforming in a secondary reactor offers flexible control of the catalytic process and enables the reacted catalysts to be recycled and reused. Among the catalysts used for secondary catalytic gasification, nickel-based catalysts are commonly used by researchers and industry due to their effective catalytic activity for tar reduction and their comparatively low price. Although noble metals, such as ruthenium and rhodium, have been reported to be more effective than nickel-based catalysts, they are not commonly used in industry because of their high cost.¹⁶⁰ A comprehensive review has been carried out on the various types of Ni-based catalyst in the catalytic gasification process, including Ni/Al₂O₃, Ni/CeO₂/Al₂O₃, Ni/dolomite and Ni/olivine, *etc.*¹⁶¹ It was concluded that Ni/Al₂O₃ prepared by the impregnation method is a typical nickel-based catalyst for the gasification process; however, Ni/Al catalysts prepared by co-precipitation have better catalytic activity. Magnesium has been reported to be an effective promoter for nickel-based catalysts since its addition results in an increase in the physical strength of the catalyst and the high reactivity of Mg-added catalyst with steam prohibits coke deposition on the surface of the catalysts. Olivine, dolomite and zeolites have also been regarded as good supports for nickel-based catalysts.

3.3 Gasification Reactors

3.3.1 Fixed-bed Gasification. The fixed-bed reaction system is one of the most common systems used for gasification. Two basic types of traditional fixed-bed gasifiers are up-draft (counter-current) and down-draft (co-current) gasifiers, shown in Figures 9 and 10, respectively. Both of the fixed-bed reactor types are based on natural slowly descending fuel-flow under gravity.

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. Ash falls through the grate at the bottom and 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. The bottom ash is usually completely oxidised. Due to the low temperature of the gas products leaving the gasifier, the overall energy efficiency of the process is high. In addition, up-draft gasifiers can accept raw materials with high moisture (up to 60 wt%).¹⁶²

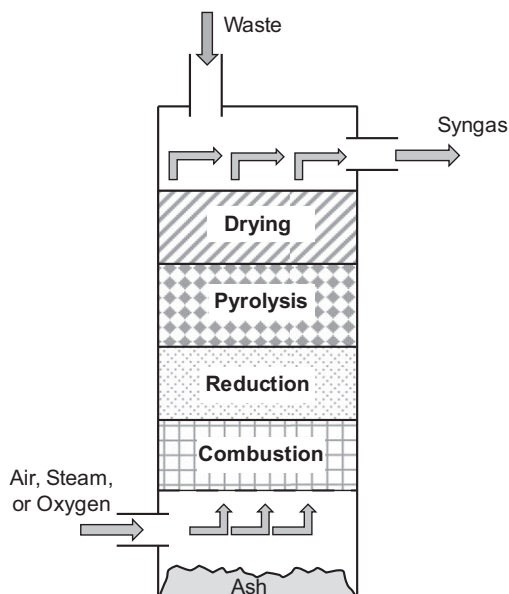


Figure 9 Up-draft fixed-bed gasification reactor.

The down-draft gasifier is one of the most widely used fixed-bed gasification systems due to the comparative low tar content in the gas outlet. In a down-draft gasifier, the feed and the gasification agent (air) move in the same direction. The volatiles from pyrolysis pass through the oxidation zone, where the tar is partially cracked. The gas products leave at the bottom with a low tar content. Because of the high temperature of gases leaving the gasifier, the overall energy efficiency is relatively lower than that of the up-draft gasifier.

Another type of fixed-bed gasifier is the cross-flow gasifier, where the gasification agent (air) is introduced from the side; the gases leave from the opposite side of the reactor at the same level. A gasification/combustion zone forms near the entrance of the air, with the pyrolysis and drying zones formed higher up in the reactor. This type of gasifier gives high tar content in the gas stream and low overall energy efficiency.

The advantages of the fixed-bed gasifier are:

- i. High carbon conversion;
- ii. High ash content feedstock possible; and
- iii. Molten slag possible.

The disadvantages of fixed-bed gasifiers are:

- i. Non-uniform temperature distribution;
- ii. Poor heat exchange;

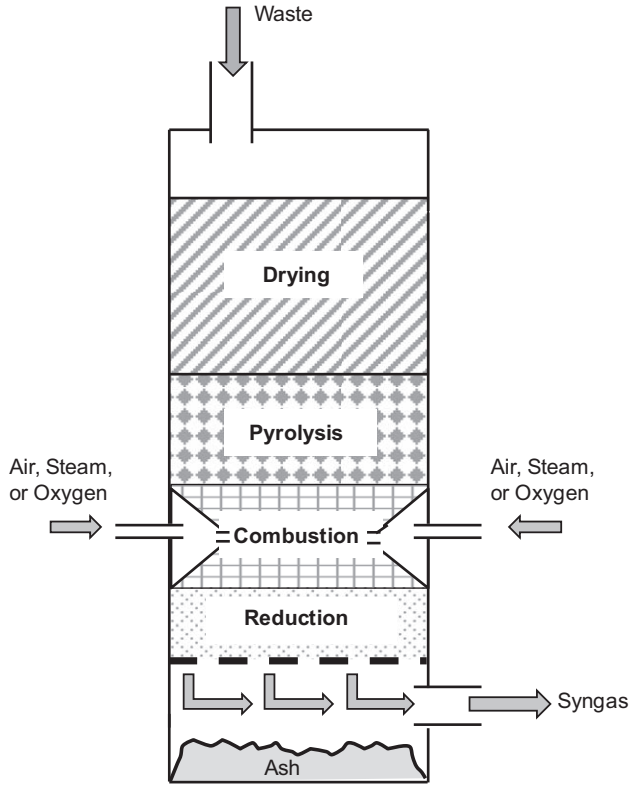


Figure 10 Down-draft fixed-bed gasification reactor.

- iii. Long periods for heat-up;
- iv. Strictly requirement of material size; and
- v. Limited scale-up potential.¹⁶³

3.3.2 Fluidised-bed Gasification. The two main types of fluidised-bed gasifier are the circulating fluidised bed and the bubbling bed. In the circulating fluidised bed, the bed materials are circulated between the gasification reactor and a cyclone separator, where the ash is removed and the bed materials return to the reactor. In the bubbling-bed gasifier, the fluidising velocity is low, and very few solids are transported out of the reactor. The advantages of fluidised beds are:

- i. Good solid contact and mixing;
- ii. Good heat-up;
- iii. Possible broad particle size distribution;
- iv. Good temperature distribution; and
- v. Low investment requirement.

The disadvantages are:

- i. High dust content in gaseous products;
- ii. Strict requirement for low ash content; and
- iii. Conflicting temperature requirement for good conversion efficiency (high temperature required) and preventing melting of ash components (low temperature required).¹⁶³

3.3.3 Entrained-flow Gasification. With entrained-flow gasifiers the feed of raw material and gasification agent (air) flow co-currently and the gasification reactions occur at temperatures high than 1000 °C. Extra gas-cooling requirements are needed for the entrained-flow gasifier compared with other types of gasifiers. In addition, the entrained-flow gasifier is more suitable for coal gasification, since significant pre-treatment is needed to generate very small particles that are very energy-intensive for materials like biomass.

3.3.4 Other Novel Gasifiers. Due to the variability in chemical composition, water and ash content, heating values and the heterogeneous nature of waste, feedstock preparation plays an important role in any thermal waste conversion process. Most of the single-stage gasifiers for solid biomass and waste can be used if the requirements placed on product gas quality are low, as is the case for direct thermal gas use, such as co-combustion of raw gas in coal boilers or use as fuel gas in a cement process. To improve the gasification process, especially for hydrogen production from thermal degradation of waste plastics, gasification of waste plastics can be separated into several stages, including separate pyrolysis and gasification units. Catalysts are commonly used in the second gasification stage to enhance reaction rate and improve hydrogen production. However, the formation of coke in the gasification process results in the deactivation of the catalyst. Generally, the coke is formed in two ways. One is during the pyrolysis stage before the catalyst bed. The other is by secondary reactions in the catalyst bed. Therefore, if the coke or soot formed during the pyrolysis of hydrocarbons can be gasified before entering the catalytic zone, coke formation on the surface of the catalyst can be reduced. However, it has been reported that gasification with steam requires high temperature (more than 900 °C) and long reaction time.¹⁶⁴ Therefore, limited amounts of oxygen can be introduced to the gasification system, since the oxidation rate is high. However, the derived volatiles might be oxidised before the removal of coke, because the reactions between oxygen and volatiles are much faster than soot gasification. Therefore, the basic idea is to separate the oxygen oxidation of soot from the steam gasification of volatiles. Hayashi *et al.*¹⁶⁴ presented the basic concept for the rapid and complete conversion of solid fuel at low temperatures. This separates the oxygen oxidation from the steam gasification reactions and the O₂ oxidation reportedly reduces the coke or soot formation.

A 100 kW two-stage gasifier was designed by the Technical University of Denmark for the purpose of reducing tar content in the product gas.¹⁶⁴

The two-stage gasifier consists of a pyrolysis unit and a gasification unit. Air is injected between these two units for partial oxidation of the volatile pyrolysis products. Gas products pass through a charcoal bed and leave the reactor. The system gives low tar-gas products. A novel air-gasification process was reported by Cao *et al.*¹³¹ The two-stage gasifier is a combination of a fluidised bed and a separate tar decomposer with the partial recirculation of fuel gas to maintain a suitable temperature. Secondary air is injected for the complete combustion of the circulating fuel gas. A moving-bed gasifier has been reported by Susanto *et al.*¹⁶⁵ In the moving-bed gasifier, part of the pyrolysis gas was drawn into a separated combustion stage and the generated flue gases were recycled to the pyrolysis process; therefore, heat transfer was found to be greatly improved and a more complete pyrolysis of solid feedstock was obtained. In addition, a modified down-draft gasifier, using oxygen–steam as the gasification agent instead of air/steam, has also been reported by Lv *et al.*¹⁶⁶

3.4 Examples of Commercial and Semi-commercial Gasification Systems

A number of gasification companies have developed plants for commercial and semi-commercial gasification of biomass and wastes.^{167–173} Examples are shown in Table 11.

Table 11 Examples of commercial and semi-commercial plants for biomass and waste gasification.

<i>Company</i>	<i>Location</i>	<i>Reactor Type</i>	<i>Feedstock</i>	<i>Output</i>	<i>Capacity</i>
Vienna University of Technology	Guessing, Austria	circulating fluidised bed	biomass	heat & power	8 MW
Xylowatt, Belgium	Gedinne, Belgium	down-draft	wood chips	heat & power	-
ITI Energy Ltd, UK	Teeside, UK	cross-draft	solid waste recovered fuel	power	6.86 MW
Host, Netherlands	Santiago de Besteiros, Portugal	circulating fluidised bed	chicken manure and forestry waste	heat & power	5 MW
Host, Netherlands	Galati, Romania	circulating fluidised bed	biomass	heat	4.5 MW
Gas Technology Institute, USA	Skive, Denmark	fluidised bed	wood	heat & power	12 MW
Energem Technologies, Canada	Alberta, Canada	fluidised bed	MSW	syngas, bioethanol	-
Ebara, Japan	Skata, Japan	fluidised bed	MSW	heat & power	2 MW
Ebara, Japan	Kawaguchi, Japan	fluidised bed	MSW	heat & power	12 MW

MSW = Municipal Solid Waste.

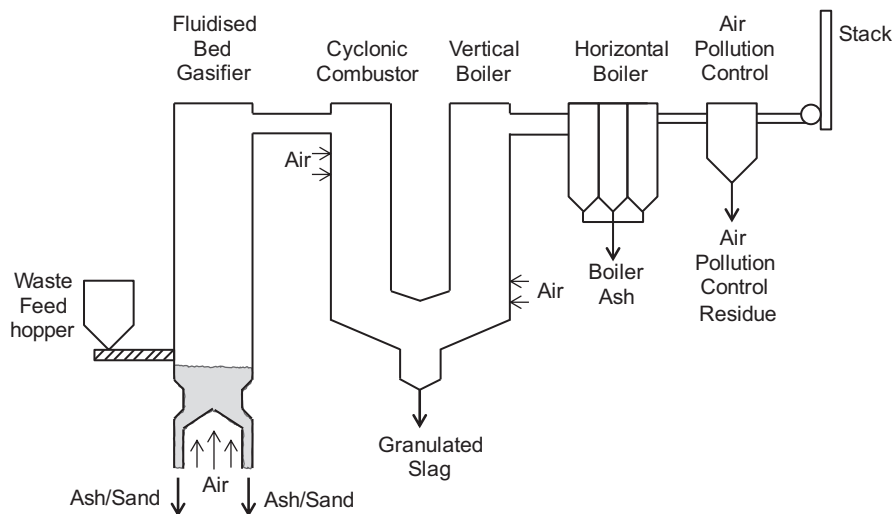


Figure 11 Schematic diagram of the Ebara TwinRec gasification system.^{174–176}

Figure 11 shows an example of a large-scale commercial gasifier: 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 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 combustion chamber 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.

Combined pyrolysis–gasification plants exist, notably the Thermostelect system (see Figure 12), with several plants operating in Japan utilising industrial wastes and municipal solid waste.

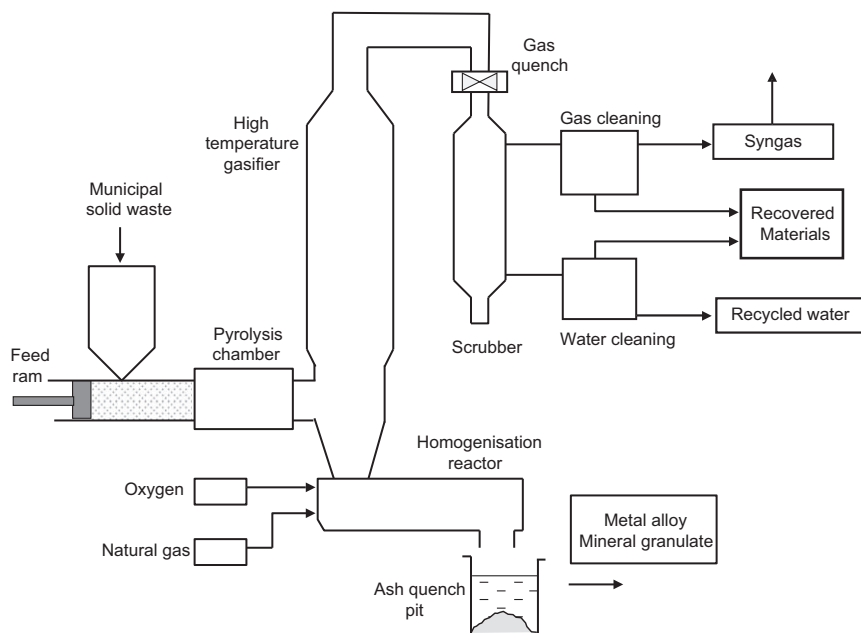


Figure 12 The combined pyrolysis-gasification Thermoselect system.^{177,178}

For the Thermoselect process, untreated waste is compacted at high pressure to 10% of its original volume to form plugs of waste devoid of most of the air; these are then fed to the pyrolysis reactor, which is heated indirectly at 600 °C. The resultant organic pyrolysis gases, vapours and char are fed to a high-temperature gasification chamber, operated at approximately 1200 °C, with oxygen as the gasifying agent. The product synthesis gas is shock-quenched to 90 °C and undergoes several cleaning steps to produce a clean gas suitable for use as a chemical feedstock or for energy recovery applications. At the base of the gasification reactor, temperatures of 2000 °C produce melting of the metal and mineral components of the waste. The liquid melt flows to a homogenisation chamber at 1600 °C where sufficient residence time allows the separation of two phases: a metal alloy and a mineral phase. Rapid quenching of the melt produces a granulate mineral material for use as aggregate in road building and construction, and a metal alloy for recovery of metals. Other products recovered are sulfur from the gas-cleaning process, zinc and lead concentrate, sodium chloride and purified water from the water-treatment process.

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