

Chapter 2

Gasification of Waste Derived Fuels in Fluidized Beds: Fundamental Aspects and Industrial Challenges

Fluidised beds are the most popular technologies for gasification as they are considered to be more robust and versatile than other more conventional reactors. Most of the commercial fluid bed gasifiers (FBG) were originally developed for operation coal and/or pure biomass. The translation of the systems to operation on waste is the issue which represents the most significant technical difficulty, and from this cascade particular concerns regarding the ability to achieve long term stable operation, as well as wider confidence in commercial viability. The purpose of this Chapter is to appraise the fluidized bed gasification systems in light of the exotic characteristics of alternative fuels derived from waste materials. Given the technology's heritage there is extensive technical information available regarding the modus operandi of fluidized bed reactors. However, given the relatively limited track record of operation on waste, this depth of information is helpful in appraising the expected performance of a waste-fed fluid bed system and the technical issues associated therein.

In meeting this aim, the analysis is structured in four parts:

- Waste fuel characterization;
- Process overview on fluidized bed gasification;
- Ash behaviour and agglomeration issues;
- Tar formation and reduction measures.

A summary of key points from the appraisal is also provided at the end. By definition many of the observations herein presented are judgements made by the Author, matured in 4 years of direct experience of operating thermal waste treatment facilities (including fluid bed systems), and backed up where possible by specific references to the literature. All photos in this appraisal were taken by the Author during his staying on plant, unless stated otherwise.

2.1 Fuel Characterization

The overall focus of this study is the use of solid waste as a gasification feedstock.

Waste fuels are derived from a number of sources, in turn destined for various handling, processing and disposal routes. This creates a complex mix of materials characteristic to each original waste stream—the arisings and composition of which are influenced by a wide range of factors. The composition of the waste feedstock, and properties therein, has a major bearing on the performance of a fluidized bed gasifier in terms of energy conversion and environmental emissions. This is especially true for a heterogeneous MSW-type feed—varying in the type, format and relative quantity of component materials. Understanding the properties and composition of feed is therefore the first step to understand the process.

This section looks at the waste feed on a macro-material basis. This provides a foundation for a more in-depth micro-elemental perspective in later sections. From the overall review the inter-connection between these perspectives and the role they play in fluidized bed gasification will become apparent.

2.1.1 Fuel Preparation

Before energy can be extracted systematically from the waste, the base material has to be sorted into its different fractions (combustibles, ferrous and non-ferrous metals, glass and unclassifieds) through mechanical or mechanical-biological processing. The recovered fraction of higher calorific value material is known as refuse derived fuel (RDF). This refuse material has been used for providing heat and power to a diverse range of industries from paper mills to cement production to power generators (Shibagaki and Nishiyama 1999; Mokrzycki and Uliasz-Bochenczyk 2003).

This thesis refers as consistently as possible to RDF gasification in general as ‘waste gasification’. It must be noted, however, that is not the original waste (e.g. MSW) that is treated, but the RDF which is a derivative product. According to the ASTM standard (2006), RDF is a shredded fuel derived from solid waste which most of metal, glass and other inorganic materials have been removed and has particle size 95 wt% passes through a 5 cm² mesh screen. In the UK this term is generally reserved for the processed paper, card, wood and plastic fractions of municipal, commercial or industrial wastes (Gendebien et al. 2003). As such, RDF can contain a wide range of plastics, fibre, textiles, putrescible materials, rubber, metallic components, ceramics and dusts, which complicate its classification (Fig. 2.1).

The transformation process from the base material to the final RDF consists in general of:

- Separation at source;
- Sorting or mechanical separation;
- Size reduction (shredding, chipping and milling);



Fig. 2.1 Refuse derived fuel (RDF)

- Separation and screening;
- Drying and pelletising (optional);
- Packaging and storage.

Typically, the waste material is screened to remove the majority of the recyclable fraction (e.g. metals), the inert fractions (such as glass) and separate the fine wet putrescible fraction (e.g. food and garden waste) containing high moisture and high ash material before being shredded. The wet organic materials can then undergo further treatment such as composting or anaerobic digestion, and can be used as a soil conditioner for landfill restoration work or be landfilled (Gendebien et al. 2003). In some cases, the putrescible fraction is kept in place to enable the mass of material to be dried through biological treatment (the process of ‘dry stabilisation’). The coarse fraction is either rejected or returned to the shredder. The medium fraction, consisting of paper, card, wood, plastic and textiles can either be gasified directly as coarse fuel (floc form) or dried and pelletised into dense RDF (d-RDF). The decision as to whether or not to pelletise is usually based upon the technology used for gasification (i.e. bubbling fluid bed, circulated fluid bed, etc.), and location of the RDF manufacturing facility relative to the gasification facility.

Size reduction and pre-processing of the waste is expensive from an energy and maintenance standpoint and should generally be kept to the minimum required to meet recycling objectives. Diaz and Savage (2007) reported that drying and pelletizing are liable to be expensive in terms of energy usage (~ 85 kWh/t), die wear, and so on. Moreover, the optimum route has not yet been determined; hence a degree of uncertainty is involved in installing a process line (Haley 1990).

The quantity and quality of RDF produced per tonne of waste varies depending on the type of collection, treatment process and quality requirement. Caputo and Pelagagge (2001) reported that, in the conversion of waste to a refuse derived fuel, the yield of recovered fuel decreases markedly with increased quality of the prepared fuel. For example, from a raw MSW feed of 9.2 MJ/kg and 35 % moisture, the recovered energy content is close to 100 % when producing a relatively crude RDF with an net calorific value (NCV) of 15 MJ/kg and <15 % moisture. This falls

to ~80 % when producing a higher (cement) grade RDF or solid recovered fuel (SRF); e.g. NCV 18–20 MJ/kg and <15 % moisture. Furthermore, producing a more refined fuel means also co-producing a stream which is not usable as a fuel due to the poor quality, and therefore destined to be landfilled. Therefore, in order to effectively plan waste treatment activities it is important to assess under which technical conditions a waste pre-treatment plant may be able to produce a RDF that meets the prescribed quality standards and the economic feasibility.

2.1.2 Component Materials

As stated before, wastes are generally made up of numerous different materials. A standard list of these and their categorisation (in line with Defra (2004) guidance) for a generic MSW is presented in Table 2.1. An indication of those materials contributing to its biodegradable, recyclable and combustible content is also provided. In this list there are 15 primary and 48 secondary material categories, which in turn may accommodate numerous related materials. Other materials may include plastics and paper from commercial and industrial activities (i.e. packaging waste or rejects from manufacturing), waste tyres, biomass waste (i.e. straw, untreated waste wood, dried sewage sludge), waste textiles, residues from car dismantling operations (automotive shredder residues—ASR) and hazardous industrial wastes with high calorific value, for example, waste oils, industrial sludge, impregnated sawdust and spent solvents (WRc report 2003). This illustrates the extent to which the composition of solid wastes and hence properties of RDF can vary.

The waste stream also contains a number of composite materials, for example drinks cartons (i.e. card body with plastic and other coatings), waste electrical and electronic equipment (WEEE) (i.e. plastics casing, metal frame, and electrical and mechanical components made from numerous different materials) and furniture (i.e. wooden frame, metal springs, synthetic foam and textiles etc.). Such materials are difficult to recycle and predominantly end up in the residual waste stream. Domestic or household hazardous waste (HHW) is another heterogeneous material category comprising of various composite materials. Both WEEE and HHW are likely to contain trace amounts of hazardous compounds (for example, lead, mercury, paints and pesticide) that could pose plant, operational and environmental risks.

From the above one can appreciate the challenging in trying to accurately characterise RDF and in turn, the influence this has on fluid bed gasification.

2.1.3 Organic Content

As with most material, many of the compounds contained within the waste component materials have an organic content. ‘Organic’ is a catch-all term for substances containing carbon. This includes matter: derived from once-living

Table 2.1 Categorisation of the materials which constitute MSW

Material categories		Biomass content		Recycling/composting		Energy recovery	
Primary	Secondary	Biomass	Bio-degradable	Potentially compostable	Potentially recyclable	Combustible	Renewable
Paper	Newspapers	y	100	~	y	y	y
	Magazines	y	100	~	y	y	y
	Other recyclable paper	y	100	~	y	y	y
	Paper packaging	y	100	~	~	y	y
	Non-recyclable paper	y	100	~		y	y
Card	Card packaging	y	100	~	y	y	y
	Board packaging	y	100	~	y	y	y
	Liquid cartons	y	100	~	y	y	y
	Other card	y	100	~		y	y
	Bottles				y	y	x
Dense plastic	Other packaging				y	y	x
	Other					y	x
	Packaging film				y	y	x
Plastic film	Other					y	x
	Textiles	~	50		~	y	~
Glass	Shoes	~	50		~	y	~
	Bottles				y		
	Jars				y		
	Other						

(continued)

Table 2.1 (continued)

Material categories		Biomass content		Recycling/composting		Energy recovery	
Primary	Secondary	Biomass	Bio-degradable	Potentially compostable	Potentially recyclable	Combustible	Renewable
Misc combustible	Treated wood	y	100			y	y
	Untreated wood	y	100	~	y	y	y
	Furniture	~	50		~	y	~
	Disposable nappies	~	50*			y	~
	Carpet and underlay	~	50*			y	~
	Other	~	50*			y	~
Misc non-combustible	Construction and demolition				y		
	Other						
Ferrous metal	Food containers				y		
	Beverage cans				y		
	Other				~		
Non-ferrous metal	Food containers				y		
	Beverage cans				y		
	Other				~		
WEEE	White goods				~	~	x
	Large electronic goods				~	~	x
	TV's and monitors				~	~	x
	Other				~	~	x
	Household batteries						
HHW	Car batteries						
	Engine oil					~	x
	Identifiable clinical waste	~				~	~

(continued)

Table 2.1 (continued)

Material categories		Biomass content		Recycling/composting		Energy recovery	
Primary	Secondary	Biomass	Bio-degradable	Potentially compostable	Potentially recyclable	Combustible	Renewable
	Other potentially hazardous					~	x
Organic catering	Home compostable kitchen waste	y	100	y	y	y	y
	Non-home compostable kitchen waste	y	100	y	y	y	y
	Garden waste	y	100	y	y	y	y
Organic non-catering	Soil	~					
	Other organic	y	100			y	y
Fines	Fines (<10 mm)	~	50*	~		~	~

Source Material categories adapted from Defra (2004)
Note Biodegradable content factors based on English and Scottish Regulations (E/S) and EA Guidance (WRAP 2010); *EA list includes additional materials; ~ possibly/partially

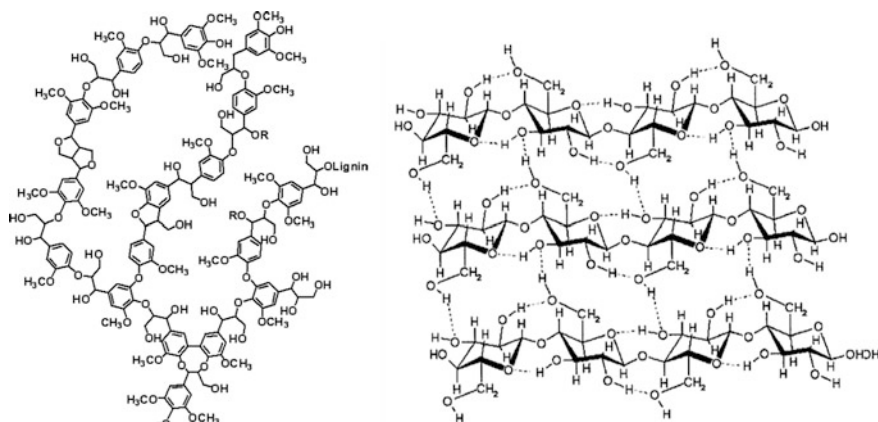


Fig. 2.2 Molecular structure of lignin (*left*) and cellulose (*right*)

organisms; capable or the product of decay; or composed of organic compounds. Tchobanoglous (2003) notes that, in addition to plastics, rubber and leather, the organic content of RDF includes: water soluble constituents (i.e. sugars, starches, acids), hemicellulose, cellulose, fats, oils and waxes; lignin, lignocellulose, and proteins.

The biomass and biodegradable content of RDF is important since, further to defining the biogenic fraction of the waste (i.e. fraction that does not contribute to GHG emissions), can result in harmful emissions when thermally treated (devolatilization products). In fact, the complex chemical structure of the parent substrate is likely to reflect in the gas products, which maintain a large portion of the same organic functional groups. For example, lignin represents a potential precursor for polycyclic aromatic hydrocarbons (PAH) formation, due to the aromatic nature of this polymer (Bai et al. 2014) (Fig. 2.2).

In a similar manner, the organic sulphur content is also reflected in the devolatilising products. Struis et al. (2008) reported the presence of organic disulfide, methylthiol and organic sulfonate or organic sulfate in samples of Norway spruce, both in the sap and heartwood, but in different concentrations. When thermally treated these compounds are normally released as H_2S , COS, thiophenes, thiols and mercaptans, all of which are extremely dangerous for the plant, due to corrosion and catalyst poisoning issues.

2.1.4 Ash Content and Composition

The chemical composition of RDF ash is described in terms of the alkali and alkaline earth metals contents (Ollila et al. 2006). Ash analysis tends to be reported in terms of oxides (wt%), in spite of the constituents not occurring as oxides.

Alkali metals are important elements in the ash fraction, and are found in waste-derived fuels as organically-bound sodium (Na) and potassium (K) and salts, such as chlorides (e.g. NaCl, KCl, etc.) and alumino-silicates, dispersed in the mineral phase. A large fraction of the inherent inorganic material in RDF, and probably the dominant fraction in the ashes, is associated with oxygen-containing functional groups (K_2O and Na_2O). Knowing the alkali metals content is important since these components are commonly associated with fouling deposits in gasification plants, resulting from the vaporisation and subsequent condensation on heat transfer surfaces that can trap fly ash particles and elutriated material. The most important factor that influences the nature of these deposits is the mode of occurrence of alkali in RDF and the extent to which competing reactions with other mineral species can reduce the alkali volatility (see Sect. 2.3.3). In addition, the alkalis are fluxing agents that can form low melting point eutectics in the thermal process, limiting the temperature of operation of the gasifier to around 800–850 °C. This operational limit is necessary to avoid clinkering and deposition of material, causing significant and expensive disruptions of the plant.

Alkaline earth metals (mainly calcium and magnesium) are the other main components of RDF ashes. They are known to occur in the RDF primarily as carbonates and under local oxidative conditions are expected to decompose to the oxides, which can then react with sulphur and chlorine gases. For this reason, alkali and alkaline earth metals have been largely used in the incineration industry as additives to increase the acid gas control (Broström 2010). Another class of contaminants present in the inorganic fraction consists of heavy metals, i.e. those elements with a density of approx. 5000 kg/m³ or higher, such as Cd, Pb, Hg, Zn and Cu. These constituents are usually expressed as mg/kg ash. They occur normally in RDF, being originated from small residual metal pieces, solder, plasticisers and paints present in waste-derived fuels. These elements may pose a threat to the environment or to human health by dispersion in the atmosphere or leaching from the solid residues.

2.1.5 Moisture Content

Moisture in RDF is stored both on the surface and within the porous structure, i.e. in the spaces within the dead cells and within the cell walls. When the fuel is dried the stored moisture equilibrates with the ambient relative humidity. Equilibrium is usually about 20 % in air dried fuel (Demirbaş 2001). Moisture percentage of RDF varies from 10 to 30 %, depending on the fuel preparation process. Heating value of RDF decreases with increasing of moisture content of the fuel.

2.1.6 Element Content

Both the chemical and the physical composition of RDF are important determining factors in the characteristics of gasification. RDF can be analyzed by breaking it down into structural components (called proximate analysis) or into chemical elements (called ultimate analysis).

2.1.6.1 Ultimate Analysis

Ultimate analysis (UA) reports both the elemental (including the C, H, O, N, S and sometimes Cl) and ash content of solid waste material on a mass percentage basis (wt%). Carbon, hydrogen and oxygen are the main elements contributing to the material's heating value (Niessen 2002). Nitrogen in contrast, is a minor contributor; however, it is responsible for NO_x generation during partial combustion. Sulphur and chlorine (i.e. organic and inorganic species) arise in smaller amounts still, yet they can be problematic, producing acid gas (i.e. H₂S and HCl) leading to plant corrosion and pollutant atmospheric emissions.

The occurrence of various elements in the RDF feed will depend on the elemental content (i.e. UA) associated with each component material in the original MSW (Table 2.2). From the ultimate analysis data presented in Table 2.2 it is apparent that carbon is the most prominent fuel element amongst RDF component materials (i.e. ~48 wt% on average for combustible components—dry, Cl-free basis), apart from metals and materials with a high ash content (for example, glass and other non-combustibles). Fossil fuel based materials such as plastics have especially high carbon content (at ~66 %). Oxygen at ~31 % is the next most prominent. This is especially true in cellulose-based materials (paper for example). Apart from non-combustibles, the hydrogen content of most component materials is ~7 %. Nitrogen is also found in small amounts (~1 %).

Materials with a high protein content (which contains up to 16 % nitrogen), food waste for example, are one source of nitrogen. Chloride and sulphur are lower still at 1.3 and ~0.2 %. Dense plastics, which include PVC, are shown to have a higher Cl content. Plant and animal derived material will contain sulphur sequestered naturally from the environment. Manmade sources include materials such as rubber which has sulphur added to aid vulcanisation.

2.1.6.2 Proximate Analysis

Proximate analysis (PA) includes the feedstock's moisture, combustible (including volatile combustible matter (i.e. gases and vapours driven off during pyrolysis) and fixed carbon) and ash content (see Table 2.2). The moisture content is assessed by recording the material's weight loss when it is heated to 105 °C for one hour (i.e. due to volatilisation of water and other compounds). Volatile combustible matter

Table 2.2 Analysis of raw waste and associated RDF material

Material composition	MSW wt%	RDF ^a					RDF ultimate analysis (wt%, dry basis)					Nitrogen	Sulphur	Chlorine	Ash
		wt%	Carbon	Hydrogen	Oxygen										
Paper	9.67	11.26	45.86	5.62	34.55						0.45	0.10		0.29	13.13
Card	7.14	10.9	55.14	6.52	30.79						0.34	0.12		0.32	6.77
Dense plastic	9.51	8.03	72.24	7.94	6.38						2.64	0.15		2.98	7.67
Plastic film	18.94	33.18	74.76	12.31	2.70						0.67	0.56		0.54	8.45
Textiles	4.35	9.88	57.64	5.89	22.95						1.58	0.61		0.09	11.25
Misc. combustibles	5.12	5.79	59.46	9.76	21.99						1.30	0.19		0.11	7.20
Glass	4.61	3.76	0.40	0.11	0.72						0.09	0.03		0.13	98.52
Misc. non-comb.	9.67	0.84	7.40	0.41	4.23						0.20	0.56		0.22	86.98
Ferrous metal	2.34	0.2	4.50	0.60	4.30						0.10	0.00		0.00	90.50
Non-ferrous metal	2.34	0.24	4.50	0.60	4.10						0.10	0.20		0.00	90.50
Organic catering	4.82	5.24	60.33	8.05	25.10						0.75	0.80		0.80	4.99
Organic non-cat.	5.4	9.04	45.30	7.42	20.24						2.02	0.68		0.15	24.18
Batteries	1.73	0	29.33	4.61	9.90						0.61	0.84		0.34	54.36
WEEE	3.37	0	19.93	2.56	5.71						0.30	0.15		2.27	69.08
Fines (<10 mm)	10.98	1.64	23.29	2.69	37.18						1.64	0.38		0.25	34.58
Total	100.00	100.00													
RDF weighted ultimate analysis (wt%, dry basis)			58.65	8.35	16.03						1.00	0.40		0.52	15.01
RDF proximate analysis (wt%) ^b		Moisture		Volatile matter	Fixed carbon						Ash	Gross CV (MJ/kg)		Net CV (MJ/kg)	
		5.9		70	11.2						12.9	26.95		24.82	

^aThe RDF preparation process included metal removal, shredding and rapid drying; ^b as received

refers to the additional loss in weight (i.e. exclusive of moisture) when the material is ignited at 950 °C inside a covered crucible. Fixed carbon refers to the combustible material remaining after the volatile matter has been removed. In turn, ash is that material remaining after combustion in an open crucible (i.e. representing the non-combustible content).

Looking at the proximate analysis data, the volatile matter content is high for most waste components, paper-based materials in particular—56 % on average from the data presented here. Plastics tend to have an even higher volatiles content, 69 % in this instance. Materials within organic catering and non-catering categories have a high moisture content (60 % on average). In contrast, glass and metals are reported to contribute to ash almost entirely (~98 %). Non-combustibles have a similarly high ash content (82.42 %). Fillers used in magazine stock paper, some plastics and other materials also contribute ash.

Heating values for the various component materials rise and fall depending on their volatiles, and moisture and ash contents respectively. ‘Other dense plastics’, for example, with high volatiles and low moisture and ash content report a gross calorific value of 27.9 MJ/kg. On the other hand, home-compostable kitchen waste, with a moisture content of 78.29 %, has a calorific value of only 4.17 MJ/kg—similar to fines at 4.83 MJ/kg, containing as it does, significant amounts of both moisture and ash.

2.1.7 The Energy Value of RDF

The most important characteristic of a fuel is its calorific value (CV) or heating value (HV)—referring to the amount of energy (MJ or kJ) it contains per unit of mass (kg).

For a multi-component feedstock such as RDF, the overall CV depends on the CV and relative amount of individual component materials therein. For example, a large plastics content (with a high CV of 40 MJ/kg) will increase the overall HV (Marsh et al. 2007). The volatile, ash and moisture content will also vary depending on waste source (Fig. 2.3). A plastic-rich commercial waste feedstock would generate a large volume of combustible volatiles, low moisture and low ash. Moisture and ash in the fuel reduce the CV. This is apparent in feedstocks which contain a lot of food (i.e. high moisture), paper (i.e. high ash) and plastics with a high filler content (i.e. generating ash). As stated in Sect. 2.1.1, the yield of recovered fuel decreases markedly with increased HV of the prepared fuel. A performance improvement may be attempted by adding high HV material (e.g. tyre scrap) to the blend mix. Caputo and Pelagagge (2002) reported that an input waste mix containing 10 % of scrap tyres (or high HV plastics) greatly improve the quality of the RDF in terms of heating value, even when high RDF recovery options were selected.

Overall, the energy density of the waste is rather low when compared to other fuels; for example, in the UK the energy content of RDF is around 10 MJ/kg which

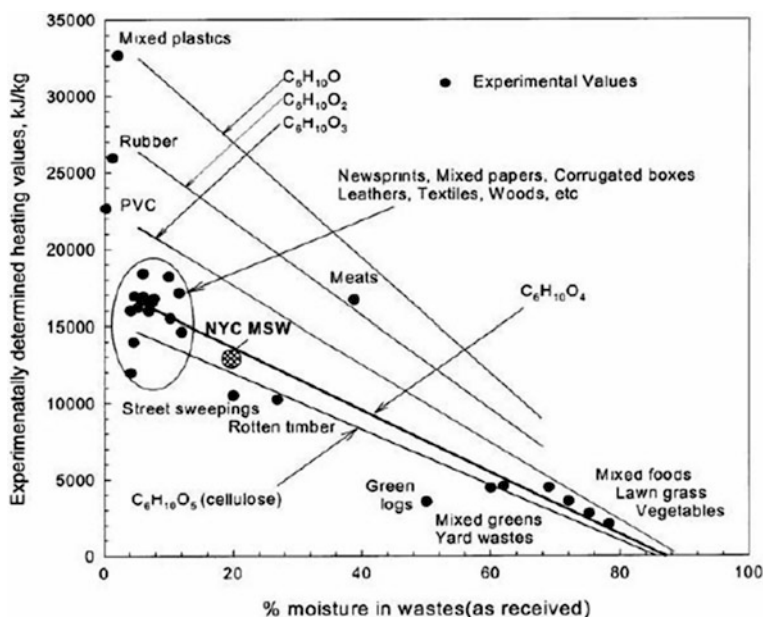


Fig. 2.3 Effect of constituents and moisture on calorific value of MSW (Themelis 2006)

compares with $\sim 23\text{--}35$ MJ/kg for coal and $14\text{--}21$ MJ/kg for dried biomass (see Table 2.3 in next Section).

2.1.8 Preliminary Considerations Based on Fuel Characterization

Historically, fluid bed gasification has centred on the utilisation of fossil fuels and, to a lesser extent, biomass, although it is widely recognised that gasification of solid waste containing biomass has a significant and growing potential for the future offering a more energy efficient, lower environmental impact alternative to fluid bed incineration (Demirbaş 2001). However, RDF has properties which make it very different from coal or biomass. These are summarised and compared in Table 2.3.

The interrelated effects of these differences are summarised below, and must be recognised when developing an efficient and reliable process for the gasification of waste streams:

- RDF is very heterogeneous in nature and contains high levels of ash and moisture.
- The composition and properties of a waste derived fuel are potentially definable; however, variations will occur depending on processing (size reduction,

Table 2.3 Physical, chemical and fuel properties of biomass, coal and RDF

Property	Biomass	Coal	RDF
Fuel density (kg/m ³)	~ 500	~ 1300	100–200
Particle size (mm)	3–10	~ 100	5–200
<i>Proximate analysis (% dry fuel)</i>			
Fixed carbon	16–19	70–80	1–6
Volatile matter	75–80	10–20	70–90
Ash	3–7	2–4	20–30
<i>Ultimate analysis (% dry fuel)</i>			
C	42–54	65–85	30–40
H	5–6	3–5	3–7
O	35–45	2–10	5–30
N	0.2–0.8	1–2	0.2–2.0
S	0.0–0.1	0.5–7.5	0.1–0.6
Cl	0.0–0.1	0.1–0.3	0.1–0.65
<i>Elemental composition of ash (%)</i>			
SiO ₂	23–49	40–60	30–40
K ₂ O	4–48	2–6	0.2–10
Al ₂ O ₃	2.4–9.5	15–25	10–20
Fe ₂ O ₃	3.4–7.5	15.5–20.0	5.0–15
CaO	10–30	5–10	14–30
Na ₂ O	1.5–6.5	0.5–1.5	1.0–4.0
Ignition temperature (K)	418–426	490–595	400–420
Friability	Low	High	High
HHV (MJ/kg)	14–21	23–35	9–15

Source Demirbaş (2001), Jenkins et al. (1998)

compaction and drying, etc.) origin, season, weather and storage duration. Therefore plant design must be based on a median definition, whilst including contingency for expected excursions.

- RDF may contain residual recoverable materials including ferrous and non ferrous metals, dense plastics and glass.
- Size reduction and pre-processing of RDF is expensive from an energy and maintenance standpoint and should generally be kept to the minimum required to meet recycling objectives.
- The energy density (i.e. heating value) of RDF is low compared to other fuels.
- RDF is likely to contain substances in varying quantities in the ash-forming fraction which can form low melting point eutectics in the thermal process (see Sect. 3.4 for further details).

- Secondary streams generated in RDF preparation processes may contain high levels of organic and heavy metal pollutants and are expensive to dispose of at permitted hazardous waste sites.
- The RDF feed contains a number of regulated pollutants and the cost and complexity of the plant is strongly influenced by the gas cleaning requirements.

New generation fluid bed gasifiers have been developed to specifically address the above issues, to provide an efficient and reliable techno-economic solution for the gasification of waste streams. Extensive experimental investigation has been carried out to date on the feasibility and performance of the fluidized bed gasification of different alternative fuels (Arena et al. 2010; Chirone et al. 2004; Barea and Thunman 2007). However, fundamental work on the comprehension of the basic mechanisms taking place during conversion of RDF has received comparatively less attention.

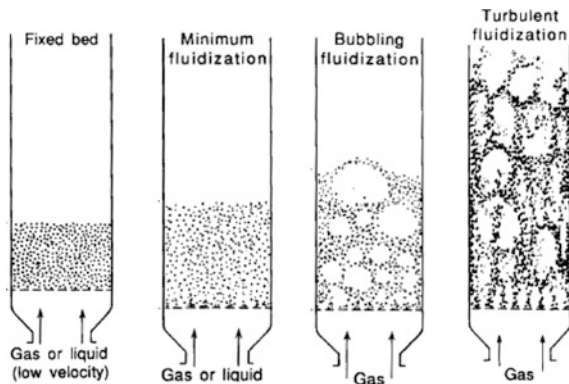
2.2 Fluidized Bed Gasification: Process Overview

The fluidized bed gasification of solid fuels is a complex process that includes a number of physical and chemical interactions that occur in series-parallel at temperatures typically higher than 550 °C. Furthermore, the different modes of fluidization, regime transition, fluid-mechanical simulation and fluid-particle interaction complicate the analysis. Before proceeding to explain the phenomena that occur within the gasifier, the fundamental technology of fluidized beds must be introduced.

Kunii and Levenspiel (1991) defined fluidization as the “*operation by which solid particles are transformed into a fluid-like state through suspension in a gas or liquid*”. More specifically, when the drag force created by an upward gas flow through a packed bed of free flowing particles equals the buoyant weight of the bed, the particles become suspended within the upward gas flow. The bed is then considered to be at minimum (or incipient) fluidisation and the upward gas velocity is called the ‘minimum fluidisation velocity’ (U_{mf}). Any further increase in the gas flow rate above U_{mf} , may (depending on the size of particles under consideration) result in the formation of bubbles rising through the bed of particles. At this stage, the particles take on the characteristics of a boiling fluid, and the bed is considered in a ‘bubbling’ state (Fig. 2.4).

The upwards and sideways coalescing movement of these bubbles provides intense agitation and mixing of the bed particles, which make fluid beds ideal for applications where high mass and heat transfer rates are required (like in combustion or gasification). In such systems (i.e. combustors or gasifiers), the particles are initially heated to above the ignition temperature of the fuel to be burned and then combustion or gasification takes place when the fuel is delivered into or onto

Fig. 2.4 Gas-solid fluidization regimes. Adapted from Kunii and Levenspiel (1968)



the heated fluidised particles. The fuel burns (completely or partly) by virtue of the oxygen within the fluidising gas (air, oxygen, steam-oxygen or enriched-oxygen air), which is delivered by a fan (or blower) through the distributor plate and upwards through the bed particles. During steady-state operation, temperature is controlled by the opposing effects of the heat input from the burning char in the bed, versus outgoing heat in the devolatilised gases and further heat ‘consumed’ by endothermic reactions in the gas-phase (e.g. steam reforming, water gas-steam carbon, etc.). The extent of exothermic reactions is determined by the equivalence ratio (ER, the amount of air/oxygen added relative to the amount of air/oxygen required for stoichiometric combustion).

Various refractory materials can be used to form the original ‘bed’ of particles, the most convenient being graded sand, around 1 mm in mean diameter, enabling fluidising velocities in the range 1–3 m/s. Alternatively, graded limestone or dolomite can be used if sulphur capture and, or, tar reforming are required (see Sect. 2.4.5).

The producer gas, or ‘syngas’, leaving the freeboard is then forced to flow through a cyclone to separate part of the elutriated material (e.g. fly ash, unreacted char, bed particles, etc.), and cooled to (say) 200 °C before going through the gas cleaning.

Making a technical survey of fluidized bed gasification involves the analysis of several other phenomena, which include:

- Materials in-feeding
- Heating and drying
- Devolatilization and volatile conversion
- Char conversion
- Particle attrition and elutriation

A more detailed description of the process in a fluid bed gasifier follows below.

2.2.1 Material in-Feeding

Fuel feeding in bubbling FBG is one of the basic problems that has to be solved in order to achieve efficient conversion. Poor mixing of inert bed particles and fuel in horizontal direction, and short fuel particle residence time are two of the main drawbacks reported for bubbling fluidization at large scale (Gómez-Barea and Leckner 2010). In this sense, the way in which waste fuel is injected to the FBG is a very critical point.

In-bed fuel feeding has been the first and most employed feeding system for fluidized bed coal boilers in the past. Fuel is crushed to a size of ~ 5 mm, and dried to ensure moisture content not higher than 6–8 %, prior to transport and feeding (Oka 2004). Material is fed into the vicinity of the distributor plate from hoppers, connected to screw augers via a rotary valve or a pneumatic conveying system, with slight nitrogen over-pressure to stop back feeding of producer gas and bed material through the in-feed. The basic advantage of this type of fuel feeding is the large residence time of fuel particles in the bed and higher conversion efficiency. However, with operation on waste, the following issues are of concern:

- If the gasifier runs at greater than atmospheric pressure, there is potential for migration or leakage of hot gas into the fuel feed mechanism.
- RDF is heterogeneous, both in composition and morphology. Bridging in hoppers and blocking of screw feeds are common issues with RDF. Vreugdenhi (2010) reports that bridging in the feeding line was the main cause that resulted in abandoning pure RDF feeding in circulated fluidized bed gasifiers. Blockages may also be caused by large inerts in RDF. Drying and pelletisation are common techniques to provide a more homogeneous fuel form to aid feeding, and also by definition remove any large inerts above the pellet size. However this comes at high costs and energy penalties.
- The high levels of volatiles, especially plastics in RDF are likely to lead to rapid devolatilisation at the base of the gasifier, on contact with the hot bed material. This could exacerbate the issue of gas transport back up the in-feed and could lead to melting of the feed in the auger and exacerbate risk of blockages.

A different option is to inject the fuel directly *over-bed* by means of screw feeders. These feeding devices were also developed for conventional fluid bed combustor boilers, and have been successfully applied in fluid bed gasification. A general advantage of over-bed feeding systems is the possibility of feeding moist and gross RDFs “as received”, with a particle range between 0 and 50 mm, although is recommended that percentage of particles smaller than 0.5 mm should not be higher than 10 % for this types of systems (Oka 2004). The deficiencies of this type of feeding are its limits in terms of the need to specify a particular particle size range and the likelihood of elutriation of small particles and their subsequent conversion above the bed (rather than inside the bed). A further general deficiency of this type of system is the requirement for recycling/disposal of unreacted fuel particle, given the high elutriation losses that are likely to be experienced (see Sect. 2.2.5).

2.2.2 Heating and Drying

Firstly, when a fuel particle is injected into a hot fluidized bed it begins to rise in temperature, dry, and eventually to shrink. This process can also start before the actual injection into the hot reactor. Heating and drying occur in a very few seconds at temperatures up to about 160 °C, as a combination of events that involve liquid water, steam and porous solid phase through which liquid moisture and steam migrate (de Souza-Santos 1989). The evaporation front moves inside the particle under the influence of an increase in the temperature of the drying surface. It is a heat transfer limited process influenced by the reactor temperature, fuel particle size and porosity. Drying and heating may also cause particle shrinkage, a reduction in the pore size, internal cracking or particle break up.

2.2.3 Devolatilization and Volatile Conversion

When the temperature exceeds 250 °C, the fuel particle organic matter starts to thermally degrade, with the detachment of the volatile matter from the solid fuel matrix (being 'char'). This step is usually referred to as pyrolysis (or devolatilization), wherein water vapour, organic liquids and non-condensable gases, such as CO, H₂, CO₂, are separated from the solid carbon and ash content of the fuel. The vapour/liquid product comprises mostly of hydrocarbons and tar (i.e. dark, oily, viscous material, consisting mainly of heavy organic and mixed oxygenates). Subsequently, the volatiles and char undergo a second gasification step and they modify their composition due to the occurrence of several reactions becoming the final syngas (see Table 2.4).

Table 2.4 Typical gasification reactions (Basu 2010)

Reaction name	Biomass gasification	Energy (kJ/mol)
<i>Exothermic</i>		
Combustion	(Char/Volatiles) $C + O_2 \rightarrow CO_2$	-398.3
Partial oxidation	(Char/Volatiles) $C + 1/2O_2 \rightarrow CO$	-123.1
Water gas shift	$CO + H_2O \leftrightarrow H_2 + CO_2$	-40.9
CO methanation (I)	$CO + 3H_2 \leftrightarrow CH_4 + H_2O$	-217.0
CO methanation (II)	$2CO + 2H_2 \leftrightarrow CH_4 + CO_2$	-257.0
<i>Endothermic</i>		
Pyrolysis	$Biomass \rightarrow Char + Volatiles + CH_4 + CO + H_2 + N_2$	+200–400
Methane steam reforming	$CH_4 + H_2O \leftrightarrow CO + 3H_2$	206.0
Water gas/steam carbon	(Char/Volatiles) $C + H_2O \rightarrow CO_2 + H_2$	118.4
Boudouard	(Char/Volatiles) $C + CO_2 \rightarrow 2CO$	159.9

Most of these reactions are endothermic and require a consistent amount of energy to proceed. In *autothermal* reactors, this is usually supplied by the exothermic reactions (char combustion in particular), within the same environment.

Since the initial devolatilization is a rapid process, it has a negligible effect on the overall conversion time. Nevertheless, the location of devolatilization significantly affects the heat release profiles throughout the reactor.

Many different works deal with the modelling of volatiles reactions. One of the most famous is the “plume” model according to which devolatilization of fuel particles is instantaneous and occurs suddenly at the feed entry ports (Park et al. 1981). If the furnace is fed from below, volatiles form an oxygen-starving plume rising through the bed, and the released volatiles may form an endogenous bubble around the fuel particles moving upwards as a consequence of the drag force. If the reactor is fed over-bed, volatiles reaction occur in the freeboard while solid residues (mainly fixed carbon and ash) drop on the bed surface. As the solid carbon-containing particles formed on initial decomposition of the fuel (or fed if the fuel is non-volatile), mix with the inert bed solids, heterogeneous reactions continues until the particle, is either converted completely, or is discharged with the bed material for bed height control, or is removed from the bed by elutriation.

2.2.4 Fixed Carbon Conversion

The residue after devolatilization is made up of char, which contains most of the fixed carbon content of the original particle. The gasification of fixed carbon is governed by several complex phenomena: mass transfer of oxygen from the bubble phase to the solid one; boundary layer and intra-particle transport of the mass (oxygen and combustion products) and heat; heterogeneous reaction on the fuel particle external and internal surfaces. Their importance varies according to fuel properties and reactor operating conditions.

Though char from RDF usually constitutes a minor fraction of the fuel, its conversion kinetics has a major effect on the performance of a gasifier, for it is the slowest of conversion processes. In fact, due to the porous nature of char, it is not always possible to achieve complete chemical control of the reaction because the diffusion within the pores limits the overall rate of reaction. When this happens, both processes, chemical reaction and pore diffusion, exert an influence on the progress of reaction, which in turn limits the conversion into valuable syngas. The extent of diffusion resistance can be reduced by properly reducing the particle diameter (to less than 1 mm) and, or, by increasing the process temperature, as it is done for example in entrained flow gasification.

2.2.5 Particle Attrition and Elutriation

This already complex picture is further complicated in a fluidized bed gasifier by the parallel ash release and comminution phenomena that can remarkably change the structure of mother fuel particles and then strongly affect its conversion process (Chirone et al. 1991; Gomez-Barea et al. 2008).

If the fuel has only a very low, friable, ash content, the fuel ash is mainly degraded by the action of the fluid bed, such that it is substantially carried away i.e. elutriated (as ‘fly ash’), within the emergent flue gases. Alternatively, if a high ash material is treated, especially one that leaves behind coarse particles of metals, bones, glass or adventitious stone, some of the ash (named ‘bottom ash’) remains in the bed. If such ash is of similar size to the original bed particles, the ash will fluidise and eventually coexist with the original bed particles (Fig. 2.5).

The process through which particle size decreases and ash is released includes the following four steps: primary and secondary fragmentation, attrition by abrasion and percolative fragmentation. Primary fragmentation (Chirone et al. 1991) occurs immediately after the injection of the fuel particle into the bed, as a consequence of thermal stress caused by rapid heating and by volatile release. It generates coarse particles whose size and shape are influenced by fuel properties such as volatile content and swelling index. Secondary fragmentation and attrition by abrasion (Chirone et al. 1989) are determined by mechanical stress due to collisions between particles and with the furnace interior: the former generates coarser and non-elutriable fragments while the latter generates finer and elutriable fragments. The phenomenon that most affect carbon conversion efficiency is elutriation. This is the process in which fine particles are carried out of a fluidized bed due to the fluid flow rate passing through the bed. Fine particles that are subjected to elutriation can directly come from the fuel fed to the FBG or, alternatively, they can be produced during the gasification process and attrition.



Fig. 2.5 *Left* Dry discharged bed (*bottom ash*) from FBG showing plenty of bones and stones and *right* presence of glass fraction on the fluidising nozzle

2.2.6 Comparison Between Conventional and Waste Fuels

Gasification of waste derived fuels in fluidized beds includes a wide variety of non-fossil solid materials, ranging from mixed plastic to municipal, agricultural and industrial waste. Although there is a certain amount of operating experience in connection with this topic (Saxena and Jotshi 1994; Anthony 1995), a complete comprehension of the phenomena occurring during gasification of these fuels, RDF in particular, is still lacking, probably due to the great difference in physical and chemical features from conventional ones. In fact, waste fuels are characterized by high moisture and volatile content, a porous and fragile structure, a low density and high intrinsic reactivity. The potential of a large quantity of moisture in fuel particles amplifies drying time and postpones devolatilization. On the contrary, low moisture and the high volatile contents lead to shorter devolatilization times and larger quantities of volatiles evolved: as a result, a larger contribution to the overall heat release is associated with drying process and homogeneous volatile reactions. When RDF is fed over bed, devolatilization is completed at (or close to) the bed surface and a large fraction of the volatile matter is released directly in the free-board: a direct consequence of bypassing the bed is that the post-conversion of volatiles in the splashing region leads to significant local overheating with respect to the bed (Scala and Chirone 2004). Besides, fine carbon particles are significantly formed by attrition and fragmentation of coarse particles: this feature reflects the propensity of such fuels to give rise to either friable chars or even to a multitude of fragments of very small size. As a result, the conversion of fixed carbon occurs as much through the generation of fines, followed by their conversion over their residence time in the bed, as through direct conversion of coarse char particles. Because of high reactivity, the fine char particles are mostly burned in the freeboard (Scala and Chirone 2004). Whereas conventional fuels like coal undergo moderate primary fragmentation: after devolatilization about 99 % of the fixed carbon can be found in coarse char particles. Consequently, coal conversion occurs primarily in the bed, mostly via coarse char particle direct combustion.

The high quantity of fly ash and volatile material in RDF can also provide a decrease in thermal output, create high ash clinkering, and increase emission of tars and particulates. In fact, FBG reactors need to be operated at lower temperatures to prevent sintering of the ashes causing defluidisation of the bed and, consequently, tend to produce a syngas containing high levels of condensable organics and gaseous hydrocarbon species which can be problematic in subsequent stages (see Sect. 2.4). Because of high reactivity, the fine char and tars conversion occurs mostly via thermal cracking and direct combustion, and are thermodynamically favoured by high temperature. Besides, raising the temperature to certain levels generally enhances the kinetics of slow reactions, producing higher yields of synthesis gas. Figure 2.6 is a composite that illustrates the effect of temperature in FBG on some key output variables: char conversion, tar concentration, heating value of producer gas, and ash sintering risk.

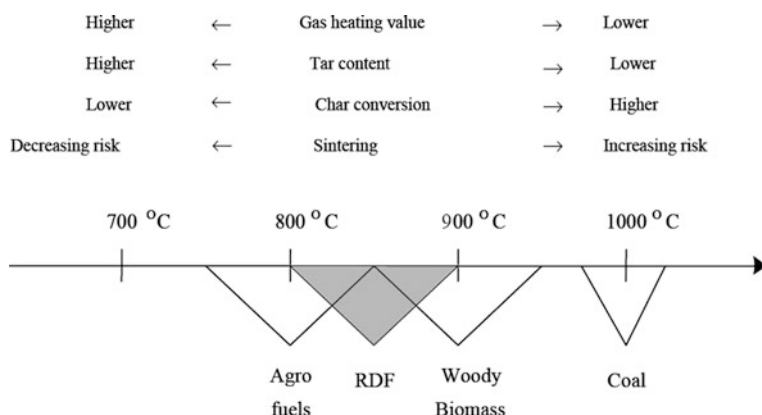


Fig. 2.6 Typical gasification temperature for various feedstock and influence of temperature change on some critical factors as reported by Hallgren et al. (1993)

Furthermore, the large quantities of gases and vapours leaving the solid matrix can entrain organic and inorganic material, even if the material itself is non-volatile, thus producing a large amount of residues downstream. As a result, the combination of high velocities in FBG and high volatile matter in RDF indicates a potential for creating significant tar condensation and fly ash deposition problems during gasification, with the severity varying significantly with the different nature of the feedstock (Oakey et al. 1989). A more detailed description of these two technical issues associated to operation of fluidized beds on waste follows in the next Sections.

2.3 Ash Behaviour and Agglomeration Issues

All the residues that remain after fuel thermal conversion processes described in the previous section are referred as to ashes. Waste gasification produces a lot of ash that may be deposited on the bed particles causing agglomeration or bed sintering, which in the worst case may result in total defluidization often leading to unscheduled downtime (Fig. 2.7). Furthermore, a waste fuel rich in coarse inert materials (e.g. glass, bones, metals, etc.) leaves behind ash particles that are significantly larger than the original bed particles, eventually causing the bed to defluidise, unless the concentration of large particles is controlled.

Attention was paid on agglomeration of bed materials in fluidized bed combustion and gasification in the mid-1970. Since then, some fundamental research on agglomeration and defluidization has been carried out (Visser et al. 2008; Öhman et al. 2000) they found that agglomeration is caused mostly by sintering of ash particles. For the agglomeration occurring in FBG of wastes, the ash chemistry is the most important. The potassium content is, along with sodium, calcium,



Fig. 2.7 Fused bed in FBG (*left*) and closer inspection of fused pan (*right*)

magnesium, silicon, sulphur and chlorine, the foremost sintering promoter. Other factors that influence agglomerate formation include temperature, fuel/oxidant ratio, flow mixing and atmosphere.

Agglomeration and sintering imply an increase in particle size through physical and chemical processes in specific circumstances. These circumstances and reactions may occur at typical fluidized bed gasifier operating temperatures, which are lower than ash fusion temperature.

2.3.1 Mechanism

Two possible mechanisms for particle agglomeration in FBG are supposed (Kunii and Levenspiel 1968). In the first one, partial melting or reactive liquid sintering, ash with high sodium, chlorine and sulphur contents may form low-melting point eutectics, which partially melt at low bed temperatures, i.e. 500–700 °C. The presence of the liquid phase makes the ash ‘sticky’ and would facilitate the transfer and adhesion of ash to the bed particles. The second mechanism, viscous flow sintering, involves melting of ash at temperatures greater than 1000 °C, producing a highly viscous liquid phase, which controls the sintering process. The high viscosity of the molten ash may keep the liquid in the glassy phase when the ash is deposited onto the bed particle surface whose temperature is normally lower than that of the char particle.

2.3.2 Effect of Temperature and Segregation Profiles

Fluidized bed gasifiers normally operate between 600 and 900 °C. In an oxidative environment (e.g. combustion, $ER \geq 1$), ash softening temperatures range from 1000 to 1250 °C. However, the softening and liquid temperatures of the ash can

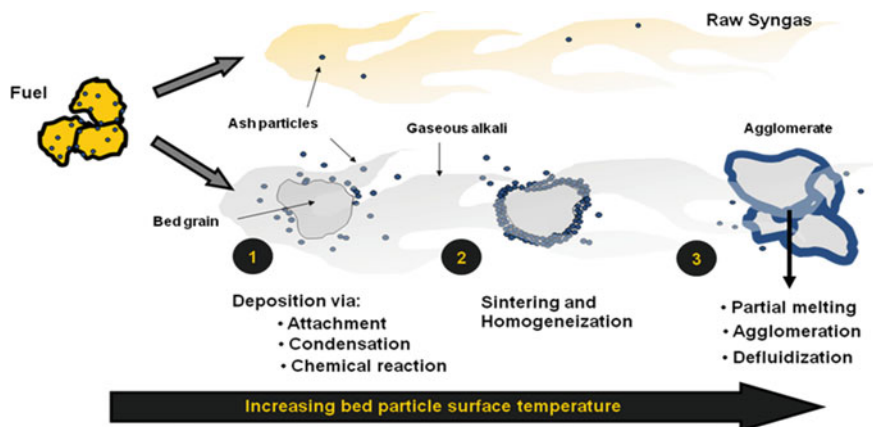


Fig. 2.8 Illustration of the important chemical sub-processes of the bed agglomeration mechanism

drop by as much as 260 °C in a reducing environment. A reducing environment ($ER < 1$) may lower the eutectic point of mineral matter present in waste fuels. If temperatures rise above normal operating temperatures, either locally or globally with the gasifier, agglomeration is imminent due to ash sintering. The conversion scheme is presented in Fig. 2.8, where it is shown the transition as a function of process temperature from primary products to potential bed ash agglomerates. Ash sintering is referred to as the agglomeration of bed particles under heat without melting (Mettanant et al. 2009). The extent of bed mixing has a direct effect on the occurrence of local hot spots within the fluidized bed reactor. Therefore, temperature profiles can be used to map fluidization patterns along the vertical axis of a fluidized bed reactor. The pressure drop across the bed may also be used to monitor the formation of agglomerates. As agglomerates form, the bed may segregate and defluidize, causing a decrease in the pressure drop.

2.3.3 Effect of RDF Ash Composition

The solids within the fluidized bed gasifier may consist of fuel particles, sulphur sorbents such as limestone or dolomite, or an inert material such as sand. A small percentage, one to five percent, of the bed material enters as fuel. General wastes are composed of carbon, mineral matter (ash), and a variable percentage of various inorganic elements (glass, metals, bones, etc.). Most of the mineral matter found in many types of wastes are clay or shale impurities. The majority of the carbon will be converted within the FBG. However, the mineral matter may reside within the bed and undergo chemical reactions and physical changes leading to agglomeration (Fig. 2.9). The various inorganic elements, including alkalis, may also play a role in

Fig. 2.9 Large agglomerate formed from RDF ash sintered and sand particles



the formation of agglomerates. Consequently, agglomerates may form even when bed temperatures remain below ash fusion temperatures.

The presence of alkali elements within the bed has been linked to deposition and agglomeration (Scala and Chirone 2004). The elements of importance are sodium (Na) and potassium (K). These elements must be volatile to have any detrimental effect. Sodium and potassium may occur in several different forms within wastes. Sodium, for example, may be deposited on RDF particle surfaces as a salt (NaCl) or may be organically bound in the biomass structure. Sodium and potassium in either of these forms readily volatilize under temperatures experienced during gasification (Mettanant et al. 2009). However, such elements are not volatile if associated with silicate mineral matter. The alkali elements which volatilize may condense on cooler surfaces within the reactor and form deposits. Agglomerates may form if alkali elements condense on bed particles.

Sodium and potassium may lower the eutectic point in a sulfate matrix. Agglomeration is proposed to take place when two particles coated with a sodium or potassium sulfate-rich material cohere due to sulfate-to-sulfate sintering (Brown et al. 1996). As volatilized sodium and potassium elements condense on cooler surfaces, they may react with calcium sulfate forming a sticky substance which acts as a glue for bonding bed particles together.

2.3.4 Entrainment, Slagging and Fouling

Mechanical attrition of the fuel, due to bed fluidisation, coupled with high bed velocities and the fragile nature of RDF, gives rise to the potential for significant carryover of fine and fly ashes from the FBG, affecting the particulate control system and its associated ash handling devices.

This problem is usually controlled by mechanical separation of particulate matter from the syngas downstream the gasifier. Cyclones, in particular, are often an integral part of the fluidized bed reactor, since they are relatively inexpensive, can be operated at the typical FBG temperatures and could increase carbon conversion efficiency by recycling coarse particulates (and bed material) to the gasifier. On the other hand, cyclones have a limited collection efficiency, i.e. 80–85 % for particles larger than 7 μm . Ceramic candle or sintered metal filters can provide an efficient high-temperature removal of the finest particles, even though they are still relatively novel and expensive. In the past, they appeared susceptible to breakdown due to mechanical fatigue, but recently ceramic candles have been utilized in a large-scale CFB gasifiers (Arena and Di Gregorio 2013). The finest particulates can also be removed by wet scrubbers or by the new-generation bag filters that can operate at temperatures up to 450 $^{\circ}\text{C}$.

However, finer sized fractions of elutriated material and inorganic vapours can still deposit in downstream parts of the installation and before gas cleaning equipment. Fines deposition has been a critical problem for many years in conventional thermal plants, the severity varying significantly with the different nature of the feedstock (Oakey et al. 1989). There are two types of deposition: *slagging* and *fouling*. Slagging arises when RDF ash, in the form of flying incandescent ‘plastic’ particles impinges on hot surfaces to provide a sticky base for the adherence of dust and grit, a formation which quickly solidifies and hardens. This is basically fused ash and it is regarded as a separate problem to fouling. Fouling occurs on the outside of heat exchangers tubing, and it has been attributed to the condensation of alkali salts onto cooled surfaces to form a sticky white layer that initiates deposition by then capturing passing fly ash (see Fig. 2.10). Alkali sulphates are usually the matrix of the fouling deposit which contains high contents of partially-fused ash (Oakey et al. 1989).

This build-up of ash deposits causes the choking of the tubes and the shut-down of the plant for cleaning. This suggests that one important objective should be to prevent solid deposits from accumulating in the high temperature zone of the convective heat transfer area (known as ‘nesting’ area), which is usually located before the conventional air-cleaning systems.

There are four possible routes to accomplish this:

- prevent either the acidic (SO_3 , Cl) or the alkali (Na, K, Ca) radicals passing from the fuel bed into the gas phase by, for example, addition of suitable chemical compounds to the fuel (or bed material) to reduce the volatilization of alkalis, or their injection into the gas phase to convert alkali sulphates into inert compounds of high melting point (Rampling and Hickey 1988);



Fig. 2.10 *Left* Fly ash deposits (*slagging*) in a plant duct. *Right* condensation of alkali components on the chilling unit (*fouling*)

- prevent the accumulation of fly ash in the ‘nesting’ area by reducing the particulate carry-over of the process;
- the installation of soot blowing appliances in currently operating units to prevent the accumulation of the initial layer of deposition;
- prevent condensation of the alkali salt onto the metal tubing, by modifying heat exchangers design and operating conditions;

Unfortunately, the accomplishment of these routes is not always possible or economically viable, and further research is needed to mitigate these problems. The first two options are part of this study and will be explored in Chap. 7.

2.3.5 Use and Disposal of Solid Residues

As discussed in the previous section, the finer sized fractions of inorganic matter are elutriated from the gasifier by the gaseous products and recovered from downstream parts of the installation and from gas cleaning equipment. At the same time, the coarser sized fractions (bottom ashes) may replenish the bed solids to maintain the bed at a fixed level during normal operation. Solids in excess of this requirement, small agglomerates and tramp material, are removed as a bed discharge stream, which serves both to regulate the bed level and to keep the bed relatively clean. Thus, in general, two waste solid residue streams, one with relatively fine and one with relatively coarse sized particles, are formed although the relative proportion and composition of each stream may vary widely according to the fuel being used and operating conditions.

These solid residues are usually classified as a hazardous waste on account of their high alkalinity and other pollutant species (e.g. heavy metals and soluble chloride and sulphate salts), and require specific treatment before disposal or reuse

(Jung et al. 2006). The latter assumes a particular importance when we consider that the recovery of materials from thermal plant solid residues is becoming a critical issue, from both an environmental and economic perspective. The recovery of high proportion of inert materials from the plant residues would reduce the dependency on primary resources, while decreasing the amount of potential toxic residuals that have to be disposed of in adequate landfill sites under severe environmental controls. Furthermore, the ash handling system in gasification plants is anything but easy. Many problems stem from inadequate understanding of the fluctuation of ash properties before and during the plant's design. The sluiceways used to transport the ash in the ash handling area can experience cementation and buildup that leads to reduced performance or clogging. The ash particles can settle more quickly than anticipated, cementing to each other and constricting flow in the sluiceways. The constrictions have to be removed from the sluiceways mechanically, adding rock salt to the slurry to promote the formation of an ionized layer around the particles and prevent them from coagulating. All this procedure is very costly and time consuming.

All these problems have led to the conception of a more efficient and sustainable way to dispose and/or reuse the inorganic fraction of gasification plants.

One possible approach involves the utilization of a high temperature refining stage, such as an ash melting furnace. The main companies that operate with combined FBG and ash vitrification systems of different kinds of wastes are Ebara, Hitachi Zosen and Kobelco, as reported in the most recent reviews of the state-of-the-art of waste gasification technology (Juniper Rating Gasification Report 2009; Arena 2012). In these processes, gasification works only as a sort of pre-treatment for the successive stages of gas combustion and ash melting (Arena and Di Gregorio 2013). The recoverable materials contained in the waste, such as iron and aluminium, are extracted from the bottom of the gasifier in an un-oxidized state after being polished by the sand used as bed material. The remaining ash fraction, the produced gas and carbonaceous particles are subsequently burned in a swirling flow melting furnace at high temperatures (above 1200 °C) and low excess air ratios (1.1–1.2) to fuse ash and produce vitrified slag and energy. The molten slag is finally quenched with water and obtained as granulate that can be sold to the construction industry. The process has the advantage of involving a reduced flue gas flow rate when compared to conventional incineration systems, which allows for a size reduction of steam boiler and pollution control units. The final amount of process residues to be sent to landfill is also remarkably reduced. However, the achieved net efficiency of electrical energy is relatively low (ranging from 9 to 17 %), strongly depending on the energy necessary for the melting system. Furthermore, these processes work at all effects as combustion plants, precluding the possibility of producing a clean syngas for chemicals or bio-fuels synthesis.

The need for more innovative sustainable solutions to the ash problem are required to ensure more efficient overall use of resources, especially with regards to inertising the ashes while producing a high quality syngas in an efficient and environmentally friendly way. One such approach is analysed in this research (see Chap. 3), and utilizes a plasma processing stage for conditioning the syngas

generated from the FBG unit and vitrifying the ash fraction of the feed which may be used as a construction material. The ash vitrification energy is provided by the plasma arc rather than from excess oxygen, thus the syngas produced is clean and of high calorific value. The plasma vitrified product, derived from both fly and bottom ashes may find direct use, for example, as a pipe bedding or unbound aggregate material (Chapman et al. 2010). However, further processing of this glass may be undertaken to produce high added value engineered materials, which can compete with commercially available products, in architectural or building applications, for example. One specific process route developed by Tetronics, relates to the treatment of incinerator ash residues, in which the plasma vitrified product is utilised as the raw material for glass-ceramic production.

2.4 Tar Formation and Reduction Measures

The other major technical obstacle faced by conventional waste gasifiers and discussed in this thesis is the high level of tars and organosulfur contamination in the syngas. This has been the primary cause of waste gasification developments failing over the last 30 years and has prevented their commercial adoption with efficient technologies for power generation (e.g. gas engines, fuel cells, etc.) and catalytic transformation to generate either hydrogen or alternative fuels (Scala and Chirone 2004).

Tars are formed during the gasification process in a series of complex reactions that start from the devolatilization of the fuel. With high volatility (more than 60 %) and low ignition temperature (250–350 °C), RDF is prone to devolatilise immediately after the injection into the reactor, making it more susceptible to tar formation and organic contaminants release when compared to other fuels, such as biomass or coal.

Tar compounds in the syngas have to be avoided since tar can cause serious problems associated with condensation and blocking in the process equipment used for the application of the syngas. Besides, the condensed tar and particulates can cause huge problems for the particle removal devices such as cyclones, filters and heat exchangers (Fig. 2.11).

Another problem usually related to waste tar is the solubility of tar in water which creates a waste water problem when scrubbing is used to clean the produced gas (Chen et al. 2011).

Nowadays, tar is the most problematic issue of waste gasifiers because it will impose serious limitations in the use of the syngas. Thus, the successful implementation of gasification technology for power production or biofuels synthesis depends much on the effective and efficient removal or conversion of tar from the producer gas.



Fig. 2.11 Tar condensation (*left*) and crystals build-up (*right*) on heat transfer surfaces

2.4.1 Tar Definition and Formation

“Tar” represents a lump term comprising thousands of single substances. Due to its complexity, different definitions have been given by various research groups working on gasification. In Milne’s review report, tar is defined as “*the organics produced under thermal or partial-oxidation regimes of any organic material and generally assumed to be largely aromatic*” (Milne and Evans 1998). A consensus on the definition of tar was agreed by the European Committee for Standardization (CEN) and “tar” is defined as “*all organic compounds present in the gasification product gas with molecular weight higher than benzene*” (Li and Suzuki 2009).

For many waste types, tar represents one of the major initial species released during devolatilisation, and its composition evolves according to a series of complex reactions. The yields and nature of these tars depend not only on waste composition but also on gasification conditions, including heating rate and residence time imposed by the reactor type, and particle size.

The tar formation scheme proposed by many researchers and summarized by Materazzi et al. (2014) is presented in Fig. 2.12, which shows the transition of tar as a function of process temperature from primary products to phenolic compounds to aromatic hydrocarbons in a lignin-plastic fuel.

The mechanism by which a carbonaceous material is degraded and evolves in the gas phase in a fluidised bed reactor is very similar to that proposed by Katheklakis et al. (1990) except that the initial material here is a refuse derived fuel. According to this mechanism, the degradation process starts at 300–400 °C with the desorption of moisture, some light gases (e.g. H₂O, CO, and CO₂), and primary tar components (mainly aliphatic). Tar yield increases initially with temperature, going through a maximum (between 500° and 600 °C for lignin and heavy plastics), beyond which secondary tar destruction reactions in the freeboard cause a decline in observed trend. The temperature at which the tar yield maximum occurs appears to depend on the chemical structure of the parent substrate. For example, lignocellulosic substrates, normally present in RDF, appear to cleave readily to give

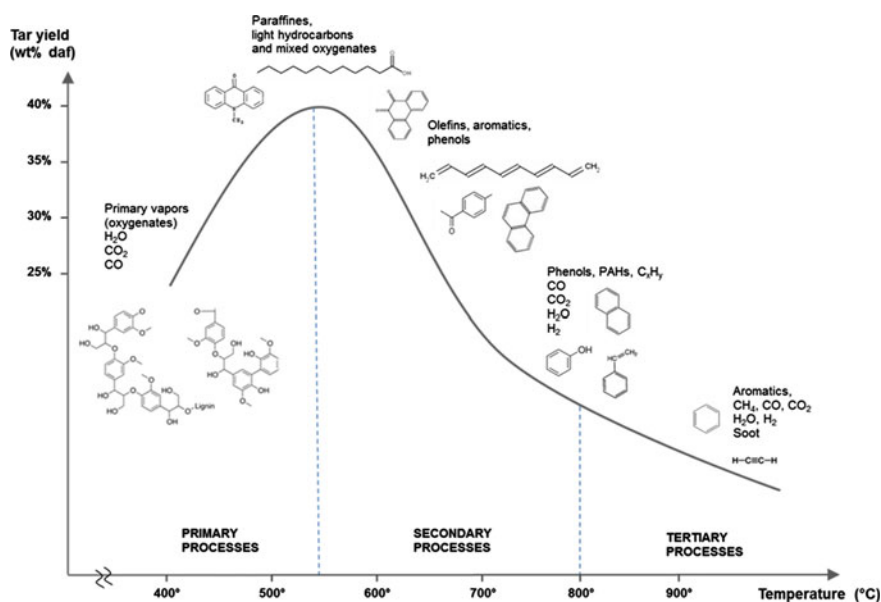


Fig. 2.12 Tar yields in a generic gasification process as a function of temperature. Results are qualitative and given on the basis of wt% dry ash-free (*daf*) lignin-plastic mixture, as representative for waste material (Katheklakis et al. 1990; Fraga et al. 1991; Li et al. 2013)

relatively small, compact and relatively stable molecules able to evaporate completely at temperatures around 500 °C (Fraga et al. 1991). Hence, this tar yield maximum is expected to occur at considerably lower temperatures during the devolatilisation of materials richer in cellulose and light plastic, which are known to decompose more easily (Font Palma 2013a; Grammelis et al. 2009; Werther et al. 2000; Miller and Bellan 1997).

Conversely, total gas yields at temperatures above that of the tar yield maximum are observed to increase monotonically with increasing temperature, while tar yields decline, suggesting cracking and steam reforming (to give syngas and lighter volatiles) as the predominant mechanism for tar loss in the freeboard. Major tar components often occurring in concentrations higher than 5 % are toluene, naphthalene and phenol, for the process lower than 800 °C. In addition, for temperatures over 800 °C, macromolecular components with up to seven benzene rings may occur.

Milne and Evans (1998) proposed a classification of tars according to how the tar components are formed in the gasifiers:

- Primary tar, characterized by cellulose-, hemicellulose-, plastic- and lignin-derived products, i.e. product from the main components of the RDF.
- Secondary tars, characterized by phenolics and olefins, and are product from the conversion of primary tars.

- Alkyl tertiary tars, characterised by methyl derivates of aromatics (styrene and/or xylene), and organo-sulphur compounds (thiophenes).
- Condensed tertiary tars, i.e. the polyaromatic hydrocarbons (PAH) without substituents.

The amount and the composition of each tar class produced are strongly dependant on the gas composition, gasification temperature, equivalence ratio, type of bed material, and gas residence time inside the gasifiers. Based on this, the most common tar conversion processes can be lumped into four generic categories: thermal, steam, partially oxidative and catalytic processes. All these processes can occur in situ (inside the gasifier reactor), or in separate units by chemical methods (e.g. catalytic cracking, thermal cracking, etc.).

2.4.2 Effect of Temperature

The temperature is one of the most influential factors affecting the overall gasification process. Temperature can influence the amount of tar formed as well as the composition of tar. Kinoshita et al. (1994) observed that the total number of detectable tar species produced from sawdust gasification decreased with increasing temperature. Lower temperatures favoured the formation of more aromatic tar species with diversified substituent groups, while higher temperatures favoured the formation of fewer aromatic tar species without substituent groups. Li et al. (2004) reported that the amount of tar obtained from biomass gasification decreased drastically from 15 to 0.54 g/Nm³ as the average temperature increased from 700 to 820 °C. Figure 2.13 shows the effect that temperature has on tar composition, with

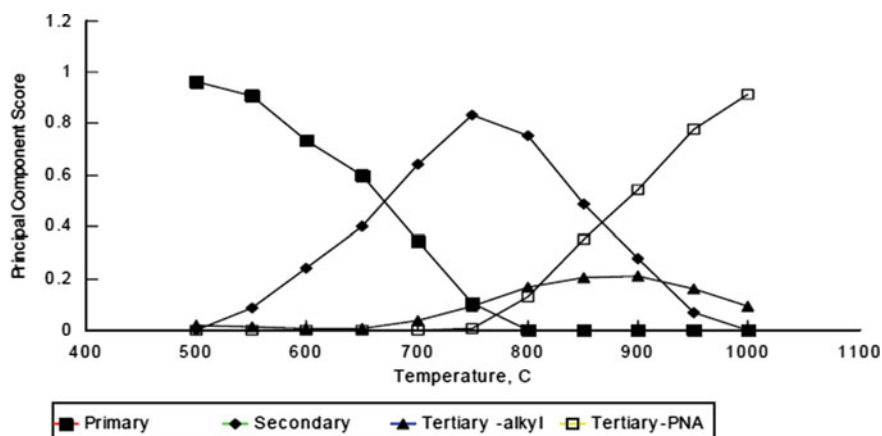
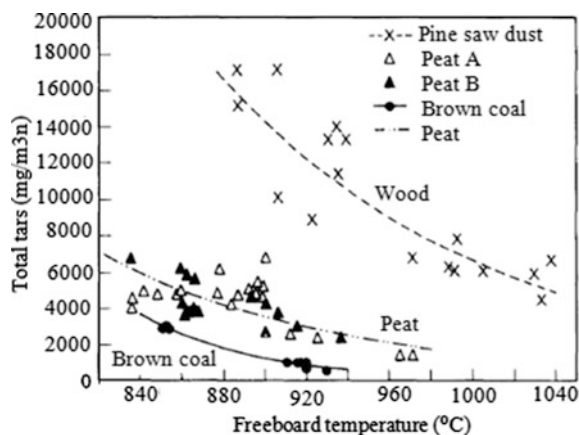


Fig. 2.13 The distribution of the four “tar” component classes as a function of temperature at 300 ms (0.3 s) gas-phase residence time (Milne and Evans 1998)

Fig. 2.14 Effect of freeboard temperature on the total amount of tar+benzene in the PFB gasification with different feedstocks (Kurkela et al. 1993)



primary tars more prominent between 500 and 600 °C and tertiary PAHs increasing above 800 °C.

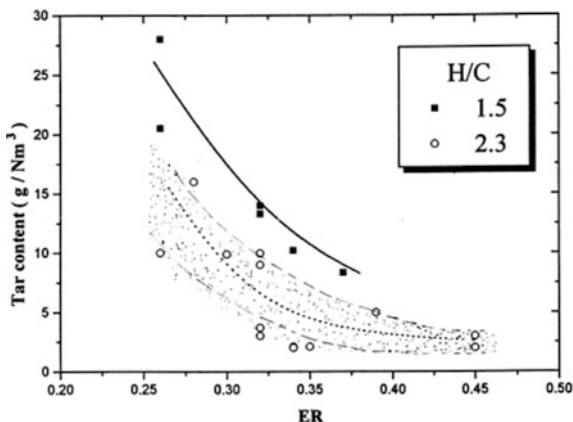
Kurkela et al. (1993) and Simell et al. (1992) studied the effects of operational conditions on the formation of tar produced from different feedstocks ranging from hard coals to wood wastes gasification in a pressurized fluidized bed (PFB) gasifier. They found that the total tar concentration in the PFB product gas seems to depend mainly on the feedstock and on the gasification temperature, which can be clearly seen in Fig. 2.14 which shows the tar content produced from for wood, peat, and brown coal gasification in the PFB gasifier at different freeboard temperatures.

The consensus seems to be that temperatures in excess of 1000 °C are necessary to destroy the refractory unsubstituted aromatics. In order to avoid melting of the inorganic phase and total defluidization of the bed described in previous sections, such high temperatures are not achievable in a stand-alone FBG, and a separate unit (called ‘thermal cracker’) is normally needed. Apart from the economics and materials problems, such thermal stage produces soot that can be even more troublesome for some process than the aromatics.

2.4.3 Effect of Equivalent Ratio and Steam

The ratio of gasifying gas to waste is given as Equivalent ratio (ER) for the gasification operation. Similar to temperature, an increase in ER also has a beneficial effect on reducing tar formation. Narvaez et al. (1996) studied operational conditions on the product gas produced from pine sawdust gasification with air in an atmospheric bubbling fluidized bed (BFB) gasifier. The effect of ER on the tar yield in the product gas is shown in Fig. 2.15 for two H/C ratios in the gasifier.

Fig. 2.15 Tar concentration at different ER values at gasification temperature 800 °C (Narvaez et al. 1996)



From Fig. 2.15 it can be seen that the tar content produced from pine sawdust gasification at a temperature of 800 °C decreased with increasing ER and a tar content of about 2–7 g/Nm³ was obtained at an ER value of 0.45. Meanwhile, the H/C ratio is also very important and the tar content decreases with increasing H/C ratios. Lv et al. (2004) reported that the lower heating value (LHV) of the product gas decreased with an ER increase due to strengthening oxidation reactions of product gases.

When also steam is used as the gasification medium, other index is used instead of ER. Steam to biomass ratio (SBR) is the ratio of the weight of H₂O fed to the gasifiers divided by the weight of RDF used. The value of this index also depends on the moisture content of RDF because when the waste has high content of moisture then less steam can be fed to the gasifiers. Steam to biomass ratio (SBR) also influences tar formation due to tar steam reforming reactions. Herguido et al. (1992) reported that the amount of tar sharply decreased from 8 wt% to negligible content with an increasing SBR range from 0.5 to 2.5. Aznar et al. (1998) reported that with varying GOR (steam + oxygen)/biomass mass ratio from 0.7 to 1.2 more than 85 % reduction in the total tar was achieved.

Steam or secondary oxygen can be added selectively to a certain stage, such as in secondary zones of the FBG (above the bed or in the freeboard), or in separate units (e.g. thermal cracker) to preferentially oxidise and reform certain tar compounds (Jensen and Joergensen 1996). However, contact of oxygen and tar is difficult to control, and a portion of the syngas (e.g. H₂ and CO) can be inevitably combusted, lowering the energy conversion efficiency.

2.4.4 Effects of Residence Time

The gas residence time determines the time for the reaction to occur and proceed. Since tar formation is a multi-step process involving several consecutive reactions

where each has a certain reaction time for completion, the gas residence time will determine how many, and to what extent, consecutive reactions can take place at certain temperature. This will eventually determine how much tar content and composition formed in the gasifiers. According to Kinoshita et al. (1994) residence time can significantly influence the composition of tar, but slightly affect tar yield. With increasing residence time, yields 1- and 2-ring compounds (except benzene and naphthalene) decreased whereas that of 3- and 4-ring compounds increased in the total tar fraction.

Longer residence times can be achieved with a multiple-stage design of the gasifier. The basic concept of a multiple-stage design is to physically separate the principal unit operations of pyrolysis-preliminary gasification zone from the final conversion zones, involving different levels of heat intakes (see Sect. 3.5.1). This strategy will provide longer residence time whilst making a more efficient use of the oxygen required to support the endothermic steam reactions. Most such processes have been based on two sequential reactors where this can be achieved more easily.

2.4.5 Effect of Active Materials

There are many active materials which may act as catalysts available for gasification which are classified into different categories by different researchers. Devi et al. (2002) divided catalysts into three groups: dolomites, fluid catalytic cracking (FCC) catalysts and nickel and other metals such as platinum, palladium, and rhodium. Devi (2005) divided them into dolomites, alkali metals and nickel catalysts. Abu El-Rub et al. (2004) divided them into two classes based on their production methods: minerals (calcined rocks, olivine, clay mineral and iron ores) and synthetic catalysts (char, FCC, alkali metal-based, active alumina and transition metalbased). Most of these active materials act on the tar loading by promoting hydrogenation and/or steam reforming of the organic structures (Li and Suzuki 2009). Analogously, other organic contaminants, such as sulphur-substituted hydrocarbons and dioxins, are converted into H_2S , NH_3 , etc. (Kaufman Rechulski et al. 2014).

So far, only a few of these materials have been tested as active bed materials inside the gasifier during waste gasification. Olivine showed some promising results in the control of tar content obtained in fluidized bed biomass gasifiers. For instance, Rapagnà et al. (2000) investigated the catalytic activity of olivine and observed that it has a good performance in terms of tar reduction and the activity is comparable to calcined dolomite. More than 90 % reduction in average tar content was observed, leading to a tar amount of 2.4 g/Nm^3 compared to 43 g/Nm^3 with only sand. Arena et al. (2009) reported that the use of a natural olivine as an in situ tar reduction agent greatly catalyzes the reactions of heavy hydrocarbon cracking and carbon formation and considerably improved the quality of the syngas. Siedlecki et al. (2011) studied the effect of magnesite as bed material on tar formation in the CFB gasifier and found that magnesite largely enhanced the

water–gas shift (WGS) reaction, (steam) reforming of methane and C₂ hydrocarbons toward their equilibrium, and also reduced the tar total concentration of toluene, xylenes, PAHs and phenolics circa 6.7 g/Nm³ compared to circa 9 g/Nm³ measured during a base-case experiment with quartz sand as the bed material. Among these compounds, the concentration of PAHs and phenolics was reduced to 1.9 g/Nm³.

In order for these catalysts to be used in situ (as FBG bed additives), they must meet some fundamental criteria, i.e. they must be effective in reducing tar, should provide a suitable syngas ratio for the intended process, should be resistant to deactivation as a result of sintering and fouling, easily regenerated, strong and inexpensive. Although the above mentioned investigations reported that the use of these additives can increase tar conversion up to 90 %, still problems appear. Dolomite, for example, is a soft material and hence gets easily eroded, thus producing problems of carry over of fines. Furthermore, the extent of tar reduction that can be attained by this method is limited by the high level of ash contained in MSW waste streams, which dilute the efficacy of the added catalyst. Due to these problems, the use of catalyst in situ may not be suitable for FBG and it would be more appropriate as a secondary treatment in hot gas cleaning, thus introducing a further energy penalty and operating cost to the plant. Also metallic catalysts, such as nickel, are much more effective in secondary beds or guard beds (Kaufman-Rechulski et al. 2011). However, a limitation of Ni catalyst for hot gas cleaning of the product gases is the rapid deactivation which lead to limited catalyst life time. Sulphur-substituted tar, chlorine and alkali metals are some of the components that may be present in the gasification product which can poison Ni catalysts.

Furthermore, the duration of most reported catalyst tests has been quite short, especially considering the long activity requirements for expensive catalysts such as Ni to be economic. The ongoing research is then moving towards developing inexpensive catalysts which are active in the presence of both tars and other contaminants, and can be commercially operated at relatively mild conditions (Kaufman Rechulski et al. 2014).

2.4.6 Physical Tar Reduction Measures

Several physical approaches for tar reduction outside of the gasification stage have been reported in the literature, and are usually referred to as ‘secondary methods’ (Palma 2013). However, not all of them have been proven efficient in terms of tar removal, economically feasible, and environmentally sound. Hot barrier filters, for example, are not suitable for tar removal at large scale, due to the high maintenance requirements. Other cleaning units, such as cyclones, may remove a small portion of condensables, but the tar removal efficiency is still low, because cyclones cannot remove particles of small diameter, including tar-droplets smaller than 1 µm (Milne and Evans 1998). In this review the Author will not attempt a thorough comparison

of all tar removal technologies, but will only limit the analysis to the most employed and commercially viable ones for fluidized bed systems.

2.4.6.1 Wet ESP's for Tar Removal

Wet Electrostatic Precipitators (ESP) are used for both particulates and tar removal. As the dust and aerosol particles enter the collection tubes, located inside of the wet ESP, they become charged from a bombardment of negatively charged electrons. The negatively charged particles adhere to the wetted collection tube and are periodically flushed into the electrostatic precipitator's lower plenum. Using wet ESPs is a very efficient method to remove tars in the aerosol form with a removal efficiency of up to 99 % of materials under 0.1 μm in diameter. This removal technology has successfully been applied at an updraft gasifier in Harboore, a downdraft gasifier at Wiener Neustadt and a circulating fluidised bed gasifier at ECN (Milne and Evans 1998). However, this technology proves inefficient when tar is in the gaseous phase. Moreover, wet ESPs are significantly more expensive than any other system, and the available data for long term operations are scarce.

2.4.6.2 Wet Scrubbers

One of the most used approaches is to condense the tars from the gas stream using either water or oil washing, and attempt to recover the significant energy contained in the tar condensate by recycling to the thermal treatment stage (Chen et al. 2011). This is a combination of two basic approaches for tar removal, namely the physical removal and afterwards the destruction of the tars in the gasifier.

Using a wet scrubber to remove tar in the product gas requires a gas temperature of 35–60 °C if the scrubber liquid is water. Most waste tars are hydrophobic such that only aerosols are removed. Using more organic liquids that also act as solvents such that gas phase tar is also removed can enhance separation (Boerrigter et al. 2005). At the Güssing gasification plant in Austria, a wet scrubber is used with biooil (RME, Rape Methyl Ester) as scrubber liquid. Spent scrubber liquid saturated with tar and condensate is vaporized and recycled to the gasifier in the combustor. In addition, another scrubbing technology developed by ECN named OLGA also uses 'oil' as scrubber liquid.

OLGA is an advanced scrubbing technology where:

- The tar is removed prior to water condensation.
- Tar aerosols are removed.
- The tars are recycled to the gasifier to be destroyed.

The removal of tar is done by contacting the tar-loaded product gas with a special developed scrubbing liquid ('oil') in an absorption column. All tar aerosols, heavy and light tars are removed from the product gas in the absorption column.

The current design of the OLGA technology requires a dust free gas so a hot gas filter is used to ensure this.

The special scrubbing liquid, containing all the tars, is then drained to the so-called stripper column. In the stripper column, the scrubbing liquid is regenerated by removing the tar. The tar is released to the stripper gas (air), which is then used as fluidisation gas in the gasifier where the recycled tars in the air are destroyed. The outlet temperature of the gas is kept above the water dew point at all times. This ensures that mixing of condensed water and scrubbing liquid is avoided.

According to ECN, the OLGA operated such that 99 % of phenol was removed. At those operating conditions essentially all heavy (≥ 4 aromatic rings) and light tars (2–3 aromatic rings) are removed from the product gas. BTX (Benzene, Toluene and Xylenes) removal efficiencies range from ~ 50 % for benzene to 90 % for the xylenes. This has been tested in a small downstream bubbling fluidised bed gasifier called WOB (lab-scale).

2.4.6.3 Use and Disposal of Collected Tars

All wet gas cleaning systems generate waste streams that are contaminated with organic and inorganic pollutants. Even when other fluids are used as scrubber media (such as in OLGA), there is an absolute quantum in terms of wastewater production: it is the condensable water contained naturally in the producer gas. Recycling/reuse of these waste streams, as proposed in Abatzoglou et al. (1997), introduces technical obstacles, and environmental issues. Several technologies are available to separate tars and water, but they are not complete as some organic components may chemically dissolve into the solvent. Furthermore, particularly in the treatment of wastes, contaminants including sulphur, chlorine, heavy metals and particulates are then inevitably concentrated in the recycle stream. This may limit or even preclude the possibility of tar recycling, leaving a problematic waste for disposal and/or clean-up which is not only highly toxic but typically embodies around 10 % of the energy value of the input fuel (Chen et al. 2011). This stream could be incinerated or combusted separately to generate steam. The steam can be used as gasification agent. In a new process developed by Babcock and Wilcox Volund, the water mixed with tar is cleaned using a new-patented technology named TARWATC, used by the Haboore gasifier. However, the cleaning and reuse of process fluids introduce further technical and economic challenges given the high concentration of pollutants (primarily sulphur and chlorine based) both in the solid residue and in the emissions from the combustor. Moreover, although such removal systems have been designed and operated on fuel gases generated from low tar/sulphur biomass feedstocks (such as hard wood), their application to waste fuels, where the complex spectrum of contaminants generated is very different, has not been reliably tested.

Lastly, it should be taken into consideration that tars formed during the gasification process at temperatures less than 800 °C can be handled using standard

safety practices, while tars formed at temperatures above 800 °C are much more hazardous to human health (Milne and Evans 1998).

Accordingly, in the gasification of waste streams, one should consider that the most rational approach to tar reduction is to reform/crack the tars into simple gaseous products (predominantly H₂ and CO), without relying on delicate capture, processing and recycling systems. The challenge in this case is to ensure that this process is conducted in an energy efficient and economic way. Results have been variable but several systems appeared to be quite promising for waste syngas conditioning following minor modifications.

2.4.7 Thermal and Plasma Cracking

As noted in Sect. 2.4.2, temperature is an important parameter in tar conversion, as it is particularly at higher temperatures—of the order of 1200 °C or higher (also depending on the residence time)—that the radicals responsible for the cracking and further reaction of tars are generated. Cracking in the absence of a solid (i.e. in an empty, inert reactor) is referred to as ‘thermal’. A separate thermal cracker is historically used associated with FBGs, since the temperature of the gasifier is limited to prevent agglomeration issues. Examples are found in the Thermoselect and Noell dust cloud gasification processes and in the large-scale Creusot-Loire two-stage plant, which was built in the mid-1980s and is still in use (Rabou et al. 2009).

The products of thermal tar cracking are gaseous (mainly hydrogen and light hydrocarbons) as well as solid, as it converts a small to large portion of the tars into carbon (= carbon-rich dust or soot). This has two consequences for the use of thermal cracking to remove tar in waste gasification plant. The first is that, if the fuel gas is used in a gas engine or turbine or in synthesis processes, the carbon needs to be removed first by means of a (bag) filter. The second is that, as a result, thermal cracking makes only part of the energy content of the tars available to the lower heating value (LHV) of the fuel gas, as the carbon will not be used to generate energy if the gas is burned in the engine or turbine or converted in the synthesis. In order to reduce soot formation, other ways have been explored in which radicals are produced, such as:

- The presence of radicals from other combustion reactions (e.g. partial oxidation or the admixture of combustion products)
- Raising the energy content of a molecule by means of electromagnetic radiation, e.g. microwaves or UV radiation
- The presence of a plasma

The new technologies deployed for handling the post-FBG fumes are numerous and often includes all the sources above. Most of them, as it is the case for thermal plasma, operate at very high temperatures. The main benefits are that almost

complete tar conversion is achieved (the tar contents at the output of a gasification stage by thermal plasma are 1000 time less than that obtained by autothermal fluidized bed) and that temperature, speed of the process and rate of heat transfer can be controlled to change the composition of the products. In particular, the water gas shift reaction, which drives the hydrogen to carbon monoxide ratio of the syngas, can be controlled via a modification of the external energy into the reaction system. These results can be very interesting for applications of synthesis gas in second generation biofuel that require tar concentration below 0.1 mg m^{-3} and high content of H_2 .

Therefore, the role of the plasma treatment associated with fluid bed technologies is twofold: it allows, on the one hand, a significant purification of gas by converting all tars and on the other hand, producing a synthesis gas enriched in hydrogen. Depending on the coupling configuration, the high temperatures involved have also the advantages to convert the portion of the inorganic fraction entrained with the gases into an inert vitrified glass so that the ash remaining to be landfilled is significantly reduced.

The current market for plasma-assisted gasification plants is shared by some companies including Alter NRG (Westinghouse subsidiary), CHO-Power (Europlasma subsidiary), Advanced Plasma Power (APP), InEnTec, Hitachi Metals Ltd., Plasco Energy Group Inc., EnviroParks Limited, Sunbay Energy Corporation, Green Power Systems, Pyrogenesis, PEAT... However, plants currently installed are of medium size (few MW of electricity produced by plant), and mainly demonstration units to promote plasma technology for waste gasification and ash vitrification (see Sect. 3.6). The efficiency of secondary reforming by plasma seems to be validated but the economic viability and reliability of this technology must be proven before to be accepted by the industry. This part will be largely covered in Chap. 3.

2.5 Remarks and Conclusions

Refuse derived fuels (RDF) may provide solutions to the disposal of non-recyclable waste fractions, and can be used as a direct substitute for primary fossil fuels in gasification. With hundreds commercial units in operation worldwide, fluid bed gasifiers (FBG) are frequently employed in thermal conversion technologies due to their ability to handle relatively coarse and chemically heterogeneous materials. However, most of the commercial fluid bed gasifiers were originally developed for operation coal and/or pure biomass. The translation of the systems to operation on waste is the issue which represents the most significant technical difficulty, and from this cascade particular concerns regarding the ability to achieve long term stable operation, as well as wider confidence in commercial viability.

Based on the results reported in the literature, as well as the hands-on experience of the Author, the practical implications with operating on waste can be summarised in the following:

- Materials in-feed to FBG systems are technically challenging.
- The introduction of RDF into a fluid bed gasifier adds a fuel whose dominant reaction sequence is volatilization, and gas-phase reactions, rather than char formation and gas-solid oxidation as in the dominant gasification process for biomass and coal.
- The fast devolatilization, and corresponding char residence time are all inter-dependent on the chemistry and morphology of the RDF. Changes in material feed rate, morphology and chemistry, including ash, will have an instantaneous effect on the rate of gas evolution and buoyancy of particles, which in turn feeds back to the autothermal operation of the FBG.
- The low level of fixed carbon with RDF upsets the energy balance in the system, such that either a support fuel is required, or that a proportion of producer gas is combusted in the reactor.
- RDF is likely to contain substances in varying quantities in the ash-forming fraction which can form low melting point eutectics. This limits the temperature of operation of the FBG to around 750–800 °C, in order to avoid agglomeration and ultimately defluidization of the bed.
- The high level of ash will alter any catalytic effect achieved by specific bed material in the FBG.
- Secondary ash and deposit streams contain high levels of pyrolytic carbon, organic, and heavy metal pollutants and are expensive to treat or dispose of at permitted hazardous waste sites.
- The nature of the ash in RDF is such that high dust loading is expected in the producer gas which the downstream units must be able to accommodate.
- Sulphur and organo-sulphur levels may be high in RDF gasification and can result in process issues.
- Tar formation at high level is an inevitable consequence of low intensity gasification (due to temperature limitation) and high fraction of volatile matter.

From the above it is evident that a FBG system, on his stand-alone basis, has characteristics which could make it inherently unstable on RDF, thus affecting his operability for clean syngas generation at industrial scale. In fact, achieving high levels of availability required with a heterogeneous waste derived fuel may be technically difficult, especially when a high quality and consistent quantity of syngas (as opposed to fuel gas for external combustion) is required.

Ashes and tars separation and removal and disposal were identified as the main obstacles to waste gasification in fluidized beds at large scale. There are three primary approaches for dealing with these; removal from the system for disposal, separation for recycling, or destruction. Nevertheless, it is not feasible to imagine different physical systems for separate tar and ash particles removal, since the cost would be prohibitive. Consequently the design of such systems must be based on the optimization of the simultaneous removal and/or conversion of these two entities.

New generation systems are designed to remove tars and fine particulate (via wet scrubbing) and recycle them back to the gasification stage. This strategy is a rational

approach for separating tars for recycling and is well thought through in terms of underlying principles and engineering. Compared with conventional physical cleaning systems, they are believed to be somewhat less susceptible to changes due to waste operation, although are not without risks. The dominant effect is expected to be a higher dust loading which could adversely affect the scrubber operation and create an additional hazardous waste stream. There may also be a change in tar loading and composition, which could require design changes.

By contrast, an additional thermal stage based on selective tar conversion and ash capture would be inherently more forgiving and stable. This can be achieved with the use of thermal plasma, which has been successfully used in conjunction with conventional thermal treatment units, for its ability to ‘polish’ the producer gas by organic contaminants and collect the inorganic fraction in a molten (and inert) state. The tar and ash removal by plasma methods is one of the most concern topics for current scientific research and is the main subject of next Chapter.

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