

CRANFIELD UNIVERSITY

DIMITRIS E. BALAMPANIS

COMPARATIVE STUDY ON THE COMBUSTION AND GASIFICATION OF
SOLID RECOVERED FUELS. EMPHASIS ON RESIDUES
CHARACTERISATION AND CHLORINE PARTITIONING

SCHOOL OF APPLIED SCIENCES

PhD THESIS

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Academic Year 2009-2010

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Supervisor: Dr. Raffaella Villa

October 2009

This thesis is submitted in partial fulfilment of the requirements for the degree
of Doctor of Philosophy

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Abstract

Thermal treatment is recognised as a valid option within the waste management hierarchy for the recovery of the energy content of waste. Recent developments in the field are signposted from emergent technologies and the standardisation of solid recovered fuels.

This work comparatively examines the fluidised bed combustion and gasification of a novel material; East London's solid recovered fuel. Emphasis is given on the characterisation of the solid residues produced from the two thermal treatment techniques and chlorine partitioning, in particular. Chlorine mass balances are studied under steady state conditions for combustion and gasification. Furthermore, trace metals content, chlorobenzenes, major elements, crystalline structures, and leaching behaviours are compared in the two residues types. For the characterisation of these residues a series of analytical methods have been applied and compared for their efficiencies.

Results indicate that gasification produces 5-6 times less HCl than combustion. Furthermore, gasification residues retain higher amounts of Cl and in less water soluble forms. However, gasification residues have 3-8 times higher organochlorides load, expressed as chlorobenzenes.

This work generates novel data on the comparative characterisation of waste thermal treatment residues. These data contribute towards the technical confidence for further utilisation of solid recovered fuels, and the knowledge over the residues' properties.

Acknowledgements

I would like to thank my supervisor Dr. Raffaella Villa, for her unlimited support and encouragement. Dr. Nigel Simms, my co-supervisor, is also greatly acknowledged for his persistence and inspiration. Without the help of these two people, this work would not be completed.

Dr. Phil Longhurst played a key role in this project. He is greatly acknowledged for his professionalism, ethics and support. I would also like to thank numerous anonymous members of staff, such as lecturers and technicians in the School of Water Sciences, the Energy Technology Centre and the Centre for Resources Management and Efficiency that contributed towards the completion of this work.

Last but not least, a great thanks to all the wonderful friends that stood next to me during these years.

*‘A deep mistrust of that which certain seems,
A hope of that which reason doubtful deems.’*

Farewell to False Love
Sir Walter Raleigh

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Acronyms

APC Air Pollution Control

ASR automobile shredded residues

CBs Chlorobenzenes

CEN (Comite Europeen de Normalisation)- European Comity for Standardisation

CFD Computational Fluid Dynamics

CHP Combined Heat and Power

CPs Chlorophenols

EPA Environment Protection Agency (America)

ESP Electrostatic precipitators

FBC Fluidised Bed Combustion

GC Gas Chromatography

HF Hydrofluoric acid

ICP-MS Inductively Coupled Plasma- Mass Spectrometry

IGCC Integrated Gasification Combined Cycle

L/S Liquid to solid ratio

MBT Mechanical Biological Treatment

MCFC Molten Carbonate Solid Oxides

MS Mass Spectrometry

MSDS Material Safety Data Sheets

MSW Municipal Solid Waste

MSWI Municipal Solid Waste Incineration

NCV Net Calorific Value

NIR Near Infrared

Pa-s Pascal- second

PAHs Polycyclic Aromatic Hydrocarbons

PAN peroxyacetal nitrate

PCCS (Programmable Computer Control Systems)

PCDD/Fs Polychlorinated Dibenzodioxins Dibenzofurans

PDF Packaging Derived Fuels

PM Particulate Matter

POPs Persistent Organic Pollutants

POV Piston Operated Valve

PTFE Polytetrafluoroethylene

PWF Packaging Waste Fuels

RDF Refuse Derived Fuel

ROCs- Renewable Obligation Certificates

RSD Relative Standard Deviation

SEM-EDS Scanning Electron Microscopy-Energy Dispersive Spectroscopy

SBG Spouted bed Gasification

SRF Solid Recovered Fuels

SOFC Solid Oxide Fuel Cells

TC Total Carbon

TGA Thermogravimetric Analysis

TOC Total Organic Carbon

WDF Waste Derived Fuel

WID Waste Incineration Directive

WMH Waste Management Hierarchy

WTT Waste Thermal Treatment

Chapter 1. Introduction

1.1 Study context within the integrated waste management framework

Waste thermal treatment is a traditional environmental engineering practice, which has been used for centuries for the mass and volume minimisation of wastes. Modern waste thermal treatment is considered as one of the integrated waste management practices, within the waste management hierarchy (WMH) (Figure 1.1). According to the latter, waste should be reduced, reused, and recycled, prior to any energy recovery process.

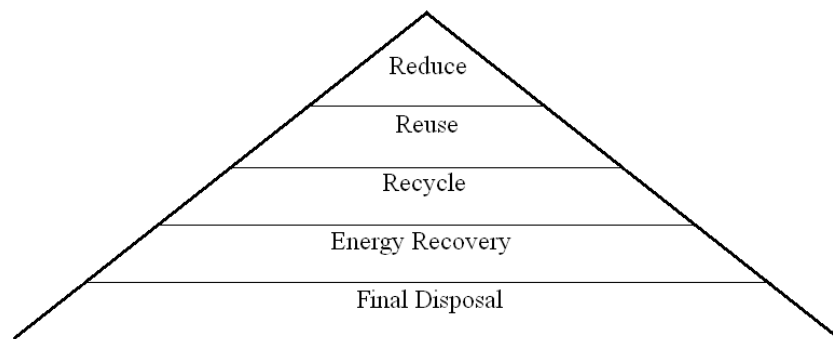


Figure 1.1. The waste management hierarchy

Waste energy recovery is met with different terms in literature, such as ‘energy from waste’, or ‘waste to energy’. The term includes a wide range of technologies, e.g. thermal treatment, anaerobic digestion, and landfill gas utilisation. The scope of these technologies is the recovery of the remaining energy content of wastes prior to their final disposal.

This work focuses on the comparison of two modern waste thermal treatment methods; combustion and gasification. Furthermore, the study examines the behaviour of wastes that have undergone through the previous stages of the WMH, and comparatively characterises the output materials of the two processes. In this context, the generation of detailed process data for one of the layers of the WMH is achieved.

1.2 Current status and trends in waste thermal treatment

Further to the minimisation of the mass and volume of waste, other factors the last decades have promoted waste thermal treatment (WTT). The diversion of biodegradable waste fractions from landfills, the increasing cost of land, the continuing interest in renewable energy sources, the changes in earth's climate, and the potential exhaustion of fossil fuel stocks, are only some of the incentives for the energy and materials recovery from solid wastes.

As a result, extensive research and commercial applications have been developed worldwide, including a variety of waste thermal treatment technologies. Some of these are: waste mass-burn grate incineration, combined heat and power (CHP) applications, utilisation of refuse derived fuels (RDF) in cement kilns and fluidised bed reactors, and the emergent technologies of gasification, pyrolysis, and plasma.

In 2000, only 2.6% of British waste was treated in WTT facilities (Defra, 2005), and it was early recognised that this percentage could rise. Porteous (Porteous, 2005) described why energy from waste is essential for UK's responsible environmental management, and identified opportunities for the utilization of waste as feedstock in cement production furnaces. Other studies indicated that the UK waste management practices in the waste hierarchy, do not optimise the energy recovery from biomass

waste (Biomass Task Force, 2005). Nowadays this proportion has reached about 11%, regarding MSW in the UK (Defra, 2009a). Europe 8-50% of the produced waste is treated in WTT facilities with Denmark, Netherlands, France, Sweden and Luxemburg being first in the ranking (Defra, 2009b). In US the equivalent percentage is 7.4% (Psomopoulos et al., 2009), and in China a cumulative capacity of ca. 50000 tones per day by 2010 is estimated (Wan et al., 2006).

Furthermore, applications that utilise new technologies operating in a starved oxygen environment, such as gasification, pyrolysis and plasma have achieved commercial success in the last few years. Detailed references of the latter can be found in literature (Heerman et al., 2003; Fichtner, 2004; Malkow, 2004; Longhurst et al., 2006). Gasification in particular, due to its enhanced capabilities for energy recovery, has attracted additional interest. The energy recovery of integrated gasification combined cycle (IGCC) processes, for example, is often advocated to be double than the incineration one (see paragraphs §2.2.2-§2.3.2).

Despite the technological innovations in the field of WTT and the regulatory framework that defines their environmental safe operation (EC, 2000), public opinion is often against their development (Luria, 2008; Psomopoulos et al., 2009). The major reason behind the negative perception of WTT is the generation of toxic flue gases and hazardous solid residues, which are the inevitable by-products of thermal treatment applications. The increased concern regarding these by-products is due to their enrichment with persistent organic pollutants and heavy metals.

However, some of the newest WTT technologies that operate under starved oxygen environment are claimed to be more environmental friendly in terms of toxic by-products production (Heerman et al., 2003; Malkow, 2004). These claims are often used for the commercial promotion of these technologies to highlight the

technological and environmental benefits of the latter, against traditional waste incineration.

1.3 Research question

A research question can be formulated within this context. Does sub-stoichiometric waste thermal treatment has advantages over incineration, in terms of toxicity of the generated by-products? In this work, the research question is addressed through the experimental comparison of fluidised bed combustion (FBC) and fluidised bed gasification (FBG), using waste derived fuels as feedstock. The breakdown of the research question to more particular questions is attempted. Particularly, the following questions are addressed:

- Is there a difference on the organochloride load of the two types of residues?
- Is there a difference in the trace metals concentration between the two types of residues?
- Is there a difference in the pollutants load of the leachate of the two types of residues?

The narrow-down of the research question to specific toxic species in the solid residues, along with the aims and objectives are analysed in the following paragraphs.

1.4 Original hypothesis- aims and objectives

1.4.1 Original hypothesis

The role of oxygen in combustion processes for the formation of organochloride pollutants like dioxins is described in the literature (see paragraph §2.5). Sufficient

oxygen supply ensures the complete combustion of unburned hydrocarbons which are major dioxin precursors (McKay, 2001). At a later combustion stage though, excess oxygen serves the de-chlorination of HCl through the Deacon reaction (paragraph §2.5.2- equation 2-10) and the subsequent chlorination of benzene rings (reconstructed by the 'de novo' process); both reactions are thermodynamically favoured and form dioxins precursors (Aracil et al., 2005).

The above imply that excess oxygen might play a controversial role in the formation of dioxins and generates the question of the performance of gasification against the same organochlorides indicators. Thus, the research question could be expressed by the following hypothesis.

H_1 : FBG produces less toxic organochloride pollution than FBC

Vs

H_0 : FBG doesn't produce less toxic organochloride pollution than FBC

Organochloride pollutants include a wide range of chemical compounds each of which has a specific toxic potential. The term dioxin, for example refers to 210 congener species. This number rises to 419 when the congener PCBs, chlorobenzenes (CBs) and chlorophenols (CPs) are added to the count (McKay, 2001). The toxicity of all these pollutants can be compared using the 2,3,7,8- Tetrachlorodibenzodioxin (the most toxic dioxin) as reference value according to the international (I- TEF) or World Health Organisation- toxic equivalency factors (WHO- TEF).

The workload and the cost of a detailed detection and quantification of all the congener species was beyond the capabilities of the present work. It was decided that a key performance indicator corresponding to I or WHO-TEF values should be utilised instead. An extended volume of information regarding the correlation of

gaseous dioxin precursors and I/ WHO- TEF values can be found in literature, rising from the analytical difficulties during 90's for the identification and quantification of the specific pollutants. The most important indicators and their correspondent correlation indicators with I-TEF are:

- Pentachlorobenzene (Kato and Urano, 2001a) $r^2 = 0.84$
- Hexachlorobenzene (Oberg and Bergstrom, 1985) $r^2 = 0.58$
- Sum of penta- and hexa- chlorobenzenes (Kaune et al., 1994) $r = 0.52 - 0.93$

From the indicators presented above, the sum of penta and hexa- chlorobenzenes was chosen as the reference value for the acceptance, or the rejection of the original hypothesis. Based on the above analysis, H_1 should be accepted if the concentration of penta- and hexa-chlorobenzenes produced during SRF (Solid Recovered Fuels) gasification is lower than the one produced by combustion of the same fuel. In any other case H_1 will be rejected and H_0 accepted.

$[Cl_{5,6}Bz]_{SRF \text{ gasification}} < [Cl_{5,6}Bz]_{SRF \text{ combustion}} \rightarrow H_1 \text{ accepted}$ $[Cl_{5,6}Bz]_{SRF \text{ gasification}} \geq [Cl_{5,6}Bz]_{SRF \text{ combustion}} \rightarrow H_1 \text{ rejected} \rightarrow H_0 \text{ accepted}$

Technical issues that evolved during the experimental work did not allow replicate trials and the subsequent data collection for the hypothesis testing. These issues will be discussed in the limitations paragraph (§ 5.4). However, aims and objectives were adjusted consequently to partially address the initial hypothesis as described in the following paragraphs.

1.4.2 Aims

The aim of this work was limited to the study of transfer phenomena and partitioning of chlorine and heavy metals in the solid by-products of the two processes.

Chlorine was selected because of its role in environmental pollutants and corrosive species. Cl is found in several POPs like poly-chlorinated biphenyl's (PCB's) and polychlorinated dibenzo-dioxins/ furans (PCDD/ F's). It is also the basic element of corrosive species like hydrogen chloride (HCl) and salts, such as potassium and sodium chlorides (KCl, NaCl). Furthermore, it is used by the waste management sector as a quality indicator for solid recovered fuels, (SRF) and as a legislative signpost for the characterisation of waste as 'hazardous'.

Waste derived chlorine enters thermal treatment processes either in an inorganic form, namely salts in food residues, or other organic waste. Extended literature is available regarding Cl behaviour, mass balances and partitioning issues in waste derived fuels incineration, and a few characteristics can be identified as common in most of these contributions:

- Artificial feedstock is used as test material (Chiang et al., 1997; Wey et al., 2001; Wey et al., 2006; Wey et al., 2008). This strategy ensures the necessary knowledge of the waste fuel composition. Furthermore the experimental work is simplified by the avoidance of complicated sub-sampling procedures. The trade-off in this case is to overlook the effects that heterogeneous waste feedstock can have in the Cl behaviour; e.g. different metals, or metal chlorides, namely copper and iron can have a catalytic effect on the organochlorides formation process (Liu et al., 2000; Wikstrom et al., 2003; Gilardoni et al., 2004).
- Bench scale examination (Chiang et al., 1997; Guo et al., 2001; Liu et al., 2001; Watanabe et al., 2004; Hilber et al., 2007a). In most

experimental works the apparatus is characterised by its small scale and the feedstock test quantity does not exceed a few grams. The advantage of this approach is usually very good control over the experimental conditions, and the reproducibility of results. However, valuable information about the kinetics of the process and/ or the memory effect influencing the generation of organochlorides is not examined.

The characterisation of solid residues, in terms of heavy metals concentrations, was also included in the aim of the study. However, high metals concentration in WTT solid residues has an oxymoron meaning. Although high concentrations are problematic in terms of residues stabilisation and final disposal, they can also be beneficial when we refer to the low boiling point metals. Thus the comparison of the two types of residues for their heavy metals content can provide further information on the potentials of FBC and FBG for metals volatilisation.

Furthermore, leaching behaviours were examined both for chlorine and heavy metals, as well as for other leaching species. This analysis is believed to provide a holistic view on the comparison of the processes through their produced residues, under the final disposal prism.

1.4.3. Objectives

It is important to highlight that the technical challenges that this work faced, suggested a slight change to the scope from ‘comparison of WTT processes’ to ‘comparison of WTT residues’. In this context, a slight shift from the original hypothesis allowed this study to set the following objectives:

1. Studying chlorine behaviour (phases, partitioning, and mass balances) for FBC and FBG using 'real' waste derived fuel.
2. WTT solid residues characterisation, with emphasis on Cl, heavy metals, and leaching behaviour from a scale that approaches pilot plant dimensions, offering 'in vivo' conditions.

1.5 Structure of thesis

The first chapter presented the research context within the WMH. Furthermore, the latest trends and developments in the field of WTT have been presented. These are signposted from the standardisation of waste derived fuels and emergent WTT technologies. Chapter one concludes with the presentation of the research question, hypothesis, and aims and objectives that this work investigates.

The second chapter is the literature review of this work. The background of WTT is investigated and the different available technologies are presented and classified. Separate sections with further details on combustion and gasification are given to provide the necessary information for the comparison of the two processes. Furthermore, additional information is provided for SRF, which is the feedstock of the experimental section. The role of chlorine in WTT and the chlorine pathways in furnaces are presented in detail, to complete the literature review chapter.

The third chapter is dedicated to the combustion experiments in the FBC. In this chapter the materials and methods used for the analysis of the combustion residues are presented in detail. This detailed presentation is a reference for the fourth chapter, regarding the gasification experiments and the gasification residues analysis, where the same analytical methods are used. Thus, chapter four focuses directly to the presentation of the gasification experimental conditions and the residues characterisation.

The fifth chapter presents a discussion over the comparison of the two processes/experiments; FBC and FBG. Furthermore, the differences between the two types of residues are discussed, based on the selected toxicity indicators.

The final chapter summarises the major conclusions of this work, as well as the limitations, the novelties, and the challenges for further work.

1.6 Synopsis

WTT is one of the approaches for the recovery of the energy content of waste within the WMH. This work focuses on the comparison of two modern waste thermal treatment methods and their solid residues; FBC and FBG. Studying chlorine behaviour for FBC and FBG using ‘real’ waste derived fuel, and solid residues characterisation, with emphasis on Cl, heavy metals, and leaching behaviour from a scale that approaches pilot plant dimensions are the objectives of this study.

Chapter 2. Waste Thermal Treatment- Literature Review

2.1 Introduction

2.1.1 Background

The increase in the standard of living in developed countries has led to increasing volumes of generated wastes. Although the most profound solution to this problem is the reduction of the generated wastes through a change in consumption patterns, (McKay, 2001), several environmental engineering approaches are historically, and currently available for the management of wastes.

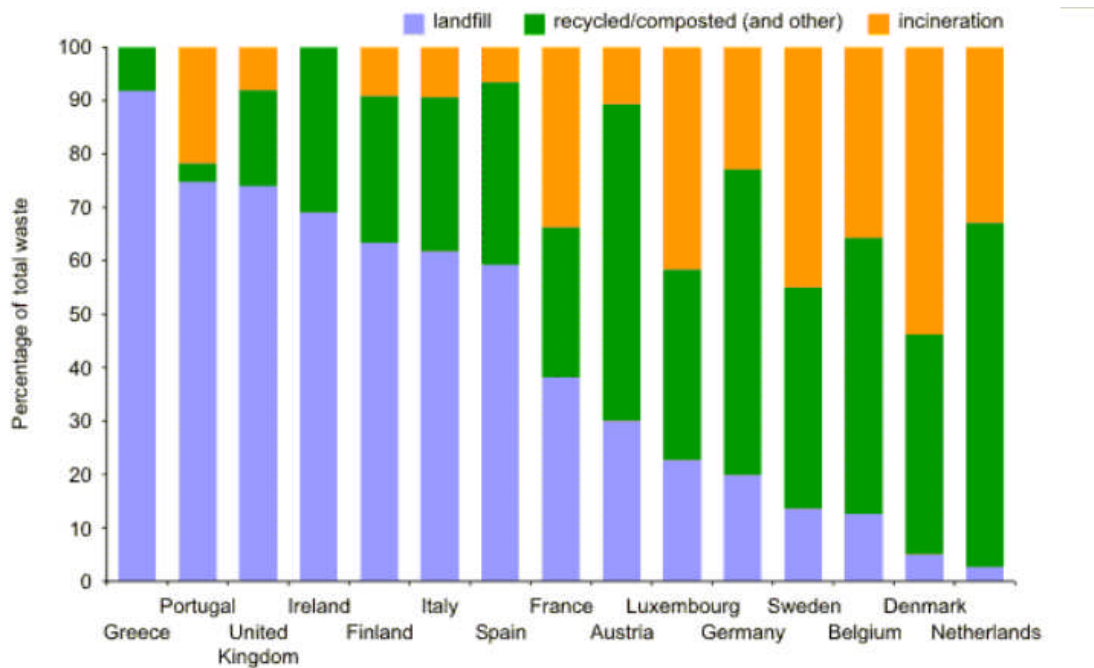
Traditional landfilling is nowadays considered increasingly expensive due to the cost of land (Liu et al., 2000), and a rather wasteful option, as valuable resources are lost. Moreover, landfills contribute ca. 35-73 Tg of methane per year to the global atmospheric CH₄ budget (IPCC, 2001), promoting global warming phenomena. Legislative initiatives (EC, 1999) are in place to resolve the abovementioned issue with the reduction of the biodegradable fraction of wastes from landfills. In the same context, UK has developed the landfill tax scheme. Except from the implementation of the abovementioned directive, the scheme acts as an economic tool that promotes further reduction of biodegradable waste, from landfills and the development of alternative waste treatment technologies (Morris and Read, 2001).

These legislations coupled by the depletion of fossil fuels, energy security issues, and the interest in renewable energy sources are considered as the incentives for 'waste to energy' research and commercial applications. Although 'waste to energy' is a generic term, referring to a wide range of technologies such as landfill biogas utilization, anaerobic digestion, thermal treatment, etc., this work focuses on WTT.

Waste incineration was traditionally used to reduce the volume of wastes. Although the first incinerators with energy recovery appeared in UK during 1895, these were rather insufficient due to the lack of cheap fuels (Morcos, 1989). Since then, waste incineration practices have been maturing, often facing public acceptance issues (McKay, 2001; Luria, 2008) until the universal scientific acceptance of the waste management hierarchy. The hierarchy consists of practices that aim to waste minimisation, reuse, recovery (of materials and energy) and finally landfilling (Porteous, 1997).

Thus, in replacement of traditional mass grate thermal treatment, the use of the combustible output fractions from mechanical- biological treatment (MBT) plants could further support a sustainable short/middle- term approach for the management of the increasing volumes of wastes, especially in dense metropolitan areas (Caputo and Pelagagge, 2002). This integrated waste treatment approach has increased its presence in Europe, with MBT plants that reach a capacity of 2 million tons per annum (Velis et al., 2009).

Recent data, as illustrated in Figure 2.1 (Defra, 2009b) indicate that EU countries such as Denmark, Netherlands, Belgium, Sweden, Luxemburg, Germany, France and Portugal, incinerate more than 20% of their generated municipal solid waste, while the equivalent percentage in the USA is ca. 17.2 % (Themelis et al., 2002).



Source: <http://www.defra.gov.uk/environment/statistics/waste/kf/wrkf08.htm>- Accessed on 29/5/09

Figure 2.1: Waste management practices in the EU(15)

In 2000, 2,6% of British waste was treated in WTT facilities (Defra, 2005), while nowadays this proportion has reached about 11% for MSW (Defra, 2009a) as illustrated in Figure 2-1. Developments in other EU countries and the literature indicate that this percentage is expected to rise. Porteous (2005) describes why energy from waste is essential for UK's responsible environmental management, and identifies opportunities for further utilization of waste as feedstock in cement production. In other reports (Eckardt and Albers, 2003; Murphy and McGeogh, 2004) an increase in energy recovery from waste fractions is foreseen. It is indicated elsewhere that current UK waste management practices in the waste hierarchy, don't optimise the energy recovery from biomass waste (Biomass Task Force, 2005).

With modern plants at the commissioning stage (CIWM, 2009), the UK is expected to follow the rising European trends in WTT and further technological maturity stages should be expected.

2.1.2 Classification of technologies

The science behind waste thermal treatment involves three types of thermal volatilization with different O₂ requirements (Tchobanoglous et al.1993):

- Incineration: with the exact amount of oxygen (the oxidising agent might be pure oxygen, or ambient air) needed for complete combustion, known as stoichiometric combustion. However, in practice excess oxygen is provided to ensure complete oxidation.
- Gasification: can be regarded as combustion with less oxygen than the stoichiometric requirements (the oxidising agent might be pure oxygen, ambient air, or steam).
- Pyrolysis: the thermal degradation of a fuel in the complete absence of oxygen.

Furthermore, the technology of plasma, initially developed for steel processing, evolved to gas cleaning systems and has recently been incorporated in medium scale applications for hazardous waste gasification systems (Moustakas et al., 2005; Lemmens et al., 2007).

The similarity of combustion, pyrolysis and gasification in terms of products is obvious. Although the definitions of the processes are strict and regard the amount of oxygen participating in each one of them, one should be aware that in real processes pyrolysis, gasification and combustion reactions might occur simultaneously, at least during part of the time taken by these processes. That might involve simultaneous reactions in different parts of the same reactor, or sequentially reactions in the same particles. Actually it is almost impossible to have combustion without the typical reactions of gasification (Santos, 2004). A good practice though, that seems to be

favoured in the literature is classification of technologies based on their primary products and oxygen requirements, and not based on the actual reactions that take place; for example a main difference is that pyrolysis produces an oil type fuel, while gasification doesn't (Figure 2.2).

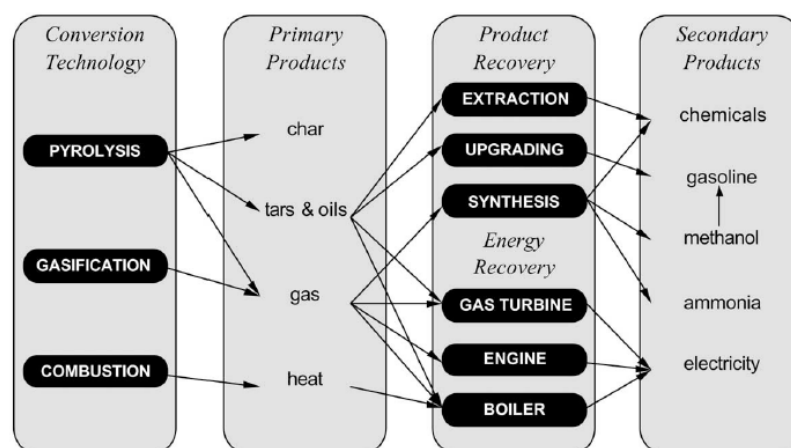


Figure 2.2. Categorisation of thermal treatment technologies
Source: Bridgewater et al, 1994

The combination of processes is often met in commercial applications. Pyrolysis followed by gasification and combustion, for example, has met commercial success (Malkow, 2004; Hacket et al., 2006; Thermoselect, 2006). A detailed reference to particular commercial technologies is out of the scope of the present work, and can be found in literature (Heerman et al., 2003; Fichtner, 2004; Malkow, 2004; Longhurst et al., 2006). This review focuses mainly in combustion and gasification and their detailed presentation follows in the next paragraphs.

2.2 Combustion

2.2.1 General Description

Waste incineration has historically been a management practice for the treatment of excess by-products from production processes, and the utilization of their calorific value. Rice mills, sugar mills, olive-oil production units and wood-product plants are only a few of the industrial applications that traditionally treated their waste in order to generate power in the form of thermal, mechanical and electrical energy (Prasad, 1995; Gelfand and Wong, 2001).

Autret et al. (2006) give a comprehensive description of a waste to energy incineration process: “Basically, incineration is the chemical reaction of oxygen (oxidation) with a combustible material. Waste is generally a highly heterogeneous material, consisting essentially of organics, minerals, metals and water. During incineration, the flue gases created contain the majority of the available fuel energy as heat. The organics in the waste will burn in gas phases when they have reached their necessary ignition temperatures and come into contact with oxygen. The actual combustion process takes place in gas phase in fractions of seconds and simultaneously releases energy. This leads to a thermal chain reaction and self-supporting combustion... Incineration of municipal and assimilated wastes also generates a solid slag, called “bottom ash”, which takes the form of a grey-coloured chunks, a mixture of metals, glass, silica, alumina, limestone, lime, unburned matter and water.” (Autret et al., 2006)

The development of waste to energy incineration plants to full scale units for the treatment of a variety of waste streams has the following advantages (Hester and Harrison, 1994):

- The immediate reduction of the volume (up to 90%) and weight (up to 75%) of wastes for final disposal.
- The destruction and detoxification of hazardous wastes, to render them more suitable for final disposal, e.g. pathologically contaminated materials, toxic organic compounds, or biologically active materials.
- The combustion of the organic component of biodegradable waste for the avoidance of fugitive landfill gas (LFG, mainly consisting of carbon dioxide and methane) emissions to the atmosphere from final disposal.
- The recovery of energy from organic wastes with sufficient calorific value.
- The replacement of fossil-fuel for energy generation with consequent beneficial impacts in terms of global warming.

However, incineration has a number of disadvantages, which consequently raise problems and criticism (McKay, 2001):

- Some waste materials are not suitable for combustion, either because they may generate harmful substances, or because they are more valuable for recycling.
- Poor operating practices and the chlorine level within MSW may lead to emissions containing dioxins and furans in flue gases and solid residues.

- The control of air emissions in terms of trace metals can be problematic.
- The commissioning of a new plant might involve excess capital and operating costs.
- Supplementary energy sources (fuels or electricity) are required to achieve the necessary combustion temperatures and the proper operation of air pollution control (APC) systems (e.g. afterburners, plasma, etc.).

The different stages and the operating conditions of a waste incineration process are described in detail in literature (Tchobanoglous et al., 1993; Asri and Baxter, 2004). At the front-end of the process some kind of fuel (waste) pre-treatment is considered essential for the removal of bulky, hazardous and inert materials. The mixing, shredding, drying and homogenization of the waste feedstock are among the practices that ensure good process performance to the combustion system.

The next stage is the feeding of the treated waste into the incinerator, which is in most cases achieved through a crane that moves the waste from the reception (or pre-treatment) pit to a hopper. The feeding technique can affect the whole process efficiency, as shown in previous studies where automated feeding systems combined with experienced crane feeder operators can provide optimum operation conditions (Chen, 2003).

The combustion of the materials occurs sequentially in an incineration chamber. The type of combustor is related to engineering choices regarding the feedstock characteristics: e.g., for mass burn facilities (mixed and untreated waste) mass grate incineration systems are used, while for Solid Recovered Fuels (SRF) smaller and more efficient systems such as fluidised bed combustors can be used (Tchobanoglous

et al., 1993; Eckardt and Albers, 2003). Other incineration systems such as rotary kilns which are used successfully in the cement industry, are described elsewhere (Murphy and McGeogh, 2004). The air necessary for the combustion is usually injected from the bottom (or the front end) of the combustion chamber, while secondary air injection at the top (or the back end) of the reactor ensures complete oxidation of unburned organic particles in the product gases.

The recovery of heat from the flue gases is the next stage in modern waste incineration facilities. Water-walls in the combustion chamber and/or heat boilers are usually employed to transfer the heat from the wastes and the flue gases to a steam production unit capable of providing district heating or electricity through a steam turbine. Detailed description and examples of the heat recovery mechanisms are provided in the following references (Horton, 1985; Priest, 1985; Weinberg, 1986) and a typical waste incinerator is illustrated in Figure 2.3. The final, but one of the most important sections in 'waste to energy' plants is the air pollution control (APC) system. Air emissions monitoring and effective control is crucial for every similar plant due to the risk associated with hazardous substances affecting ambient environment and humans.

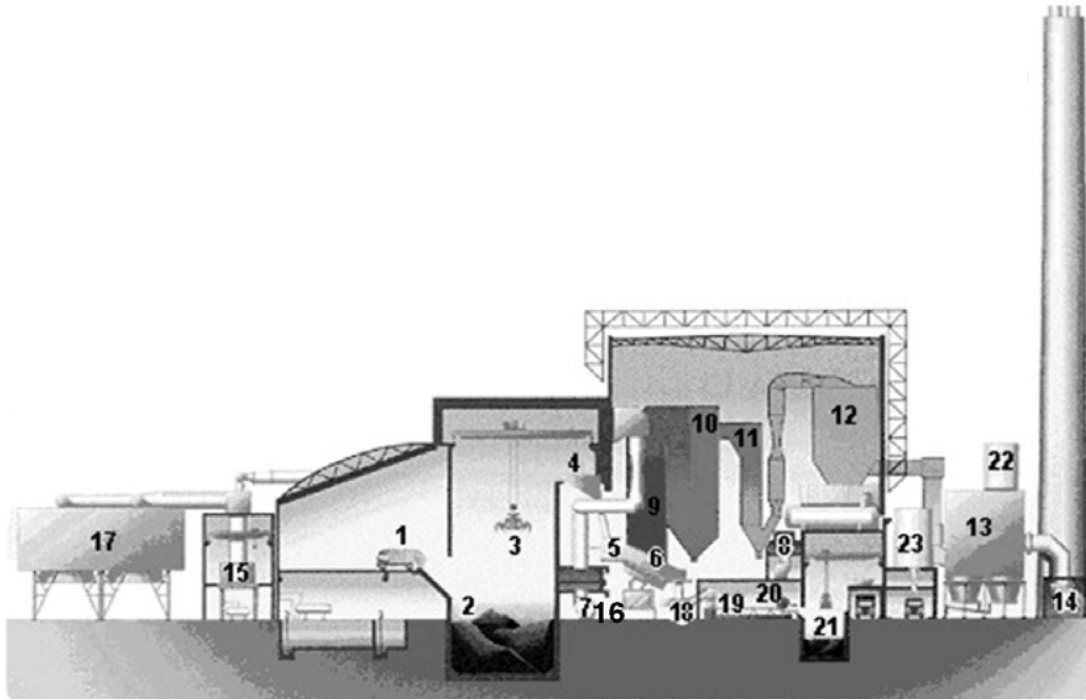
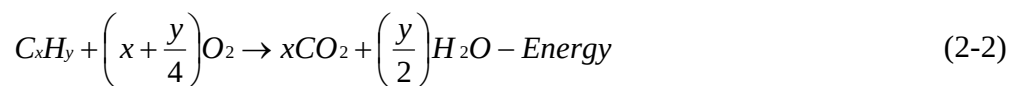


Figure 2.3: Typical arrangement of a mass grate incinerator (Amutha Rani et al., 2008): 1. Collection vehicle, 2. Refuse bank, 3. Crane, 4. Feed hopper, 5. Hydraulic ram feeders, 6. Storage grate, 7. Forced draught fan, 8. Overfire air fan, 9. Steam boiler, 10. Super heater, 11. Economiser, 12. Gas scrubber, 13. Bag-house filter, 14. Induced draft fan, 15. Turbine hall, 16. Air preheater, 17. Air cooled condensers, 18. Ash discharger, 19. Residue handling system, 20. Magnetic separator, 21. Residue pit, 22. Lime storage silo, 23. Ash silo

2.2.2. By- products

2.2.3.1 Energy

In general terms the combustion of hydrocarbons produces energy according to the following exothermic equations:



Typical arrangements for the collection and utilisation of the energy produced can be found in the literature (Horton, 1985; Priest, 1985; Weinberg, 1986; Prasad, 1995):

The heat is absorbed through the boiler's waterwalls or other heat exchangers (e.g.

steam boilers- Figure 2.3) to generate saturated steam, which is then piped to a steam engine, or turbine to generate rotary motion through a shaft. The kinetic energy is then transformed to electricity by an alternator. When additional subsystems are used, downstream the steam engine/ turbine, to collect the excess heat from the generated steam, then we refer to combined heat and power applications (CHP). CHP configurations utilise the amount of heat that would otherwise be wasted in the form of steam. In these systems the energy recovery levels are significantly higher, as the energy from the exhaust gases is transformed to electricity (Murphy and McGeogh, 2004; Dong et al., 2009). However the energy recovery levels expressed in different energy qualities (e.g. electrical and thermal terms) are not directly comparable (Patterson, 1996) and quotes on energy recovery should take into account the parameters described in the following paragraph.

The energy recovery (ratio of energy output to energy input) from waste fuelled steam power systems is affected by a number of factors. These are namely the feedstock's moisture and ash contents, the combustion chamber's efficiency, the losses of energy from flue gases and ashes that exit the system without effectively interacting with the heat exchanging mechanisms, the use of auxiliary fuels (parasitic energy demand), and the prime mover's and alternator's characteristics (Prasad, 1995). Different CHP technological arrangements can enhance the overall efficiency of a system by trade-offs between electrical and thermal outputs e.g. re-circulation of hot flue gases for the drying/ preheating of the waste feedstock prior to combustion (Heerman et al., 2003). Although experimental (Bujak, 2009) and theoretical approaches (Prasad, 1995) are available in literature using various 'work potential' indicators (e.g. Gibbs free energy- ΔG)(Patterson, 1996) for the harmonisation of different quality energies in WTT systems, comparison of literature data on recovery efficiencies should be

carefully examined. The following table (Table 2.1) summarises some of the available literature values.

Table 2.1
Energy efficiencies of MSWI systems

Type of system	Energy efficiency	Source
Fixed bed- 3 cylinder POV engine	Max 22% el. Actual 8.4- 11.9 % el.	(Prasad, 1995)
Field studies on various systems	15.3% el., 42.5% th.	(Murphy and McGeogh, 2004)
Typical MSWI system	20% el.	(Daskalopoulos et al., 1998)
Typical MSWI incinerator	Max 23% el.	(Belgiorno et al., 2003)
FBC- Steam turbine	18-3 22.4 % el.	(Yassin et al., 2009)
Waste fired CHP	60%	(Ilex Energy Consulting, 2005)
Waste fired CHP	45- 90%	(Eriksson et al, 2007)

Other authors express the energy efficiency in hybrid indicators in respect to specific waste feedstock characteristics, and/or resources saved from MSWI applications etc. Porteous (2005) for example, describes that 1 Mg of MSW can save 2.5 Mg of steam (400 °C, 40 bar), or 30 Mg of hot water (130-180 °C), or 500 kWh electricity when incinerated. In another example (Bujak, 2009), it is stated that 100kg of medical waste in a specific WTT system correspond to 660–800 kW of usable energy in the form of 1000–1200 kg of saturated steam. It is therefore obvious that the quoted energy efficiencies of WTT are process- specific, and highly heterogeneous data can be found in literature, which are not directly comparable.

2.2.3.2 Flue gases

Except from nitrogen, carbon dioxide is the major component of the MSWI flue gases. About 98-99% of carbon entering MSWI processes is converted to CO₂ (Ferrari et al., 2002). Besides CO₂ and steam which are the basic components of every incineration process, a number of impurities are present in the gaseous by-products, as listed in Table 2.2, and a short description on their formation and properties is given below.

Table 2.2

Classification of impurities in flue gas from waste incinerators

Particles	Gases
Heavy metals Cd, Pb, Cr, Ni, parts of mercury	Acidifying HCl, SO ₂ , HF, HBr, NO _x
	Heavy metals, mainly mercury
Dioxins, furans and similar chlorinated hydrocarbons	Dioxins, furans

(Carlsson, 1988; Wey et al., 2001)

- Nitrogen oxides (NO_x). The importance of nitrogen oxides in environmental degradation is because they are precursors to the formation of ozone (O₃) and peroxyacetal nitrate (PAN), the photochemical oxidants known as smog (Tscobanoglous et. al, 1993) and for their contribution to acid rain, ozone depletion in the upper atmosphere and global warming as relatively strong greenhouse gases. NO_x are minimized through effective combustion control and injection of ammonia (Tchobanoglous et al., 1993; Baukal, 2004).
- Sulphur Oxides. Sulphur oxides (SO_x) are recognized as significant air pollutants. SO₂ can be very corrosive in the presence of water although this is not generally of significant concern compared to its contribution to acid rain, through the formation of sulphuric acid (H₂SO₄). The majority of sulphur entering the WTT process can be found in the raw material, the waste feedstock usually in the form of sulfates or sulfides from, food waste, garden waste and rubber (Manahan, 1991; Baukal, 2004).
- Other acid gases. The presence of chlorine (Cl), fluorine (F) and bromine (Br) in the waste feedstock and in the auxiliary fuels during the combustion process can lead to the formation of acid gases with

corrosive characteristics such as hydrogen chloride (HCl), hydrogen fluoride (HF), and hydrogen bromide. Fluorine and bromine can be found in trace amounts in many products, while chlorine is found primarily in plastics, chiefly polyvinyl chloride (PVC), polystyrene (PS) and polyethylene (Tchobanoglous et al., 1993). Acid gases (HCl, HF, HBr, SO_x) emissions can be minimized by dry and wet scrubbing with sodium carbonate (Na₂CO₃) and lime (carbonate, oxides and hydroxides of calcium)(Tchobanoglous et al., 1993; Baukal, 2004). A more detailed discussion on chlorine behaviour in WTT is given on another paragraph of this chapter (§2.5).

- Dioxins, furans and chlorinated hydrocarbons. Besides the above mentioned pollutants, a complex range for pollutants such as dioxins and furans and other chlorinated hydrocarbons is related to waste thermal treatment. Dioxins are formed during the incineration process where oxygen, chlorine and hydrogen are present. Polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs), often referred to as “dioxin like” chemicals are persistent organic pollutants, which are highly toxic for humans. (McKay, 2001; Oberg, 2004). Due to the role of chlorine in PCDD/Fs formation, their detailed description is given in another paragraph (§2.5).
- Heavy metals. Heavy metals can not be destroyed in the combustion process but are either collected in the ashes, collected in the pollution control devices, or emitted to the atmosphere (Gilardoni et al., 2004). As illustrated in Figure 2.4 this distribution is called “partitioning” (Sullivan and Woods, 2000), and is related to their volatility and other

factors. These factors relate to combustion conditions such as temperature, moisture, pressure and the absorbents used in full scale processes (Durlak et al., 1997; Chiang et al., 2001). Heavy metals can also play a catalytic role in the formation of other pollutants, primary organochlorides in the flue gases (Öberg et al., 2007).

The release of flue gases from WTT plants is regulated by the Waste Incineration Directive (WID) (EC, 2000) that covers all the abovementioned pollutants. Their control is achieved through optimum operating conditions and APC systems. These systems include cyclones for bigger particles, electrostatic precipitators, fabric filters (bag-house filters), and wet, dry, semi dry scrubbers, absorption columns, condensers, and selective non- catalytic reduction mechanisms (for NO_x). Their detailed presentation is available in literature (Perry et al., 1997). Extensive literature on the fine tuning of APC systems is also available, e.g. the modelling and minimisation of Hydrogen Chloride (HCl) and Polycyclic Aromatic Hydrocarbons (PAH's) by the use of additives (Jannelli and Minutillo, 2006), the optimisation of lime spraying for semi-dry scrubbing systems (Huang, 2008), and the partitioning of heavy metals during sewage sludge incineration with waste co-combustion (Toledo et al., 2005) are only a few examples.

2.2.3.3 Ashes

The solid residues from WTT plants are generally generated from the 'bottom ash' (the ash and inert materials that are rejected from the bottom of the thermal reactor) and the APC operation and service by-products. Although other types of residues might be produced in solid or slurry form from the injection of additives for flue gas cleaning purposes, e.g. mostly lime residues from scrubbers (He et al., 2004; Amutha

Rani et al., 2008; Quina et al., 2008a; Quina et al., 2008b) this work focuses in bottom and 'fly ashes' only. The term 'fly ash' according to the International Ash Working Group (IAWG, 1997) refers to the particulate matter (PM) carried away from the combustion chamber and separated from the gas stream, prior to the addition of any additives.

Bottom ash consists of about 80% of the generated ashes in MSWI and is generally characterised as a non hazardous material, embedding no particular environmental concerns (Lundin and Marklund, 2007). However, fly ash can contain significant amounts of leachable salts, organic pollutants and heavy metals. About 0.1- 0.4% of the carbon entering a MSWI process is found in fly ashes in 200 different hydrocarbon compounds (Ferrari et al., 2002). These compounds are mostly consisted of PCDD/Fs, PCBs, PAHs, benzenes, phenols and other products of incomplete combustion (Huang et al., 2003; Liljelind et al., 2003). Furthermore, fly ash particles from 1 to 100 μm (Gilardoni et al., 2004) have a rather high concentration of heavy metals and salts in leachable forms (He et al., 2004; Quina et al., 2008b; Hyks et al., 2009). For the abovementioned reasons, fly ashes are characterised as hazardous waste (European Waste Catalogue number 190107*) (EU, 1994) and require further treatment prior to disposal, or disposal in special landfills.

Several methods are available for the de-contamination of APC residues like washing, chemical stabilisation, solidification and thermal treatment, a detailed presentation of which is available in the literature (Huang et al., 2003; Jung et al., 2005; Lundin and Marklund, 2007; Amutha Rani et al., 2008; Quina et al., 2008a).

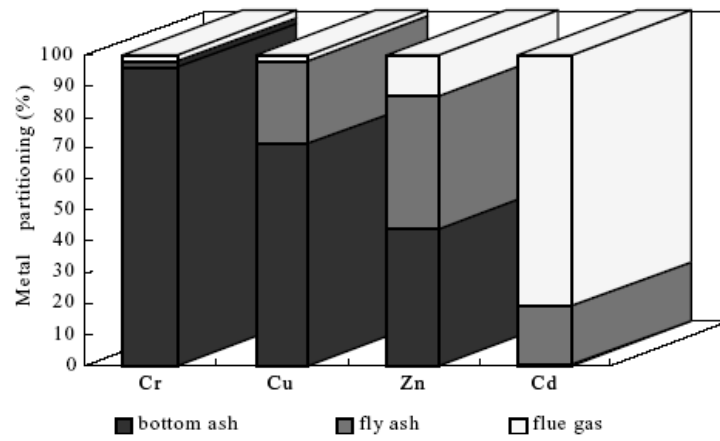


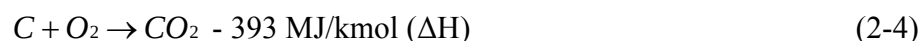
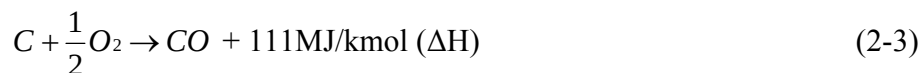
Figure 2.4: The partitioning of heavy metals during MSW incineration in the process outputs
(Chiang et al., 2001)

2.3 Gasification

2.3.1 General description

Gasification is a technology with a history of over a century and it was initially employed for the production of combustible gas from coal and biomass (Vick, 1981; Belgiorno et al., 2003). Gasification is the general term used to describe the process of partial combustion of a carbonaceous material with much less oxygen than stoichiometrically needed at temperatures between 600-1200 °C. The thermochemical conversion changes the chemical structure of feedstock to be quickly volatilized into gas and vapours by means of different heterogeneous reactions with an oxidising agent (air, steam or oxygen) (Belgiorno et al., 2003). In general terms the gasification process is the total or partial transformation of solid fuels into gases. This is accomplished by thermal conversion, chemical reactions, and a combination of both. Pyrolysis and combustion reactions, can be found between the numerous complex reactions that take place in a typical gasification process. The more (in standard conditions) important are (Morlando and Manahan, 1997; Santos, 2004; Abdul Salam and Bhattacharya, 2006; Lemmens et al., 2007):

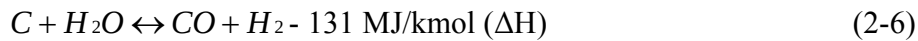
- Heterogeneous (gas- solid) reactions for the oxidation of carbon



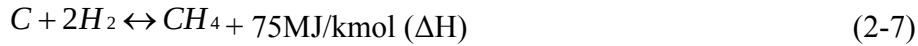
- The heterogeneous reaction between carbonaceous solids and carbon dioxide forming carbon monoxide, known as Boudouard reaction



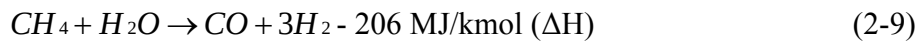
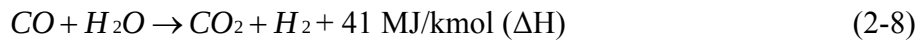
- The reaction of carbonaceous solids with water forming carbon monoxide and hydrogen



- The reaction of carbonaceous solids with hydrogen forming methane



- The homogeneous (gas phase) reactions for hydrogen formation



Through the above reactions the feedstock is gradually converted to syngas, a medium calorific value combustible gas, which is the main product of the process, mainly consisting of carbon monoxide, hydrogen, methane and other gas phase hydrocarbons. In general terms, any hydrocarbon can be gasified. The more the carbonaceous material in the waste feedstock the better the energy yields for gasification. The less inert content in the feedstock, the less process, economic and environmental problems for gasification WTT plants. The above requirements formulate a feedstock suitable for gasification in a specific range of carbonaceous medium calorific value, dried and shredded materials. In this range household, commercial, green waste, plastics, papers, tyres, cardboard, dewatered sewage sludge, automobile shredded residues (ASR) and agricultural waste is included (Higman and V.D. Burt, 2003).

As a rough rule, gasification reactions are endothermic, thus a proportion of oxygen serves the combustion of carbon in the feedstock, to provide the necessary heat for the reactions. In a typical gasification plant pre-treated waste is fed to the gasifier where the organic part is volatilised forming mainly a gas, while inert materials, unburned carbon, and ash leave the gasifier in the form of char. The so-called syngas, after cleaning up, can be used for energy production through integrated gasification

combined cycle (IGCC), or in a conventional boiler plant (Morris and Waldheim, 1998; Ando et al., 2005).

In WTT applications, gasification is advocated to have certain advantages in comparison to incineration. These are:

- Possibilities for improved energy recovery through a variety of technologies e.g. hydrogen for fuel cells (Kuramochi et al., 2005).
- Better process control and thus less emissions of thermal NO_x, PCDD/Fs and unburned combustibles (Belgiorno et al., 2003; Kantarelis et al., 2009)
- The production of chemicals such as methanol and ammonia (Bridgwater, 1994)
- Benefit from flexibilities of scale as gasification plants can be built in a modular manner and economic benefits from renewable fuels credit claims e.g. renewable obligations certificates (ROCs) (Yassin et al., 2009)

The benefits of gasification compared to incineration of wastes are also demonstrated in other technical reports (Murphy and McGeogh, 2004; Bebar et al., 2005). Extended information for commercial applications on the gasification of wastes can be found in the bibliography (Tchobanoglous et al., 1993; Higman and V.D. Burt, 2003; Malkow, 2004; Santos, 2004; Min et al., 2005; Longhurst et al., 2006) and Figure 2.5 represents a typical arrangement of an IGCC plant.

Despite the advantages of waste gasification, only a few full scale applications have achieved commercial success (Longhurst et al., 2006; Heerman et al., 2003). This fact is recognised from other authors when comparing the different WTT technologies (Consonni et al., 2005). The sophisticated technical requirements (Figure 2.5), along with the capital and operational expenditure for a gasification plant, could justify the popularity of waste gasification in commercial applications.

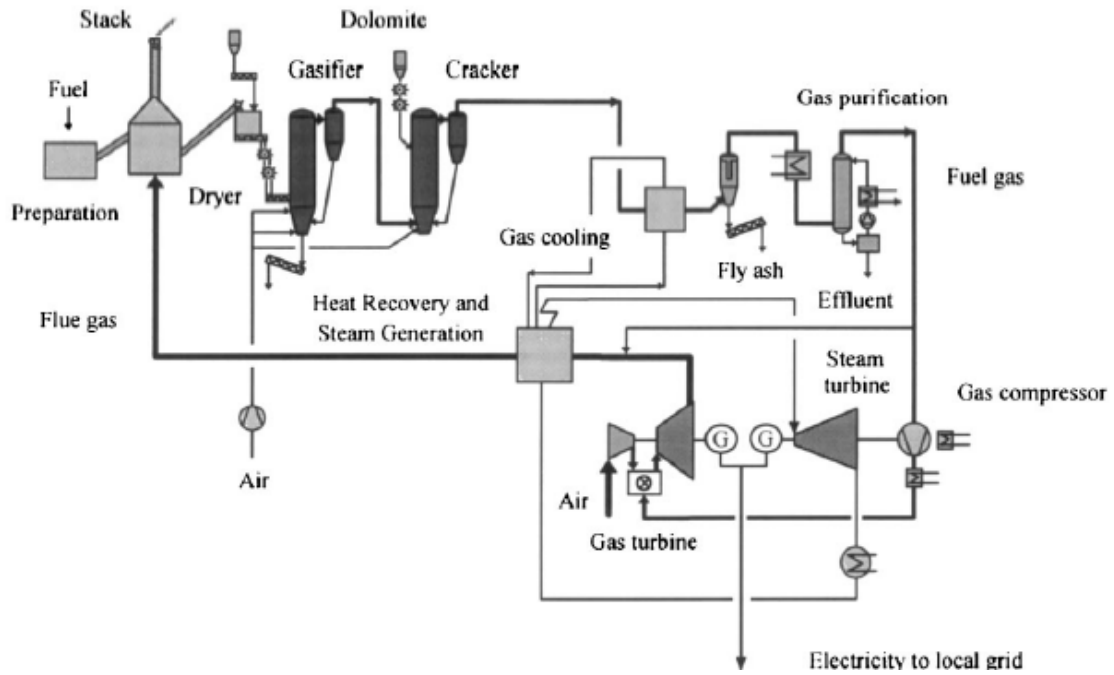


Figure 2.5: Typical arrangement of a Combined Gasification Cycle plant (Morris and Waldheim, 1998)

2.3.2 By- products

2.3.2.1 Energy

The main interest related to waste gasification is the potential of further utilization of the syngas in gas engines and gas turbines to overcome the efficiency of the steam cycle, to replace some quantities of fossil fuels (Kwak et al., 2005), etc. Indicative efficiencies vary from 12.5% for the gas engine up to 35.5% for the gas turbine, and efficiencies for various gasification systems are illustrated in the following table (Table 2.3).

Table 2.3

Energy efficiency rates for WTT gasification applications

Type of system	Energy efficiency	Source
FBG - Diesel Engine	30 % th.	(Min et al., 2005)
Down draft gasifier- gas engine	12. 5% el.	(Wu et al., 2002)
Circulating FBG- Gas engine	17% el.	(Wu et al., 2002)
Gasifier- gas turbine Combined Cycle	35.5% el.	(Morris and Waldheim, 1998)
Gasifier- gas furnace	27.8 % el.	(Morris and Waldheim, 1998)
Theoretical efficiencies	27.2% el. - 30% th.	(Murphy and McGeogh, 2004)
FBG- Gas engine	23.3- 24.7 % el.	(Yassin et al., 2009)
FBG- Gas turbine combined cycle	24.4- 26.8 % el.	(Yassin et al., 2009)

Generally, energy efficiency in ‘waste to energy’ systems is a multivariate value as described in § 2.2.3.1, influenced by the feedstock characteristics, the scale of the plant, the gasifier-boiler type, the energy recovery technique etc. In addition to what applies to incineration it should be noted that gasification reactions (equations 2-3,7,8) are endothermic, thus an amount of energy is absorbed in the process to sustain the gasification reactions. This energy should be provided by the simultaneous exothermic combustion reactions. However, in practice auxiliary fuels, or electricity are also used. Despite this trade-off the utilisation of syngas can allow enhanced energy recoveries compared to incineration. The modelling of such a multivariable value like energy efficiency in WTT gasification systems is given by Filippis et al. (2004). These data can be used as a guide for the prediction of the outcomes in terms of electrical power, according to different waste feedstock (Table 2.4).

Table 2.4

Modelled gasification conditions, syngas quality and electric power generation (Integrated Gasification Combined Cycle) for a 15 ton/ h plant treating various waste feedstock

Waste feedstock	O ₂ (m ³ (STP)/kg)	Outgas temperature (C°)	Energy efficiency	Produced syngas (m ³ (STP)/kg)	CO (%)	H ₂ (%)	Electric power (MW)
Methane	1.20	1141	0.88	4.20	28.48	47.75	92.31
Landfill gas	0.31	868	0.90	2.11	35.70	48.40	47.85
Waste oil	1.70	882	0.80	3.45	22.46	24.01	51.24
MSW1 ^a	0.70	873	0.62	1.49	3.75	3.54	9.75
RDF ^b	0.70	873	0.77	1.72	21.49	20.41	23.10
MSW2 ^c	0.40	859	0.87	1.56	43.79	32.21	32.37
RDF and waste oil	1.13	1304	0.79	2.30	22.65	12.83	32.62
MSW1 and landfill gas	0.67	875	0.77	1.70	17.72	19.26	21.52

^a Municipal solid waste typical of a low-income Asian country.

^b Refuse derived fuel made from MSW1.

^c Municipal solid waste of a high-income country.

Source: (De Filippis et al., 2004)

Further to the ‘in-situ’ use of IGCC for energy recovery, the process can be fine-tuned for the maximisation of hydrogen in the syngas, e.g. by providing steam as gasifying agent (Bangala et al., 1997; Skoulou et al., 2009). This can lead to applications for ‘ex-situ’ utilisation of hydrogen rich syngas as a transportation fuel (Bjorklund et al., 2001; Assefa et al., 2005), or in high temperature fuel cells like solid oxide (SOFC) and molten carbonate fuel cells (MCFC) (Kuramochi et al., 2005). However, different syngas cleaning requirements apply for each one of these applications.

2.3.2.2 Syngas

Syngas is a combustible gas containing mainly carbon dioxide, carbon monoxide, hydrogen, nitrogen, methane, water, trace amounts of higher hydrocarbons, inert gases present in the gasification agent, various contaminants such as small char particles and ash and tars (Bridgwater, 1994; Williams and Onwudili, 2006). The quality of syngas is defined by its yields in H₂ and CO and varies according to the waste characteristics, the oxidising agent, the gasifier type, temperature etc. Indicative

information is given by Aznar et al. (2006) in Figures 2.6 and 2.7, which illustrate syngas composition for different types of waste feedstock. Other sources (Kwak et al., 2005) report higher yields that reach ca. 33% and 30% per volume for H_2 and CO , respectively from MSWI gasification in double diffusion flame burners.

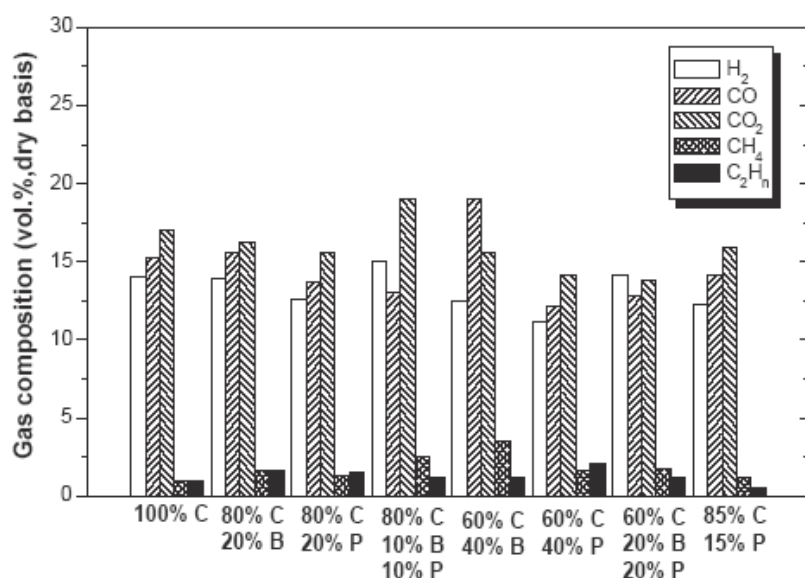


Figure 2.6: Effect of fuel composition on syngas composition for different mixtures of Coal, Biomass and Plastics waste (Aznar et al., 2006)

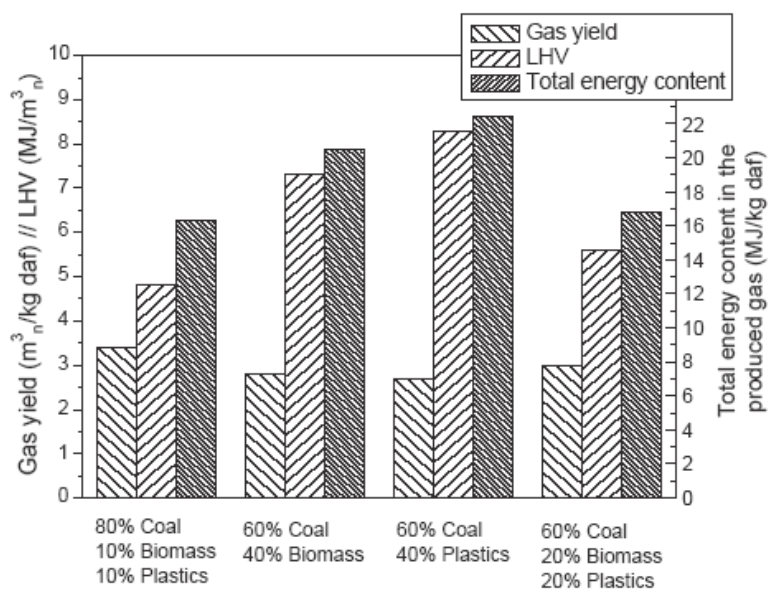


Figure 2.7: Effect of fuel composition on gas yield, LHV, and total energy content for different mixtures of waste feedstock (Aznar et al., 2006)

Furthermore, the experiments of utilising powdered tyres in a fluidised bed gasifier and the behaviour of product yields for various particle sizes and feeding rates (Leung and Wang, 2003), co- gasification of plastics with coal and biomass and the produced gas properties (Aznar et al., 2006) and the modelling of the working parameters of wood waste (saw- dust) gasification (Altafini et al., 2003), are available in literature. These studies indicate that the more homogenized the feedstock is, the better the syngas yields. In mono-stream biomass gasification for example (Lv et al., 2007), the hydrogen content achieved was over 50% per volume. However, it should be noted that waste derived feedstock is highly heterogeneous and with lower heating value, thus the expected syngas should be of lower quality. Finally as an indication on the effect that the type of gasifier can have on the product yields, Table 2.5 is provided, which illustrates the composition of syngas for various types of gasifiers.

Table 2.5
Syngas characteristics subject to different boiler types

	Gas composition, %v/v dry					HHV, MJ/Nm ³	Gas quality	
	H ₂	CO	CO ₂	CH ₄	N ₂		Tars	Dust
Fluid bed air-blown	9	14	20	7	50	5.4	Fair	Poor
Updraft, air-blown	11	24	9	3	53	5.5	Poor	Good
Downdraft, air-blown	17	21	13	1	48	5.7	Good	Fair
Downdraft, oxygen-blown	32	48	15	2	3	10.4	Good	Good
Multi-solid fluid bed	15	47	15	23	0	16.1	Fair	Poor
Twin fluidised bed gasification	31	48	0	21	0	17.4	Fair	Poor

(Bridgwater et al., 2002)

Syngas is often contaminated with solid residues and relatively small quantities of liquid/vapour fractions, e.g. vapours that later condense into tar (§ 2.3.2.3). Thus, the gas produced must undergo a series of cleaning treatment prior to any utilization. This treatment ensures protection of WTT from operational problems like pipe blockages,

particulates deposit, slugging and fouling etc. (Skoulou et al., 2009). If the syngas is combusted in high temperature combustion chambers to provide energy through the steam cycle then the requirements regarding contaminants are more elastic in comparison to the use of syngas in a gas engine or steam turbine (Bangala et al., 1997; Belgiorno et al., 2003) where the complete elimination of tar particulates is required.

2.3.2.3 Tar

The process has also a solid residue that has the form of char, containing mostly carbon, ash, inert material originally present in the waste feedstock, and tar. Tar is the generic term used in literature that describes a heterogeneous group of organic species including phenols, naphthalene, PAHs, chlorinated aromatics etc. (Bangala et al., 1997). A classification of tar components has been proposed by Van Paasen and Kiel (2004) as cited in Skoulou et al. (2009), using 5 different categories to allow consistent presentation and comparison of different results. According to that, class 1&5 represent GC undetectable and heavy chars, class 2 heterocyclic compounds with high water solubility, class 3 light aromatic hydrocarbons and class 4 poly-aromatic hydrocarbons.

The minimisation of tars is of major interest in every gasification process and various methods have been investigated for their control. These methods vary from fine tuning, thermal and catalytic cracking/ reforming, to plasma technologies and a detailed review is available in literature (Han and Kim, 2008).

2.3.2.4 Other products

Other products of gasification WTT applications can include flue gases and ashes similar to the ones produced by incineration (§ 2.2.3.2- 2.2.3.3). As in incineration,

gasification solid residues can be stabilized using techniques like solidification with cement and chemical agents, vitrification, etc. (Calaminus and Stahlberg, 1998; Jung et al., 2005; Amutha Rani et al., 2008; Quina et al., 2008a), while the final gaseous emissions are regulated by the relevant legislation (EC, 2000).

2.4 Waste derived fuels

2.4.1 Introduction

In almost every front-end of WTT systems, some kind of fuel preparation is performed that should exclude fractions of waste unsuitable for combustion. In harmonisation with the waste management hierarchy, pre-treatment systems support WTT by providing the following functions (Fichtner, 2004):

- The recovery of valuable recyclables.
- The removal of inert objects.
- The formation of smaller waste particulates, through grinding for the purposes of complete combustion.
- Drying for odours, storing and moving waste feedstock through MBT.
- The elevation of the calorific value of the waste feedstock.

In this context, bulky objects, ferrous and non ferrous metals (e.g. iron particles/ aluminium cans), mineral constructive materials (e.g. bricks-stones), hazardous goods (e.g. batteries, light bulbs-containing heavy metals), glass (e.g. bottles) and some plastics (e.g. PVC), should be excluded from the combustible fraction. This stage will ensure the minimization of the above materials in the feedstock but will not eliminate their presence in the process (Higman and V.D. Burt, 2003).

Furthermore, the pre-treatment stage includes size reduction, drying and homogenization according to the requirements of the end user (Eckardt and Albers, 2003). These requirements may vary in terms of particles size, moisture content, calorific value, or contamination from unsuitable substances according to the boiler

type and the process used for energy recovery. In the cement production for example, alkali conditions within rotary kilns can allow higher levels of Cl in the feedstock than conventional boilers like FBCs (Tchobanoglous et al., 1993). Figures 2.8 and 2.9 illustrate the medians and variations of the net calorific values and particle sizes of refuse derived fuel (RDF) used in various WTT plants.

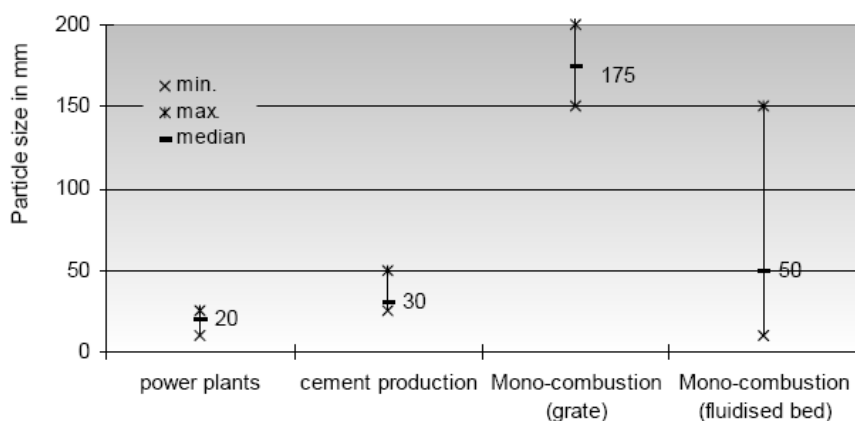


Figure 2.8: Required limits for particle sizes for various types of RDF utilization
(Eckardt and Albers, 2003)

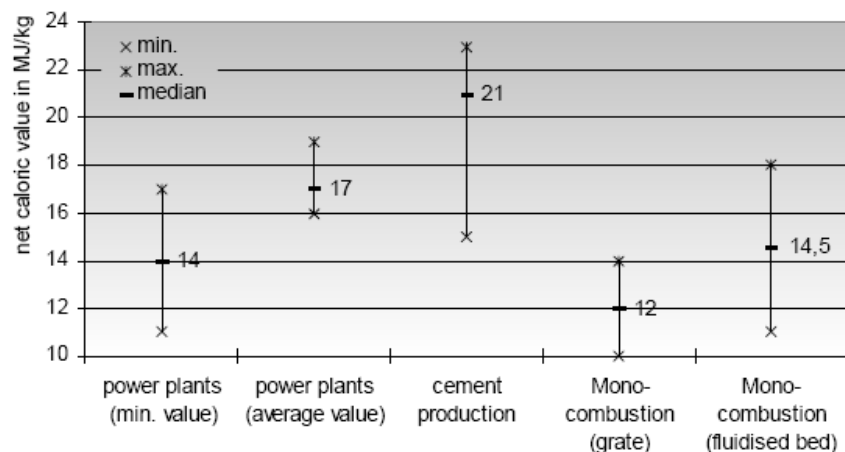


Figure 2.9: Requirements for the net calorific value of RDF in different combustion plants
(Eckardt and Albers, 2003)

The history of waste derived fuels (WDF) was not initially successful. Until 1984, over 50 different plants were built in UK and Germany, but could not satisfy demand

in terms of chlorine and heavy metals content of the feedstock produced, causing problems with co- combustion applications (Rotter et al., 2004). This led to a temporary decrease of interest in WDF technologies until the introduction of the Waste Landfill Directive (EC, 1999) which was estimated to increase the production of WDF to over 13 milion tones in EU (CEN, 2003). Furthermore, the development of MBT technologies could support this trend, as it will be analysed in the following paragraph.

2.4.2 Mechanical Biological treatment

Mechanical Biological Treatment (MBT) is defined as the processing and/or conversion of municipal solid waste (MSW) through a combination of mechanical, physical and biological processes, aiming at the stabilisation of the biodegradable organic matter contained in waste, the minimisation of methane emissions, landfill leachate, and the final volume and mass of waste to be deposited (Lornage et al., 2007). As this definition notes, and other researchers report (van Praagh et al., 2009), MBT processes were initially developed to stabilise waste in the context of the Landfill Directive, prior to landfilling. However, MBT technologies can be fine-tuned to produce improved WDF for thermal energy recovery (Velis et al., 2009).

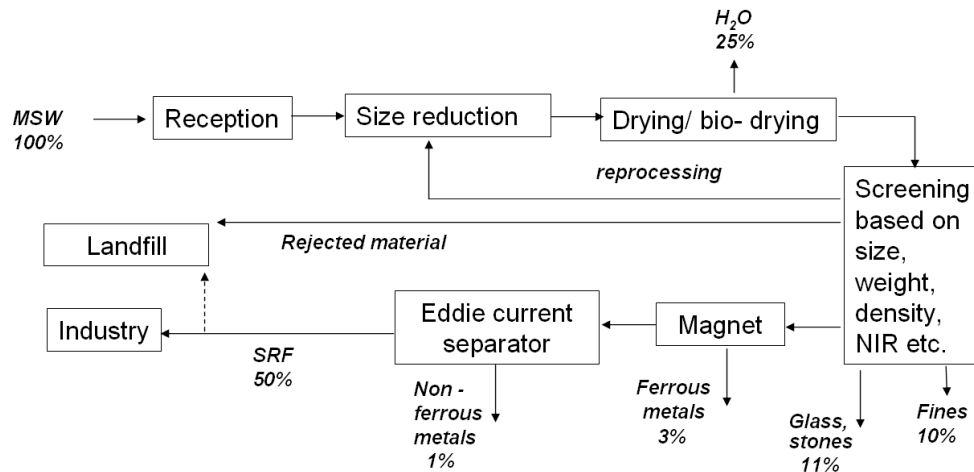


Figure 2.10: Arrangement and materials balance in a typical MBT plant.
Adapted from (Gascoyne, 2008)

Figure 2.10 illustrates the layout and the materials balance in a typical MBT plant. The initial size reduction can be achieved through a series of shredders and screens that re-circulate oversized materials. Dewatering of the material in the next step can be achieved through drying and bio-drying processes, where the heat released through aerobic decomposition of readily degradable organics is combined with excess aeration to dry the unsorted waste (Velis et al., 2009). The dried material has then a better behaviour in mechanical processing and separation methods using air classifiers, magnets, Eddie-current separators and optic techniques to remove materials unsuitable for thermal recovery, for the production of WDF according to the end users requirements. An extended presentation of the various separation techniques can be found in literature (Tchobanoglous et al., 1993; Caputo and Pelagagge, 2002; Rotter et al., 2004).

2.4.3 Solid recovered fuels

Waste derived fuels have been given various names and subsequent acronyms over the last years. WDF, RDF, PDF (packaging derived fuels), ASR etc. are only a few. The various names are representative of the numerous waste streams and components from which alternative waste fuels were produced. As a result no common basis, either for a wider scientific study, or wider commercial utilisation was available until recently. The last decade a series of efforts (Frankenhaeuser, 2008) has led to the standardisation (CEN/ TS 15359, 2006) of the various WDF according to their combustion characteristics.

According to the abovementioned standard, SRF is distinguished from the classical term of refuse derived fuel (RDF), as the initial characterization criterion is a non-hazardous waste source (Figure 2.11) and the final criterion is a quality assured (QA) classification according to the following properties (Table 2.6):

- The mean value for net calorific value (NCV). The relevant standard (CEN/ TS 15359, 2006) defines NCV as the lower heating value (LHV): *“calculated value of the energy of combustion for unit mass of a solid recovered fuel burned in oxygen in calorimetric bomb under such conditions that all the water remains as water vapour at 0.1 MPa”*.
- The mean value of chlorine content
- The mean and 80th percentile values for mercury content

Each property is divided in five classes with range values and the combination of the properties' classes makes up the class code for each SRF.

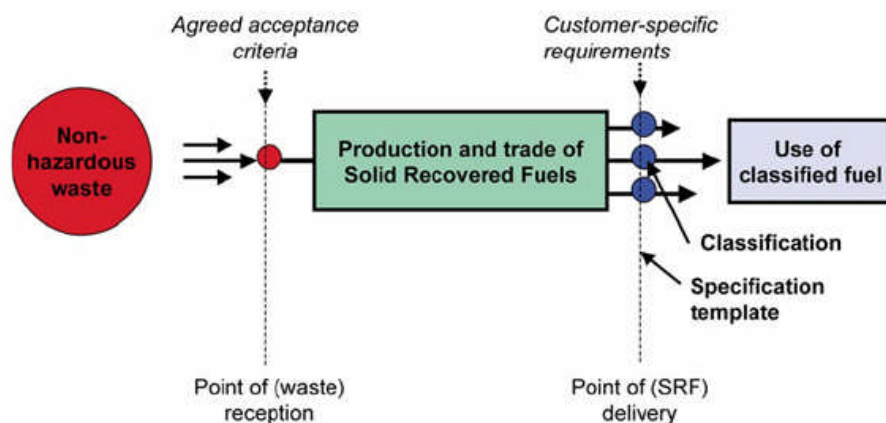


Figure 2.11: SRF context. Source: CEN/ TS 15359

The classification according to these three indicators intend to facilitate the economic (NCV), emissions (Hg), and technological (Cl) issues associated with the acceptance and marketability of waste derived fuels and related applications. As such, SRF standardization protocols can support the development and expansion of waste-fuel markets (Bernd et al., 2007; Garg et al., 2007).

CEN has produced a series of protocols that cover almost all the issues related with the investigation of the fuels properties. For statistical protocols that define appropriate sampling and sub-sampling methods (CEN/ TS 15413, 2006; CEN/TS 15442, 2006) to chemical methods for the investigation of particular properties considering the peculiarities of waste matrices e.g. biogenic content (CEN/TR 15591, 2007) or trace metals (CEN /TS 15411, 2006).

Table 2.6

Classification system for Solid Recovered Fuels

Classification property	Statistical measure	Unit	Classes				
			1	2	3	4	5
Net calorific value (NCV)	Mean	MJ/kg (ar)	≥ 25	≥ 20	≥ 15	≥ 10	≥ 3
Chlorine (Cl)	Mean	% (d)	$\leq 0,2$	$\leq 0,6$	$\leq 1,0$	$\leq 1,5$	≤ 3
Mercury (Hg)	Median	mg/MJ (ar)	$\leq 0,02$	$\leq 0,03$	$\leq 0,08$	$\leq 0,15$	$\leq 0,50$
	80 th percentile	mg/MJ (ar)	$\leq 0,04$	$\leq 0,06$	$\leq 0,16$	$\leq 0,30$	$\leq 1,00$

Source: CEN/ TS 15359

2.5 The role of chlorine in WTT

2.5.1 Introduction

The present work focuses in particular on the chlorine behaviour in SRF WTT utilisation. As Figure 2.12 illustrates chlorine sources in waste are either inorganic, namely salts (e.g. NaCl, KCl) in food residues and other organic waste or organic, namely plastics (PVC) (Rotter et al., 2004; Schirmer et al., 2005).

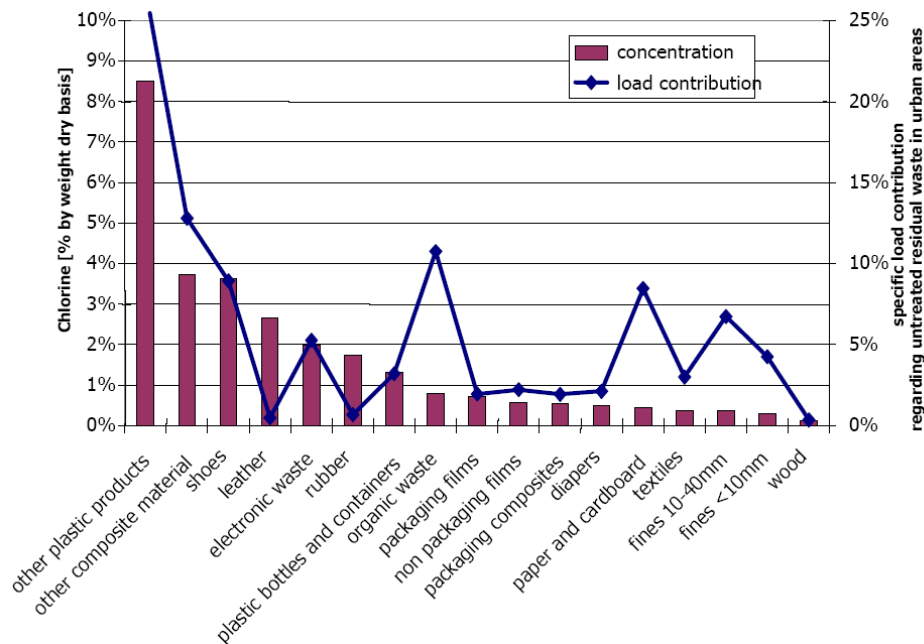


Figure 2.12: Chlorine concentration and specific load on MSW fractions

Source: (Rotter et al., 2004)

Chlorine in WTT processes decomposes at temperatures between 300-700 °C. As shown from thermogravimetric investigations organically bonded chlorine (e.g. plastics) is volatilised at lower temperatures (300-400 °C) than the chlorine in inorganic salts (600 °C) (Guo et al., 2001). When released to the gas phase, Cl is met

as HCl, gaseous Chlorine (Cl_2), chlorine radicals, or bounded to ash particles, again in the form of salts (Wikstrom et al., 2003).

The chlorine pathways from the point of its volatilisation in WTT furnaces include several homogeneous and heterogeneous reactions. Some of the most common gas-solid reactions are the reaction of HCl with alkali metals and alkaline earth metals to form salts (e.g. NaCl, KCl, and CaCl_2 , respectively). The addition, for example, of calcium compounds (e.g. dolomite $\text{CaMg}(\text{CO}_3)_2$) in the bed material and lime (CaO) assists the retention of HCl in the bottom ash and semi-dry scrubbers, respectively in WTT applications (Huang, 2008). The reaction of HCl with metals in the particulate matter to form metal chlorides (e.g. CuCl) is an other example that triggers catalytic phenomena for the formation of organochloride pollutants.

From the point of volatilisation onwards, a series of complex reactions initiates that affect two different phenomena; the formation of toxic organochloride pollutants in the flue gases and fly ash, and corrosion phenomena. These two processes are further analysed in the following paragraphs.

2.5.2 Formation of organochlorides

Waste derived chlorine in combustion processes is the major precursor for a series of toxic organic contaminants such as chlorobenzenes (CBs), chlorophenols (CPs), PCBs and PCDD/Fs (Wey et al., 2007). Although the detailed presentation of the formation mechanisms of these pollutants are out of the scope of the present work, a brief description is considered essential for the understanding of the broader research context.

McKay (2001) and others (Wang et al., 2003) summarize the organochlorides formation theories: (i) already present in the fuel, (ii) formation during combustion and (iii) 'de novo' formation in the post combustion chamber.

The last two theories seem to be more likely than the first based on recent research work (Stanmore, 2002; Wikstrom et al., 2003):

- Reactions involving elemental carbon and organic and inorganic chlorine in the fly ash characterised as 'de novo' synthesis and
- Heterogeneous catalytic reactions between particulates and chlorinated gas phase precursors (i.e. CBs and CPs) seem to be another dominant formation mechanism.

The role of CBs and CPs as precursors for PCDD/ Fs formation was identified early. Several researchers (Oberg and Bergstrom, 1985; Oberg and Bergstrom, 1987; Kaune et al., 1994) reported correlations between CPs, CBs and PCDD/Fs, or I -TEQ values. These attempts resulted from a need for PCDD/Fs estimation through indicator parameters due to the analytical difficulties for their determination and quantification. PCDD/Fs are persistent organic pollutants (POPs), which are highly toxic for humans. They are reported as Toxic Equivalent or International Toxic Equivalent (TEQ and I-TEQ respectively- there are 75 PCDD's and 135 PCDF's congener species, each differing in the number and position of the chlorine atoms) following a classification according to the most toxic dioxin (2,3,7,8 tetra-chlorodibenzo- dioxin)(McKay, 2001).

More detailed parameters affecting the formation mechanism have also been reported:

- In the study of Wikstrom et al. (2003) the ash bonded chlorine is reported to be more significant than the gas phase one for the formation process.

- Molecular chlorine formed through the Deacon reaction is more likely to undergo aromatic substitution reactions to produce dioxins than HCl (Liu et al., 2000; Aracil et al., 2005).



- Different metals, or metal chlorides, namely copper and iron can have a positive catalytic effect on the formation process (Liu et al., 2000; Wikstrom et al., 2003; Gilardoni et al., 2004; Öberg et al., 2007). Furthermore, other metal oxides like chromium, cobalt and vanadium can have a negative catalytic effect on the formation of chlorinated aromatics (Oberg et al., 2008).

Researchers have tried to find the relationship between the chlorine content of the waste feedstock and the dioxins at the end tail of various waste incineration facility types. For every molecule of PCDD/ PCDF two or more molecules of chlorine are necessary. In relevant reports where artificial waste samples of plastics, newspaper and pulp, impregnated with inorganic chlorides were tested, it was discovered that there is an obvious relationship between chlorine content and dioxin formation and TEQ value ($r^2 = 0.97$ and 0.99 respectively) (Yasuhara et al., 2002).

The chlorine content of the feedstock has a direct relationship with the amount of the specific pollutants. The above claim is confirmed for the '1% threshold'. For example, the correlation of PCBs and PCDD/Fs with Cl content in the fuel is only confirmed for concentrations of the latter $>1\%$ (Wikstrom et al., 1996) as indicated in Figure 2.13. This might be due to the 'memory effect' (pollutants get accumulated inside the combustor and are released at a later stage) especially in large scale incinerators, to the sensitivity of the PCDD/Fs capturing and detection methods, or

even the sensitivity of the detailed analytical detection of chlorine in the original feedstock (Schirmer et al., 2005). In another study (Wang et al., 2003) the threshold range 0.8- 1.1% of chlorine content in the fuel is reported as more important. Below that range PCDD formation dominates, while above that, PCDF formation rates increase faster. Positive correlation of the chlorine content in waste samples with dioxins formation is reported in several experimental works, but full scale experiments do not always reach the same conclusions; probably due to the effect of pollution control systems (e.g. the temperature inside the electrostatic precipitator that affect significantly the 'de novo' formation of dioxins) or other operating parameters (Everaert and Baeyens, 2001).

Finally, inconclusive evidence has been published on the effect of the chlorine origin: organic or non organic. Wikstrom (2003) observed no significant difference in the production of dioxins, but these results do not agree with other studies (Wey et al., 2001).

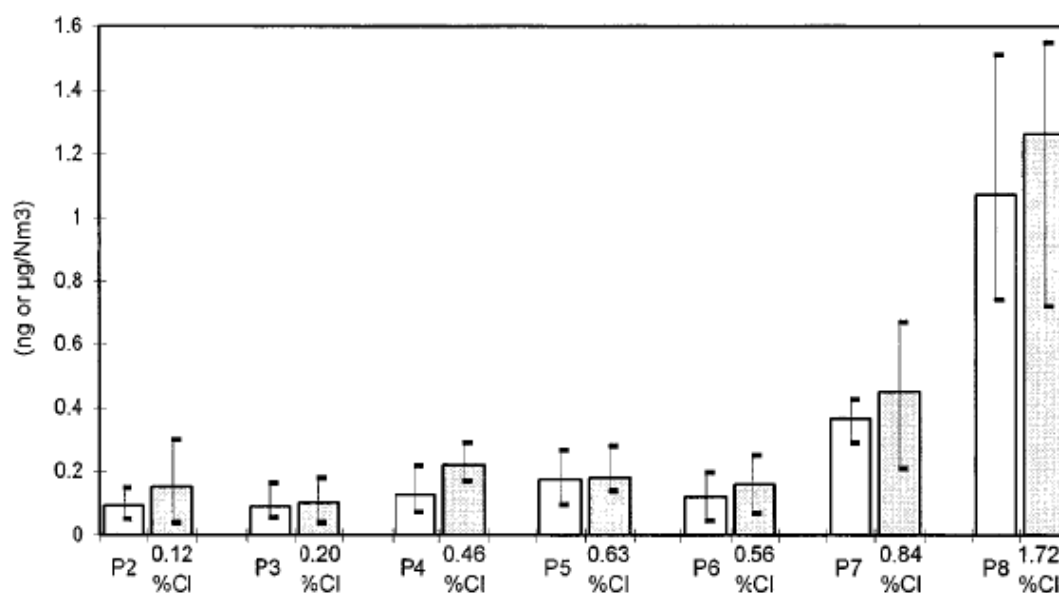


Figure 2.13: Average, minimum, and maximum values of the I-TEQ ng/Nm³ (shaded bars) and Σ3-6 PCBs µg/Nm³ (open bars) as a function of chlorine content in the fuels.

Source: Wikstrom et al 1996

It is evident from the above that the PCDD/Fs formation mechanisms are complex and depend on several parameters. It is also evident that the production of organochloride pollutants during waste derived fuels incineration is also affected by other elements in the feedstock. In full scale WTT processes PCDD/Fs prevention and abatement techniques have been studied and employed. These techniques have resulted to a dramatic reduction in the generated organochlorides and pollutants in general from similar processes, resulting in the characterisation of WTT as one of the cleanest sources of energy by the American EPA (Psomopoulos et al., 2009)

Some of the pollutants preventions and destruction mechanisms are summarised as following (McKay, 2001):

- Combustion Temperature $> 1000\text{ }^{\circ}\text{C}$, for complete destruction of PCDD/F molecules.
- Chamber Turbulence, $Re > 50000$ (Reynolds number), for adequate aeration inside the combustion chamber and minimization of unburned particles
- Gas combustion residence time $> 2\text{ sec}$
- Post combustion temperature: rapid quench cooling from $^{\circ}\text{C } 400$ to $^{\circ}\text{C } 250$
- Air pollution control devices: semi dry scrubber, bag filter, activated carbon injection.
- Process control: automated PCCS (Programmable Computer Control Systems) with interlocks and automatic MSW feed shut- off.

2.5.3 Inorganic chlorides and corrosion

The impact of inorganic chlorine species from a technological point of view is probably as important as the organic one from an environmental view. Chlorine participates in various complex reactions throughout the combustion process assisting the formation of corrosive phenomena in different parts of the combustion systems. The following corrosive mechanisms have been identified in literature as the most important (Daniel et al., 1988; Fordham et al., 2002; Sroda et al., 2006):

Gaseous corrosion by HCl: The mechanism is also known as ‘active oxidation’ where gaseous HCl and/or Cl_2 molecules react with the metal in the tubes of superheaters to form volatile metal chlorides. These products move outwards to the gas interface via porosity and crack metal surfaces before liberated to the gas stream. In oxygen rich environments the metal chloride oxidizes and the chlorine continues the circle promoting further material degradation.

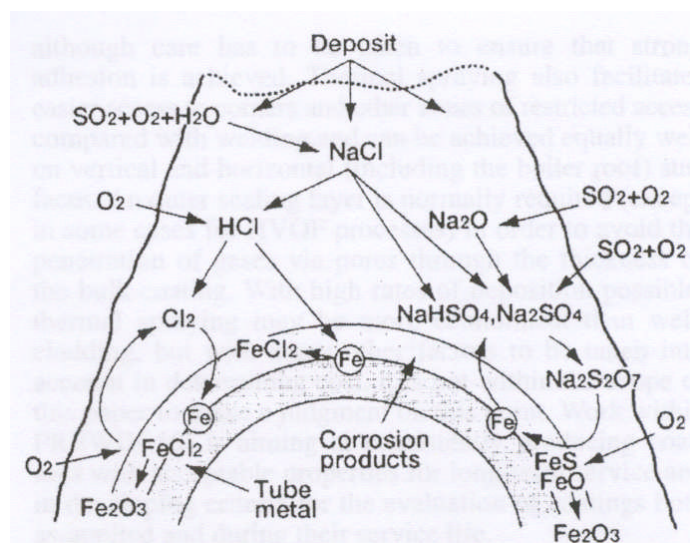


Figure 2-14. Simplified illustration of the complex corrosion interactions (Fordham et al., 2002)

Hot or high temperature corrosion: The phenomenon is also found in the literature as ‘deposit corrosion’ and ‘fireside corrosion’. The metal surfaces are covered with deposits containing salts, sulphites, metal chlorides etc. These species can react further to form eutectics (mixtures characterised by a low temperature melting point)

that breakdown the metal oxide layers of the tubes in water-walls and super heaters. Interaction between the flue gases and the deposits followed by further interaction between the deposits and the metal tubes form a circle of continuing degradation. Figure 2-14 illustrates the complex reactions of the mechanism.

Dew point corrosion: At low temperatures, HCl, sulphuric and hydrochloric acids have a corrosive effect on economisers and flue gas cleaning systems such as wet scrubbers and bag filters. The phenomenon also occurs during shut-down periods.

It is evident from the above that the amount of chlorine in waste derived fuels has a severe impact in the degradation of materials used in the combustion facilities. HCl and salts promote the gaseous and high temperature corrosion phenomena, respectively, in oxygen rich environments. These reactions can result to the failure of heat exchangers after a few hundreds of hours as demonstrated in recent experiments with waste derived fuels in full scale applications (Watson, 2008). Figure 2.15 illustrates pictures from the super-heaters and water walls of such installations.



Figure 2.15: Fouling phenomena to tubing (up) and water walls (b) that lead to flaking and failure (Watson, 2008)

2.6 Synopsis

Waste thermal treatment has historically been one of the management practices for the minimisation of the volume and mass of wastes and the recovery of their energy content. The recent interest in WTT is related to a number of factors such as the depletion of fossil fuels, energy security issues, the interest in utilisation of renewable fuels, and the diversion of biodegradable wastes from landfills due to global warming phenomena etc.

The recent developments in the field of WTT are signposted from two major changes. The first one is the development of advanced WTT applications such as gasification. Gasification in comparison to combustion has significant energy recovery advantages, due to the production of a combustible gas, mainly consisting of hydrogen and carbon monoxide that enables its utilisation in combined cycles for energy generation.

The second change, is a change in the production of waste derived fuels. The quantities of readily available mono-stream or MSW recovered fuels are increasing, especially in dense metropolitan cities. Furthermore, the quality of these fuels is also changing due to the development of MBT technologies, capable of mastering the heterogeneous nature of wastes to deliver fuels according to the end users requirements. This quality has been recently subjected to standardisation that is expected to enhance the marketability of SRF.

Despite these changes, there are technological and environmental concerns regarding WTT and the behaviour of pollutants like chlorine and trace metals in high temperature environments. Chlorine in particular, takes part in complex reactions that trigger corrosion phenomena, and the generation of POPs in the flue gases and solid

residues. These factors limit the development of WTT technologies and are considered as major research challenges for the success of full scale applications.

Chapter 3. Combustion experiments

3.1 Introduction

The present chapter describes the experimental conditions of the SRF FBC, the analytical methods for the characterisation of the produced by-products, and the obtained results. The experiments took place from January 2007 to February 2008 at the Energy Technology Centre in Cranfield University. Several tests took place during this period that served different objectives: training on the operation of the combustion rig; testing of the available feeding systems and the examination of various feeding rates; testing of the available analytical instrumentation; the production of preliminary ash and gas samples; tests and fine tuning of the analytical protocols etc.

During these tests a number of technical and operational problems were revealed. Most of these problems related to the nature of SRF and the feeding procedure, since the available test rigs were purpose built for the utilisation of coal or other granular feedstock (e.g. biomass pellets). SRF is a material with physical heterogeneity, high moisture content and a relative low bulk density, when compared to conventional fuels (Table 3.1). These characteristics caused bridging (cohesive arching) problems during the tests and blockages that resulted in erratic furnace operation and finally the termination of trials. Similar operational problems were reported recently from full scale applications (Watson, 2008) using similar fuels. These facts indicate that ready flow of SRF in feeding systems is a general challenge that the WTT sector needs to address and not a particular weakness of our test rigs.

Table 3.1
Comparison of SRF with coal-indicative attributes

Attribute	SRF	Coal
NCV- MJ/ Kg	18	31.5
Moisture w/w %	15	1.7
Ash w/w %	13	5
Bulk density kg/m ³	120	603
Chlorine w/w %	0.5	0.1

Source: adapted from Gascoyne, 2008 and Phyllis biomass database (www.ecn.nl/phyllis- accessed on 11/12/2008)

For the achievement of steady state conditions, ‘low technology’ approaches were often used; e.g., researcher with rod manually mixing the fuel to facilitate normal flow. Other factors that characterised a ‘successful combustion trial’ were the duration of the trial, the target temperature, the production of adequate gas and ash samples etc. When all the above conditions were achieved, the experiment was characterised as successful and the analysis of samples followed.

A detailed presentation of a successful trial and the subsequent analytical methods used for the analysis of the produced samples follows in the next paragraphs.

3.2. Materials and Methods

3.2.1 Feedstock properties and sub-sampling procedure

SRF derived from East London’s Waste Authority, as processed by a private contractor in a sequential separation, shredding, and aerobically bio-drying MBT process, classified as a “NCV 3; Cl 2; Hg 1” class SRF was the feedstock for the trial. A batch of 100kg was sampled from the MBT plant and it was later sub-sampled as a ‘static pile’ according to the relevant standard (CEN/TS 15442, 2006). Twenty four piles of equal volume were created, after homogenisation by mixing, and an equal

number of increments, with an arbitrary mass of 100g each was collected by sub-sampling 33g from the top, the middle and the bottom of each pile. The resulting 2400g lab sample was shredded to <4mm (Retsch- SM 2000 cutting mill), and by mixing and quartering (CEN/ TS 15413, 2006) was further reduced to 300g. Three replicates of 100g were produced, shredded to 0.5mm (Retsch- ZM 200 centrifugal mill), and 1g from each replicate was finally tested for Cl content using the oxygen bomb method (CEN/ TS 15408, 2006) and was found to be 0.4 ± 0.02 %wt dm. Figure 3.1 illustrates the sampling plan. The remaining data on ultimate analysis (Table 3.2) were provided by the SRF producer based on routine QA/QC analysis.

Table 3.2
SRF properties

Proximate analysis (%wt ar)	
Moisture content	13.2 ± 1.5
Ash content	13.7 ± 2
Ultimate analysis (%wt dm)	
C	47.4 ± 4.2
H	5.7 ± 2.9
N	0.8 ± 0.3
S	0.1 ± 0.02
Cl	0.4 ± 0.02
O	31.9^*

* By difference/ including errors

Based on the ultimate analysis, and the assumption that SRF comprises mostly of lignocellulose materials (Bangala et al., 1997), an approximate theoretical formula was estimated ($C_6 H_9 O_4$) for the feedstock. This approach, as indicated in literature (Themelis et al., 2002), can simplify the stoichiometric calculations for heterogeneous materials.

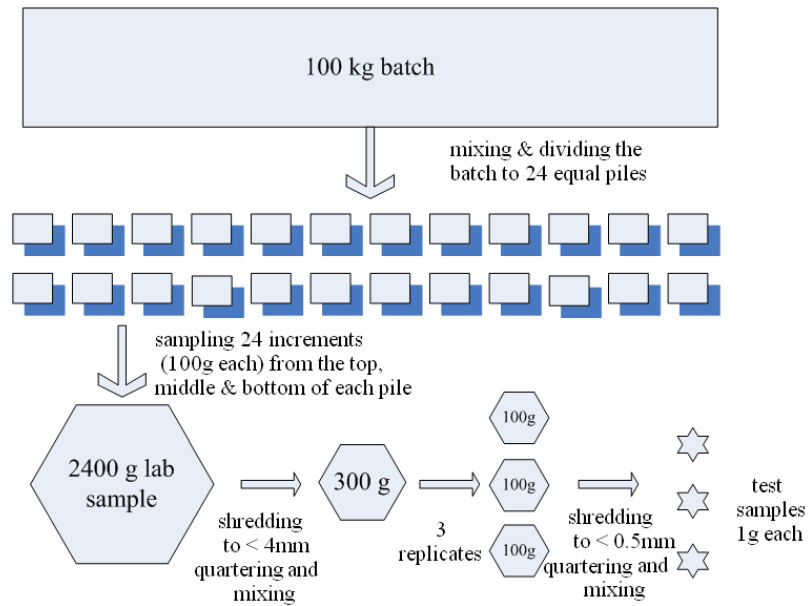


Figure 3-1. Schematic of the SRF sampling plan

3.2.2 Fluidized bed combustion rig operating conditions

The 50kW fluidized bed combustor (Figure 3-2) used for the trial consisted of a screw feeding hopper, the main bed chamber (dimensions 173*30*30 cm), a secondary combustion chamber that leads to a vertical ash deposition/combustion system, a water cooled heat exchanger, a cyclone and an exhaust fan prior to the stack. The rig was monitored by: 19 thermocouples; CO, CO₂, and O₂ online gas monitoring systems, HCl and gaseous chlorobenzenes capturing bubblers. The bed area was filled with 30.2 kg of silica sand (particle size 1.00 – 0.5 mm, 16/30 grade, density 1556 g/l, bed static dimensions= 30*30*15.35 cm). The FBC was vacuum cleaned the day before the experiment for the removal of residual ash and particles from previous trials. Furthermore, it was operated overnight, burning natural gas resulting in a bed temperature of 460 °C for the elimination of organic species. The supply of primary, secondary air and natural gas before the SRF feeding was 500, 400 and 25 l/min,

respectively. The SRF incoming flow varied throughout the trial with a mean value of 117g/min and a lambda [λ] coefficient equal to 1.7. The duration of the test was 300 minutes and the bed temperature was at 800 ± 20 °C. The flue gases were monitored by an on line gas analyser. The gas sampling line passed through a particles' trap and a glass wool filter, both situated in an ice bath. Thus, the following measurements are assumed to be in room temperature. The CO₂ levels had a mean value of 3.55% and ranged between 1.18 and 5.86%. The O₂ concentration had a mean value of 17.6 ppm and ranged between 0.5 and 20.6 ppm. The CO levels had a mean value of 64 ppm and ranged between 6 and 160 ppm.

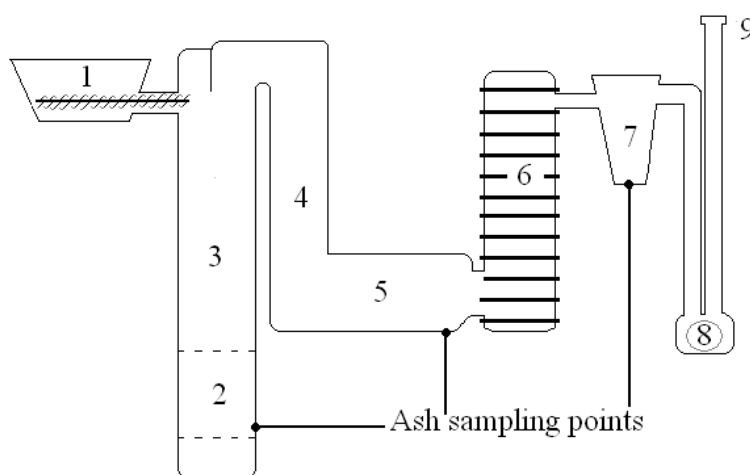


Figure 3.2. Fluidized Bed Combustor- 1: screw feeding hopper, 2: FB chamber, 3: bed area, 4: vertical secondary chamber, 5: horizontal secondary chamber, 6: water cooling tower, 7: cyclone, 8: exhaust fan, 9: stack

3.2.3 Analysis

The airborne chlorobenzenes were captured using the apparatus presented in Figure 3. The sampling train, as described in the literature (Kato and Urano, 2001b) is a modified standard (BS EN 1948, 2006) rig, and has a proven capturing efficiency >85% for Cl₅₋₆Bz recovery. The sampling lasted 30 minutes during steady state

conditions. After the experiment the deionised water and diethylene glycol were mixed (mix A). The gas traps and glass- PTFE tubing were washed twice with 50 ml of ethanol, and 50 ml of toluene. The rinsing solvents were added to mix A and extracted twice (liquid to liquid extraction) with 100 ml of toluene for each 1 litre of mixture.

The extracts were evaporated to 5 ml using a rotary evaporator (38 °C, 68 mbar) and cleaned up using ‘Waters Sep-Pak light silica’ cartridges attached to gas tight syringes. The cleaned- up extracts were further evaporated down to 1ml using a nitrogen flow, spiked with $1.6\mu\text{g ml}^{-1}$ 1,2 dichlorobenzene-d₄ (recovery standard) and stored at 4 °C for GC-MS analysis. The GC-MS parameters are given in § 3.2.4.4.

The HCl was captured using a set up similar to the one presented in Figure 3.3 with 2 gas traps filled with deionised water and the amount of Cl anions was determined with titration using silver nitrate.

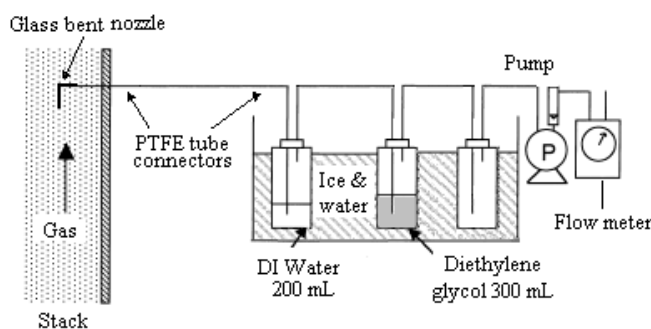


Figure 3.3. Chlorobenzenes sampling train

After the experiment, the rig was disassembled and the mixed silica sand/bed ash were collected, weighted, and emptied into a tank with DI water. The tank was mechanically agitated for 3 hours and 6 replicate samples were taken, centrifuged and filtrated. The horizontal chamber and cyclone ash were vacuum-cleaned and collected separately in clean pre-weighted vacuum bags; due to the visual difference in particle dimensions (SEM pictures on § 3.3.4), these ashes will be referred herein and after, as

coarse fly ash and fine fly ash, respectively, according to the literature definitions for fly ash (IAWG, 1997; Quina et al., 2008a): “*the particulate matter carried over from the combustion chamber and removed from the flue gas stream prior to addition of any type of sorbent material*”. Finally the ash samples were homogenised using a mortar and screened through a 0.5 mm sieve.

3.2.4.1 Total and water soluble Cl

Three replicates, of one gram each, from each fly ash type, were analysed for total Cl by an external laboratory, using a standard method (ASTM, 1991).

Six replicates of a gram each, of coarse and fine fly ash were diluted in 200 ml of DI water and agitated for three hours. The mix was centrifuged and decanted and the filtrate was stored in polypropylene bottles, at 4 °C for chloride ions analysis (Dionex, UK- Ion Chromatographer, column: Ion Pac As9- HC 4*250 mm).

3.2.4.2 Heavy metals

Standard methods (ASTM, 2004) for the determination of heavy metals in combustion residues, involve the utilisation of hydrofluoric acid (HF). These methods were excluded from this work due to their adverse effects on instrumentation and for health and safety reasons. The literature was reviewed for HF- free digestion methods and the following references with the equivalent recoveries were taken into account (Table 3.3):

Table 3.3:
HF- free digestion methods and the achieved recoveries in literature

Matrix	Materials & Methods	Instrumentation	Metals	HFF- RR* (%)	Source
1 Soils	Aqua Regia Hot plate digestion/ reflux condenser	Flame & Electrothermal AAS		-	(British Standards, 1995)
2 Coal	MWAD** 220- 240 °C, 2.5- 4 MPa H ₂ O ₂ & HNO ₃	ICP- OES ICP- MS	Cu Cr Ni Cd Pb Zn	95- 100 94.8- 98.5 99-113 120- 170 92.5- 103 -	(Wang et al., 2004)
3 Soils, sediments, sludge, organic waste	Aqua Regia Hot plate digestion/ reflux condenser	ICP- MS F- AAS	Cu Cr Ni Cd Pb Zn	95.7- 105 - - 95.7- 101.6 95.5- 111 94.7- 119	(Sastre et al., 2002)
4 Coal / coal fly ash	MWAD (110- 130 °C) H ₂ O ₂ & HNO ₃	ICP- AES GF- AAS HG- AAS	Cu Cr Ni Cd Pb Zn	47 77 49 - 45 44	(Iwashita et al., 2007)
5 Sewage sludge/ waste Fly ash	MWAD HNO ₃	F- AAS ICP- AES GF- AAS	Cu Cr Ni Cd Pb Zn	101- 106.8 ^a 66.8- 136 ^a 76.4- 93.6 ^a 80.5- 139.1 ^a 99.7- 117.3 ^a 91.2- 100 ^a	(Mester et al., 1999)
6 Coal fly ash	MWAD (110- 130 °C) H ₂ O ₂ & HNO ₃	GF- AAS ICP- AES	Cu Cr Ni Cd Pb Zn	48 75 49 - 38 44	(Iwashita et al., 2006)
7 Coal	MWAD (110 °C) H ₂ O ₂ & HNO ₃	ICP- AES	Cu Cr Ni Cd Pb Zn	86- 102 70- 96 47- 93 - 87- 103 90- 95	(Xu et al., 2005)
8 APC residues	150 °C - 6 h closed vessel digestion Aqua Regia/ HNO ₃	F- AAS	Cu Cr Ni Cd Pb Zn	No statistically significant difference between the acid mixtures ^a	(Quina et al., 2008b)
9 Coal	MWAD 200- 250 °C 7.5 MPa HNO ₃	ICP-MS ICP- OES FI- ICP- MS	Cu Cr Ni Cd Pb Zn	86.1- 98.3 85.9- 94.1 86.3- 106.4 96- 197 80- 100.2 105.8- 166.6	(Wang et al., 2006)

F-AAS: Flame atomic absorption spectrometry, ICP: Inductively coupled plasma spectrometry, MS: Mass spectrometry, OES: Optical Emission Spectrometry, GF- AAS: Graphite furnace atomic emission spectrometry, AES: Atomic emission spectrometry

* Hydrofluoric Acid Free method Relative Recovery (Found/Certified) - Range of Values

** Microwave Assisted Digestion

^a Hydrofluoric Acid Free method Relative Recovery (Found /digestion with HF) - Range of Values

Based on the available instrumentation and the expected recoveries, four HF free digestion methods were tested for their recoveries, using a certified reference material (CRM). The CRM was MSW incineration fly ash (BCR-176R, Joint Research Centre, Institute for Reference Materials and Measurements, EC) and a summary of the digestion methods is presented in Table 3.4.

Table 3.4
Summary of digestion methods

Method	Reagents	Digestion conditions
A	8 ml HNO ₃	Open vessel digestion 16 hours MWAD 190°C, 18 bar
B	3 ml H ₂ O ₂ + 5 ml HNO ₃	Open vessel digestion 16 hours MWAD 190°C, 18 bar
C	8 ml HNO ₃	Open vessel digestion 16 hours MWAD 190°C, 18 bar + ultrasonication
D	21ml HCl+ 7 ml HNO ₃	Equilibration 16 hr, reflux 2 hr

An Anton Parr Multiwave 3000 microwave oven unit was utilised for the microwave assisted digestion (MWAD) methods (A, B, and C), and compared against standard reflux with aqua regia (method D) (BSI, 1995). For method A, seven replicates of 400 ±1 mg CRM and three method blanks were placed in the PTFE pressure vessels with 8 ml of concentrated (15.8 M) nitric acid. The vessels were left 16 hours in a fume cupboard to equilibrate, to avoid elevated pressures inside the vessels at the MWAD stage. The following MWAD programme was applied: 20 minutes for the instrument to reach 18 bar and 190 °C, where held for 20 minutes and finally another 20 minutes for the vessels to cool down. The mixture was then filtered using 0.45µm Whatman cellulose filter papers and diluted with ultra pure (MiliPore) water, to a volume of 100 ml.

Method B was performed exactly as method A, but with a different acid mix: 5 ml of nitric acid and another 3ml of hydrogen peroxide (100 volumes). Method C was performed exactly as method A, with the difference that ultrasonic waves were

applied through a 600W probe (Langford Ultrasonics- Sonomatic), to test whether ultrasonication could enhance the digestion reactions.

Method D was tested on 7 CRM replicates of $3 \pm 0.001\text{g}$ each, and three method blanks. 21 ml of concentrated hydrochloric acid (12 M) were added in 250ml reaction flasks, followed by 7ml of nitric acid. Condensers with continuous flowing cold water completed the digestion rigs. The mix was allowed to oxidise at room temperature for 16h, and then heated to reflux conditions for 2h. After cooling down, it was filtered (0.45 μm Whatman cellulose filter papers) and made up to 100ml using ultra pure water. All chemicals were trace analysis grade and purchased from Fischer Scientific UK. The quantification was achieved through a graphite furnace/flame- atomic absorption spectrometer (GF/F-AAS) A-Analyst 800 Perkin Elmer instrument, equipped with an air/acetylene flame and an AS-90 autosampler. The limits of detection (LOD) and limits of quantification were calculated according to the following formula

$$\text{LOD (LOQ)} = b_{\text{ave}} + 3(5) s_b \quad (3.1)$$

Where b_{ave} is the mean concentration of the analytical blank controls and s_b is the standard deviation of the analytical blank controls.

3.2.4.3 XRD, TOC & SEM-EDS analysis

The coarse and fine fly ashes were also analysed for their total C, H, N, and TOC content using an elemental analyser (Vario EL III), and further examined in a SEM-EDS microscope (Philips XL 30) to determine their major elements composition. The mean concentration of elements (% wt> 1) in the SEM- EDS analysis was obtained from a spectrum over a 4 mm^2 and 0.16 mm^2 area for coarse and fine fly ash, respectively. Furthermore, the reported deviations (§ 3.3.4) represents 4 different

scans in smaller areas, on each one of the quadrants of the originally scanned areas. Finally, XRD (Siemens ED 5005) analysis was employed for the determination of the ashes' crystalline phases.

3.2.4.4 Organics- Chlorobenzenes

Penta- and hexa-chlorobenzene were selected for the evaluation of the organochloride load of the fly ashes. In this context, alternative sample preparation methods to the traditional Soxhlet were compared for their recoveries, precision and ease of use. Furthermore, the mass spectrometry- selected ion monitoring (MS-SIM) and electron capture detection (ECD), chromatographic detectors were also compared. ECD has theoretically lower detection limits (5 fg) compared to mass spectrometer in single ion monitoring (SIM)(25fg-100pg) mode (Harris, 2003). Moreover, ECD is extremely sensitive to halogenated compounds and could provide better integration parameters in the generated chromatograms, eliminating the need for extensive sample preparation.

A wide range of methods is described in literature for the extraction and quantification of CBs in solid matrices (Table 3.5), but no standard method is yet available. Usually a pre-treatment stage such as grinding (Dionex, 2005), and/or acid digestion (Huang et al., 2003; Liljelind et al., 2003; Lundin and Marklund, 2007) ensures the homogenisation, and/or the increase of the internal surface of the matrix, and the transfer of the target species to a liquid phase.

For the extraction step, Soxhlet, whether traditional, Dean-Stark modified, or automated, is the most frequently applied technique, and often used as a reference for the efficiencies of other extraction methods. Major disadvantages of Soxhlet extraction include the amount of time needed (18- 48h per sample), the large volume

of solvent used (120-400ml per sample)(Sun et al., 2006; Lundin and Marklund, 2007), and the subsequent losses of volatile and semi-volatile species during concentration of extracts, ranging from 5 to 20% for highly chlorinated benzenes, depending on the evaporation method used (Liljelind et al., 2003).

Table 3.5

Pre-treatment, extraction, clean-up methods and instrumentation for the quantification of chlorobenzenes from solid matrices

Pre-treatment	Extraction	Clean- up	Detection	Reference
Acetic acid	Soxhlet- Dean-Stark	Silica gel column	GC-MS	Liljelind et al., 2003
HCl digestion	Refluxing	Multilayer silica gel column	HRGC-LRMS ^a	Huang et al., 2003
-	Soxhlet	-	HRGC-MS-SIM	Oberg et al., 2008
-	Ultrasonication	-	GC-MS-SIM	Pekárek et al., 2007
-	Ultrasonication	Filter paper	LVI ^b -GC-MS	Korenkova et al., 2006
-	Soxhlet	Multilayer silica gel column	GC-MS	Sun et al., 2006
Acetic acid	Soxhlet- Dean-Stark	Multilayer silica gel column	GC- MS-MSD ^c	Lundin and Marklund, 2007
Grinding	ASE	Silica/ alumina column	GC-MS-MS/ GC-HRMS	Dionex, 2005
-	Ultrasonication	Alumina column	GC-MS-SIM-ECD	Liu et al., 2001

^a LRMS: Low resolution mass spectrometry

^b LVI: Large volume injection

^c MSD: Mass selective detection

Pressurised fluid extraction (PFE), also described in the literature as accelerated solvent extraction (ASE), utilises elevated temperature and pressure conditions, and thus smaller amounts of solvents (10-50ml per sample) and time (10-40min) (Bautz et al., 1998; EPA, 2000; Dionex, 2005). More recently, ultrasonic extraction has been employed in fly ash samples for the extraction of chlorinated benzenes and recoveries equivalent to Soxhlet have been reported (Korenkova et al., 2006). Furthermore, ultrasonication has the same advantages as ASE in terms of volume of solvents, and time needed for the analysis, compared to traditional Soxhlet. Other techniques have

been employed for the extraction of CBs from fly ash, such as microwave assisted extraction (Sun et al., 2006) however, these methods will not be investigated here.

The selection of the clean-up method and the GC detector used, depends on the expected concentrations of the target pollutants and the expected interferences from the matrix. A multilayer silica gel column (anhydrous Na₂SO₄, 10% AgNO₃ silica gel, 22% H₂SO₄ silica gel, 44% H₂SO₄ silica gel, KOH silica gel)(Sun et al., 2006) has been reported to absorb interferences from fly ash enabling their detection with GC/MS. In Korenkova et al. (2006), chlorobenzenes are extracted by ultrasonication, and the quantification is achieved simply after paper filtration and large volume injection (LVI) GC/MS. Therefore, the need for extensive sample clean up, is also related to the available instrumentation. Other combinations of clean-up methods and detection instruments are illustrated in Table 3.5.

The extraction method for the specific matrix and samples was a combination of methods for PCDD/F's and CB's extraction, found in the literature (He et al., 2004; Sun et al., 2006). For this experimental stage only fine fly ash was used due to the availability of sample quantity.

The fly ash was collected using vacuum from the cyclone of the 50 kW_{th} fluidised bed combustor. Sample replicates of 10 ± 0.01g each, were homogenised using a mortar and screened through a 0.5 mm sieve. The samples were spiked with 1ml of 800ng ml⁻¹ 1,3,5-tribromobenzene in toluene (extraction standard). Thirty ml of dichloromethane was added, to cover the ash in a conical flask, and shaken mechanically at least for 24 hours, until dry, to allow the incorporation of the standard within the ash matrix. The schematic representation of the following extraction methods is shown in Figure 3.4.

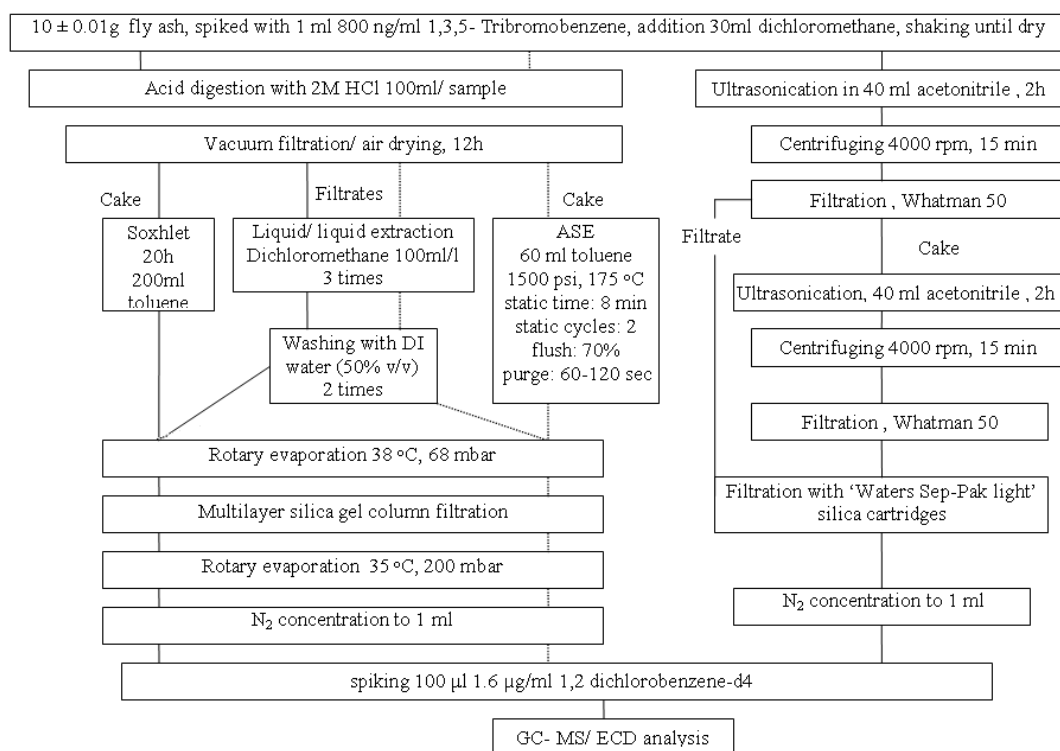


Figure 3-4. Summary of tested extraction methods

Ultrasonic extraction

Seven replicates of spiked fly ash samples, and a blank matrix sample consisting of decontaminated silica sand were placed in 50ml PTFE tubes with 40ml of acetonitrile. The samples were extracted using an ultrasonic bath at 30°C for 2h, centrifuged (15min, 4000rpm) and filtered (Whatman-50 filter papers). The extraction was repeated under the same conditions, with fresh solvent, and the two filtrates were mixed and evaporated under a gentle nitrogen flow to 1ml. Optimum extraction conditions (ultrasonication time, solvent/ matrix ratio, ultrasonication cycles, and filtration method) were the same as reported by Korenkova and co-workers (2006). A lipid phase residue observed in the final concentrate, prevented direct chromatography injection, and a further purification step was employed using ‘Waters Sep-Pak light silica’ cartridges attached to gas tight syringes, and eluted with 5 ml acetonitrile. Finally the samples were concentrated again with a nitrogen flow down to 1ml, and

each was spiked with 100 μ l of 1.6 μ g ml⁻¹ 1,2 dichlorobenzene-d4 (recovery standard).

Soxhlet and ASE

Fourteen replicates and two blank matrix samples were each digested with 100ml of 2M HCl in conical flasks. The flasks were shaken periodically for about an hour, until no further foaming reaction was observed. The mix was separated using vacuum filtration and the cake was washed with deionised water to reduce acidity. Continuous vacuum was applied for 12h to allow the air drying of the cakes, which were then transferred with the filter papers in the Soxhlet cellulose thimbles, and the ASE extraction cells.

Half of the cakes were extracted with Soxhlet using 200ml of toluene for 20h, and the other half with Dionex ASE 200 accelerated extractor using approximately 60ml of toluene and the following settings: 175°C, 1500psi, static time=8min, static cycles=2, flush=70%, purge=60-120sec. The aqueous solutions were extracted three times with 100ml of dichloromethane per litre of solution. The solvent extracts were washed twice with deionised water for pH adjustment (50% v/v). The two extracts from each sample were mixed, concentrated using a rotary evaporator (38°C, 68mbar), filtered through a multilayer silica gel column (anhydrous Na₂SO₄, 10% AgNO₃ silica gel, 20% H₂SO₄ silica gel, 40% H₂SO₄ silica gel, 30% KOH silica gel) and eluted with hexane, double the height of the column. The column's elutes were further evaporated using a rotary evaporator (35°C, 200mbar) and finally concentrated to 1ml using a nitrogen flow concentrator. The samples were finally spiked with 100 μ l of 1.6 μ g ml⁻¹ of 1,2 dichlorobenzene-d4 (recovery standard).

Multilayer silica gel column preparation and principle

Preparation:

The multilayer silica gel column was prepared using neutral silica gel, 70- 230 mesh (Sigma Aldrich catalogue number 288624). The gel was packed in an open chromatography column and rinsed with methanol and dichloromethane each twice the column length of the silica. The gel was activated at 130 °C for 24 hours and stored at 130 °C until further utilisation.

Activated silica gel and sulphuric acid at ratios 3:2 and 4:1 by weight were shaken at room temperature, until dry for the preparation of the 40% and 20% H₂SO₄ silica gels, respectively.

KOH pellets (22 g) were thoroughly dissolved in 100 ml of methanol in a glass flask. Activated silica gel (40 g) was added and the flask was attached to a rotary evaporator with a water bath at 55 °C and no vacuum for 2 hours. The gel was then packed at a chromatography column and rinsed with methanol and dichloromethane each twice the height of the column. After drying it was stored at room temperature.

The silver nitrate silica gel was purchased ready made from Sigma Aldrich (catalogue number 248762).

An open chromatography column with an internal diameter of 15mm was packed (bottom to top) with 20mm 30% KOH silica gel, 20mm 40% H₂SO₄ silica gel, 20 mm 20% H₂SO₄ silica gel, 20mm 10% AgNO₃ silica gel and 20 mm anhydrous Na₂SO₄. The column was rinsed with hexane twice the height of the column (BS 1948, 2006; Wright, 2007).

Principle:

The sample is transferred with a Pasteur pipette to the top of the column. The first layer of anhydrous sodium sulphate absorbs any remaining water traces. The silver nitrate silica gel reduces sulphides as they can interfere with following clean up steps. The 40% H₂SO₄ silica gel layer oxidises interfering organic material such as lipids or carbohydrates. The 20% H₂SO₄ silica gel layer acts as a contingency layer in case of the breakthrough of similar organics. The KOH silica gel layer is there to neutralise possible displacements of acid from the H₂SO₄ layers, which could damage subsequent adsorption systems e.g. the top of the GC column. The elution with hexane ensures the transfer of target species from the column to the collection flask at the bottom of the column. Furthermore, excess hexane cleans the column from trace species and makes it ready for the next sample. The layers were replaced with new after the clean-up of every six samples, or between the clean up of samples extracted with different methods (Wright, 2007).

Analysis

All samples were stored at 4 °C prior to the GC-MS/ECD analysis. The solvents used for the extraction were all HPLC grade (Rathburn, UK). The glassware (separation funnels, transfer vials, rotary flasks, micro syringes) was decontaminated using a two step process with acetone and dichloromethane. The extraction standards were prepared in-house (Sigma-Aldrich catalogue number 140066). The recovery standards were purchased already prepared (Sigma-Aldrich catalogue number 48068). The detection and quantification limits were calculated according to equation 3.1.

The chromatographic conditions used for the two detection systems were identical consisting of a Thames-Restek Rtx ®- 1MS- 100% dimethyl polysiloxane column

(length 15m, internal diameter 0.25 mm, film thickness 0.25 μm), an initial oven temperature of 50 $^{\circ}\text{C}$, rising 30 $^{\circ}\text{C min}^{-1}$ up to 125 $^{\circ}\text{C}$, and then 15 $^{\circ}\text{C min}^{-1}$ up to 300 $^{\circ}\text{C}$ where was held for 6 min. The carrier gas was helium and the injection volume was 1 μl at a split ratio 100:1 at 300 $^{\circ}\text{C}$. The GC-ECD analysis was performed in an Agilent Technologies – 6890N Network GC system equipped with a ^{63}Ni ionisation source, and the identification was based on the retention times of the target species. The GG/MS analysis was performed in a Perkin Elmer- Autosystem XL/Turbo Mass Gold instrument (70 eV) operated in SIM mode. The selected masses were: m/z = 150, 148, 152 corresponding to the $[\text{M-H}^{+}]$ ions of 1,2- dichlorobenzene- d_4 , m/z = 235, 74, 75 corresponding to the $[\text{M-H}^{+}]$ ions of tribromobenzene, m/z = 252, 250, 248 corresponding to the $[\text{M-H}^{+}]$ ions of pentachlorobenzene, and m/z = 284, 286, 282 corresponding to the $[\text{M-H}^{+}]$ ions of hexachlorobenzene. A typical sequence of injections consisted of one blank, six unknowns, one blank, four standards, one blank, and an analytical blank etc.

3.2.4.5 Leaching tests

Further to the abovementioned analysis, leaching tests were performed for the coarse and fine fly ashes. Although the available leaching standards define liquid to solid (L/S) ratios between 2-10 (BSI, 2002), the available samples quantity did not allow such ratios. However, these standards serve the legislative characterisation and control of wastes within management frameworks (e.g. landfill acceptance criteria). Moreover, greater L/S ratios can simulate long term leaching of wastes, as indicated in literature (Hyks et al., 2009).

In these leaching tests a L/S ratio equal to 50 was employed. Seven replicates of 1g each, from each ash type were diluted in 50 ml of deionised water. The replicate

mixes were agitated overnight and filtrated with Whatman filter papers (pore size 0.45 µm). The leachates were stored at 4 °C and analysed with ICP-MS (Inductively Coupled Plasma- Mass Spectrometry- Perkin Elmer- ELAN 9000) for aluminium, magnesium, cadmium, chromium, copper, mercury, nickel, lead, zinc, tin, titanium, phosphorous, potassium, vanadium, manganese, and sodium. For the quantification of the above elements the LOQs were calculated using equation 3.1

3.3 Results and discussion

3.3.1 Cl mass balance

The chlorine mass balance, considering the water soluble chlorides in the gas and solid by- products, closes at 92.8% (Figure 3.5). The remaining 7.2% represents the organically bonded Cl species and any losses in the collection or capturing of the ashes and flue gases respectively. The mass balance has been calculated according to Equation 3-2.

$$C_{in} = C_b + C_h + C_c + C_g \quad (3-2)$$

Where: C_{in} , is the total Cl in the input; C_b , is the Cl found in the bed ash; C_h , is the Cl of the horizontal chamber ash; C_c , is the Cl of the cyclone ash; and C_g , the Cl volatilized as HCl..

From the original Cl in the SRF feedstock, 18.4% was found at the bed area, 28.2% in the horizontal chamber (coarse fly ash), 17.2% in the cyclone (fine fly ash) and 29% volatilised as HCl.

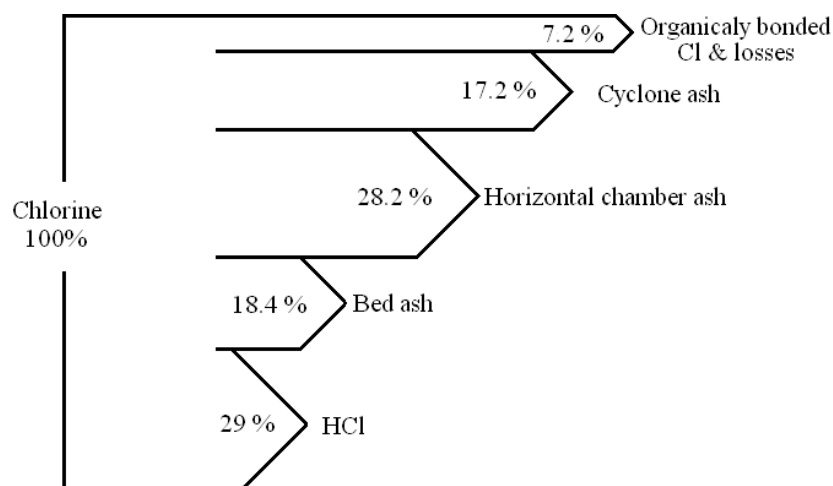


Figure 3.5. Shankey diagram- Cl mass balance

The measurement and expression of the Cl content in the bed ash presented a few peculiarities. The ash could not be distributed and homogenized with the silica bed particles, resulting in big deviations in the originally sampled replicates. Furthermore, an amount of unburned particles, mainly glasses and ceramics, were found, as expected in the bed ash, and the expression of the results of the Cl content on a w/w basis would be confusing. The emptying of the whole bed to a tank full of deionised water and the measurement of the total water soluble chlorine seems to overcome this problem.

The chlorine mass balance presents certain challenges regarding the partitioning of organically bonded and inorganic species. There is an amount of Cl, for example in the cyclone ash, that is either bonded to organic molecules, or to inorganic salts physically trapped in the ash matrix, but still insoluble in water. A similar issue has been discussed for coal fuels (Cox et al., 1984). Furthermore a detailed measurement of the organically bonded chlorine would require extensive identification and quantification of trace species.

Finally the results are in general agreement with other figures in the literature that examine the Cl mass balance in FBC (Hilber et al., 2007b). In comparison with data from other rigs used to measure the volatility of Cl in waste, e.g. quartz moving furnace (Liu et al., 2001), the figures in this experiment present lower HCl values. This fact suggests that the results are process specific. Moreover, one of the most popular advantages of FBC against other furnaces is the low HCl emissions (Weinberg, 1986). The fluidisation conditions succeed good mixing of the reactants and products, within the furnace. As a result, the volatilised HCl can further react with alkali metals and alkaline earth metals to form salts, or metals to form metal chlorides (further details in § 2.5.1).

Another explanation for the low HCl levels of the experiment is the operating temperature, and SRF particles' residence time. As discussed in other parts of this work (§ 5.2.2), heterogeneous SRF particles emit HCl under different temperatures and in different periods. Thermogravimetric experiments, for example, indicate that plastic emits HCl more rapidly than food (Guo et al., 2000). Thus, some SRF particles need greater residence time to volatilise their whole chlorine content.

3.3.2 Water soluble Cl

Figure 3.6 demonstrates the amount of water soluble chlorides that leached from each ash type. As expected the bed ash contained the lowest levels of Cl as most of it was volatilised in the process to form HCl, Cl₂, or Cl radicals. The bed ash contained an amount of non- combustibles that were visible between the bed material, thus a rather abnormal and heterogeneous distribution of chlorides in these particles should be expected. Although the determination of chloride ions was made with a much greater L/S ratio than characterisation protocols suggest (200/1 instead of 20/1) (BSI, 2002),

the bed ash, based on the leached Cl^- , would be accepted for co-disposal in a non hazardous landfill ($\text{Cl}^- < 15,000 \text{ mg kg}^{-1}$), according to the existing legislation (EC, 2002) for granular waste. According to the same legislation the coarse fly ash would be accepted in a hazardous waste landfill without further treatment ($\text{Cl}^- < 25000 \text{ mg kg}^{-1}$), while fine fly ash would require further stabilisation before final disposal.

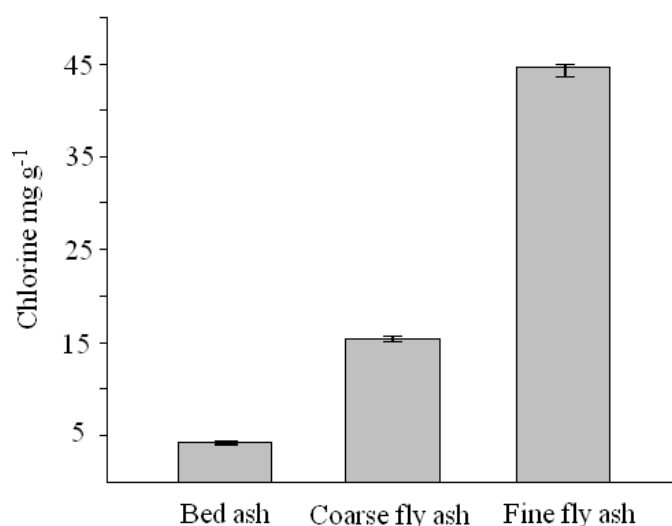


Figure 3.6: Water soluble chlorine content per ash type

3.3.3 Heavy Metals

The four HF-free fly ash digestion methods were compared for their recoveries from CRM and the results are reported in Figure 3.7. The overall recoveries ranged between 59% and 94%, except from Cr which ranged at lower levels ca. 19- 38%. A one way ANOVA at a confidence interval of 95%, confirmed that there was no single method that significantly recovered higher amounts for the whole range of the examined metals. However, some exceptions were found in method B, which recovered significantly higher quantities of Pb, and in the aqua regia method (D) which recovered significantly lower amounts of Cu and Cd. Furthermore, neither the

addition of H_2O_2 in the digestion vessels, or ultrasonication as post-digestion treatment, improved the recovery of the metals. Thus, single step HNO_3 MWAD proved sufficient for the solubilisation of heavy metals in waste derived fly ashes, as reported in other studies (Mester et al., 1999; Quina et al., 2008b).

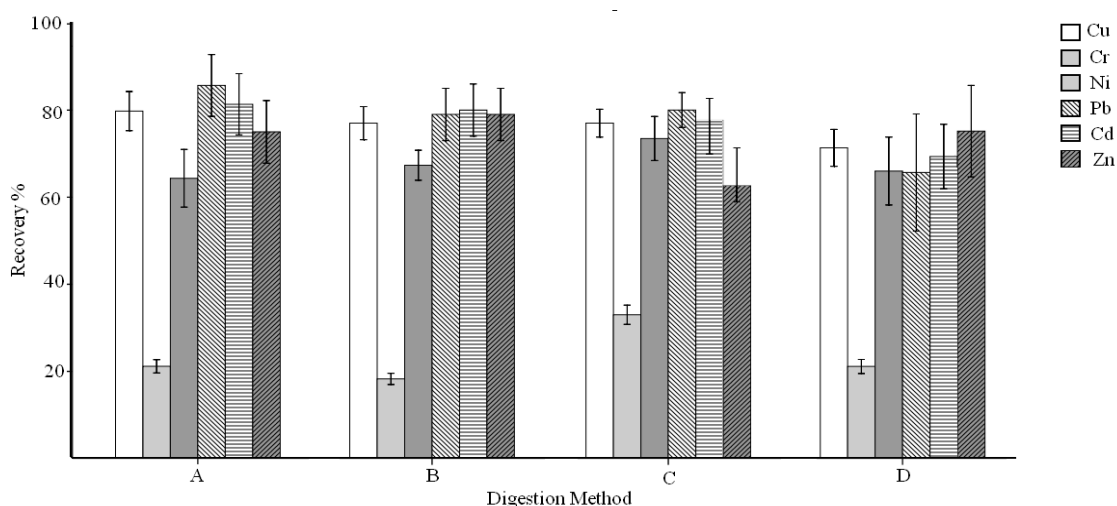


Figure 3.7: Recoveries of metals from CRM between different MW-AD methods (error bars indicate minimum and maximum values, n=7)

The fly ashes were further analysed for their content in Cu, Cr, Ni, Pb, Cd, and Zn using method A and the results are presented in Figure 3.8. Coarse fly ash contained higher Cu, Pb and Zn quantities than the fine fly ash fraction, which had higher Cr and Ni contents. The Cd values were relatively low ranging at $3.6 \pm 0.6 \text{ mg kg}^{-1}$ and $7.3 \pm 0.2 \text{ mg kg}^{-1}$ for fine and coarse fly ash, respectively. Finally, it should be noted that the actual concentration of Cr in both ash types could be higher than the ones presented in Figure 3.8, as the HF free digestion method used gives a relative poor recovery of the element.

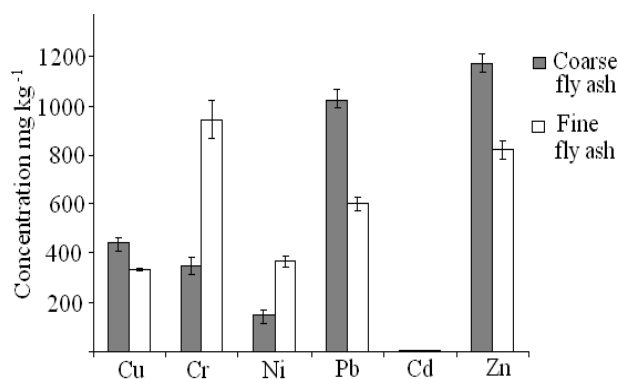


Figure 3.8: Concentration of metals in SRF coarse and fine fly ash (error bars indicate minimum and maximum values, n=7)

3.3.4 Minerals and carbon

The rough (%wt >1) composition of the elements in the ashes, as recognised in SEM-EDS analysis is presented in Table 3.6. Calcium, silica, aluminium, chlorine, sodium, potassium, iron, sulphur, and phosphorus were the most common elements, besides carbon, which was 8.6 ± 0.1 % and 9.6 ± 0.2 % for the coarse and fine fly ash, respectively. This slight difference in the total carbon content is probably due to the greater residence time of the bigger and heavier coarse particles (Figure 3.9) in the combustion zone, resulting to higher C to CO₂ conversion. This finding is confirmed by the TOC levels that ranged at 6 ± 0.4 % and 6.8 ± 0.1 % for coarse and fine fly ash particles. In respect to the SEM-EDS sensitivity, another conclusion is that fine fly ash had about double the amount of chlorine than the coarse one. This finding is confirmed by the amount of water soluble chlorides that leached from each ash type (§ 3.3.3).

The mineralogical analysis recognised the main crystalline phases of the ashes by means of XRD and the diffractograms are presented in Figure 3.10. These were similar for both ash types: Calcite (CaCO₃), quartz (SiO₂), halite (NaCl), sylvite

(KCl), calcium sulphate (CaSO_4), except from calcium silicate (CaSiO_4), which was only detected in fine ash particles. The XRD patterns are similar to most MSWI fly ashes as reported in other works (Wan et al., 2006; Quina et al., 2008b; Wang et al., 2008; Shi and Kan, 2009) with the exception of calcium silicate. This finding is of particular importance as layers of CaSiO_4 can interfere as heat transfer barriers in flame retardant applications (Hamdani et al., 2009), however its presence was not confirmed at the heat-exchanger surfaces (coarse fly ash sampling point), but only at the cyclone (fine fly ash collection point).

Table 3.6

SEM-EDS results on elemental composition (x: mean, s: standard deviation)

Composition (%wt, ar)	Coarse fly ash		Fine fly ash	
	x	s	x	s
Na	1.3	0.7	1.7	0.3
Al	1.7	0.5	2.5	0.3
Si	5	2.7	5.5	2.8
P	1.3	0.8	1	0.2
S	1.2	0.6	1.4	0.2
Cl	2.2	0.7	5.5	0.7
K	1.4	0.5	2.3	0.4
Ca	11	1.2	9	0.7
Fe	1.3	0.5	1.6	0.3

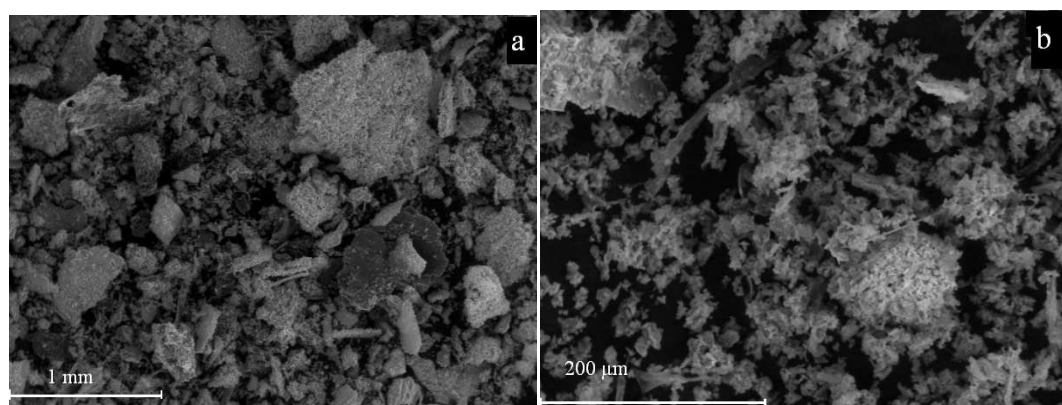


Figure 3-9. SEM pictures. (a) coarse, (b) fine fly ash

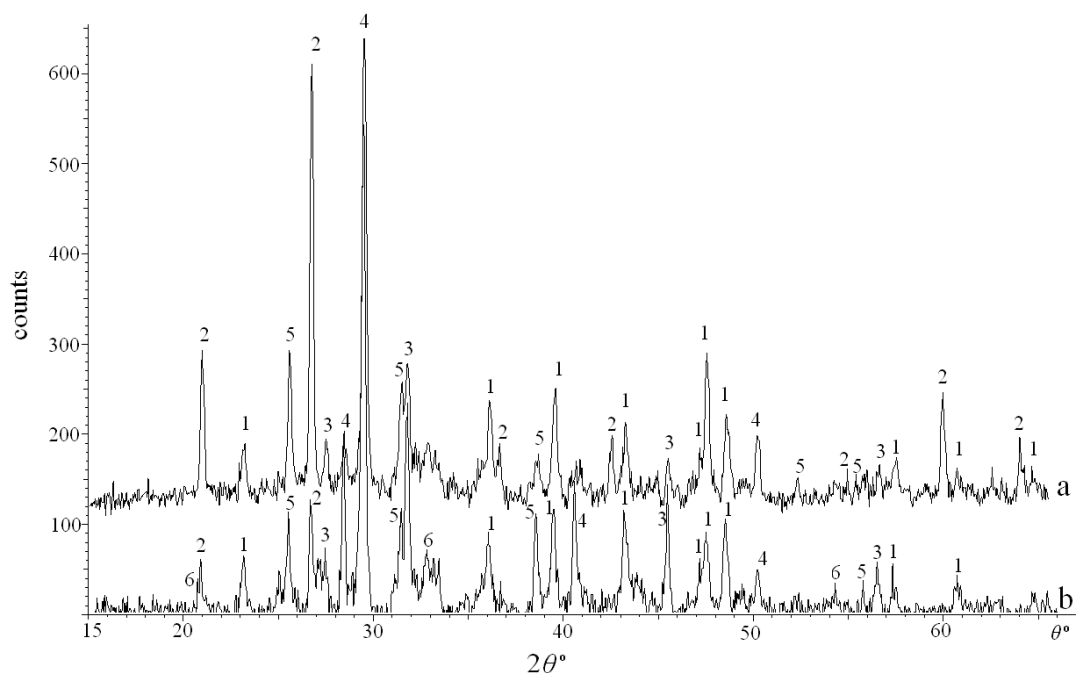


Figure 3.10. X-ray diffractogram (a) coarse, (b) fine fly ash (step 0.05°). Crystalline phases recognised: 1. Calcite; 2. Quartz; 3. Halite; 4. Sylvite; 5. Calcium sulphate; 6. Calcium silicate

3.3.5 Organics-Chlorobenzenes

The quantification of gaseous chlorobenzenes delivered results only for pentachlorobenzene. This ranged at $4.4 \pm 0.4 \text{ } \mu\text{g/ m}^3$. Hexachlorobenzene was below the quantification limit, however technical difficulties during the analysis might be the reason for that.

Regarding solid phase chlorobenzenes, extraction efficiencies, calibration coefficients, LOQs, and mean concentrations for penta- and hexa-chlorobenzene obtained for each sample preparation method and the two investigated systems of detection are summarised in Table 3.7. These results concern fine fly ash as mentioned in § 3.2.4.4. The values for coarse fly ash ranged from 5.1 to 8.9 ng g⁻¹ with an average value of 6.6 ng g⁻¹ and a standard deviation of 1.42 ng g⁻¹ for

pentachlorobenzene. The equivalent range for hexachlorobenzene was 0.9 to 4.5 ng g⁻¹ with an average value of 2.68 ng g⁻¹ and a standard deviation of 1.3 ng g⁻¹.

Table 3.7

Extraction efficiencies, calibration coefficients, LOQs, and values for penta- and hexa-chlorobenzene for the three sample preparation methods and the two detectors

Detector	Sample	Sample preparation method					
		Soxhlet			ASE		
		Extraction efficiency %	*Cl ₃ Bz ng g ⁻¹	*Cl ₆ Bz ng g ⁻¹	Extraction efficiency %	*Cl ₃ Bz ng g ⁻¹	*Cl ₆ Bz ng g ⁻¹
MS-SIM	1	146	7.62	- ^a	145	20	11.47
	2	208	13.57	- ^a	147	9.37	12.64
	3	195	9.12	- ^a	134	12.5	15.67
	4	218	6.77	- ^a	166	8.5	11.26
	5	222	12.5	- ^a	169	10.8	11.27
	6	193	- ^a	- ^a	195	- ^a	10.29
	7	-	-	-	158	8.72	15.73
	mean	197	9.92	-	159	11.65	12.62
	± s	25	2.67	-	19	3.9	2
	RSD (%)	13	2.7	-	12	3.4	1.6
ECD	1	71	8.6	8.27	89	18.40	8
	2	92	14.78	3	106	12.82	8.23
	3	81	11.7	2.46	134	12.31	5.53
	4	84	8.45	1.5	105	14.98	7.83
	5	89	11.3	1.44	136	13.78	5.94
	6	79	9.33	1.87	90	19.73	10.9
	7	-	-	-	114	15	10.26
	mean	83	10.68	3.34	111	15.28	8.11
	± s	7.5	2.4	2.8	19	2.8	2
	RSD (%)	9	2.3	8.5	17	1.8	2.5
	LOQ		0.25	1.44		0.21	2.9
	r ²		0.9999	0.9999		0.9999	0.9999
* Corrected values according to extraction and recovery efficiencies							
- ^a Values lower than LOQ							

3.3.5.1 GC detection systems: ECD vs MS-SIM

Comparison of the LOQs obtained from the two detectors showed a difference, with ECD being able to detect traces approximately 15 and 10 times lower for pentachlorobenzene and hexachlorobenzene, than MS-SIM, respectively. The quantification of the 1,3,5 tribromobenzene extraction standard showed over efficiencies in SM-SIM, for all the sample preparation methods: $197 \pm 25\%$ for Soxhlet, $159 \pm 19\%$ for ASE, and $114 \pm 31\%$ for ultrasonication, against $83 \pm 7.5\%$, $111 \pm 19\%$, and $67 \pm 17\%$, respectively when analysed with ECD. Over- efficiency was also observed in the recovery of the deuterated standard for the MS-SIM analysis that ranged between 158- 228% against 94-105% on ECD. In general, the background noise in the ECD was lower than the noise of the MS-SIM. Figure 3.11 illustrates the above finding with indicative chromatograms of the same sample, extracted by Soxhlet, with signal to noise 4 times higher for ECD in comparison to MS-SIM. Figure 3.12, gives the graphical presentation of the S/N definition from the equivalent standard (British Standards, 2006).

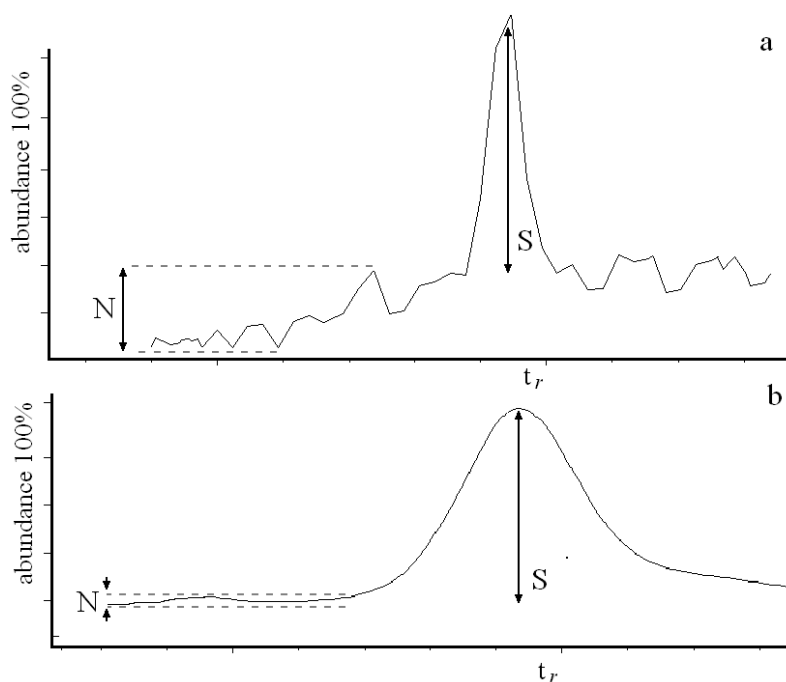


Figure 3.11. Pentachlorobenzene, indicative chromatograms for the same sample extracted by Soxhlet
(a) MS- SIM $m/z = 252$ - $S/N = 19$, (b) ECD- $S/N = 84$

These results suggest that sample matrix may strongly interfere with the quantification ions in the MS-SIM, and contribute to the over-efficiency obtained for both control and target compounds. Further purification of samples would be required for improving accuracy of final measurement e.g. purification using an aluminium oxide filtration column (Liu et al., 2001). Furthermore, when MS-SIM is used the utilisation of $^{13}\text{C}_{12}$ isotopes as extraction/recovery standards is essential for the minimisation of sample matrix interferences.

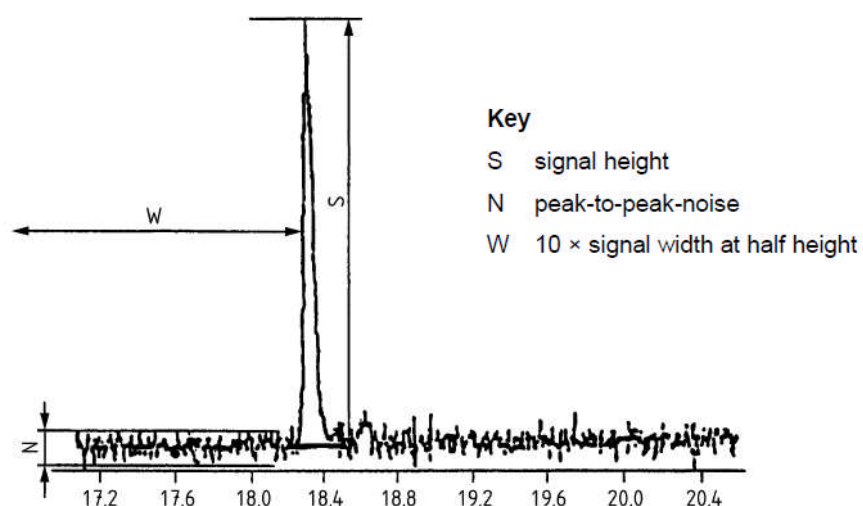


Figure 3.12. Graphical representation of signal to noise (British Standards, 2006)

This noise is disregarded in the ECD, where the halogenated compounds significantly affect the detector's signal, in comparison to other noise e.g. trace hydrocarbons, which build up the peak of interest at a specific retention time. This is confirmed by the absence of over- efficiency in the recovery of the standards. The results regarding the detectors are in agreement with those reported in the literature. These studies describe the ECD performance as being better than MS-SIM (Abreu et al., 2006; Leong and Huang, 2008), when the identification of compounds based on mass resolution is not needed, and equivalent to HRGC/HRMS (Fujita et al., 2009). In this case the advantages of ECD are based on the complexity of the environmental matrix studied, and the sensitivity of ECD for halogenated compounds, resulting to better chromatograms for CBs, and eliminating the need for extensive sample purification. Given these results, the ECD readings have been used in the subsequent analysis for the comparison of the extraction/ sample preparation methods.

3.3.5.2 Comparison of extraction methods

Soxhlet performed relatively well showing the lowest relative standard deviation (RSD) of the three methods; 9% against 17% for ASE and 26% for ultrasonication (Table 3.7). ASE and ultrasonication were over and under efficient, respectively, compared to Soxhlet, with both methods presenting large distributions around the mean values. A one way ANOVA ($p=0.05$) confirmed that there is a statistically significant difference in the extracted pentachlorobenzene, with ASE giving greater values ($15.28 \pm 2.8 \text{ ng g}^{-1}$), than Soxhlet ($10.68 \pm 2.4 \text{ ng g}^{-1}$) and ultrasonication ($9.77 \pm 3.9 \text{ ng g}^{-1}$). This finding is partially explained by the over-efficiency of ASE. Furthermore, the supercritical conditions in the extraction cells can result in better extraction efficiencies, and the circulation of solvent in a closed system, can minimise the losses of analytes. ASE also extracted more hexachlorobenzene ($8.11 \pm 2 \text{ ng g}^{-1}$) than Soxhlet ($3.34 \pm 2.8 \text{ ng g}^{-1}$), while the values for hexachlorobenzene using ultrasonic extraction were below the LOQs.

The poor performance of the ultrasonication highlights the importance of the matrix digestion for the specific analysis. Some of the chlorobenzenes are possibly formed under ‘de novo’ conditions, through heterogeneous (ash particles/flue gases) reactions and are therefore deeply incorporated within fly ash. In this case the matrix is the pollutant, and further examination of the efficiency of ultrasonic extraction in digested matrices would be interesting for future comparisons.

Although, the methods present differences in the sample preparation, extraction and the clean-up techniques, a comparison of their general efficiency can be based on the detector’s signal against the background noise, and thus the extraction against the clean up efficiencies, respectively. The results are plotted in Figure 3.13, which

illustrates that Soxhlet and the subsequent multilayer silica gel column clean up give better results for both compounds between the examined methods.

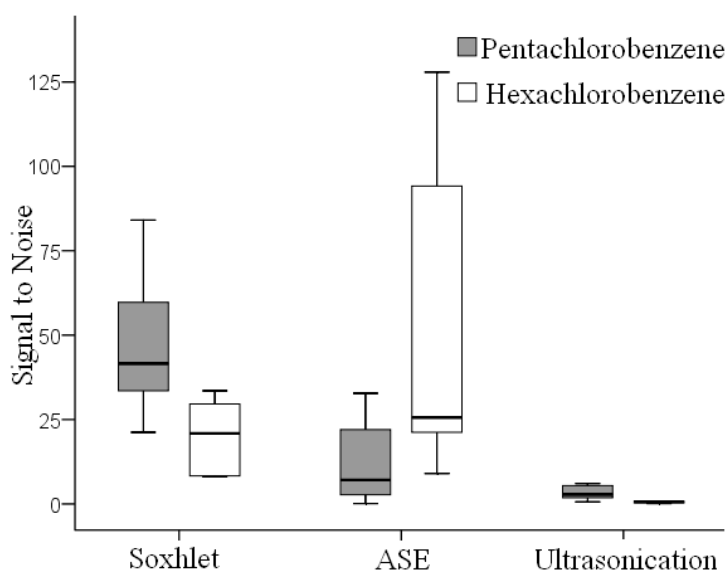


Figure 3.13. Comparison of ECD signal to noise ratio for penta-, hexachlorobenzene between the extraction methods

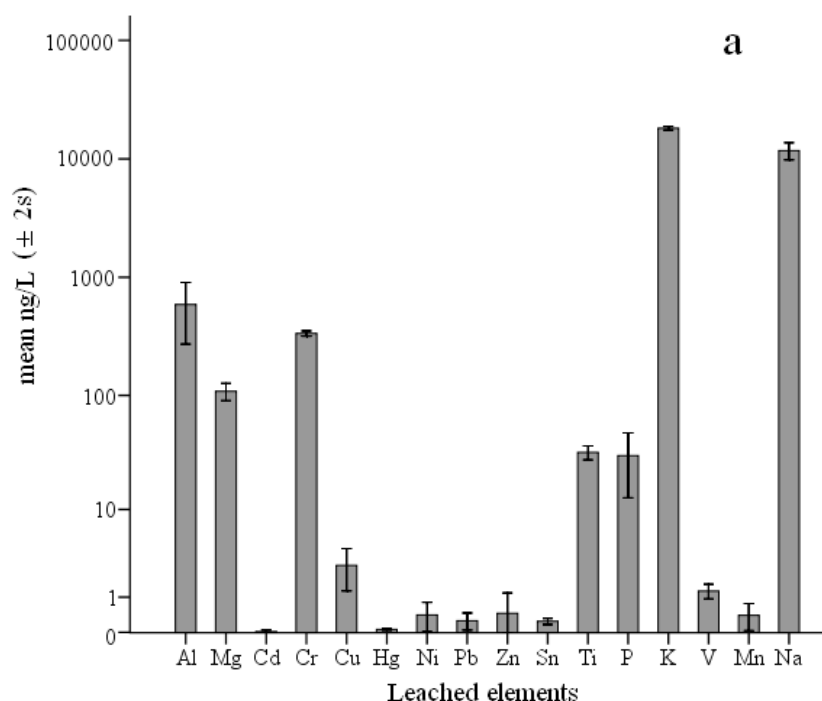
Based on these results, one can argue that ASE gave relatively good results compared to Soxhlet. The disadvantages of ASE were the over- efficiency and a wide RSD (17%) among replicates. Finally the method that incorporated ultrasonication showed poor performance in terms of extraction efficiency, S/N, and precision (RSD 26%) compared to Soxhlet and ASE.

3.3.6 Leaching tests

The leaching tests on the fine and coarse fly ash present a similar leaching pattern for the two types of fly ashes (Figure 3.14). The high amount of water soluble Na, and K, confirms the presence of salts in both types of residues and t tests (95% confidence

intervals, degrees of freedom=6), confirmed that the amount of the latter are significantly higher in the fine fraction.

Further analysis was not performed in the leaching data. The nature of the leaching test (high L/S) did not allow comparisons with other literature values, and an extensive comparison between the leaching of minor elements that come from the same process was out of the scope of this work. However, these data are further analysed and discussed in comparison to the leaching tests from the gasification residues.



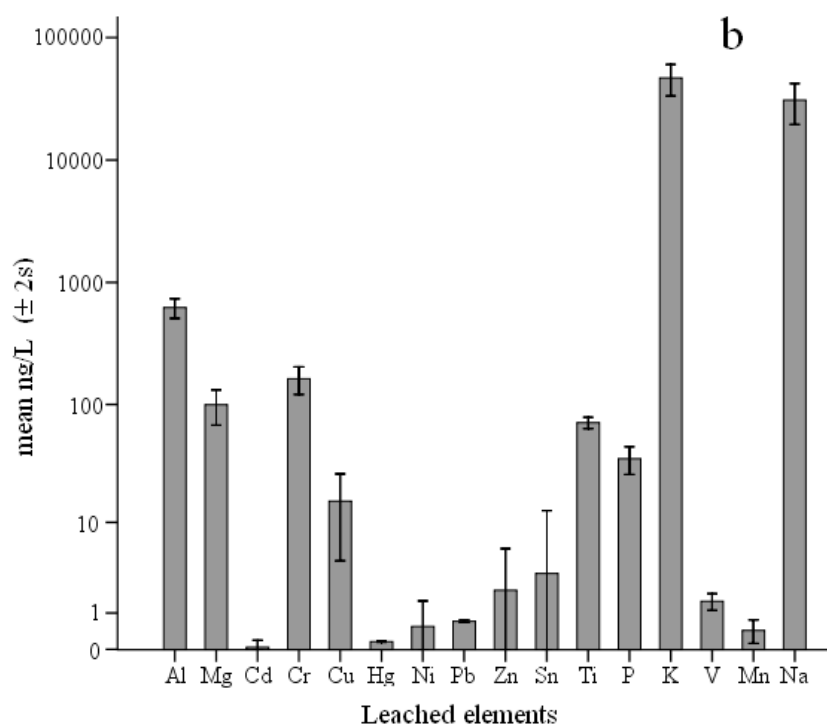


Figure 3-14. Results of leaching tests.(a) coarse, (b) fine fly ash

3.3.7 Comparison of SRF fly ash with literature values

Comparisons against literature values are often limited by the heterogeneity of available data, due to the complexity of the ash products, and the high number of available methods for residues characterisation, leaching protocols etc. Table 3.8 presents the toxicity indicators determined in this work, against equivalent values from MSWI derived fly ashes in literature. These values represent different APC residues that might differ from the classic definition of fly ash (§ 3.2.3), such as bag-filters, electrostatic precipitators, semi-dry scrubbers etc. However, a common practise is the mixing of the different APC residues for the purposes of co-treatment. Thus, although different, these residues are often studied as a single stream. The

selection of the literature data was based on the quality of the reported results, and the methods used to obtain them.

The results indicate equivalent or lower levels of pollutants in SRF- derived fly ashes compared to the reported values in literature. The chlorobenzenes in the examined samples range at an order of magnitude lower than other reported figures. The same result is obtained when comparing the heavy metals content of the SFR fly ashes with the equivalent metals load from other works. While Cr and Ni range in the same levels as other reported values, Cd, Cu, Pb and Zn are significantly lower. Furthermore, the leached chlorides levels lay on the lowest reported ranges within literature.

The reported values in literature might involve data from thermal treatment technologies different than FBC, e.g. mass grate incineration, and this can enhance the heterogeneity of data. As reported in other works (Lind et al., 2007) when comparing grate firing and FBC, there were differences in the levels of As and Sb in the generated fly ashes. However, the low pollutants ranges presented in Table 3.8 clearly reflect to the low chlorine and metals content of the particular fuel. This fact indicates the importance of modern separation technologies that are used in MBT plants for the removal of components rich in metals and chlorine like electronic waste and hard plastics, respectively, resulting to the removal of heavily polluted components from the combustible output fractions (Rotter et al., 2004).

Table 3.8

Comparison of East London's SRF fly ash indicative toxicity indicators with literature values

	This study	MSWI fly ash UK ^a	MSWI fly ash Sweden ^b	MSWI fly ash other ^c	MSWI fly ash other ^d
Cl [*] mg g ⁻¹	15-45	140-170	6-81	45-380	nd
TOC mg g ⁻¹	56- 69	10- 250	nd	4.9- 17	1.6- 400
Cd mg g ⁻¹	0.003- 0.007	0.1- 0.15	0.0035- 0.31	0.016- 1.6	0.2
Pb mg g ⁻¹	0.76- 1.22	2.5- 3.5	0.73- 36	0.25- 27	0.88
Zn mg g ⁻¹	0.8- 1.23	4- 8.5	4.9- 44	4.3- 104	21.3
Cu mg g ⁻¹	0.36- 0.47	0.35- 0.6	0.22- 1.8	0.016- 2.22	1.74
Cr mg g ⁻¹	0.41- 1.07	0.012- 0.2	0.2- 1.6	0.072-0.57	0.121
Ni mg g ⁻¹	0.18- 0.42	0.015- 0.035	0.036-0.11	0.02-0.71	nd
Cl ₅ Bz ng g ⁻¹	5.1- 14.8	nd	43- 610	nd	189- 355
Cl ₆ Bz ng g ⁻¹	0.9- 8.27	nd	47- 260	nd	113- 249

nd- not determined

^{*} Water soluble or total

^a Aqua regia total metals (Amutha Rani et al., 2008). Values include different APC residues types such as, bag filter residues, semi-dry absorber residues, electrostatic precipitators etc. Furthermore, the APC residues derive from different technologies than the experimental conditions of this work.

^b Total content (Öberg et al., 2007)

^c Total (Quina et al., 2008a)

^d Total (Huang et al., 2003)

3.4. Synopsis

In this chapter, the experimental conditions of the fluidised bed combustion (FBC) of East London's NCV 3, Cl 2, and Hg 1 class SRF were described. Furthermore, the resulting residues and especially the coarse and fine fly ashes are characterised. The following toxicity indicators have been thoroughly studied: leachable chlorine, organochlorides expressed as pentachlorobenzene and hexachlorobenzene, and the heavy metals Cu, Cr, Cd, Zn, Ni, and Pb. Furthermore the mineralogical pattern of the ashes has been studied by means of XRD and SEM- EDS. From this analysis the following conclusions can be drawn:

- A Cl mass balance has been calculated for the process with losses that ranged $< 7.2\%$. From the original Cl in the SRF feedstock, 18.3% was found at the bed area, 28.7% in the horizontal chamber (coarse fly ash), 17.2% in the cyclone (fine fly ash) and 29% volatilised as HCl.
- The results, when compared with other literature values indicate that, these SRF derived fly ashes have lower values in Cu, Cd, Pb, Zn, leachable Cl and organochloride load than other traditional thermal treatment applications. This fact highlights the importance of modern separation technologies employed in MBT plants for the removal of components rich in metals and chlorine from the combustible output fraction of SRF.

Furthermore, the extensive testing of the analytical methods and instrumentation for the residues characterisation provided significant conclusions over the methods' efficiencies and ease of use. These conclusions can serve as recommendations for future users:

- For the determination of highly chlorinated benzenes in fly ash, three different extraction methods have been compared. The results suggest that matrix digestion followed by Soxhlet extraction and multilayer silica gel column filtration, produce precise results with better signal to noise chromatograms than ASE and ultrasonication.
- The detection limits and the consistency of the readings of ECD against MS-SIM have been investigated for the quantification of chlorobenzenes. The results demonstrated that ECD can provide less noise, and thus better peaks integration than MS-SIM for the detection of penta- and hexa-chlorobenzene in fly ash extracts. The use of ECD minimises the need for extensive sample clean up, and subsequent solvent use, or $^{13}\text{C}_{12}$ labelled standards. When mass resolution is needed, further sample purification and/or high efficiency instrumentation (HRGC/HRMS) is essential for the quantification of penta- and hexa- chlorobenzenes in relevant matrices.
- For the determination of the heavy metals content in fly ashes, four HF free digestion methods were tested for their recoveries. A one way ANOVA at a confidence interval of 95%, confirmed that there was no single method that significantly recovered higher amounts for the whole range of the examined metals. Furthermore, neither the addition of H_2O_2 in the digestion acid mix, or ultrasonication as post-digestion treatment, improved the recovery of the metals. Thus, single step HNO_3 MWAD proved sufficient (with the exception of Cr) for the solubilisation of heavy metals in waste derived fly ashes.

The results, although rig and feedstock specific, can be considered as a guide for issues related to the utilization of SRF in similar processes, such as fine tuning of gas cleaning suites, and as a contribution to the technical literature/ confidence for the utilization of SRF in energy recovery processes.

Chapter 4. Gasification Experiments

4.1 Introduction

This chapter describes the gasification experimental conditions, the analytical methods used for the analysis of the gasification by-products, and the obtained results. The gasification tests took place between February 2008 and April 2009 in the spouted FBG of the Energy Technology Centre in Cranfield University. Although the tests were scheduled for March 2008, several technical problems led to 13 months of delays before achieving steady state gasification conditions within the rig.

These delays were mostly related to the feeding of SRF to the gasifier. The physical heterogeneity of SRF led to cohesive arching problems within various alternative feeding mechanisms for the gasifier, as reported in paragraph §3.1, regarding the combustion experiments. Conventional fuel manipulation, that worked in the combustion tests, was not a valid option. Due to stoichiometric limitations, a gas tight feeding system was required, as exposure to atmospheric conditions could alter the oxygen starved environment that was required for the gasification. Furthermore, gastight conditions were required for health and safety reasons to prevent CO and H₂ leakages. After numerous trials, the development of a pneumatic feeding system, based on the Venturi principle, facilitated the needs for steady state conditions with minimum trade-offs in regard to stoichiometry.

The minimum conditions for the acceptance of an experiment as successful, in this case, were the following:

- The gasification of an ‘adequate quantity’ of SRF under steady state conditions. The adequate quantity was defined as a quantity of SRF that fell in the same order of magnitude as the FBC tests.
- A temperature above 700 °C in the fluidisation chamber, to facilitate a coherent comparison for chlorine mass balance and partitioning.

The resulting gasification residues were analysed for total and leachable chlorine, organochlorides expressed as pentachlorobenzene and hexachlorobenzene, and the heavy metals Cu, Cr, Cd, Zn, Ni, and Pb. The composition and mineralogical structure of major components of the ashes and chars has been studied by means of XRD and SEM- EDS. Furthermore, leaching tests were performed in the gasification chars. For these residues characterization the analytical methods and materials presented elsewhere in this text (§3.2), were used. Coherent references to the appropriate sub-paragraph are given to guide the reader to the applied methods.

4.2 Materials and methods

4.2.1 Feedstock properties and sub-sampling procedure

A 100 kg batch of SRF was sampled from the MBT plant in East London. The material was shredded to <4mm (Retsch- SM 2000 cutting mill), to facilitate two different requirements:

Small particles' size. The gasification rig was half of the size of the combustion rig (dimension data reported in paragraph §4.2.2). Furthermore, the dimensions of the pneumatic system required smaller particles' size to support feeding of the SRF in a constant rate. Subsequently, shredding of the material was decided.

Sub-sampling. The cutting mill was perceived as an extra function in the SRF production line. Its use formulated the conditions for sub-sampling from a drop flow (CEN/TS 15442, 2006). The time needed for the shredding of the whole batch was calculated, according to lab tests. This time was divided in 24 periods, and 24 increments of an arbitrary mass of 100 g each, were collected accordingly, by manual intervention of a scoop between the exit of the cutting mill and the SRF collection container (Figure 4.1).

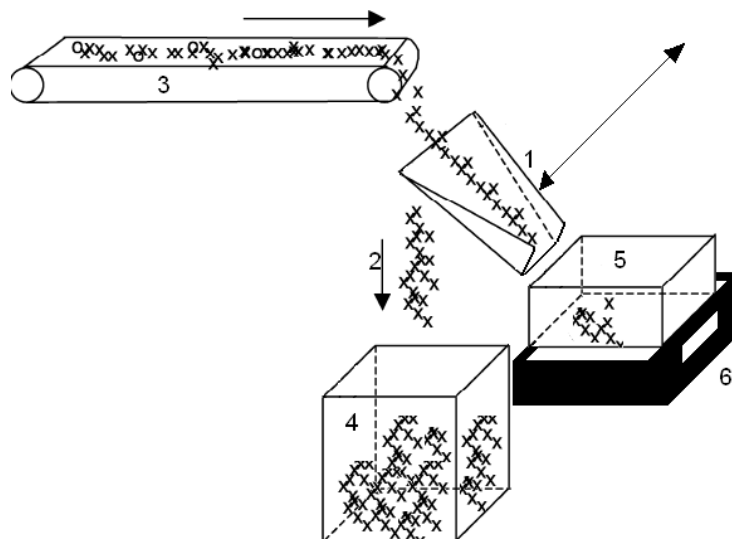


Figure 4.1. Drop flow sub-sampling. (1) manually operated scoop, (2) SRF drop flow, (3) exit of cutting mill, (4) SRF collection container, (5) sub-sample collection container, (6) balance. Re-sketched from CEN/TS 15442, 2006

The resulting 2.4 kg lab sample was further reduced to 300g by mixing and quartering (CEN/ TS 15413, 2006). Three replicates of 100 g were produced, shredded to 0.5mm (Retsch- ZM 200 centrifugal mill), One gram from each replicate was finally tested for Cl content using the oxygen bomb method (CEN/ TS 15408, 2006) and was found to be 0.49 ± 0.04 %wt dm. The remaining lab sample was used for the proximate analysis test and the results are given in Table 4.1. Values for the elemental analysis, except from chlorine, were provided by the SRF producer, according to QA/QC tests. The data reported in Table 4.1 confirm that the SRF batch that was used for the gasification experiments was similar to the one used for the FBC experiments. However, a slightly higher Cl value is noted (0.49 ± 0.04 %wt dm), and a rather lower moisture content. The moisture content is believed to have been affected by the size reduction process.

Table 4.1
SRF properties

Proximate analysis (%wt ar)	
Moisture content	9 ± 2
Ash content	15.1 ± 2
Ultimate analysis (%wt dm)	
C	48.4 ± 4.2
H	6.3 ± 2.9
N	0.9 ± 0.3
S	0.2 ± 0.04
Cl	0.49 ± 0.04
O	43.7*

* By difference

4.2.2 Fluidised bed gasification rig and operating conditions

The spouted fluidised bed gasifier used for the trial is presented in Figure 4.2. The feeding system was designed and constructed in-house, to facilitate steady feeding rates of the SRF feedstock. It consisted of a feeding hopper with continuous stirring flaps, a rotating valve and a pneumatic SRF entraining system. The rotating valve was delivering SRF at regular intervals and a pressure difference at the two ends of the Venturi jet was created by providing 1700 l/min of nitrogen at 8 bar. The resulting vacuum was capable of entraining the SRF and supplying it at a steady rate of 80g/min to the main bed chamber.

However, the feeding system was not faultless, and had two main drawbacks that limited the duration of the experiments. The first one had to do with the compressed nitrogen, which decompressed and created a cooling effect at the injection point of the SRF to the gasification vessel. This resulted eventually in an undesired lower temperature in the middle part of the gasifier (from 700 °C gradual temperature drop to 600 °C, within half an hour). To recover the required temperature, the feeding and

consequently the experiment had to be stopped, and restarted. The second drawback was air-leaks. As atmospheric air was vacuumed into the system from the Venturi nozzle, these leaks introduced atmospheric water vapours, which condensed to droplets, in the feeding lines from the decompression of nitrogen. These droplets caused SRF to block downstream the feeding system, through a bridging mechanism, limiting the duration of the experiments.

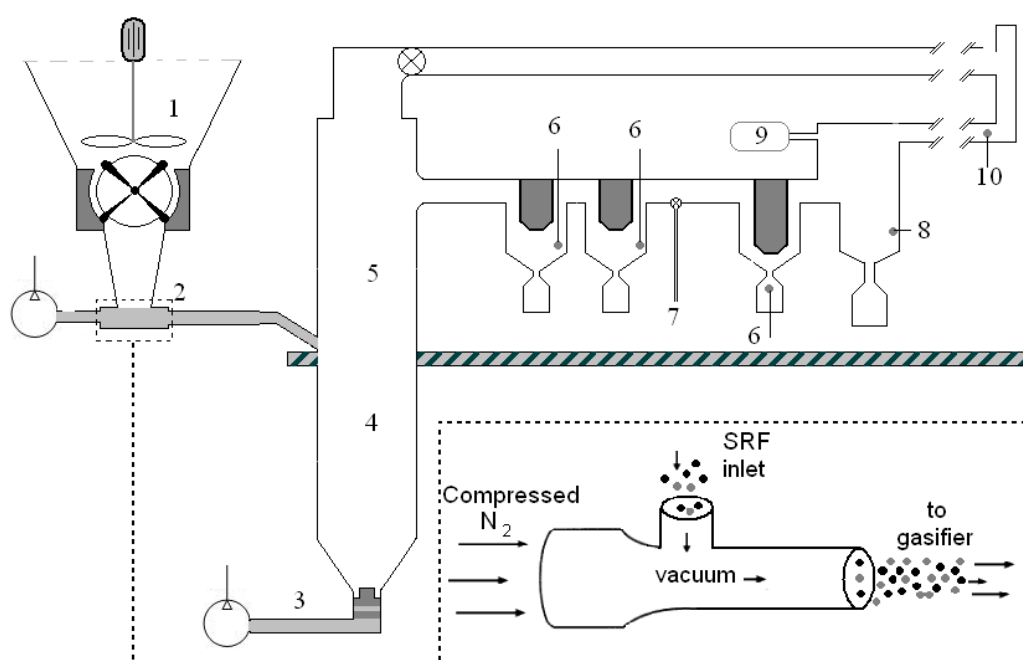


Figure 4.2: Schematic of spout bed gasifier and Venturi details. 1. Feeding hopper, 2. SRF Venturi entraining system, 3. Fluidisation air mix inlet, 4. Combustion zone, 5. Gasification zone, 6. Tar and ash traps, 7. HCl sampling point, 8. Cyclone, 9. Flare, 10. Airborne chlorobenzenes sampling point

The rig's main bed chamber (dimensions 120cm* 22cm- h*i.d.) was filled with 8200 g of silica sand (particle size 1.00 – 0.5 mm, 16/30 grade, density 1,556 g/l), and was maintained at 700 ± 20 °C by ceramic electric heaters, mounted on the external surface of the vessel. Ninety litres per minute of pre-heated atmospheric air and 80 l/min of preheated N_2 were provided to the spout at the bottom of the vessel, regulating stoichiometry and fluidisation conditions. The lambda coefficient (λ) ranged between 0.27 and 0.4.

In order to facilitate the comparison with the combustion experiments, the elimination of the possible effect of the different fluidised bed set ups (bubbling FB versus spouted FB- Figure 4.3) was attempted. Literature suggests (Weinberg, 1986) that excess bed material combined with minimum fluidisation velocities in spouted beds simulates the operation of bubbling FBs. In our experiments, the minimum fluidisation velocity (U_{mf}) was calculated according to equation 4-1. The fluidisation mix volume provided, through the spout, was calculated to slightly exceed the U_{mf} , and the actual fluidisation conditions were monitored by pressure gauges at the top and the bottom of the main chamber.

$$U_{mf}^2 + U_{mf} \frac{150(1-\varepsilon_{mf})\mu}{1.75\rho_g d} - \frac{g(\rho_p - \rho_g)\varepsilon_{mf}^3 d}{1.75\rho_g} = 0 \quad (4-1) \text{ (Weinberg, 1986)}$$

Where U_{mf} is the minimum fluidisation velocity, ε_{mf} the bed voidage at U_{mf} (here 0.45), μ the gas viscosity (here 18×10^{-6} Pa·s), ρ_g the gas density (1.25 g/l), d the bed particles diameter (mean value 0.75 mm), ρ_p the particles density (1600g/l), and g the acceleration of gravity. Equation 4-1 gives two roots: $U_{mf \text{ I}} = 0.69$ m/s, and $U_{mf \text{ II}} = -0.7$ m/s (rejected).

A series of gas/particles separation chambers were positioned further down the main gasification chamber. These were kept at temperatures of 500-600 °C, to avoid condensation of hydrocarbons that could cause blockages in the rig. Three ash/tar traps, where big particles were retained, a flare and a cyclone were located prior to the flue gas sampling point.

Between the tests, the rig was disassembled, the tar/ash traps, and gas sampling lines were emptied and cleaned, and new bed material was installed. The most successful

gasification experiment lasted 38 minutes, providing enough gas and solid samples for comparison with the combustion experiments.

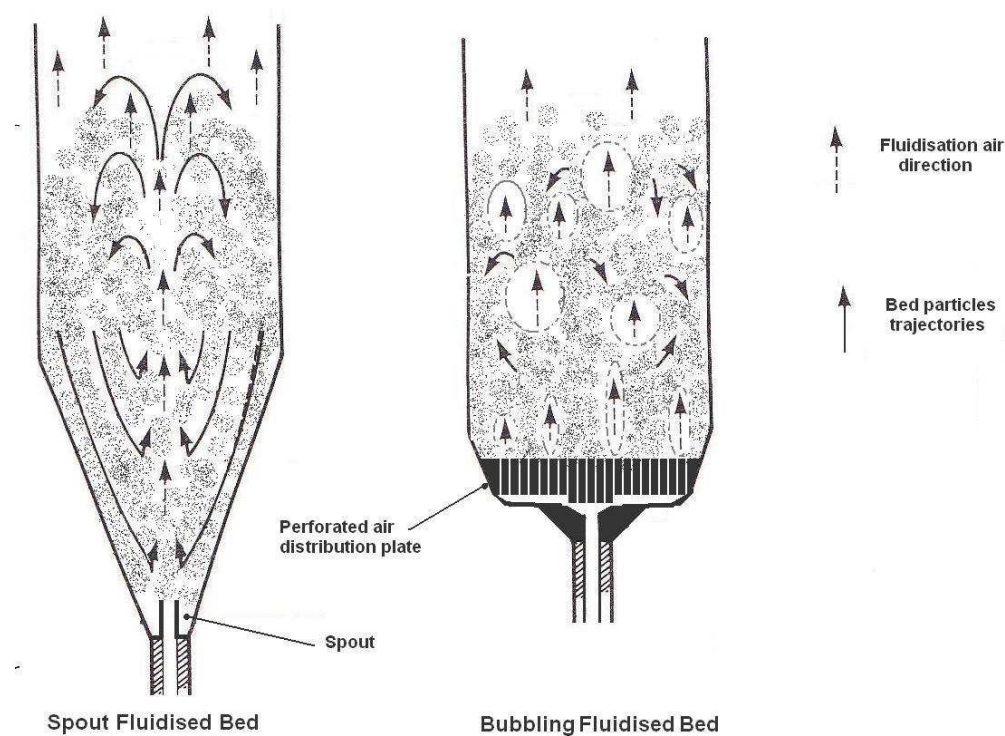


Figure 4.3: Spout and bubbling FB boilers- Re-sketched from Weinberg, 1986

4.2.3 Analysis

The airborne chlorobenzenes, and HCl were captured, and analysed using the materials and methods presented in chapter §3.2.3. The sampling period was 30 minutes for both organic and inorganic chlorine gas species.

4.2.3.1 Total and water soluble chlorine

Due to the design of the gasification rig, the collected solid residues included ashes, chars and tars. These residues were analysed both for total chlorine and for water soluble chlorides using the methods described in paragraph §3.2.4.1. However, bed ash particles were not thoroughly analysed. The collection of the bed material in a deionised water tank, and the subsequent analysis, measured only water soluble chlorine.

For combustion residues the difference between total and soluble Cl can be neglected (Liu et al., 2001), as the residues include mostly inorganic, thus highly water-soluble chlorides. However, the same assumption does not apply for the gasification residues. For this reason, some losses in the mass balance calculations were expected.

4.2.3.2 Heavy metals

In the absence of gasification CRM's, or standard analytical methods for heavy metals determination for the specific matrix (Richaud et al., 2000), the gasification residues were analysed for their heavy metals content according to the materials and methods described in paragraph §3.2.4.2. As the presence of tars in the residues was foreseen, a relatively high organic content was expected in the residues. The use of hydrogen peroxide could ensure the sufficient solubility of the target elements in the organic sub-matrices (Zhang, 2007). For this reason the nitric acid and hydrogen peroxide mix (5+3 ml, respectively- Method B) was selected in the MWAD process.

4.2.3.3 XRD, TOC & SEM-EDS analysis

The exact same conditions as the ones described in paragraph §3.2.4.3 were used for the XRD, TOC, & SEM-EDS analysis of the gasification residues.

4.2.3.4 Organics- Chlorobenzenes

The extensive comparison of the analytical methods for extraction, detection, and quantification of penta- and hexa-chlorobenzenes in the combustion fly ashes, facilitated the selection of the most suitable method for the gasification residues analysis. Soxhlet extraction, multilayer silica gel clean up, and GC-ECD detection were employed for the determination of the organochloride load in the gasification tars/ashes.

The analytical conditions used for the CBs analysis were exactly the same as the ones presented in paragraph §3.2.4.4. The only variation was the replicates mass, that was 20g (double the weight of the combustion replicate samples). The main reason for this change was that the amount of CBs in the gasification residues was unknown, thus difficulties could occur in the target species detection. Doubling the sample quantity, would increase the amounts of target compounds per replicate, and assist the detection and quantification process.

4.2.3.5 Leaching tests

The exact same condition as the ones described in paragraph §3.2.4.5 were used for the leaching tests of the gasification residues.

4.3 Results and discussion

The gasification experiment volatilised 87 wt % of the material. The remaining 13% was converted into ashes and tars. Furthermore, bulk density tests in the SRF and the produced residues revealed a volume reduction greater than 98% (98.6%). Due to the set up of the experimental rig, these residues were collected, and thus analysed as a homogeneous product.

However, these figures might contain errors of two types. The first type of error concerns losses of materials within the experimental rig. Char might have been retained, for example, in 'blind spots' within the rig, where its retrieval was practically impossible. Furthermore, the abovementioned figures are based on the nominal values from the SRF subsample. Differences between the actual test material and the subsample can bias the mass and volume transformation calculations. These differences represent the second type of possible error.

4.3.1 Chlorine mass balance

As illustrated in Figure 4.4, the majority of chlorine in the feedstock ends up in the solid residues. The quantity of Cl found in the bed material was minor (<1%). Almost 82% of Cl that entered the gasifier was converted to solid organic products of incomplete combustion e.g. chlorophenols, chlorobenzenes, etc. and salts in the tars, ashes and char. The amount of chlorine that volatilised as HCl in the process was only 5%. This figure is 5-6 times lower, when compared to tests using the same feedstock, in similar rigs, under excess oxygen environments (Balampanis et al., 2008). This

finding is of particular importance as it verifies that gasification can potentially be a safer process than combustion in terms of gaseous organochlorides generation.

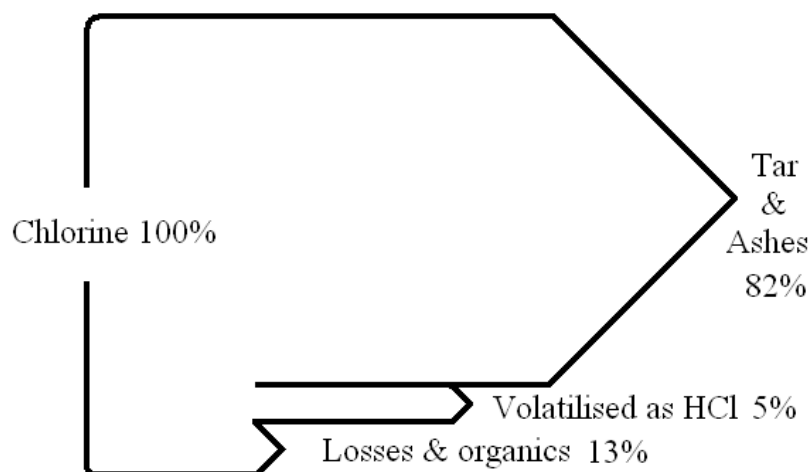


Figure 4.4. Sankey diagram of Cl mass balance

Various explanations can be given for the low HCl levels. The gasification reactions are roughly endothermic, thus an amount of energy is absorbed in the process. That leads to lower temperatures inside the upper part of the reactor that can retain Cl in the feedstock from passing to the gaseous phase. This can obstruct the volatilisation of inorganic Cl species that volatilise at higher temperatures than organically bonded Cl (e.g. PVC).

In addition to that, experimental studies using coal and biomass (Kuramochi et al., 2005; Takeda et al., 2006) have shown that the evolved HCl can react further with metal impurities, alkali metals, or active carbon structures within the produced tars-ashes-chars to be further retained in the gasification solid residues. If one assumes that the particles do not participate in the gasification reactions, when trapped in the cyclones, that hypothesis is confirmed in our case. Figure 4.5 illustrates that the Cl

content within the residues increased downstream the reactor, proportionally to the particles' residence time (for particles' traps 1, 2, and 3).

Although the relationship governing the particles Cl enrichment seems linear, the absence of data regarding the particles residence time, can not support linearity (Figure 4.5, X- axis is not calibrated). The calculation of the particles' residence time within the rig would require complex computational fluid dynamics modelling, and such work would be out of the scope of the particular study.

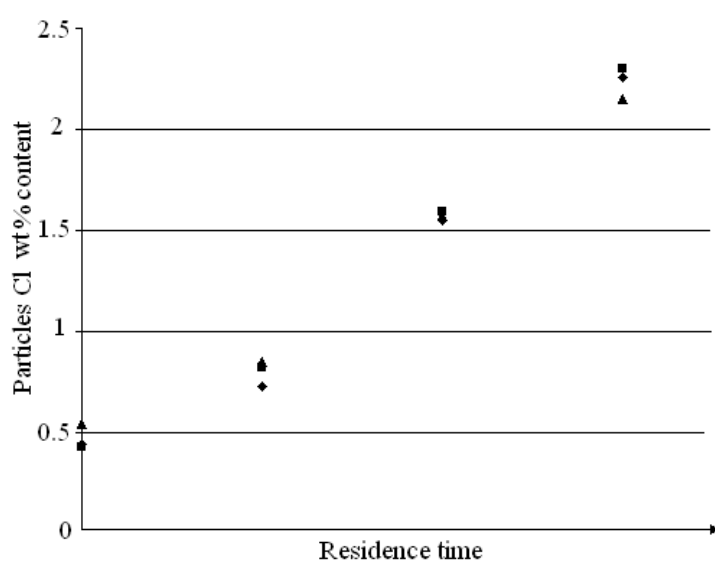


Figure 4.5. Total chlorine content of ashes-tars as a function of particles' residence time

4.3.2 Water soluble Cl

The results for the water soluble chlorine content of the gasification residues are presented in Figure 4.6. The Cl anions ranged between 1.74- 2.09 mg/g, for the first particles' trap, between 8.17- 8.9 mg/g for the second, between 11.9-12.9 mg/g for the third, and between 2.64- 4.7 for the post- flare cyclone.

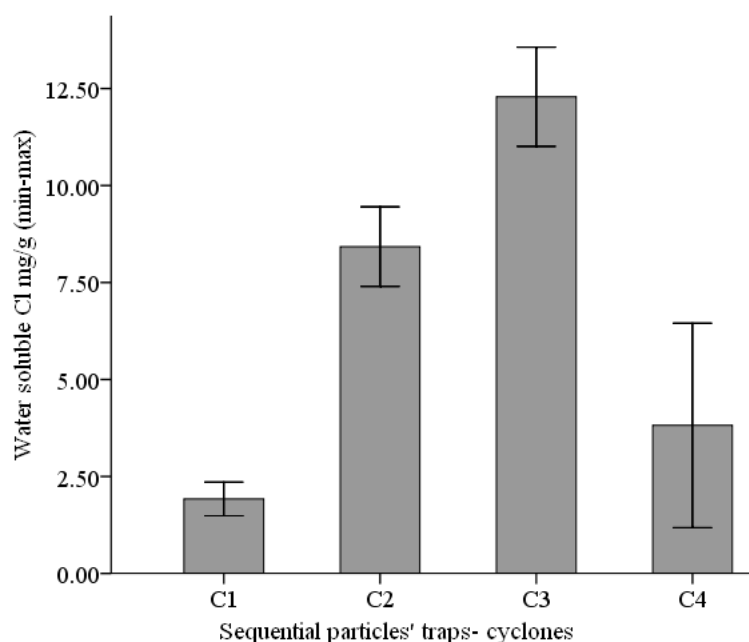


Figure 4.6. Water soluble Cl for gasification residues per collection trap

4.3.3 Heavy metals

The concentrations (range, mean, first and third quartiles) of various metals in the gasification solid residues are illustrated in Figure 4.7. Copper ranged between 0.37- 1.57 mg/g, cadmium ranged between 2.7- 54.5 $\mu\text{g/g}$, nickel ranged between 0.3- 0.63 mg/g, zinc ranged between 0.62- 1.5 mg/g, lead ranged between 0.32- 0.63 mg/g, and chromium ranged between 1.6- 2.2 mg/g. Chromium's actual concentration in the gasification residues could be higher than the one presented in Figure 4.7. This assumption is based on chromium's low recovery on the incineration CRM.

A comment can be made when these values are compared with the ones from combustion residues, from literature (Table 3.8). While Cd, Pb, and Zn are in the lower reported ranges, Cu, Ni, and Cr range at the same, or higher levels than conventional incineration derived fly ash. Thus, lower temperatures and reducing

conditions (the same reasons than retain Cl in the solid phase) can play a role in the phase distribution of heavy metals as well, as reported elsewhere (Malkow, 2004). However, this comparison is biased from the heterogeneity of the primary waste feedstock and no statistical safe conclusion can be made. Further examination is required for the study of heavy metals distribution differences between combustion and gasification. Unlike chlorine, no particular difference was observed in the concentration of metals in samples collected from different particles' traps.

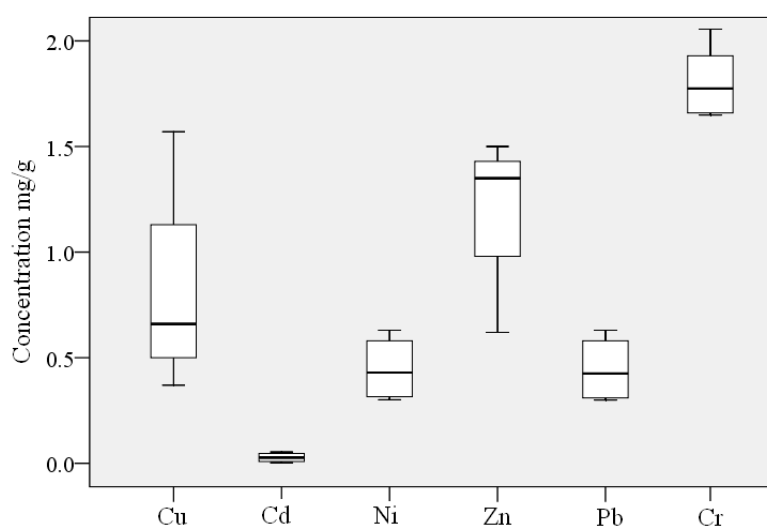


Figure 4.7. Concentration of various heavy metals in gasification tar- ash

4.3.4 Minerals and carbon

The rough (%wt>1) composition of the elements in the gasification residues, as recognised in SEM- EDS analysis is presented in Table 4.2. The instrumentation and conditions of analysis were exactly the same as the ones described in paragraph §3.3.4.

Table 4.2

SEM- EDS results on elemental composition (x: mean, s: standard deviation)

Composition (%wt, ar)		
	X	s
Na	1.7	0.4
Al	3.1	0.4
Si	4.2	1.3
P	1	0.5
S	1.1	0.1
Cl	3.2	0.3
K	1.4	0.5
Ca	12	1
Fe	2.5	0.9

The TC and TOC levels in gasification residues ranged between 5-5.7 and 3.7-6.6%, respectively. This indicates a carbon conversion of about 97% (the original SRF TOC content was $45\pm0.5\%$). The remaining carbon, according to literature volatilised to form hydrogen, carbon monoxide, carbon dioxide, and other trace hydrocarbons. Due to the particular set up of the gasification rig and the high volumes of nitrogen that were introduced in the process, the measurement and characterisation of the syngas wasn't feasible. This issue is discussed in detail in a following paragraph (discussion- limitations §5.4).

The stoichiometric conditions of the experiment, and the physical and chemical properties of the resulting gasification residues, provided sufficient evidence for the characterisation of the test as successful. Figure 4.8, for example, illustrates a SEM picture, of cracked, micro-porous particles, typical of gasification derived residues.

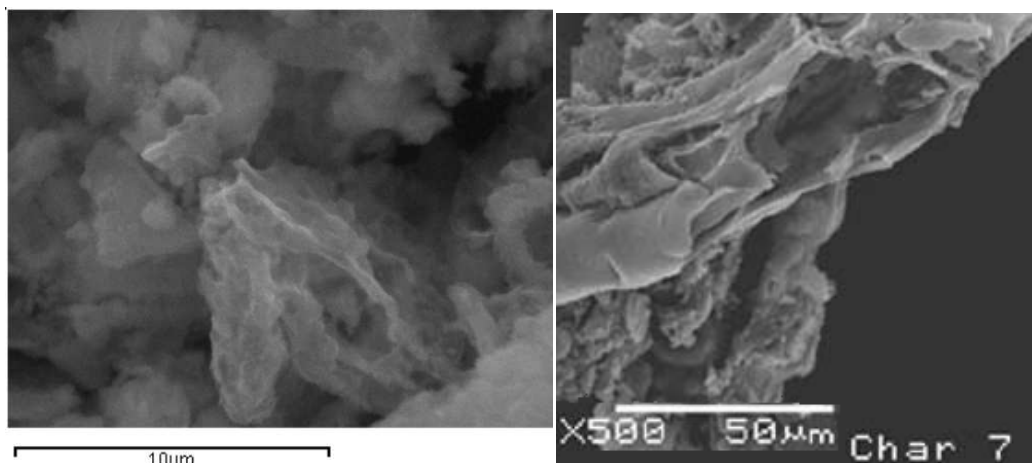


Figure 4.8. SEM picture of gasification residues indicating the cracked, micro-porous structure of the particles. This work (left) and Joyce et al. (2006) (right)

The mineralogical analysis on the gasification residues, by means of XRD (Figure 4.9), recognised the following crystalline phases: quartz (SiO_2), calcium silicate sulphate ($\text{Ca}_5(\text{SiO}_4)\text{SO}_4$), potassium aluminium oxide ($\text{K}_2\text{Al}_{22}\text{O}_{34}$), nepheline ($\text{K}_3\text{Al}_4\text{Si}_4\text{O}_{16}$), potassium perchlorate (KClO_4), silicon oxide deca-docacasil (SiO_2 -hexagonal crystalline structure), and calcite (CaCO_3). The gasification residues contained some crystalline structures that are quite common in ash residues, such as quartz and calcite (Wan et al., 2006; Quina et al., 2008b; Wang et al., 2008; Shi and Kan, 2009). Other inorganic salts, such as KClO_4 that decomposes above 600°C (Lee et al., 2001), can be considered as a product that did not volatilise due to insufficient residence time in the higher temperature zones of the gasifier (more details at limitations paragraph §5.4).

The remaining inorganic crystals in the residues are relatively rare and their presence can be considered as a minor by-product of the thermal process. Potassium aluminium oxide, for example, is a minor by-product of the aluminium refining industry (Hashimoto and Yamaguchi, 1999). For the rest of the recognised inorganic crystals no particular references were found in literature.

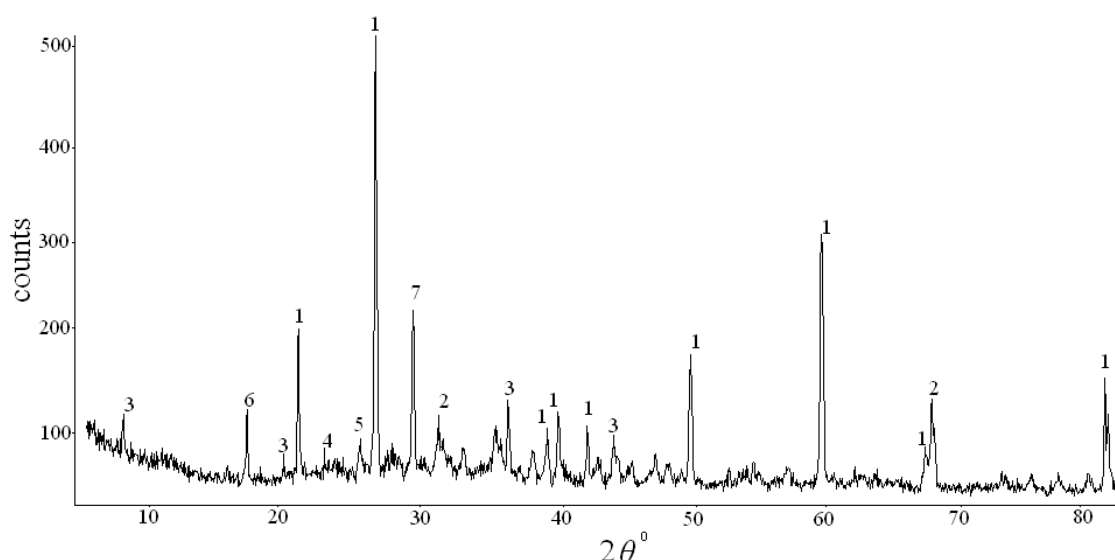


Figure 4.9. X-ray diffractogram of gasification ash/tars (step 0.05°). Crystalline phases recognised: 1. Quartz; 2. Calcium silicate sulphate; 3. Potassium aluminium oxide; 4. Nepheline; 5. Potassium perchlorate; 6. Silicon oxide Deca-docasil; 7. Calcite

4.3.5 Organics- Chlorobenzenes

Table 4.3 presents the results of the extraction and quantification of chlorobenzenes from the gasification residues. The extraction efficiency was relatively good and ranged between 64 and 101% with a mean value of 78.7 and a RSD of 16. The mean values for Cl₅Bz and Cl₆Bz were 34.8 ng g⁻¹ and 29.5 ng g⁻¹ with 31 and 37 RSDs, respectively. The deficient homogenisation of the gasification residues, during the original samples preparation, might be the reason for the relatively high RSDs. However, all the obtained values were an order of magnitude higher than the LOQs and the calibration coefficients (r^2) were satisfactory.

Table 4.3

Extraction and quantification of Cl_{5,6}Bz in gasification residues

Sample	Extraction efficiency %	*Cl ₅ Bz ng g ⁻¹	*Cl ₆ Bz ng g ⁻¹
1	86	20	11.6
2	68	55	49.4
3	64	37	34
4	101	34	30
5	83	32	24.8
6	77	39	27
7	72	27	29.4
mean	78.7	34.8	29.5
± s	12.6	11	11.3
RSD (%)	16	31	37
LOQ		0.23	0.12
r ²		0.9993	0.9998

Gaseous chlorobenzenes were below the quantification limits. This issue is further discussed at the limitations paragraph (§5.4)

4.3.6 Leaching tests

The results of the leaching tests are presented in Figure 4.10. Aluminium ranged between 0.66- 3.81 mg/L , magnesium ranged between 14-578 ng/L, cadmium between 0.2- 0.8 ng/L, chromium between 9- 47.3 ng/L, mercury between 0.05- 0.11 ng/L, nickel between 3.2-3.4 ng/L, lead between 0.14-0.5 ng/L, tin between 0.45-2.69 ng/L, titanium between 23.1-33.2 ng/L, phosphorous between 21.2-36.6 ng/L, potassium between 4.66- 7.62 mg/L, vanadium between 1.45-2.83 ng/L, manganese between 1.54-1.8 ng/L, and sodium between 6.4- 10.6 mg/L . The values for zinc and copper were below the quantification limits.

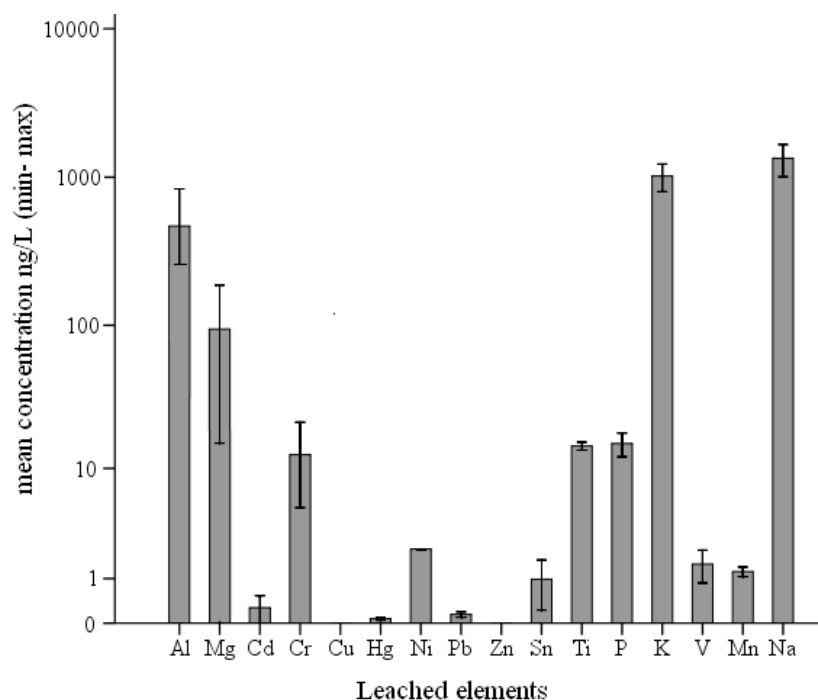


Figure 4.10. Leaching test results

The LOQs obtained were: 16 ng/L for aluminium, 11.8/L ng for magnesium, 0.1 ng/L for cadmium, 4.2 ng/L for chromium, 13.6 ng/L for copper, 0.1 ng/L for mercury, 1.4 ng/L for nickel, 0.1 ng/L for lead, 15.3 ng/L for zinc, 0.2 ng/L for tin, 0.4 ng/L for titanium, 10.7 ng/L for phosphorous, 0.1 mg/L for potassium, 0.3 ng/L for vanadium, 0.4 ng/L for manganese, and 0.4 mg/L for sodium.

The high content of soluble salts is confirmed in the gasification residues, through the high amount of leached K and Na. Other metals and minerals, such as Al, and Mg, were detected in high concentrations, but the majority of leached elements ranged close to, or far below, 10 ng/L of leachate.

The leaching tests were performed with a high L/S ratio, for sample preservation reasons, as reported in paragraph § 3.3.6. Thus, the reported values do not serve the characterisation of leachate according to the existing standards (BSI, 2002), as landfill

acceptance criteria. However these values will be further analysed when compared to the leaching behaviour of the combustion residues, in a later paragraph (§ 5.3.4).

4.4 Synopsis

The SRF gasification experiments and the subsequent results were presented in this chapter. The used materials and methods were identical to the ones presented in chapter 3, and only deviations from these methods were presented.

Extremely intense efforts and technical- intensive work led to successful gasification experiments with 13 months delay. The delays were mostly related to the feeding of the SRF in the gasifier under steady state conditions. These problems were solved with the design, and construction of a pneumatic feeding system, based on the Venturi principle, that allowed successful gasification trials of around 30 minutes. Although the feeding system had specific drawbacks, it allowed the generation of gasification samples to facilitate coherent comparisons with the combustion ones.

The following indicators have been thoroughly studied in the gasification residues: total and leachable chlorine, organochlorides expressed as pentachlorobenzene and hexachlorobenzene, and the heavy metals Cu, Cr, Cd, Zn, Ni, and Pb. Furthermore the crystalline compounds in ashes, tars and chars have been studied by means of XRD and SEM- EDS. Finally, leaching tests for the determination of various elements have been performed, that will later facilitate comparisons with the FBC samples.

From this analysis the following conclusions can be drawn:

- The gasification experiments reduced the incoming SRF mass and volume to 87 wt%, and 98 vol%, respectively.
- The majority (84%) of the Cl in the input (SRF) is found in the solid residues in the output. Moreover, the detected HCl was only 5% of the original Cl input. This indicates that the amount of volatilized Cl is much lower than the one obtained in the combustion experiments.

Thus, gasification can potentially be a safer process than combustion in terms of gaseous organochlorides generation.

- The mineralogical analysis recognised crystalline structures in the gasification residues which are quite common in ash residues, such as quartz and calcite. The presence of potassium perchlorate however, might be an indication of insufficient particles residence time within the high temperature zones of the gasifier. The above assumption though, can only be partially truth, as the gasification residues presented a typical cracked- microporous structure (SEM analysis) and a carbon conversion of ca. 97%

Other results presented in this chapter, such as the chlorobenzenes concentration, and the leaching tests data, will be discussed in chapter 5, as the comparison with the combustion data is of major interest.

Chapter 5. Discussion on the differences between FBC and FBG

5.1 Introduction

This chapter will cover a comparative analysis of the combustion and gasification experiments. Although specific results were discussed in chapters 3 and 4, further examination of the processes and the produced residues is given. This comparison will highlight the advantages and disadvantages of the two SRF thermal treatment techniques.

The chapter is divided in three main paragraphs. The first part examines the processes in terms of SRF mass and volume reduction. Furthermore, the Cl mass balances are compared. Although, the original scope of this PhD included further comparison of the two processes e.g. organochlorides formation, this was only partially achieved. Technical difficulties and time and cost limitation changed the scope of the work from ‘comparison of processes’ to ‘comparison of residues’.

The second part comparatively examines the solid residues produced by the two processes. This part of the discussion highlights the differences of the two residues for various toxicity indicators. Total and water soluble chlorine, organochlorides, heavy metals, and the leaching behaviour of various elements in the residues are discussed.

The third part of this chapter deals with the limitations of this work. These limitations explain the lack of control on reproducible trials that changed the scope of the work.

5.2 Comparison of processes

5.2.1 Mass and volume transformation

Mass and volume reduction are considered as the primary functions of waste thermal treatment. For the combustion experiments, the mass input was 35100g, and the resulting ashes were 3990g, which is equivalent of a mass reduction equal to 91.5% (equation 5.1). The mass of SRF that entered the gasifier was 2960g and the total mass of the resulting ashes and tars was 376g. This corresponds to a mass reduction of 87%.

$$\text{Mass (volume) conversion efficiency} = \left(1 - \frac{\text{Output mass (volume)}}{\text{Input mass (volume)}}\right) \times 100 \quad (5.1)$$

When considering the bulk density values for the incoming SRF (12.5 L/kg) and the bulk density of the resulting fly ashes (1.5 L/kg), combustion will account for a volume conversion of 98.6%. The equivalent values for gasification were 9.1 L/kg, 1.2 L/kg, and 98.8%, respectively. The volume reduction coefficients do not include the volume of the bed ash in both of the reactors, as there were no practical means for this measurement. Moreover, any manipulation of the resulting bed material could lead to losses of ash, and subsequent losses for the Cl mass balance.

Existing nominal literature values from waste derived fuels indicate mass and volume reduction of about 75% and 90%, respectively (Hester and Harrison, 1994). Although direct comparisons have little meaning, the rates achieved in our experiment were significantly higher. The low ash- inert materials content of the SRF, and the conversion efficiency of fluidised beds in comparison to other furnace types (e.g.

moving grates) (Tchobanoglous et al., 1993), can be considered as one of the reasons for the improved conversion rates in this work.

5.2.2 Cl mass balance and gas/solid phase distribution

Although, the mass balances have losses that range from 7.2% to 13%, for combustion and gasification, respectively, their comparison presents interesting results on the phase distribution of Cl. Gaseous inorganic chlorine, expressed as HCl was only 5% of the Cl input for gasification, against 28% in combustion.

One of the most reasonable explanations for this difference is the temperature profile of the two processes. Although the Cl to HCl conversion in most of waste materials stabilises at temperatures around 600 °C, some components, like textiles emit HCl mainly at higher temperatures (600- 700 °C), as indicated in Figure 5.1. As discussed in chapter 4, the introduction of compressed nitrogen in the gasification chamber, through the Venturi feeding system, resulted in the formation of cold spots. Moreover, gasification as an endothermic process absorbs an amount of energy. This results to the inherent partial volatilisation of waste materials, and the subsequent partial volatilisation of Cl.

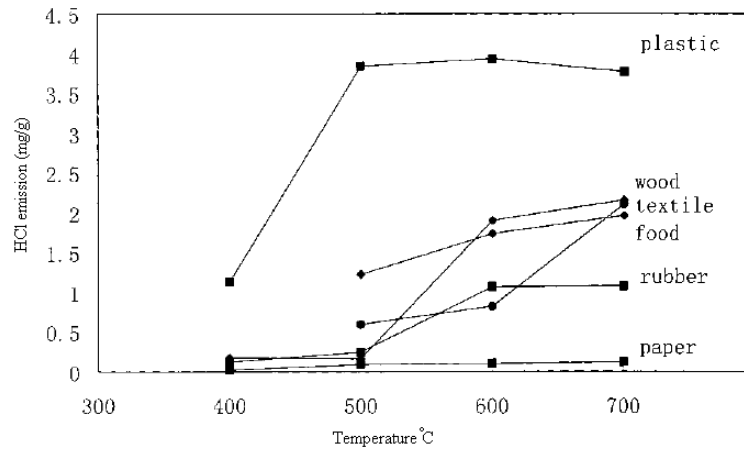


Figure 5.1 HCl volatilisation for different waste materials (Guo et al., 2001)

Chlorine volatilisation is related to the mass loss of the waste materials in thermal processes. As TGA analysis indicates, (Figure 5.2) different waste materials have different volatilisation behaviours. Plastic for example, volatilises more rapidly (at about 673 K- 400 °C) than food waste that volatilises gradually at temperatures between 473- 1073 K (200- 700 °C). As a result, different waste fractions require different residence time within high temperature zones of the gasifier, for the complete volatilisation of their Cl content. Thus, the insufficient residence time of some waste fractions is another possible explanation for the low HCl emission levels in the gasification experiment.

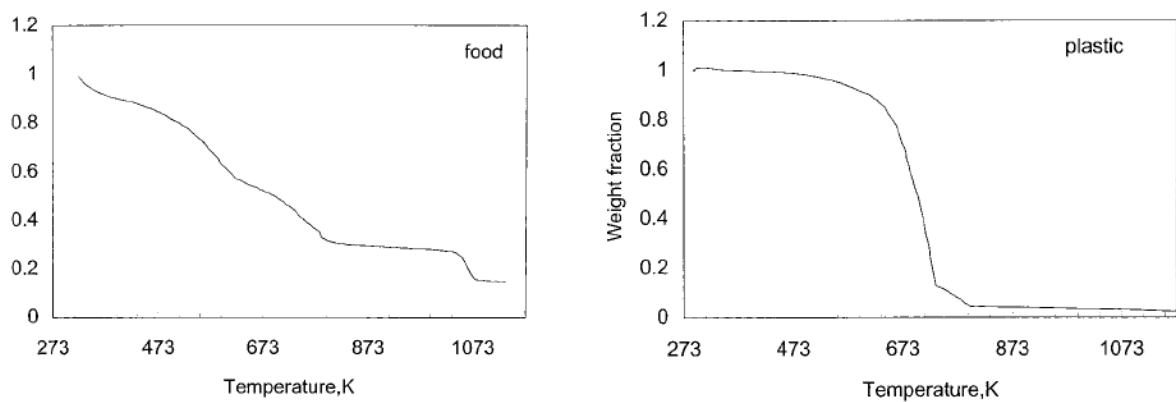


Figure 5.2 TGA graphs- Volatilisation behaviour of different waste fractions, Guo et al, 2001

The difference in the Cl content, between the two processes is also reflected in the solid residues. Combustion retained 63.8% (18.4% bed ash, 28.2% coarse fly ash, 17.2% fine fly ash) of the incoming Cl in the solid phase, while the equivalent percentage for gasification was 82%. This difference, matches roughly the difference in the HCl formation levels, in respect to the mass balance errors.

As discussed in paragraph 4.3.1, experimental studies using coal and biomass have shown that the evolved HCl can react with the residues produced, to be further retained in the gasification tars/chars. This can happen through different mechanisms involving either alkaline earth metals, or carbon active structures. In the first case for example, HCl can react with CaO, or CaCO₃ to form CaCl₂ (Takeda et al., 2006). Further interaction of Cl with trace metals is also favoured in gasification conditions due to reducing conditions. Partial pressure of oxygen (pO₂), for example, is much lower in gasification environments, promoting the abovementioned interaction (Brooker, 1993).

The second mechanism involves the reaction of HCl with active carbon sites such as nascent char (Li et al., 2005) to form covalent C-Cl bonds. The latter is one of the basic chlorobenzenes/dioxins formation mechanism, described as heterogeneous reactions (paragraph §2.5.2). Although these mechanisms are only confirmed for biomass and coal, it is apparent that they contribute to the HCl retention in waste gasification as well.

Another major difference was observed between the two experiments. While FBC retained ca. 18% of the incoming Cl in the bed ash, the equivalent percentage for the FBG was below 1%. One explanation for this difference could be the large N₂ flow, through the Venturi entraining system in combination with the small SRF particles'

size in the gasification experiment. The small SRF particles were volatilised fairly quickly, and the resulting tars, ashes, and chars were carried away further down the main gasification chamber. On the contrary, the fluidisation air in the combustor did not favour such transfer phenomena, and retained heavier ash particles within the main bed chamber.

The results presented in this section, regarding the mass balances, are biased from three different types of errors. The first error concerns the information regarding the Cl input. This value was determined through random sampling, according to the relevant standard (CEN/TS 15442, 2006). Random sampling means that a sample was taken from a lot in a way that ensures that all possible samples have the same probabilities of being taken. However, small differences in the Cl content between the test sample and the actual lot should be expected. These differences can lead to the over/under-estimation of the actual Cl that entered each processes, and subsequent errors in the Cl mass balances calculations.

The second error concerns losses in sampling. Although considerable effort was given to the collection of samples, the scale of the experiments (pilot scale rigs) and the type of samples (ashes- flue gases) might have led to losses of Cl species.

Losses of Cl species, due to analytical methods, is finally the third type of error. The Cl content of the bed-ash, for example was determined based on the water soluble chlorides only (the whole bed material was collected in a tank with deionised water). This method was followed for practical reasons as it was not possible to separate the bed ash from the bed particles, resulting in an underestimation of the Cl bed-ash content. Organic Cl species, for example in the bed ash were not taken into account. Although, this difference can be neglected for combustion residues (Liu et al., 2001) (the residues include mostly inorganic, thus water-soluble chlorides), the same

assumption does not apply for the gasification residues. This fact could also partially explain the extremely low Cl content of the gasification bed-ash.

These three types of errors were inevitably introduced into the measurements performed. However, the recoveries regarding the mass balances resulted in relatively low losses ca. 7.2% and 13% for combustion and gasification, respectively.

5.3 Comparison of residues

5.3.1 Water soluble Cl

Chlorine occurrence in waste thermal treatment residues is in three forms (Vassilev et al., 1999):

- The partially reacted organic material (e.g. PVC)
- The fused Na, K, Ca, Fe, and Mg chlorides- salts
- The absorbed Cl in pore moisture onto and into the organic and mineral phases.

Some of these species, when in contact with water, leach Cl ions relatively easy (e.g. NaCl and KCl), while others are poorly dissolved (e.g. Friedel's salt, or PVC) (Hwang et al., 2006). While standardised leaching tests (BSI, 2002) use specific liquid to solid ratios (usually in L/kg units), to facilitate regulatory needs, higher L/S ratios can be used to simulate long term leaching behaviour. Hyks et al. (2009) for example, use an L/S ratio between 200-250, which corresponds to more than 10,000 years of leaching, in a conventional landfill.

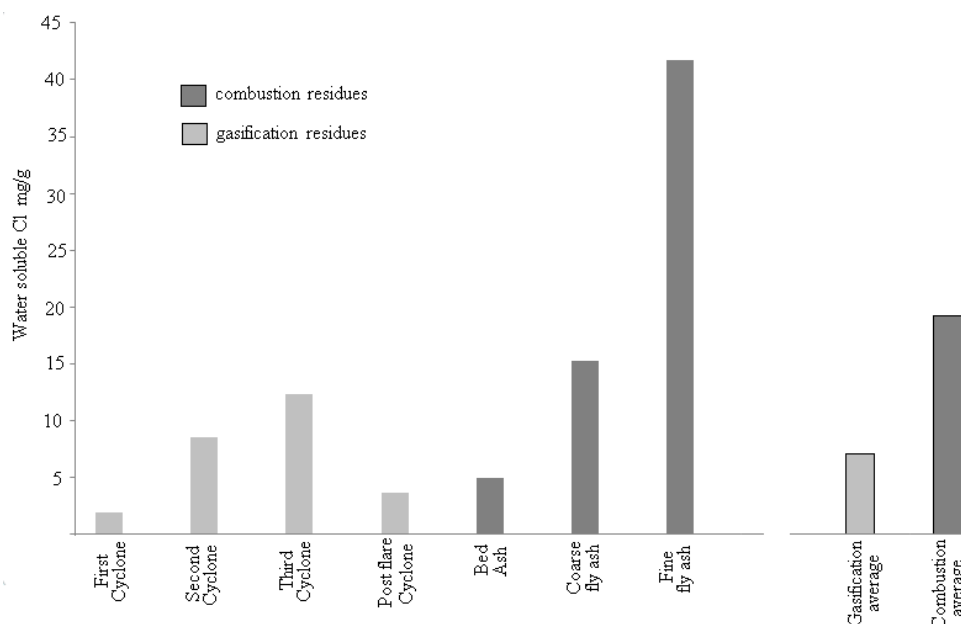


Figure 5.3. Water soluble Cl content in thermal treatment residues

In these experiments the L/S ratio was equal to 50 to facilitate sample preservation reasons. The amounts of the water soluble chlorides of the different types of thermal residues are summarised in Figure 5.3. With only the exception of the combustion bed ash, both coarse and fine fly ashes, leached 2-3 times higher levels of Cl, than the gasification residues. In average terms, the gasification residues leached 7.6 mg/g of Cl ions, while the equivalent percentage for combustion residues was 21.4%.

The fact that gasification residues leach lower amounts of chlorides is supported also by the XRD analysis. Although Cl is met in halite and sylvite crystals in the combustion residues, bonded to Na and K, respectively, these crystals were not detected in the gasification samples. On the contradict, Cl was met as potassium perchlorate (KClO_4) in the gasification ashes/tars. The solubility in water of KCl (28g/100 mL in 0 °C) is more than thirty five times higher than KClO_4 (0.75g/100 mL in 0 °C) (Sigma Aldrich MSDS, 2009). Furthermore, the presence of Cl in non

leachable forms, such as trace metal chlorides (e.g. CuCl_2) should be expected in the gasification residues.

It is concluded that the gasification residues have a greater content of partially reacted chlorine and salts with lower water solubility, than the combustion residues. It is therefore evident that the gasification residues have a much smaller potential to leach Cl, than the combustion ones, when landfilled.

5.3.2 Heavy metals content

Although the literature is extensive for the volatilisation behaviour of metals during combustion, much less information is published on the subject regarding gasification conditions (e.g. Liu, 2006). Reed et al. (1997) as cited in Richaud et al. (2000), performed thermodynamic modelling using the MTDATA software (Davies et al., 1997). They predicted that Co, Cr, Ni, and V would condense between 940- 980 °C, Cu, Mo, and Zn would mostly condense at ≥ 600 °C, Mn, Pb and Sn at ≥ 400 °C and As, Cd, Hg, and Se would still be present as gas species at 400 °C. In this work, at least one of the metals from each of the abovementioned groups is quantified. Subsequently, the concentration of Cu, Cr, Ni, Pb, Cd, and Zn content are compared between combustion and gasification residues

The heavy metals concentration in combustion related residues has an oxymoron interpretation. High concentration levels characterise the material as hazardous (BSI, 2002) and make their reuse, recycling, and final disposal challenging and costly (Quina et al., 2008a). However, when studying the kinetics of a thermal process, the heavy metals content has a different meaning. Retaining the heavy metals in the solid phase is preferable than volatilising them, in terms of environmental management. Heavy metals trapped in solid residues are a physically concentrated source of

pollution, which makes handling, transferring, decontamination, and final disposal, relatively easy. On the contrary, volatilised heavy metals can act as a non-point pollution source, if they are not properly managed. Furthermore, their management through APC can be extremely costly.

Regarding the comparison of the different residues, and based on the abovementioned concept, a higher metal content is favoured than a lower one when comparing these values. Independent t- tests at a significance level of 95% ($p= 0.05$, degrees of freedom= 6) were performed for gasification residues against coarse and fine fly ashes, for each of the examined metals. As indicated in Figure 5-4, the concentrations of Cu, Cr, and Cd were significantly higher in gasification residues. Thus, gasification retained higher amounts of Cu, Cr, and Cd in the solid residues when compared to combustion.

This difference could be temperature related for copper (condensation range 900-600 °C), but not for chromium (condensation range 940-980 °C), and cadmium (condensation range ≤ 400 °C). It is reminded that the gasification experiments were performed at an average bed temperature of 700 °C, while the combustion ones at 800 °C. This temperature difference might have affected the enrichment of gasification residues with copper. However, that assumption does not apply for chromium and cadmium, where other process-specific factors (e.g. stoichiometry, residence time, rig type) might have affected their increased concentration in the gasification ashes/tars.

The t-tests revealed further statistical significant differences. Lead and nickel, for example had a statistical significant higher and lower concentration, respectively, in the coarse fly ash fractions. However, these data are considered process- specific and do not indicate a particular pattern.

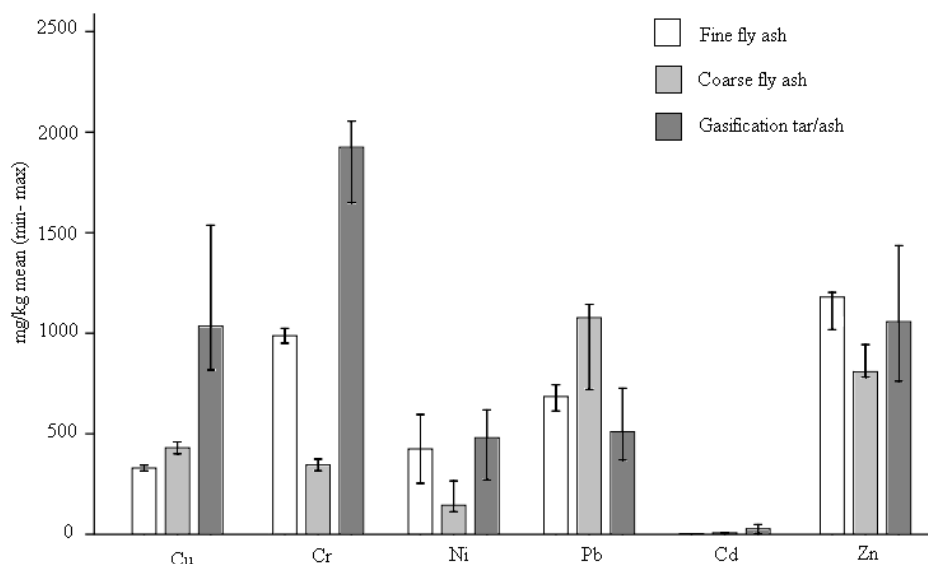


Figure 5.4. Heavy metals concentration in combustion and gasification residues

5.3.3. Organochlorides- Chlorobenzenes

Chlorobenzenes are considered as one of the most difficult species to eliminate in waste thermal treatment processes. This is due to the strength of the C-Cl bond as indicated in literature (Morlando and Manahan, 1997). Their formation is favoured in the post-combustion and post-gasification zones, also called as ‘cold zones’ in thermal treatment rigs (Lasagni et al., 2000). Regarding the experiments in this work, the fly ash samples and gasification residues were collected from the cold zones of the experimental rigs. Thus, the samples are considered as representative of the maximum organochlorides load in each process.

Figure 5.5 illustrates the concentration of pentachlorobenzene and hexachlorobenzene in the fine fly ash, the coarse fly ash, and the gasification residues. When comparing the samples from the two processes, gasification residues have 3-8 times higher concentrations of the examined organochlorides.

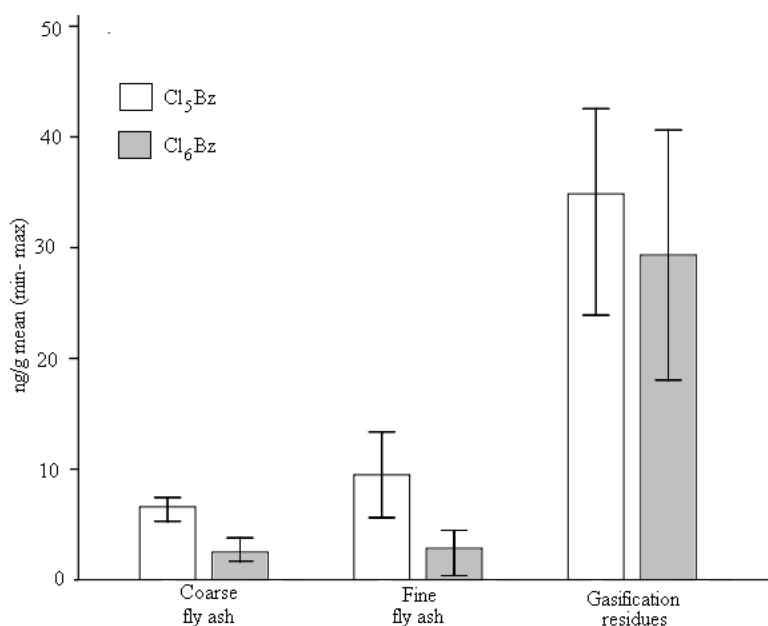


Figure 5.5. Penta- and hexa-chlorobenzene concentrations the solid residues.

Several explanations can be given for this difference. As McKay (2001) notes the destruction of organochlorides is favoured in elevated temperatures and increased residence times in thermal rigs. These conditions were relatively respected in the combustion experiments. However, the gasification experimental conditions were characterised by lower temperatures and lower particle's residence times. These factors might have contributed to the higher levels of chlorobenzenes in the gasification residues.

Furthermore, literature suggests that unburned carbon (e.g. non- reacted, native carbon) can play a significant role in the formation of PCDD/PCDFs and their precursors (e.g. chlorobenzenes) (Lasagni et al., 2000). Gasification residues, as products of incomplete combustion are expected to contain higher amounts of un-reacted carbon, thus higher amounts of organochlorides.

The above explanation is supported by the fact that gasification residues contained higher amounts of organic and inorganic Cl. This organochlorides formation

mechanism is roughly described by the de novo synthesis through homogenous reactions (Wikstrom et al., 2003). This theory suggests that ash bound chlorine alone is a sufficient source for the formation of organochlorides through homogeneous (solid to solid phase) reactions with native carbon structures.

5.3.4 Leaching behaviour

The amounts of leached alkali metals (Na and K) are illustrated in Figure 5-6. The gasification residues leach 3-9 times less potassium than the combustion residues. Regarding sodium, the gasification residues leach significantly smaller amounts than coarse fly ash (t-test, $p=0.05$, degrees of freedom=6), and 3-4 times lower amounts than fine fly ash. These results are in agreement with the chlorine leaching tests, indicating that the amount of water soluble salts are higher in combustion residues, as discussed in paragraph 5.3.1.

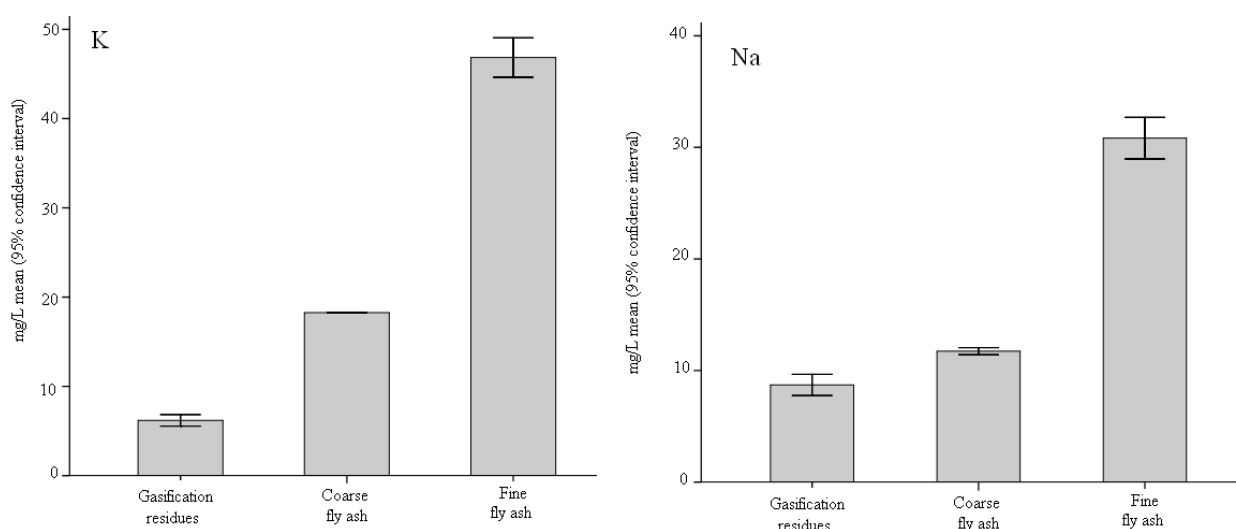


Figure 5.6. Leached K and Na in different residues types

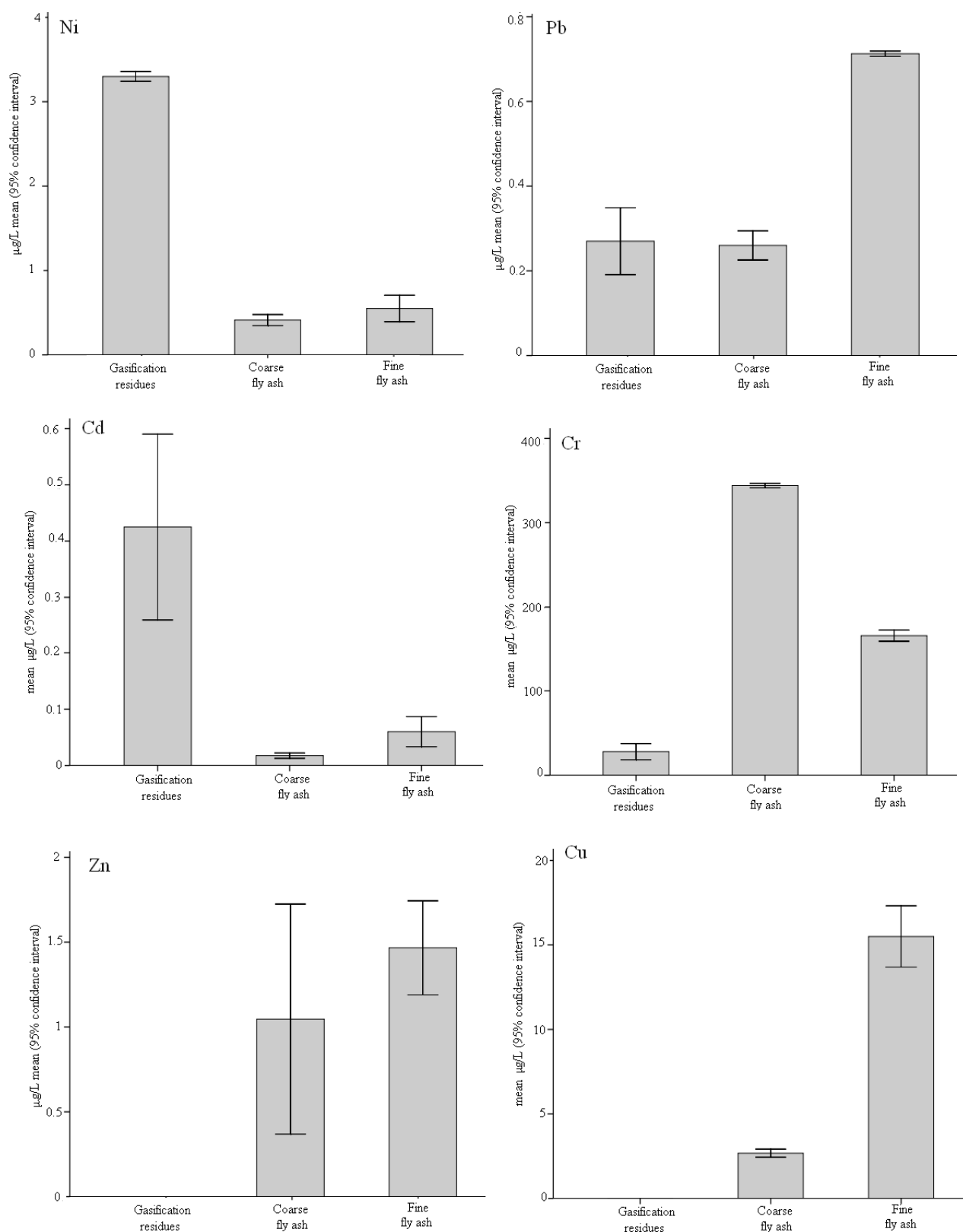


Figure 5.7 Leached Ni, Pb, Cd, Cr, Zn, Cu in different residues types

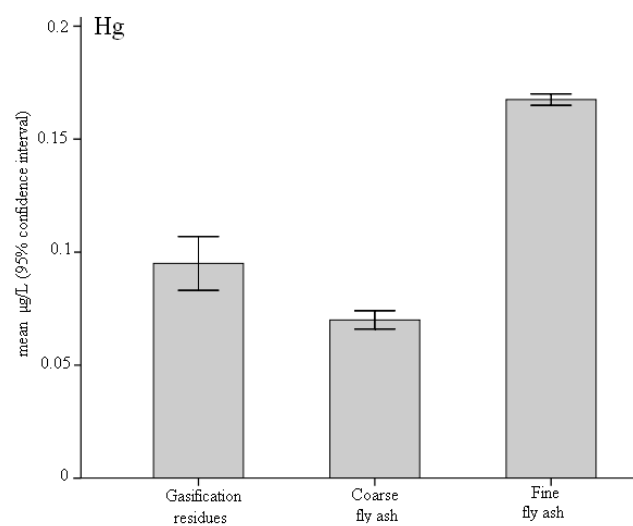
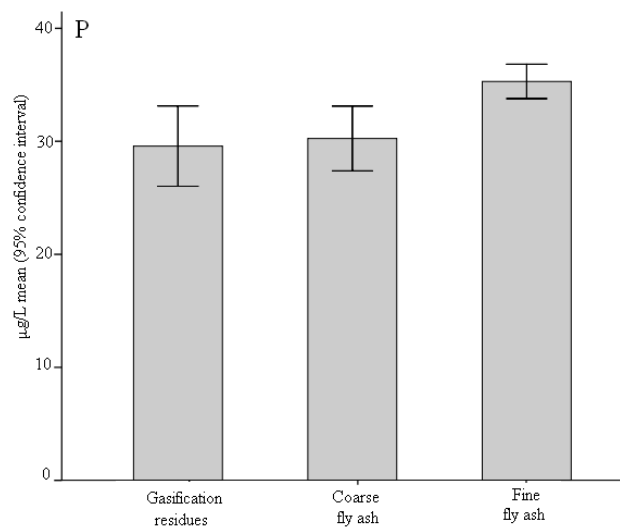
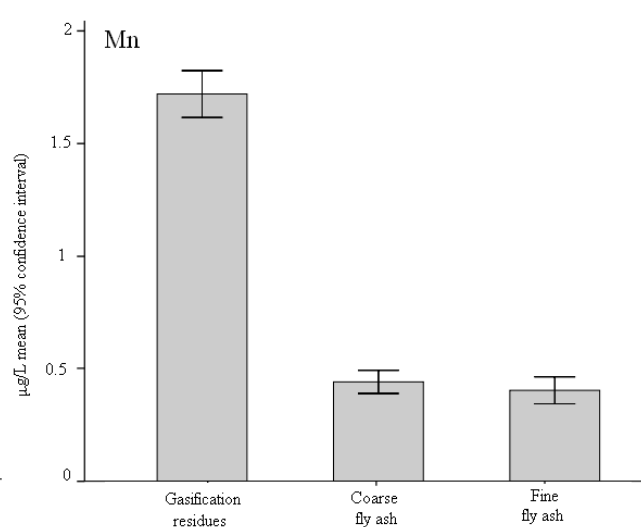
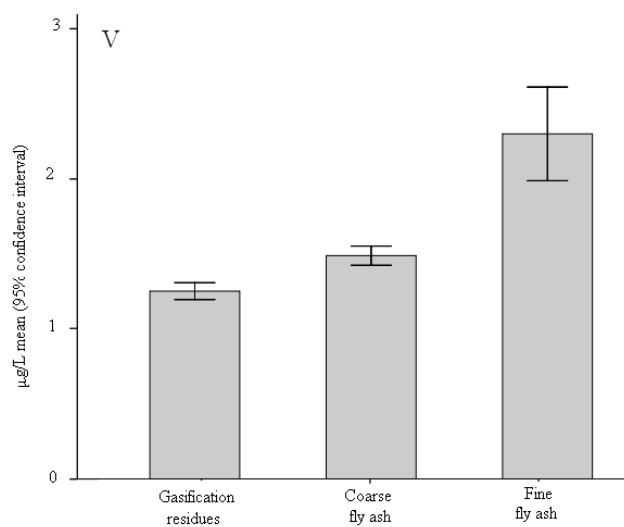
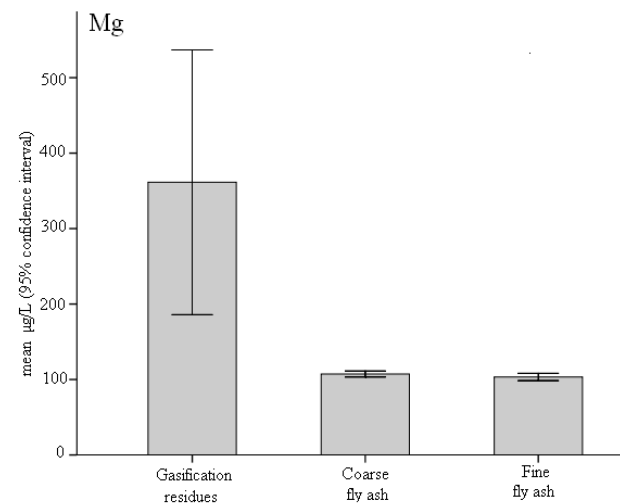
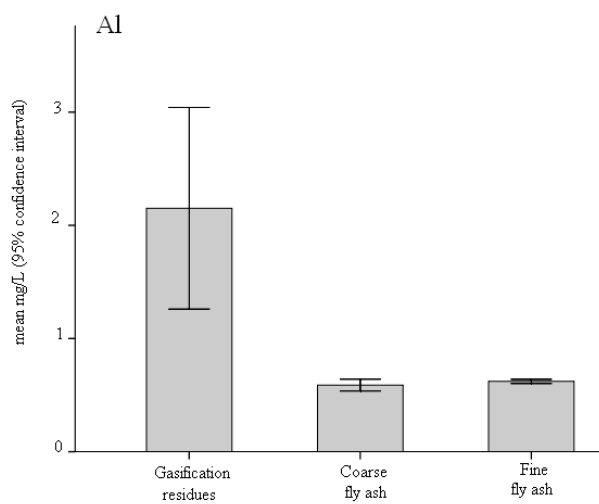
The amounts of leached heavy metals Ni, Pb, Cd, Cr, Zn, and Cu are indicated in Figure 5.7. The gasification residues leached 6-7 times higher amounts of nickel than the combustion residues. Regarding chromium, coarse fly ash leached 7-10 times higher amounts, compared to the other residues. Zinc and copper were below the quantification limits for the gasification residues, while the equivalent values for combustion residues were between 0.4-1.7 µg/L, and 3.8-17.2 µg/L, respectively. The concentration of Cd in the leachate was 2-10 times higher in the gasification residues, than the combustion ones. Finally for lead, the higher amounts were detected in the fine fly ash leachate.

An interesting conclusion can be made when comparing these values with the residues' metals content (acid digestion -Figure 5.4): there is no direct relationship between the amounts of metals that leach from thermal treatment residues and their actual metals content. The concentration of copper for example, is 2-3 times higher in gasification residues, when compared to the combustion ones. However, the amount of copper that leached from the gasification residues was below the quantification limit, and obviously lower than the equivalent amounts that leached from the combustion residues.

This conclusion was recently reported for combustion related residues (Hyks et al., 2009). However, it is confirmed in this study for gasification residues as well. Cadmium was the only exception, where the high concentration in the gasification residues was reflected in the leaching tests, respectively. However, for the rest of the examined residues no profound relationship exists between their actual and leached heavy metals levels.

The amounts of Al, Mg, Mn, V, P, Hg, Ti, and Sn that leached from the different types of residues, are illustrated in Figure 5.8. It is noted that gasification residues

leached higher amounts of aluminium, magnesium, and manganese than combustion residues. On the contrary, fine fly ash leached higher amounts of vanadium, phosphorous, mercury, titanium, and selenium, than the other residues types. However, no particular conclusion can be made, as the original concentration of the above elements in the residues is unknown.



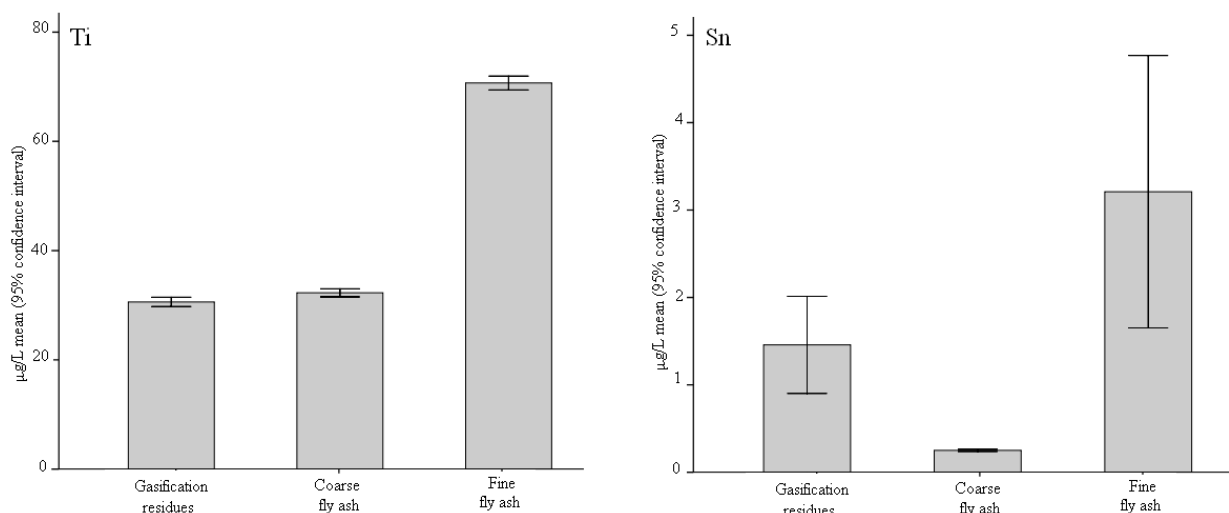


Figure 5.8 Leached Al, Mg, Mn, V, P, Hg, Ti, and Sn in different residues types

5.4 Limitations

The scope of this study was more ‘in vivo’ rather than ‘in vitro’. The nature of the feedstock and the scale of the experimental rigs, and feeding rates are indicative of the applied nature of the experimental approach. As such, the experiments are limited by a number of factors. These are as follows:

- Results from single trials. Although replicate trials were performed, the results presented in this work are from a single FBC and FBG trial. In this context, major efforts were given for the achievement of steady state conditions in pilot scale conditions, and the generation of ‘real life’ samples. Due to time and cost implications, samples from replicate trials were not analysed, but they were only used as test materials for the fine tuning of analytical methods. However, the results presented in this study derive from the most successful trials,

with the maximum operational time. Thus, they are believed to represent full scale processes.

- Variation in the particles' residence time between the two processes. The physical form of the SRF made its control in feeding systems extremely challenging. This fact, combined with the set up and operation of the available experimental rigs had a direct effect on the control of the particles' residence time. This has been a limiting factor especially in the gasification experiments, where the pneumatic feeding system was introducing large volumes of nitrogen in the gasification main chamber. Subsequently, flows other than the fluidisation air mix were affecting the turbulence in the gasifier, compared to the combustor. A solution to this problem could be given by a different type of reactor. Downdraft gasifiers for example, can ensure sufficient particles' residence time as reported in literature (Morlando and Manahan, 1997). However, the experiments were limited from the type and set-up of the available rigs in Cranfield University. Moreover, the smaller SRF particles' size in the gasification experiments might have contributed to the off-set of a limited residence time.
- Gasification gaseous species. The composition of the syngas, in the gasification experiments was not quantifiable. The reason for that was the massive dilution rate that the 1700 L/min of nitrogen created in the flue gases produced. Although traces (1-2%) of carbon monoxide were detected, other gases (e.g. carbon dioxide, methane) were not detected. Thus any quantification of the gases produced would be highly debatable. This factor limited the quantification of the airborne

chlorobenzenes as well. The GC-ECD results indicated that the gaseous CBs were below the limits of detection.

The abovementioned limitations illustrate the technical difficulties that evolved during this work. These were mainly related with the operation of the FBG with the particular form of the fuel. As work evolved, within the PhD framework, these limitations were recognised as extremely important factors that could justify a shift in the scope of the work. It became clear at a point that even if replicate trials were achieved, these wouldn't be identical in terms of SRF particles' residence time, normal operation time against start-up time, etc. Indicative of these conditions, was the fact that several aborted trials in the FBG had longer start-up/ stabilisation periods (e.g. 30-40 minutes) than the actual trials (1-2 minutes of operation).

However, the in-house designed and manufactured pneumatic feeding system, gave a 30 minutes trial under steady state conditions. Despite the drawbacks of the latter (effect on syngas quantification, leaks, etc.), an accountable amount of solid residues was produced from the experiment. This fact allowed the change of the scope of the work.

In conclusion, the abovementioned limitations led to a change of the scope in the PhD work. The emphasis on the scope inevitable shifted from 'comparison of processes' to the 'comparison of the solid residues' from SRF thermal treatment.

5.5 Synopsis

When comparing the two processes in terms of mass transformation, combustion reduced the incoming SRF to 91,5%, while gasification to 87%. The volume reduction for the two processes was 98.6%, and 98.8%, respectively. Furthermore,

gaseous inorganic chlorine, expressed as HCl was only 5% of the Cl input during gasification, against 28% in the combustion.

When comparing the two residues types, it is concluded that the gasification residues have a greater content of partially reacted chlorine and salts with lower water solubility, than the combustion ones. It is therefore evident that the gasification residues have a much smaller potential to leach Cl, than the combustion ones, when landfilled. Furthermore, gasification retained higher amounts of Cu, Cr, and Cd in the solid residues when compared to combustion. However, gasification residues have 3-8 times higher concentrations in penta- and hexa-chlorobenzenes.

The leaching tests indicated that there is no direct relationship between the amounts of metals that leach from thermal treatment residues and their actual metals content. Although, this conclusion was recently reported for combustion related residues it is confirmed in this study for gasification residues as well.

Finally, the limitations of this work were mainly related with the operation of the FBG with the particular fuel form. In conclusion, these limitations led to a change of the scope of the PhD from 'comparison of processes' to the 'comparison of the solid residues' from SRF thermal utilisation.

Chapter 6. Conclusions

6.1 Introduction

This chapter describes the major conclusions of this research project. The conclusions are grouped in five categories; analytical methods, combustion experiments, gasification experiments, comparison of processes, and comparison of residues. This arrangement follows the structure of this report, and intends to facilitate a better understanding of the highlights of this work.

Furthermore, a paragraph is dedicated to opportunities for further research. These opportunities rose from the limitations that evolved during this work, and have a rather technical nature. Among others, the experimentation with alternative gasification rigs, or rig set-ups, and computational fluid dynamics modelling, are proposed.

The chapter closes with the presentation of the novel approaches, methods, and conclusions that this study brought out. These are summarised by the utilisation of a novel fuel, and the generation of novel raw data for the characterisation of ‘in vivo’ waste thermal treatment residues.

6.2 Main conclusions

The main conclusion of this work can be summarised in the following paragraphs.

Regarding the analytical methods:

- For the determination of the heavy metals content in fly ashes, four HF free digestion methods were tested for their recoveries. A one way ANOVA at a confidence interval of 95%, confirmed that there was no single method that significantly recovered higher amounts for the whole range of the metals examined. Furthermore, neither the addition of H₂O₂ in the digestion acid mix, or ultrasonication as post-digestion treatment, improved the recovery of the metals. Thus, single step HNO₃ MWAD proved sufficient (with the exception of Cr) for the solubilisation of heavy metals in waste derived fly ashes.
- For the determination of highly chlorinated benzenes in fly ash, three different extraction methods have been compared. The results suggest that matrix digestion followed by Soxhlet extraction and multilayer silica gel column filtration, produce precise results with better signal to noise chromatograms than ASE and ultrasonication.
- The detection limits and the consistency of the readings of ECD against MS-SIM have been investigated for the quantification of chlorobenzenes. The results demonstrated that ECD can provide less noise, and thus better peak integration than MS-SIM for the detection of penta- and hexa-chlorobenzene in fly ash extracts. The use of ECD minimises the need for extensive sample clean up, and subsequent solvent use, or ¹³C₁₂ labelled standards. When mass resolution is needed, further sample purification and/or high efficiency instrumentation (HRGC/HRMS) is essential for the quantification of penta and hexa- chlorobenzenes in relevant matrices.

Regarding the combustion experiments:

- A Cl mass balance has been calculated for the process with losses that ranged $< 7\%$. From the original Cl in the SRF feedstock, 18.3% was found at the bed area, 28.7% in the horizontal chamber (coarse fly ash), 17.2% in the cyclone (fine fly ash) and 29% volatilised as HCl.
- Comparison of the residues with other literature values indicate that, these SRF derived fly ashes have significantly lower values in Cu, Cd, Pb, Zn, leachable Cl and organochloride load than other traditional thermal treatment applications. This fact highlights the importance of modern separation technologies employed in MBT plants for the removal of components rich in metals and chlorine from the combustible output fraction of SRF.

Regarding the gasification experiments:

- A pneumatic feeding system was developed to facilitate the feeding of the SRF in the gasifier, under steady state conditions. It successfully managed to achieve its goal, where other feeding systems proved problematic, due to SRF bridging problems.
- A Cl mass balance has been calculated for the process with losses that ranged $< 13\%$. The majority (84%) of the Cl in the input (SRF) is found in the solid residues in the output. Moreover, the HCl emitted was only 5% of the original Cl input.
- The gasification ash/tars/chars are relatively rich in heavy metals when compared with literature values for combustion derived fly ash. While Pb, and Zn are in the lower reported ranges, Cu, Ni, and Cr range at the same, or higher levels than conventional incineration derived fly ash.

- The XRD analysis identified crystalline structures in the gasification residues which are quite common in ash residues, such as quartz and calcite. The presence of potassium perchlorate however, might be an indication of insufficient particles residence time within the high temperature zones of the gasifier. The above conclusion though, can only be partially true, as the gasification residues presented a typical cracked- microporous structure (SEM analysis) and a carbon conversion of ca. 97%. XRD analysis though, can be debatable regarding its sensitivity and further analysis is required.

Regarding the comparison of the two thermal treatment processes:

- o When comparing the two processes in terms of mass transformation, combustion reduced the incoming SRF to 91.5%, while gasification to 87%. The volume reduction for the two processes was 98.6%, and 98.8%, respectively. Furthermore, gaseous inorganic chlorine, expressed as HCl was only 5% of the Cl input during gasification, against 28% in the combustion. This indicates that the amount of volatilized Cl is much lower than the one obtained in the combustion experiments. Thus, gasification can potentially be a safer process than combustion in terms of gaseous organochlorides and corrosive species generation. However, replicate trials are required for the confirmation of the abovementioned results.

Regarding the comparison of the two residues types:

- It is concluded that the gasification residues have a greater content of partially reacted chlorine and salts with lower water solubility, than the

combustion ones. It is therefore evident that the gasification residues have a much smaller potential to leach Cl, than the combustion ones, when landfilled.

- Gasification retained higher amounts of Cu, Cr, and Cd in the solid residues when compared to combustion.
- Gasification residues have 3-8 times higher concentrations in organochlorides expressed as penta- and hexa-chlorobenzenes.
- The leaching tests indicated that there is no direct relationship between the amounts of metals that leach from thermal treatment residues and their actual metals content. Although, this conclusion was recently reported for combustion related residues it is confirmed in this study for gasification residues as well.

6.3 Further work

The limitations of this work are considered as incentives for further research and experimental testing. In this context the following subjects are proposed:

- Replicate trials for the confirmation of the Cl mass balances for the two processes. These trials could vary in terms of temperatures. The gasification experiments for example, could be attempted at higher temperatures (e.g. 800 °C) than the ones achieved here (700 °C). This could eliminate the phenomenon of non-reacted high boiling point Cl species.
- Testing of alternative gasifier designs for SRF. The abovementioned conclusions can be tested in rigs more suitable for SRF, such as downdraft reactors. This can give an insight on the effect of the

particles' residence time on the Cl and metals behaviour. Furthermore, computational fluid dynamics (CFD) modelling can be used for the prediction and fine-tuning of the particles' residence time in the reactors.

- Quantification of syngas species and gaseous chlorobenzenes for SRF gasification. This work did not produce quantifiable data on the syngas composition and the amount of airborne organochlorides. Although the quantification of these species was in the original scope of the work, it was not achieved during our experiments. Further experimentation with alternative rigs or rig set-ups, and improved gas sampling/analysis systems could eliminate this problem.
- Experimentation with SRF pellets. The major limitations of this work were related with the feeding of the SRF in a fluff form. The production of pellets with this feedstock could eliminate relevant problems and allow further investigations (e.g. the confirmation of the Cl mass balances).

6.4 Novelties

This work embraces a few novelties which are mostly related with the type of feedstock that was tested in the thermal rigs. The tested SRF is a novel material from a new UK MBT plant, commissioned in 2007 (Gascoyne, 2008).

Although other similar plants exist in Italy that use the same MBT technology (Juniper CS Ltd., 2005), the quality of the SRF is mostly defined by the waste input. In this context, the consumers' patterns define the quality of the produced MSW, which are unique for every geographic area examined. Thus, this work uses a novel

fuel; East London's SRF. Furthermore, this particular SRF hasn't been used in FBC and FBG before. Indicative of that, is that so far the SRF was either landfilled, or used in cement kilns. Subsequently, the generation of raw data on the characterisation of residues from the utilisation of a novel fuel in the two thermal treatment processes is the major novelty of this work.

The comparative approach, in terms of residues characterisation is another novelty of this work. Although the comparison of waste combustion and gasification is a common subject in literature, discussion is usually limited to the benefits of gasification in energy recovery terms. However, there is virtually no reference for the comparison of the solid residues of the two processes, from exactly the same waste feedstock.

The scale, the fuel type, and the steady state conditions of the gasification experiment is another novelty. Recent data from high impact sources (Skoulou et al., 2009) support this claim. In this, and similar references, batch reactors are used even for 'easy handling' fuels, such as granular feedstock. Furthermore the test sample doesn't exceed a few grams, or is an artificial waste fuel. However, most of the gasification reactions are reversible (chapter 2), and these experimental conditions can only partially describe the process. On top of that some phenomena, e.g. the catalytic effect of metals in the formation of organochlorides, can not be fully examined using small test samples or artificial fuels.

The abovementioned novelties are characterised from the 'in vivo' experimental conditions that this work embraces. These conditions favoured the production of quantitative, and qualitative improved, waste derived thermal treatment residues. This approach can be described in Figure 6.1, which illustrates the positioning of this work in regard to the majority of equivalent studies in literature.

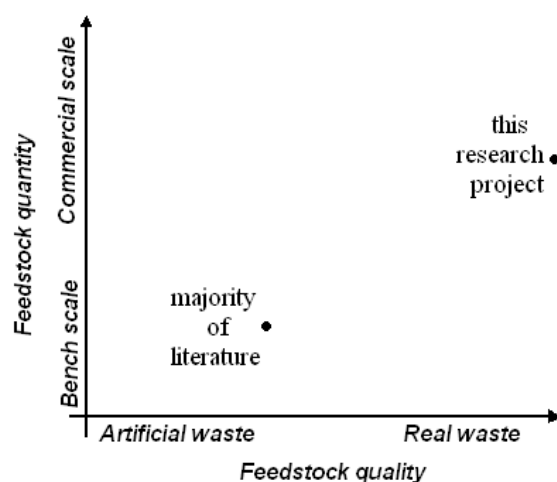


Figure 6.1 Positioning of this work in comparison to literature

One last novelty, regarding the methods used, should be noted. The comparison of the available in literature extraction- clean up methods, and the chromatographic detectors for the quantification of chlorobenzenes in fly ashes, is novel. Although different combinations can be found in literature (Table 3-4), the extraction efficiencies, precision and accuracy of the examined methods/instrumentation is reported here for the first time.

6.5 Synopsis

This chapter summarised the conclusions of this work. The conclusions regarding the comparison of processes lack confirmation from replicate trials, however sound conclusions can be made on the differences of the two types of waste thermal treatment residues. The limitations of this work can give the incentives for further research. Extended experimentation should be the scope of further work, focussing on alternative rigs/ rig set-ups and CFD modelling for gasification. In conclusion, the novelty of this project is highlighted from the use of a novel material as feedstock and

the production and characterisation of quantitative, and qualitative improved, waste derived thermal treatment residues

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APPENDICES

1. *Residues characterisation from the fluidised bed combustion of East London's NCV 3, Cl 2, and Hg 1 class solid recovered fuel-* **Paper submitted to 'Waste Management Journal'**
2. *Comparison of analytical methods for sample preparation and detection of chlorobenzenes in fly ash-* **Paper submitted to 'Journal of Hazardous Materials'**
3. *Transfer coefficients and organochloride load of a 'Class 2' solid recovered fuel in fluidised bed combustion-* **Paper presented to Venice 2008 –Second International symposium on energy from biomass and waste- CISA**
4. *Demonstration Of Experience Gained From The Gasification Of East London's Solid Recovered Fuel In A Spout Bed Reactor-* **Paper presented in the 3rd international conference on Solid Waste Management- Hellenic Solid Waste Association**

**Residues characterisation from the fluidised bed combustion of East London's
NCV 3, Cl 2, and Hg 1 class solid recovered fuel**

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Abstract

Waste thermal treatment in Europe is moving towards the utilisation of the combustible output of mechanical, biological treatment (MBT) plants. The standardisation of solid recovered fuels (SRF) is expected to support this trend and increase the amount of the generated combustion residues. In this work, the residues and especially the fly ashes from the fluidised bed combustion (FBC) of East London's NCV 3, Cl 2, and Hg 1 class SRF, are characterised. The following toxicity indicators have been studied: leachable chlorine, organochlorides expressed as pentachlorobenzene and hexachlorobenzene, and the heavy metals Cu, Cr, Cd, Zn, Ni, and Pb. Furthermore the mineralogical pattern of the ashes has been studied by means of XRD and SEM- EDS. The results suggest that these SRF derived ashes have significantly lower quantities of Cu, Cd, Pb, Zn, leachable Cl and organochlorides when compared to other literature values from traditional waste thermal treatment applications. This fact highlights the importance of modern separation technologies employed in MBT plants for the removal of components rich in metals and chlorine from the combustible output fraction of SRF resulting to less hazardous residues.

Keywords: Refuse derived fuels, thermal treatment, air pollution control residues, trace metals, chlorine leaching

1. Introduction

Thermal treatment has been recognized as a valuable technique for the recovery of the energy content of wastes within the waste management hierarchy. Recent data (Defra, 2009) indicate that countries like Denmark, Netherlands, Belgium, Sweden, Luxemburg, Germany, France and Portugal, incinerate more than 20% of their generated municipal solid waste. In addition, or in replacement, of traditional mass grate thermal treatment, the use of the combustible output fractions of MBT plants could further support a sustainable short/middle- term approach for the management of the increasing volumes of wastes, especially in dense metropolitan areas (Caputo and Pelagagge, 2002). This integrated waste treatment approach has increased its presence in Europe, with MBT plants that reach a capacity of 2 million tons per annum (Velis et al., 2009).

Despite these facts, public opinion is some times against developments regarding integrated thermal treatment applications, even in developed countries (Luria, 2008). These oppositions mainly focus on direct health effects from emissions and residues of these technologies based on past experience. Issues related to chlorine and heavy metals content of waste derived fuels have resulted to limited demand of the latter during the past decade (Rotter et al., 2004).

In this context, the standardization of SRF (CEN/ TS 15359, 2006) in terms of calorific value, trace metals and chlorine content, intends to facilitate the economic, emissions, and technological issues associated with the acceptance and marketability of waste derived fuels and related applications. According to the abovementioned standard, SRF is distinguished from the classical term of refuse derived fuel (RDF), as the initial characterization criterion is a non-hazardous waste source and the final criterion is a quality assured (QA) classification according to the following properties:

- The mean net calorific value
- The mean value of chlorine content
- The mean and 80th percentile values for mercury content

Each property is divided in five classes with range values and the combination of the property classes makes up the class code for each SRF.

SRF standardization protocols can support the development and expansion of waste- fuel markets (Bernd et al., 2007). This expansion is expected to increase the quantities of the generated combustion and air pollution control (APC) residues. In the UK this amount is expected to reach 162,000 tones per annum in 2010, from about 83,000 tones in 2000 (Amutha Rani et al., 2008). Fly ash in particular, is an issue of concern as it is enriched with heavy metals, soluble salts and organic micro-pollutants (Huang et al., 2003; He et al., 2004; Hyks et al., 2009), that could be released in the environment from its utilization or landfilling. Thus, knowledge of the characteristics of these residues is of extreme importance for their treatment within good integrated waste management practices.

This work characterizes the fly ashes produced from the combustion of East London's SRF in a fluidized bed reactor. The following toxicity indicators have been studied: TOC, leachable chlorides, organochlorides expressed as pentachlorobenzene (Cl₅Bz) and hexachlorobenzene (Cl₆Bz), and the heavy metals Cu, Cr, Cd, Zn, Ni, and Pb. Finally, XRD and SEM- EDS techniques are utilized for the mineralogical characterization of the produced fly ashes. These commonly applied indicators have been employed to facilitate comparisons with other reported values in literature. The aim of this study is to assess whether the pollutants load of SRF derived fly ashes is lower than the equivalent values reported in literature, from conventional waste fuels, and/ or traditional waste thermal treatment applications.

2. Materials and methods

2.1. Feedstock properties

SRF derived from East London's Waste Authority, processed by a private contractor was the feedstock for the trial. The fuel is produced in a sequential separation, shredding, and aerobically bio-drying MBT process, classified as a "NCV 3; Cl 2; Hg 1" class SRF. A batch of 100kg was sampled from the MBT plant and it was later sub-sampled as a static pile, according to the relevant standard (CEN/TS 15442, 2006) for the detailed investigation of proximate characteristics and chlorine content. The remaining data on ultimate analysis (Table 1) were provided by the SRF producer based on routine QA/QC analysis.

<<Table 1>>

2.2. Fluidized bed combustion rig operating conditions

The 50 kW_{th} fluidized bed combustor that was used for the trial consisted of a screw feeding hopper, the main bed chamber (dimensions 175x 30x 30 cm), a secondary combustion chamber that leads to a vertical ash deposition compartment, a water heat exchanger, a cyclone, and an exhaust fan prior to the stack. The bed area was filled with 30.2 kg of silica sand with particle size between 1.00 – 0.5 mm (16/30 grade, density 1,556 g l⁻¹), resulting to bed static dimensions of 30*30*15.35 cm. The FBC was vacuum cleaned the day before the experiment for the removal of residual ash and particles from previous trials. Furthermore, it was operated overnight, burning natural gas for decontamination and start-up purposes. The rig was monitored by 19 K-type thermocouples, CO, CO₂, and O₂ online gas monitoring systems. The SRF incoming flow slightly varied throughout the trial with a mean value of 117g min⁻¹ and a lambda coefficient equal to 1.6. The duration of the test was 300 minutes and the bed temperature was at 800 ± 20 °C. The rig and the ashes sampling points are illustrated in Figure 1. Detailed information on the experimental conditions are reported in previous work (Balampanis et al., 2008).

<<Figure 1>>

2.3. Analysis

2.3.1. Total, water soluble chlorine & chlorobenzenes

After the experiment, the rig was disassembled and the mixed silica sand/ bed ash were collected, weighted, and emptied to a tank with deionised water. The tank was mechanically agitated for 3 hours and 6 replicate samples were taken, centrifuged and filtrated. The

horizontal chamber and cyclone ash were vacuum- cleaned and collected separately in clean pre- weighted vacuum bags; due to the visual difference (Figure 5) in particle dimensions, these ashes will be referred herein and after, as coarse fly ash and fine fly ash, respectively, according to the literature definitions (IAWG, 1997; Quina et al., 2008a). Three replicates of each fly ash type were examined for total chlorine using the oxygen bomb method. Six replicates of a gram each, of coarse and fine fly ash were diluted in 250 ml of DI water and agitated for three hours. The mix was centrifuged and decanted and the filtrate was stored in polypropylene bottles, at 4 °C for chloride anions analysis (Dionex, UK- Ion Chromatographer, column: Ion Pac As9- HC 4*250 mm).

For the determination of Cl₅Bz and Cl₆Bz the following procedure was employed. Seven replicates of each ash type were spiked with extraction standards (800ng ml⁻¹ 1,3,5-tribromobenzene in toluene) and then digested with 100ml of 2M HCl. The mix was separated using vacuum filtration, and the cakes were washed with deionised water to reduce acidity, air-dried for 12h, and then extracted with Soxhlet using 200ml of toluene for 20h. The aqueous solutions were extracted three times with 100ml of dichloromethane per litre of solution, and the solvent extracts were washed twice with deionised water for pH adjustment (50% v/v). The two extracts from each sample were mixed, concentrated using a rotary evaporator (38 °C, 68 mbar), filtered through a multilayer silica gel column (anhydrous Na₂SO₄, 10% AgNO₃ silica gel, 20% H₂SO₄ silica gel, 40% H₂SO₄ silica gel, 30% KOH silica gel) and eluted with hexane, double the height of the column. The column's elutes were further evaporated (35 °C, 200 mbar) and finally concentrated to 1ml using a nitrogen flow concentrator. The samples were spiked again with recovery standards (100 µl of 1.6µg ml⁻¹ of 1,2 dichlorobenzene-d₄) and analysed through GC-MS-SIM (Instrument: Perkin Elmer-Autosystem XL/Turbo Mass Gold; Column: Thames-Restek Rtx ®- 1MS- 100% dimethyl polysiloxane column (length 15m, internal diameter 0.25 mm, film thickness 0.25 µm); Injection: 1 µl at a split ratio of 100:1; Ionisation mode: positive 70 eV; Oven temperature conditions: initial 50 °C, rising 30 °C min⁻¹ up to 125 °C, and then 15 °C min⁻¹ up to 300 °C where it was held for 6 min).

3.3.2. Heavy metals

Standard methods (ASTM, 2004) for the determination of heavy metals in combustion residues, involve the utilisation of hydrofluoric acid (HF). These methods were excluded from this work due to HF's adverse effects on instrumentation, and for health and safety reasons. Furthermore, the total content of heavy metals is not directly related to the leaching potential of fly ash, when landfilled (Hyks et al., 2009). Thus, four HF free digestion methods were tested for their recoveries, using a certified reference material (CRM). The CRM was MSW

incineration fly ash (BCR- 176R, Joint Research Centre, Institute for Reference Materials and Measurements, EC) and a summary of the digestion methods is presented in Table 2.

<<Table 2>>

An Anton Parr Multiwave 3000 microwave oven unit was utilised for the microwave assisted digestion (MWAD) methods (A, B, and C), and compared against standard reflux with aqua regia (method D) (BSI, 1995). For method A, seven replicates of 400 ± 1 mg CRM and a method blank were placed in the PTFE pressure vessels with 8 ml of concentrated (15.8 M) nitric acid. The vessels were left 16 hours in a fume cupboard to equilibrate, to avoid elevated pressures inside the vessels at the MWAD stage. The following MWAD programme was applied: 20 minutes for the instrument to reach 18 bar and 190°C , where held for 20 minutes and finally another 20 minutes for the vessels to cool down. The mixture was then filtered using $0.45\mu\text{m}$ Whatman cellulose filter papers and diluted with ultra pure (MiliPore) water, to a fixed volume of 100 ml.

Method B was performed exactly as method A, but with a different acid mix: 5 ml of nitric acid and another 3ml of hydrogen peroxide (100 volumes). Method C was performed exactly as method A, with the difference that ultrasonic waves were applied through a 600W probe (Langford Ultrasonics- Sonomatic), to test whether ultrasonication could enhance the digestion reactions.

Method D was tested on 7 CRM replicates of $3 \pm 0.001\text{g}$ each, and a method blank. Twenty one ml of concentrated hydrochloric acid (12 M) were added in 250ml reaction flasks, followed by 7 ml of nitric acid. The mix was allowed to oxidise at room temperature for 16h, and then heated to reflux conditions for 2h. After cooling down, it was filtered ($0.45\mu\text{m}$ Whatman cellulose filter papers) and made up to 100 ml using ultra pure water. All chemicals were trace analysis grade and purchased from Fischer Scientific UK. The quantification was achieved through a graphite furnace/ flame- atomic absorption spectrometer (GF/F-AAS) A-Analyst 800 Perkin Elmer instrument, equipped with an air/ acetylene flame and an AS-90 autosampler.

3.3.3. XRD, TOC & SEM- EDS analysis

The coarse and fine fly ashes were also analysed for their total C,H,N, and TOC content using an elemental analyser (Vario EL III), and further examined in a SEM- EDS microscope (Philips XL 30) for their major elements determination. The mean concentration of elements (% wt> 1) in the SEM- EDS analysis was obtained from a spectrum over a 4 mm^2 and 0.16 mm^2 area for coarse and fine fly ash, respectively; Furthermore, the reported deviations represents 4 different scans in smaller areas, on each one of the quadrants of the originally

scanned areas. Finally, XRD (Siemens ED 5005) analysis was employed for the determination of the ashes' crystalline phases.

4. Results and discussion

4.1. Inorganic chlorine and chlorobenzenes

Figure 2 demonstrates the amount of water soluble chlorides that leached from each ash type. As expected the bed ash contained the lowest levels of Cl as most of it was volatilised in the process to form HCl, Cl₂, or Cl radicals. The bed ash contained an amount of non-combustibles that was visible in the bed material. These residues were mostly glass fractions, ceramics, metals, stones etc., thus a rather abnormal and heterogeneous distribution of chlorides in these particles should be expected. Although the determination of chloride ions was made with a much greater L/S ratio than characterisation protocols suggest (BSI, 2002), the bed ash, based on the leached Cl⁻, would be accepted for co-disposal in a non hazardous landfill (Cl⁻ < 15,000 mg kg⁻¹), according to the existing legislation (EC, 2002) for granular waste. According to the same legislation the coarse fly ash would be accepted in a hazardous waste landfill without further treatment (Cl⁻ < 25000 mg kg⁻¹), while fine fly ash would require further stabilisation before final disposal.

The higher chlorinated benzenes (Cl₅Bz, and Cl₆Bz) were quantified as indicators for the organochloride load of the fly ashes, due to their reported correlations with I-TEQ values (Öberg et al., 2008). The Cl₅Bz values ranged between 9± 3.9 ng g⁻¹ for coarse, and 15± 2.8 ng g⁻¹ for fine fly ash while the equivalent Cl₆Bz values ranged between 3.3± 2.8 ng g⁻¹, and 8± 2 ng g⁻¹, respectively. These figures correspond to the lower range of reported values on organochlorides within the literature as it will be discussed at a later stage (section 4.4).

<<Figure 2>>

4.2. Heavy Metals

The four HF-free fly ash digestion methods were compared for their recoveries of the CRM and the results are reported in Figure 3. The overall recoveries ranged between 59% and 94%, except from Cr which ranged at lower levels ca. 19- 38%. A one way ANOVA at a confidence interval of 95%, confirmed that there was no single method that significantly recovered higher amounts for the whole range of the examined metals. However, some exceptions were found in method B, which recovered significantly higher quantities of Pb, and in the aqua regia method (D) which recovered significantly lower amounts of Cu and Cd. Furthermore, neither the addition of H₂O₂ in the digestion vessels, or ultrasonication as post-digestion treatment, improved the recovery of the metals. Thus, single step HNO₃ MWAD

proved sufficient for the solubilisation of heavy metals in waste derived fly ashes, as reported in older studies (Mester et al., 1999; Quina et al., 2008b).

<<Figure 3>>

The fly ashes were further analysed for their content in Cu, Cr, Ni, Pb, Cd, and Zn using method A and the results are presented in Figure 4. Coarse fly ash contained higher Cu, Pb and Zn quantities than the fine fly ash fraction, which had higher Cr and Ni contents. The Cd values were relatively low ranging at $3.6 \pm 0.6 \text{ mg kg}^{-1}$ and $7.3 \pm 0.2 \text{ mg kg}^{-1}$ for fine and coarse fly ash, respectively. Finally, it should be noted that the actual concentration of Cr in both ash types could be higher than the ones presented in Figure 4, as the HF free digestion method used gives a relative poor recovery of the element according to the CRM recovery values.

<<Figure 4>>

4.3. Minerals and carbon

The rough (%wt >1) composition of the elements in the ashes, as recognised in SEM-EDS analysis is presented in Table 3. Calcium, silica, aluminium, chlorine, sodium, potassium, iron, sulphur, and phosphorus were the most common elements, besides carbon, which ranged at $8.6 \pm 0.1 \%$ and $9.6 \pm 0.2 \%$ for the coarse and fine fly ash, respectively. This slight difference in the total carbon content is probably due to the greater residence time of the bigger and heavier coarse particles (Figure 5 a & b) in the combustion zone, resulting to higher C to CO₂ conversion. This finding is confirmed by the TOC levels that ranged at $6 \pm 0.4\%$ and $6.8 \pm 0.1\%$ for coarse and fine fly ash particles. In respect to the SEM-EDS sensitivity, another conclusion is that fine fly ash had about double the amount of chlorine than the coarse one. This finding is confirmed by the amount of water soluble chlorides that leached from each ash type (section 4.1).

The mineralogical analysis recognised the main crystal phases of the ashes by means of XRD and the diffractograms are presented in Figure 6. These were similar for both ash types: Calcite (CaCO₃), quartz (SiO₂), halite (NaCl), sylvite (KCl), and calcium sulphate (CaSO₄); except from calcium silicate (CaSiO₄), which was only detected in fine ash particles. The XRD pattern is similar to most MSWI fly ashes as reported in other works (Wan et al., 2006; Quina et al., 2008b; Wang et al., 2008; Shi and Kan, 2009) with the exception of calcium silicate. This finding is of particular importance as layers of CaSiO₄ can interfere as heat transfer barriers in flame retardant applications (Hamdani et al., 2009), however its presence was not confirmed at the heat-exchange tower (coarse fly ash sampling point), but only at the cyclone (fine fly ash collection point).

<<Table 3>>

<<Figure 5>>

<<Figure 6>>

4.4. Comparison of SRF fly ash with literature values

Comparisons against literature values are often limited by the heterogeneity of available data, due to the complexity of the ash products, and the high number of available methods for residues characterisation, leaching protocols etc. Table 4 presents the toxicity indicators determined in this work, against equivalent values from MSWI derived fly ashes in literature. The selection of the literature data was based on the quality of the reported results, and the methods used to obtain them.

The results indicate lower levels of some pollutants in SRF- derived fly ashes compared to the reported values in literature. The chlorobenzenes in the examined samples range at an order of magnitude lower than other reported figures. The same result is obtained when comparing the heavy metals content of the SFR fly ashes with the equivalent metals load from other works; The levels of, Cd, Cu, Pb and Zn were significantly lower than other reported values. Furthermore, the leached chlorides levels lay on the lowest reported ranges within literature. However, no particular difference was observed for Cr and Ni and TOC, which ranged at the same levels as other researchers report.

The reported values in literature might involve data from thermal treatment technologies different than FBC, e.g. mass grate incineration, and can enhance the heterogeneity of data. As reported in other works (Lind et al., 2007) when comparing grate firing and FBC, there were differences in the levels of As and Sb in the generated fly ashes. However, the low Cl, Cd, Cu, Pb, Zn, Cl₅Bz, and Cl₆Bz presented in Table 4 clearly reflect the low chlorine and metals content of the particular fuel. This fact indicates the importance of modern separation technologies that are used in MBT plants for the removal of components rich in metals and chlorine like electronic waste and hard plastics, respectively, resulting to the removal of heavily polluted components from the combustible output fractions (Rotter et al., 2004).

<<Table 4>>

5. CONCLUSIONS

The coarse and fine fly ashes produced from the fluidised bed combustion of a NCV 3, Cl 2, and Hg 1 class SRF have been characterised using commonly tested toxicity indicators like TOC, Cd, Pb, Zn, Ni, Cr, Cu, Cl_{5,6}Bz, and water soluble Cl. Our findings indicate that SRF

derived fly ashes have a similar mineralogical pattern with other waste- derived fly ashes, with the exception of calcium silicate, which was only detected in the fine particles.

The results, when compared with other literature values indicate that, these SRF derived fly ashes have significantly lower values in Cu, Cd, Pb, Zn, leachable Cl and organochloride load than other traditional thermal treatment applications. This fact highlights the importance of modern separation technologies employed in MBT plants for the removal of components rich in metals and chlorine from the combustible output fraction of SRF.

ACKNOWLEDGEMENTS

The authors acknowledge the financial support of ENTRUST, Shanks Group plc and Grantscape Ltd. for the completion of this project. Preliminary results of this work were presented in Venice- 2008, Second International Symposium on Energy from Waste.

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Table 1

SRF properties

Proximate analysis (%wt ar)

Moisture content	13.2 ± 1.5
Ash content	13.7 ± 2

Ultimate analysis (%wt dm)

C	47.4 ± 4.2
H	5.7 ± 2.9
N	0.8 ± 0.3
S	0.1 ± 0.02
Cl	0.4 ± 0.02
O	45.1^*

* By difference

Table 2
Summary of digestion methods

Method	Reagents	Digestion conditions
A	8 ml HNO ₃	MWAD 190°C, 18 bar
B	3 ml H ₂ O ₂ + 5 ml HNO ₃	MWAD 190°C, 18 bar
C	8 ml HNO ₃	MWAD 190°C, 18 bar + ultrasonication
D	21ml HCl+ 7 ml HNO ₃	Equilibration 16 hr, reflux 2 hr

Table 3

SEM-EDS results on elemental composition %wt> 1(x: mean, s: standard deviation)

Composition (wt%)	Coarse fly ash		Fine fly ash	
	x	s	x	s
Na	1.3	0.7	1.7	0.3
Al	1.7	0.5	2.5	0.3
Si	5	2.7	5.5	2.8
P	1.3	0.8	1	0.2
S	1.2	0.6	1.4	0.2
Cl	2.2	0.7	5.5	0.7
K	1.4	0.5	2.3	0.4
Ca	11	1.2	9	0.7
Fe	1.3	0.5	1.6	0.3

Table 4

Comparison of East London's SRF fly ash indicative toxicity indicators with literature values

	This study	MSWI fly ash UK ^a	MSWI fly ash Sweden ^b	MSWI fly ash other ^c	MSWI fly ash other ^d
Cl [*] mg g ⁻¹	15-45	140-170	6-81	45-380	nd
TOC mg g ⁻¹	56- 69	10- 250	Nd	4.9- 17	1.6- 400
Cd mg g ⁻¹	0.003- 0.007	0.1- 0.15	0.0035- 0.31	0.016- 1.6	0.2
Pb mg g ⁻¹	0.76- 1.22	2.5- 3.5	0.73- 36	0.25- 27	0.88
Zn mg g ⁻¹	0.8- 1.23	4- 8.5	4.9- 44	4.3- 104	21.3
Cu mg g ⁻¹	0.36- 0.47	0.35- 0.6	0.22- 1.8	0.016- 2.22	1.74
Cr mg g ⁻¹	0.41- 1.07	0.012- 0.2	0.2- 1.6	0.072-0.57	0.121
Ni mg g ⁻¹	0.18- 0.42	0.015- 0.035	0.036-0.11	0.02-0.71	nd
Cl ₅ Bz ng g ⁻¹	5.1- 17.8	nd	43- 610	nd	189- 355
Cl ₆ Bz ng g ⁻¹	0.5- 10	nd	47- 260	nd	113- 249

nd- not determined

^{*} Water soluble or total^a Aqua regia total metals (Amutha Rani et al., 2008)^b Total content (Öberg et al., 2007)^c Total (Quina et al., 2008a)^d Total (Huang et al., 2003)

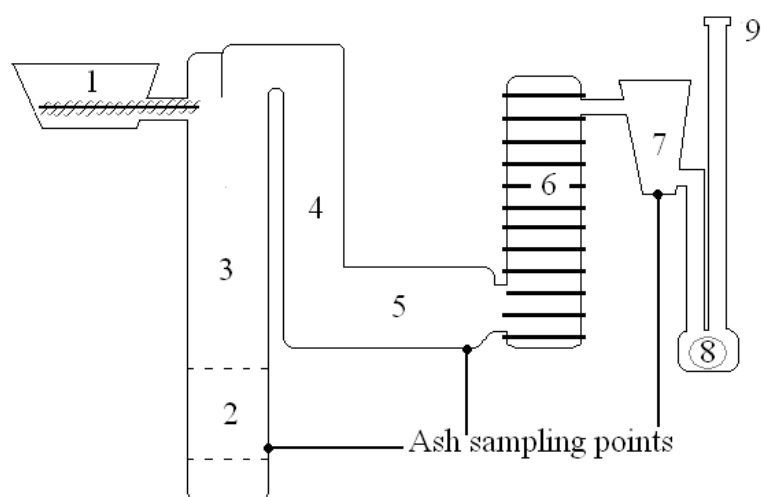


Figure 1. Fluidized Bed Combustor- 1: screw feeding hopper, 2: bed area, 3: FB chamber, 4: vertical secondary combustion chamber, 5: horizontal chamber- ash deposits area, 6: heat exchange tower, 7: cyclone, 8: exhaust fan, 9: stack

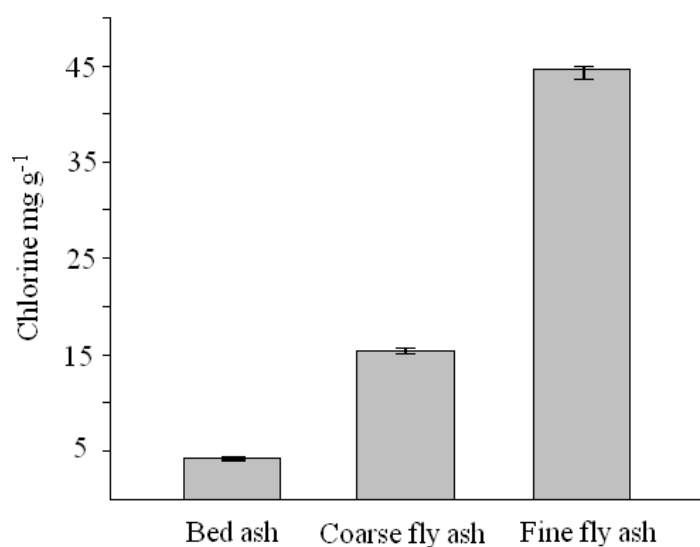


Figure 2: Water soluble chlorine content per ash type

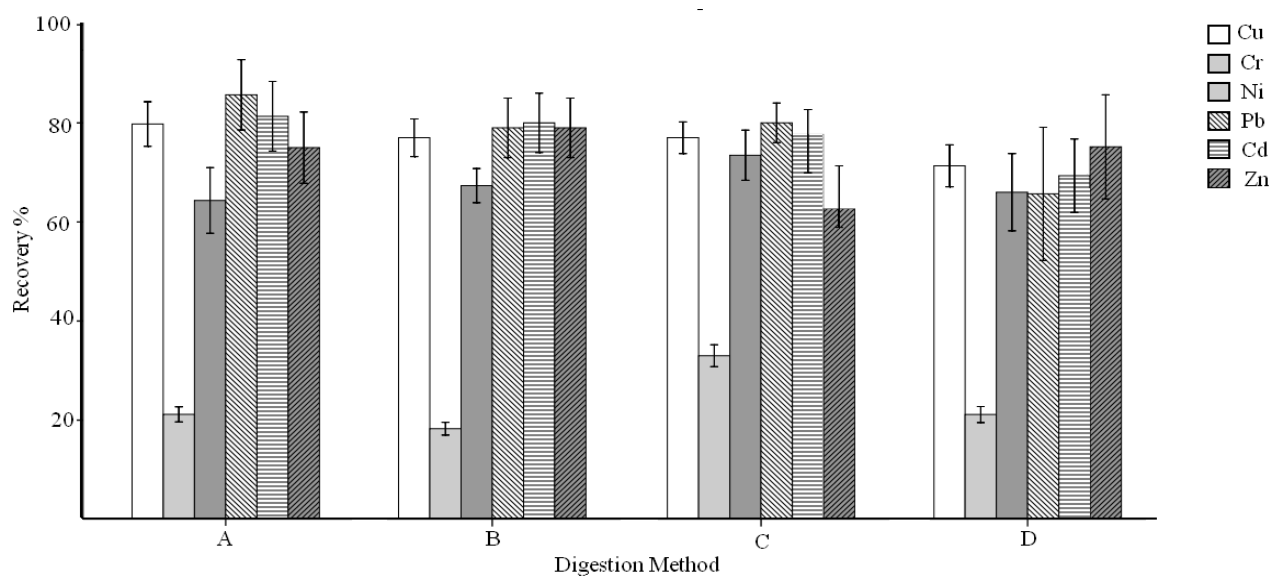


Figure 3: Recoveries of metals from CRM between different MWAD methods (error bars indicate minimum and maximum values, n=7)

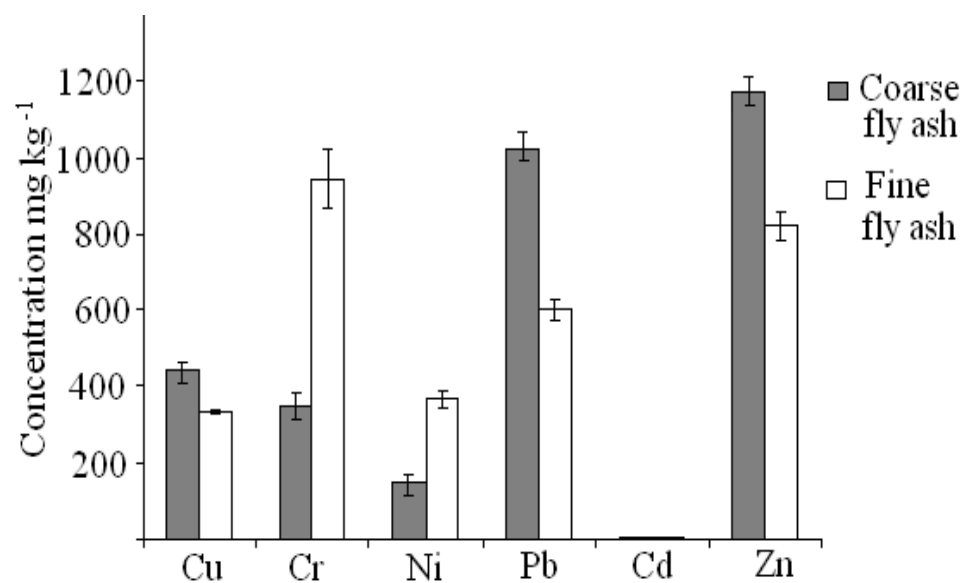


Figure 4: Concentration of metals in SRF coarse and fine fly ash (error bars indicate minimum and maximum values, n=7)

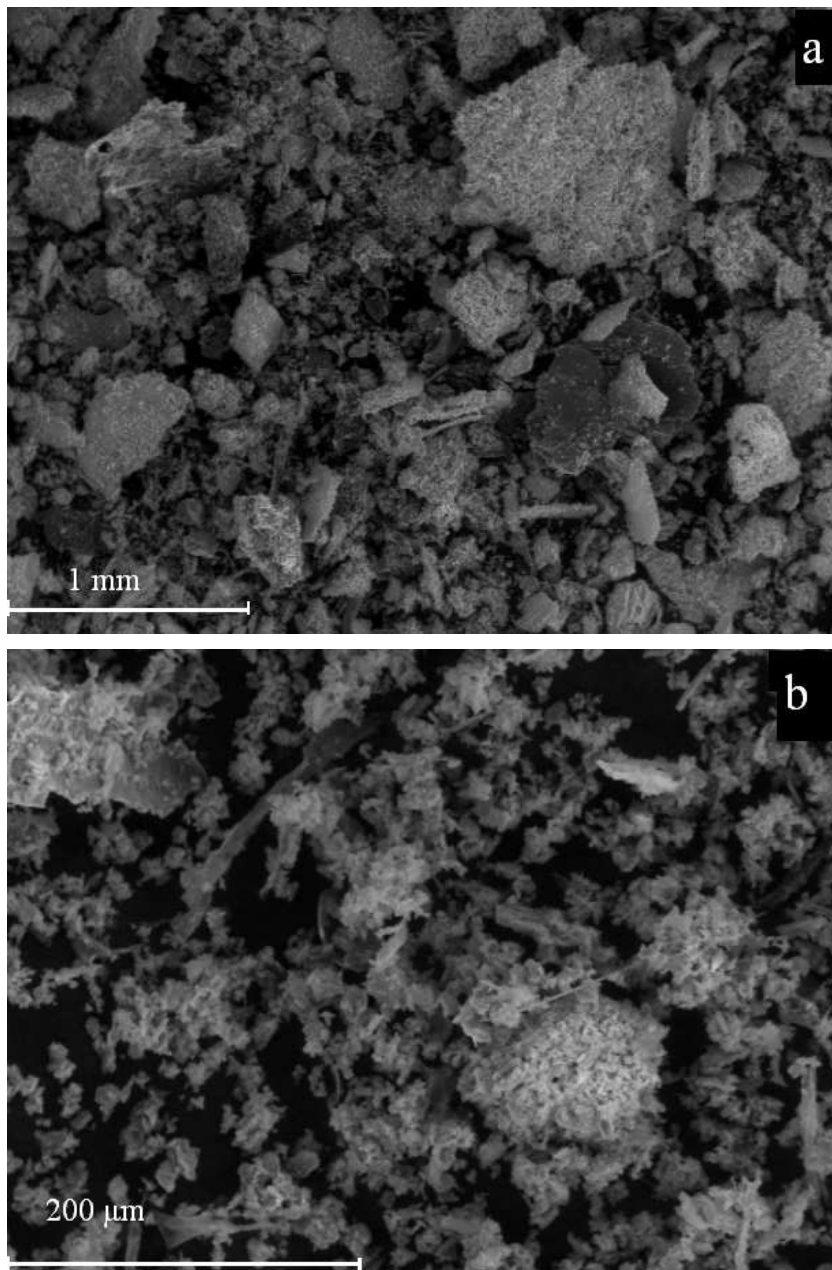


Figure 5. SEM pictures. (a) coarse, (b) fine fly ash

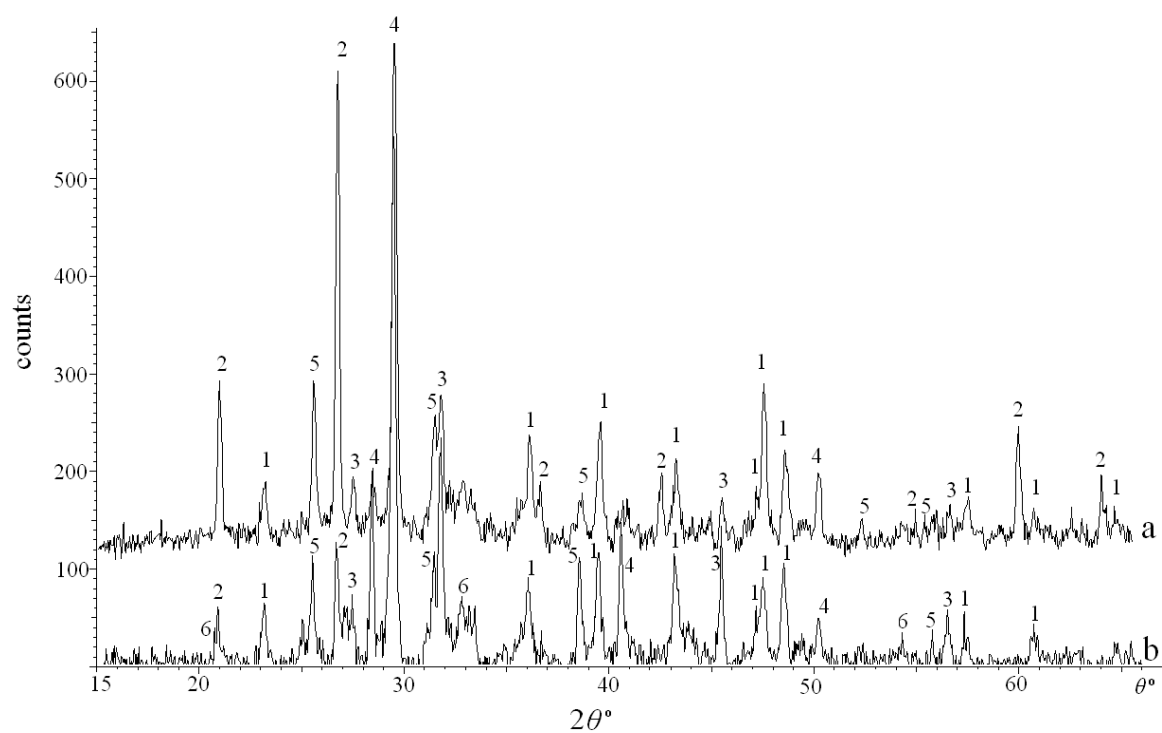


Figure 6. X-ray diffractograms (a) coarse, (b) fine fly ash. Crystal phases recognised: 1. Calcite; 2. Quartz; 3. Halite; 4. Sylvite; 5. Calcium sulphate; 6. Calcium silicate

Comparison of analytical methods for sample preparation and detection of chlorobenzenes in fly ash

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Abstract

Highly chlorinated benzenes, produced in the presence of organic matter and chlorine, are considered PCDD/Fs precursors, and are used as cost and time convenient substitute indicators for the indirect measurement of the latter. In this study penta- and hexa- chlorobenzene are quantified for the determination of the organochloride load

of fly ash from solid recovered fuel incineration. Two time efficient extraction methods involving accelerated solvent extraction (ASE) and ultrasonication, along with the equivalent clean-up methods suggested by the literature were compared to traditional Soxhlet. The extraction efficiencies achieved were $83 \pm 7.5\%$ for Soxhlet, $111 \pm 19\%$ for ASE, and $67 \pm 17\%$ for ultrasonication. Soxhlet extraction and clean-up through a multilayer silica gel column gave more precise results compared to the other sample preparation methods. Furthermore, performance comparison of gas chromatography- mass spectrometry in single ion monitoring mode (GC-MS-SIM), versus gas chromatography- electron capture detection (GC- ECD) highlighted that ECD can be used for measuring chlorobenzenes traces down to 0.21 ng g^{-1} , when the equivalent LOQ for MS-SIM was 3.26 ng g^{-1} . The results further suggest that ECD can provide better peak integration than MS-SIM in the detection of chlorobenzenes in fly ash extracts, due to the detector's sensitivity to halogenated compounds.

Keywords: Organic halogens, ultrasonic extraction, ASE, ECD, MS-SIM

1. Introduction

Polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs), often referred to as “dioxin like” chemicals are persistent organic pollutants (POPs), which are highly toxic for humans. They are produced during thermal treatment processes in the presence of chlorine and carbonaceous materials (McKay, 2001; Oberg, 2004). Their quantification involves extensive sample preparation and technical skills-intensive analytical measurements. Such a quantification, although standardised (BSI 1948, 2006), can present challenges even for specialised laboratories leading to high variations in the results, as shown from inter-laboratory comparison exercises (Stevens et al., 2001). Furthermore, high costs for instrumentation such as, high resolution gas chromatograph coupled to high resolution mass spectrometer (HRGC/HRMS), and specialised consumables ($^{13}\text{C}_{12}$ isotopes), along with time constraints due to the complexities of the extraction methods and the high number of the 210 isomers, make PCDD/Fs analysis quite demanding.

Research for a time and cost effective substitute method for the indirect monitoring of PCDD/Fs in gaseous emissions, especially in waste incineration processes, started in the 1980s. Statistical correlation patterns between the PCDD/Fs and their major precursors have been investigated, aiming to the estimation of organochloride load in flue gases without the complete quantification of dioxins. The results indicated statistical significant correlations between chlorobenzenes (CBs) and the International/World Health Organisation- toxic equivalent factors (I/WHO- TEQ) values (Oberg and Bergstrom, 1985; Oberg and Bergstrom, 1987; Kaune et al., 1994). Some empirical equations have been proposed for the relationship of CBs and PCDD/Fs, e.g. for pentachlorobenzene (Cl_5B) in flue gases e.g. $[\text{I-TEQ}_{\text{PCDDs/PCDFs}}] = 2.1[\text{Cl}_5\text{B}]$, $r^2 = 0.84$ (Kato and Urano, 2001). Similar correlations have also been derived for the fly ash residues, where the sum of tetra-hexa CBs demonstrated statistically significant correlation with I- TEQ values ($r^2 = 0.767$) (Oberg et al., 2008). Furthermore, CBs are also used as indicators of the organochloride load in fly ash residues in de-chlorination/ detoxification studies (Huang et al., 2003; Lundin and Marklund, 2007), and in studies for the catalytic effect of metals in the formation of chlorinated organics (Öberg et al., 2007; Öberg et al., 2008). It is therefore, established that CBs can provide a good indicator for the determination of the

organochloride load in fly ash when a rapid and cost effective determination is needed, e.g. when there is a high number of experiments/samples.

In this paper, penta- and hexa- chlorobenzene were selected for the evaluation of the organochloride load of fly ash, collected from the cyclone of a fluidised bed combustor, from solid recovered fuel (SRF) incineration. In this context, alternative sample preparation methods to the traditional Soxhlet are compared for their recoveries, precision and easiness of use. Furthermore, the MS-SIM and ECD chromatographic detectors are also compared. ECD has theoretically lower detection limits (5 fg) compared to mass spectrometer in single ion monitoring (SIM)(25fg-100pg) mode (Harris, 2003). Moreover, ECD is extremely sensitive to halogenated compounds and might provide better integration parameters in the generated chromatograms, eliminating the need for extensive sample preparation.

A wide range of methods is described in literature for the extraction and quantification of CBs in solid matrices (Table 1), but no standard method is yet available. Usually a pre-treatment stage like grinding (Dionex, 2005), and/or acid digestion (Huang et al., 2003; Liljelind et al., 2003; Lundin and Marklund, 2007) ensures the homogenisation, and/or the increase of the internal surface of the matrix, and the transfer of the target species to a liquid phase.

For the extraction step, Soxhlet, whether traditional, Dean-Stark modified, or automated, is the most frequently applied technique, and often used as a reference for the efficiencies of other extraction methods. Major disadvantages of Soxhlet extraction include the amount of time needed (18- 48h per sample), the large volume of solvent used (120-400ml per sample)(Sun et al., 2006; Lundin and Marklund, 2007), and the subsequent losses of volatile and semi-volatile species during concentration of extracts, ranging from 5 to 20% for highly chlorinated benzenes, depending on the evaporation method used (Liljelind et al., 2003).

Pressurised fluid extraction (PFE), also described in the literature as accelerated solvent extraction (ASE), utilises elevated temperature and pressure conditions, and thus smaller amounts of solvents (10-50ml per sample) and time (10-40min) (Bautz et al., 1998; EPA, 2000; Dionex, 2005). More recently, ultrasonic extraction has been employed in fly ash samples for the extraction of chlorinated benzenes and recoveries equivalent to Soxhlet have been reported (Korenkova et al., 2006). Furthermore, ultrasonication has the same advantages as ASE in terms of volume of solvents, and time needed for the analysis, compared to traditional Soxhlet. Other techniques have

been employed for the extraction of CBs from fly ash, such as microwave assisted extraction (Sun et al., 2006), however these methods will not be investigated here.

The selection of the clean-up method and the GC detector used, depends on the expected concentrations of the target pollutants and the expected interferences from the matrix. A multilayer silica gel column (anhydrous Na_2SO_4 , 10% AgNO_3 silica gel, 22% H_2SO_4 silica gel, 44% H_2SO_4 silica gel, KOH silica gel)(Sun et al., 2006) has been reported to absorb interferences from fly ash enabling their detection with GC/MS. In Korenkova et al. (2006), chlorobenzenes are extracted by ultrasonication, and the quantification is achieved, simply after paper filtration, and large volume injection (LVI) GC/MS. Therefore, the need for extensive sample clean up, is also related to the available instrumentation. Other combinations of clean-up methods and detection instruments are illustrated in Table 1.

2. Materials and methods

2.1. Origin and preparation of samples

Solid recovered fuel (SRF) is the term used to describe waste derived fuels from non hazardous sources, with standardized information regarding their net calorific value, chlorine and mercury content (CEN/ TS 15359, 2006). The SRF used in this case, was the combustible output of a mechanical- biological treatment (MBT) plant in East London. Details on the waste fuel, and the combustion experimental conditions under which the fly ash was produced, are reported in a previous paper (Balampanis et al., 2008).

The fly ash was collected using vacuum from the cyclone of the 50 kW_{th} fluidised bed combustor. Sample replicates of $10 \pm 0.01\text{g}$ each, were homogenised using a mortar and screened through a 0.5 mm sieve. The samples were spiked with 1ml of 800ng ml^{-1} 1,3,5-tribromobenzene in toluene (extraction standard). Thirty ml of dichloromethane was added, to cover the ash in a conical flask, and shaken mechanically at least for 24 hours, until dry, to allow the incorporation of the standard within the ash matrix. The schematic representation of the following extraction methods is shown in Figure 1.

2.2. Ultrasonic extraction

Seven replicates of spiked fly ash samples, and a blank matrix sample consisting of decontaminated silica sand were placed in 50ml PTFE tubes with 40ml of acetonitrile. The samples were extracted using an ultrasonic bath at 30 °C for 2h, centrifuged (15min, 4000 rpm) and filtered (Whatman-50 filter papers). The extraction was repeated under the same conditions, with fresh solvent, and the two filtrates were mixed and evaporated under a gentle nitrogen flow to 1 ml. Optimum extraction conditions (ultrasonication time, solvent/ matrix ratio, ultrasonication cycles, and filtration method) were the same as reported by Korenkova and co-workers (2006). A lipid phase residue observed in the final concentrate, prevented direct chromatography injection, and a further purification step was employed using 'Waters Sep-Pak light silica' cartridges attached to gas tight syringes, and eluted with 5 ml acetonitrile. Finally the samples were concentrated again with a nitrogen flow down to 1ml, and each was spiked with 100 µl of 1.6µg ml⁻¹ 1,2 dichlorobenzene-d4 (recovery standard).

2.3. Soxhlet and ASE

Fourteen replicates and two blank matrix samples were each digested with 100ml of 2M HCl in conical flasks. The flasks were shaken periodically for about an hour, until no further foaming reaction was observed. The mix was separated using vacuum filtration and the cake was washed with deionised water to reduce acidity. Continuous vacuum was applied for 12h to allow the air drying of the cakes, which were then transferred with the filter papers in the Soxhlet cellulose thimbles, and the ASE extraction cells.

Half of the cakes were extracted with Soxhlet using 200ml of toluene for 20h, and the other half with Dionex ASE 200 accelerated extractor using approximately 60ml of toluene and the following settings: 175 °C, 1500 psi, static time= 8min, static cycles= 2, flush= 70%, purge= 60-120 sec. The aqueous solutions were extracted three times with 100ml of dichloromethane per litre of solution. The solvent extracts were washed twice with deionised water for pH adjustment (50% v/v). The two extracts from each sample were mixed, concentrated using a rotary evaporator (38 °C, 68 mbar), filtered through a multilayer silica gel column (anhydrous Na₂SO₄, 10% AgNO₃ silica gel, 20% H₂SO₄ silica gel, 40% H₂SO₄ silica gel, 30% KOH silica gel) and eluted with hexane, double the height of the column. The column's elutes were further

evaporated using a rotary evaporator (35 °C, 200 mbar) and finally concentrated to 1ml using a nitrogen flow concentrator. The samples were finally spiked with 100 µl of 1.6µg ml⁻¹ of 1,2 dichlorobenzene-d4 (recovery standard).

2.4. Analysis

All samples were stored at 4 °C prior to the GC-MS/ECD analysis. The solvents used for the extraction were all HPLC grade (Rathburn, UK). The glassware (separation funnels, transfer vials, rotary flasks, micro syringes) was decontaminated using a two step process with acetone and dichloromethane. The extraction standards were prepared in-house (Sigma-Aldrich catalogue number 140066). The recovery standards were purchased already prepared (Sigma-Aldrich catalogue number 48068). The detection and quantification limits were calculated according to the following formula.

$$\text{LOD (LOQ)} = \mathbf{b_{ave}} + 3(5) \mathbf{s_b}$$

Where $\mathbf{b_{ave}}$ is the mean concentration of the analytical blank controls and $\mathbf{s_b}$ is the standard deviation of the analytical blank controls.

The chromatographic conditions used for the two detection systems were identical consisting of a Thames-Restek Rtx ®- 1MS- 100% dimethyl polysiloxane column (length 15m, internal diameter 0.25 mm, film thickness 0.25 µm), an initial oven temperature of 50 °C, rising 30 °C min⁻¹ up to 125 °C, and then 15 °C min⁻¹ up to 300 °C where was held for 6 min. The carrier gas was helium and the injection volume was 1 µl at a split ratio 100:1 at 300 °C. The GC-ECD analysis was performed in an Agilent Technologies – 6890N Network GC system equipped with a ⁶³Ni ionisation source, and the identification was based on the retention times of the target species. The GG/ MS analysis was performed in a Perkin Elmer- Autosystem XL/Turbo Mass Gold instrument (70 eV) operated in SIM mode. The selected masses were: m/z= 150, 148, 152 corresponding to the [M-H⁺] ions of 1,2- dichlorobenzene-d4, m/z= 235, 74, 75 corresponding to the [M-H⁺] ions of tribromobenzene, m/z= 252, 250, 248 corresponding to the [M-H⁺] ions of pentachlorobenzene, and m/z= 284, 286, 282 corresponding to the [M-H⁺] ions of hexachlorobenzene. A typical sequence of injections consisted of one blank, six unknowns, one blank, four standards, one blank, and an analytical blank.

3. Results and discussion

Extraction efficiencies, calibration coefficients, LOQs, and mean concentrations for penta- and hexa-chlorobenzene obtained for each sample preparation method and the two investigated systems of detection are summarised in Table 2.

3.1. GC detection systems: ECD vs MS-SIM

Comparison of the LOQs obtained from the two detectors showed a difference, with ECD being able to detect traces approximately 15 and 10 times lower for pentachlorobenzene and hexachlorobenzene, than MS-SIM, respectively. The quantification of the 1,3,5 tribromobenzene extraction standard showed over efficiencies in SM-SIM, for all the sample preparation methods: $197 \pm 25\%$ for Soxhlet, $159 \pm 19\%$ for ASE, and $114 \pm 31\%$ for ultrasonication, against $83 \pm 7.5\%$, $111 \pm 19\%$, and $67 \pm 17\%$, respectively when analysed with ECD. Over- efficiency was also observed in the recovery of the deuterated standard for the MS-SIM analysis that ranged between 158- 228% against 94-105% on ECD. In general, the background noise in the ECD was lower than the noise of the MS-SIM. Figure 2 illustrates the above finding with indicative chromatograms of the same sample, extracted by Soxhlet, with signal to noise 4 times higher for ECD in comparison to MS-SIM.

These results suggest that sample matrix may strongly interfere with the quantification ions in the MS-SIM, and contribute to the over- efficiency obtained for both control and target compounds. Further purification of samples would be required for improving accuracy of final measurement e.g. purification using an aluminium oxide filtration column (Liu et al., 2001). Furthermore, when MS-SIM is used the utilisation of $^{13}\text{C}_{12}$ isotopes as extraction/ recovery standards is essential for the minimisation of sample matrix interferences.

This noise is disregarded in the ECD, where the halogenated compounds significantly affect the detectors signal, in comparison to other noise e.g. trace hydrocarbons, which build up the peak of interest at a specific retention time. This is confirmed by the absence of over- efficiency in the recovery of the standards. The results regarding the detectors are in agreement with those reported in the literature. These studies describe the ECD performance better than MS-SIM (Abreu et al., 2006; Leong and Huang, 2008), when the identification of compounds based on mass resolution is not needed, and equivalent to HRGC/HRMS (Fujita et al., 2009). In this case the

advantages of ECD are based on the complexity of the environmental matrix studied, and the sensitivity of ECD for halogenated compounds, resulting to better chromatograms for CBs, and eliminating the need for extensive sample purification. Given these results, the ECD readings have been used in the subsequent analysis for the comparison of the extraction/ sample preparation methods.

3.2 Comparison of extraction methods

Soxhlet performed relatively well showing the lowest RSD of the three methods; 9% against 17% for ASE and 26% for ultrasonication (Table 2). ASE and ultrasonication were over and under- efficient, respectively, compared to Soxhlet, with both methods presenting large distributions around the mean values. A one way ANOVA ($p=0.05$) confirmed that there is a statistically significant difference in the extracted pentachlorobenzene, with ASE giving greater values ($15.28 \pm 2.8 \text{ ng g}^{-1}$), than Soxhlet ($10.68 \pm 2.4 \text{ ng g}^{-1}$) and ultrasonication ($9.77 \pm 3.9 \text{ ng g}^{-1}$). This finding is partially explained by the over-efficiency of ASE. Furthermore, the supercritical conditions in the extraction cells can result to better extraction efficiencies, and the circulation of solvent in a closed system, can minimise the losses of analytes. ASE also extracted more hexachlorobenzene ($8.11 \pm 2 \text{ ng g}^{-1}$) than Soxhlet ($3.34 \pm 2.8 \text{ ng g}^{-1}$), while the values for hexachlorobenzene using ultrasonic extraction were below the LOQs.

The poor performance of the ultrasonication highlights the importance of the matrix digestion for the specific analysis. Some of the chlorobenzenes are possibly formed under '*de novo*' conditions, through heterogeneous (ash particles/ flue gases) reactions and are therefore deeply incorporated within fly ash. In this case the matrix is the pollutant, and further examination of the efficiency of ultrasonic extraction in digested matrices would be interesting for future comparisons.

Although, the methods present differences in the sample preparation, extraction and the clean-up techniques, a comparison of their general efficiency can be based on the detector's signal against the background noise, and thus the extraction against the clean up efficiencies, respectively. The results are plotted in Figure 3, which illustrates that Soxhlet and the subsequent multilayer silica gel column clean up give better results for both compounds between the examined methods.

Based on these results, one can argue that ASE gave relatively good results compared to Soxhlet. The disadvantages of ASE were the over- efficiency and a wide RSD

(17%) among replicates. Finally the method that incorporated ultrasonication showed poor performance in terms of extraction efficiency, S/N, and precision (RSD 26%) compared to Soxhlet and ASE.

4. Conclusions

For the determination of highly chlorinated benzenes in fly ash from SRF fluidised bed combustion, three different extraction methods have been compared. The results suggest that matrix digestion followed by Soxhlet extraction and multilayer silica gel column filtration, produce precise results with better signal to noise chromatograms than ASE and ultrasonication. We conclude that if time efficient and solvent saving extraction methods, such as ASE and ultrasonication are to be used instead of traditional methods, they need to be clearly defined and optimised for the specific matrix and species.

Furthermore, the detection limits and the consistency of the readings of ECD against MS-SIM have been investigated. The results demonstrated that ECD can provide less noise, and thus better peaks integration than MS-SIM for the detection of penta- and hexa-chlorobenzene in fly ash extracts. The use of ECD minimises the need for extensive sample clean up, and subsequent solvent use, or $^{13}\text{C}_{12}$ labelled standards. When mass resolution is needed, further sample purification and/or high efficiency instrumentation (HRGC/HRMS) is essential for the quantification of penta and hexa-chlorobenzenes in relevant matrices.

Acknowledgments

The authors acknowledge the financial support of ENTRUST, Shanks Group plc and Grantscape Ltd. for the completion of this work.

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Figure Captions

Figure 1. Summary of extraction methodologies

Figure 2. Pentachlorobenzene, indicative chromatograms for the same sample extracted by Soxhlet
(a) MS- SIM $m/z=252$ - S/N= 19, (b) ECD- S/N= 84

Figure 3. Comparison of ECD signal to noise ratio for penta-, hexachlorobenzene between the extraction methods

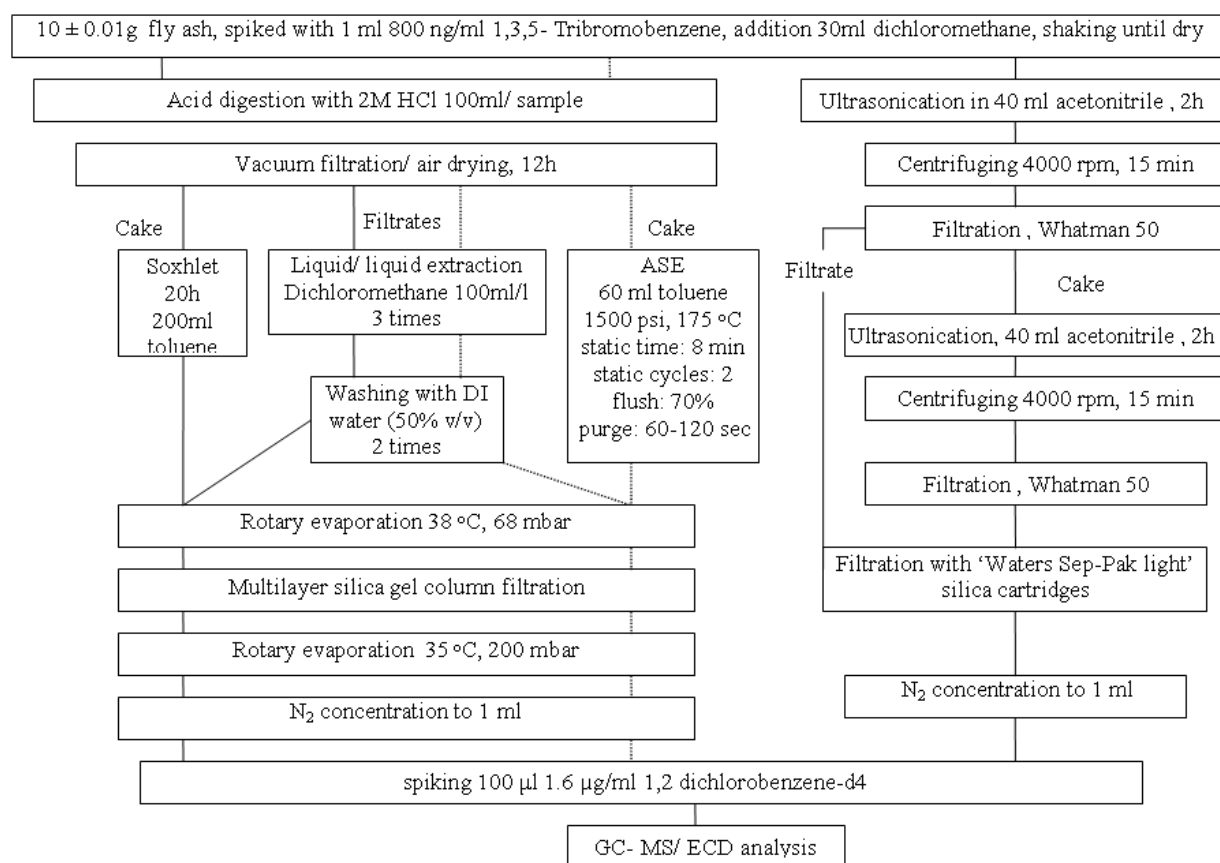


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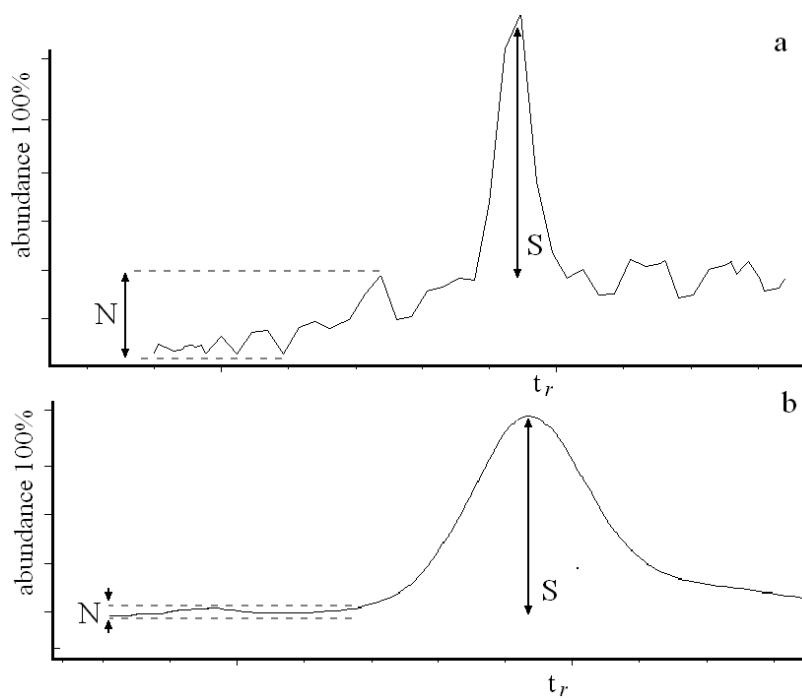


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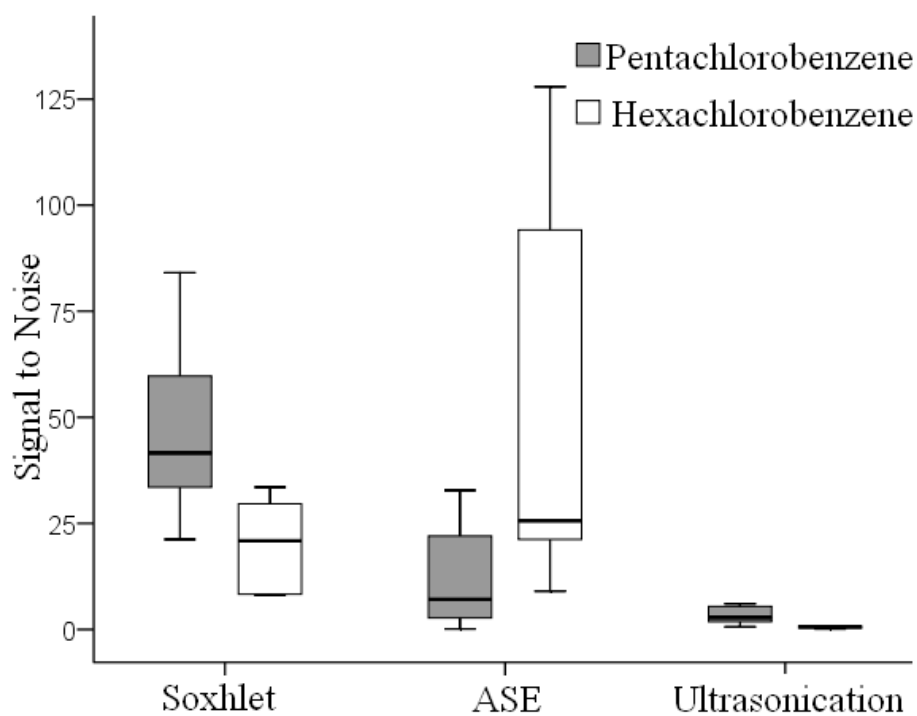


Figure 3. Comparison of ECD signal to noise ratio for penta-, hexachlorobenzene between the extraction methods

Table 1

Pre-treatment, extraction, clean-up methods and instrumentation for the quantification of chlorobenzenes from solid matrices

Pre-treatment	Extraction	Clean- up	Detection	Reference
Acetic acid	Soxhlet- Dean-Stark	Silica gel column	GC-MS	Liljelind et al., 2003
HCl digestion	Refluxing	Multilayer silica gel column	HRGC-LRMS ^a	Huang et al., 2003
-	Soxhlet	-	HRGC-MS-SIM	Oberg et al., 2008
-	Ultrasonication	-	GC-MS-SIM	Pekárek et al., 2007
-	Ultrasonication	Filter paper	LVI ^b -GC-MS	Korenkova et al., 2006
-	Soxhlet	Multilayer silica gel column	GC-MS	Sun et al., 2006
Acetic acid	Soxhlet- Dean-Stark	Multilayer silica gel column	GC- MS-MSD ^c	Lundin and Marklund, 2007
Grinding	ASE	Silica/ alumina column	GC-MS-MS/ GC-HRMS	Dionex, 2005
-	Ultrasonication	Alumina column	GC-MS-SIM/ GC-ECD	Liu et al., 2001

^a LRMS: Low resolution mass spectrometry

^b LVI: Large volume injection

^c MSD: Mass selective detection

Table 2

Extraction efficiencies, calibration coefficients, LOOs, and values for penta- and hexa-chlorobenzene for the three sample preparation methods and the two detectors

Detector	Sample	Sample preparation method					
		Soxhlet		ASE		Ultrasonication	
		Extraction efficiency %	*Cl ₅ Bz ng g ⁻¹	*Cl ₅ Bz ng g ⁻¹	*Cl ₅ Bz ng g ⁻¹	Extraction efficiency %	*Cl ₅ Bz ng g ⁻¹
MS-SIM	1	146	7.62	20	11.47	73	3.6
	2	208	13.57	9.37	12.64	125	- ^a
	3	195	9.12	12.5	15.67	156	- ^a
	4	218	6.77	8.5	11.26	151	- ^a
	5	222	12.5	10.8	11.27	93	3.4
	6	193	- ^a	- ^a	10.29	88	- ^a
	7	-	-	8.72	15.73	- ^a	8.2
	mean	197	9.92	11.65	12.62	114	3.5
	± s	25	2.67	3.9	2	31	0.1
	RSD (%)	13	2.7	3.4	1.6	28	0.3
ECD	1	71	8.6	18.40	8	90	6.36
	2	92	14.78	12.82	8.23	73	9.14
	3	81	11.7	12.31	5.53	79	4.98
	4	84	8.45	14.98	7.83	74	10.88
	5	89	11.3	13.78	5.94	57	9.45
	6	79	9.33	19.73	10.9	59	10.41
	7	-	-	15	10.26	38	17.21
	mean	83	10.68	15.28	8.11	67	9.77
	± s	7.5	2.4	2.8	2	17	3.9
	RSD (%)	9	2.3	1.8	2.5	26	4.0
	LOQ		0.25	0.21	2.9		0.28
	r ²		0.9999	0.9999	0.9999		0.9999

* Corrected values according to extraction and recovery efficiencies

-^a Values lower than LOQ

TRANSFER COEFFICIENTS AND ORGANOCHLORIDE LOAD OF A 'CHLORINE CLASS 2' SOLID RECOVERED FUEL IN FLUIDIZED BED COMBUSTION

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SUMMARY: 'Solid Recovered Fuels' is the term used to describe waste derived fuels from non hazardous sources with standardized information regarding their net calorific value, chlorine and mercury content. Chlorine in particular is considered an important factor for the technical establishment of an SRF as an alternative fuel, due to its role in corrosive phenomena inside boilers, and the formation of organochloride pollutants. Transfer coefficients have been developed in the present study for a 'chlorine-class 2' SRF, in a pilot scale fluidized bed combustor. Furthermore the organochloride pollutants load in the flue gases and the fly ash, expressed as penta-chlorobenzene, has been determined. The results can be considered as a guide for issues related to the utilization of SRF in similar processes, e.g. fine tuning of gas cleaning suites, and as a contribution to the technical literature/ confidence for the utilization of SRF in energy recovery processes.

1. INTRODUCTION

Thermal treatment is considered a valuable technique for the recovery of the energy content of wastes. After the universal acceptance of the waste management hierarchy, a shift from mass grate incineration towards more efficient technologies that use the combustible output fractions of mechanical- biological treatment [MBT] plants is expected. These developments are supported by efforts for the standardization of solid recovered fuels [SRF](CEN/ TS 15359, 2006) in terms of calorific value, trace metals and chlorine content to address the economic, emission, and technological issues arising from the utilization of waste fuels in energy recovery processes.

Solid recovered fuels, according to the abovementioned standard, are distinguished from the classical term of refuse derived fuel [RDF]; the initial acceptance criterion is a non-hazardous waste source and the final criterion is the classification according to the following properties:

- The mean value for net calorific value- on an as received basis [ar]
- The mean value of chlorine content- on a dry matter basis [dm]
- The mean and 80th percentile values for mercury content [ar]

Each property is divided in five classes with limit values and the combination of the properties classes makes up the class code for each SRF.

The chlorine content in particular, is considered an important factor for the technical establishment of a SRF as an alternative fuel for the following reasons:

- Chlorine participates in complex reactions that trigger corrosion phenomena inside boilers.
- Emissions of HCl, dioxins, and furans [PCDD/Fs] are related to the Cl content of fuels.
- The amount of soluble salts in the combustion residues is also an issue of concern, regulated in several countries.

In this context, the development of transfer coefficients for chlorine and a detailed mass balance including quantitative organochloride species information, contributes to the build up of technical confidence for the utilization of a 'Cl class 2' SRF in fluidized bed combustion.

2. AIM AND OBJECTIVES

The present work focuses on the chlorine mass balance, and its partitioning in SRF combustion by-products. Waste derived chlorine enters thermal treatment processes either in an inorganic form, namely salts [e.g NaCl, KCl] in food residues and other organic waste, or in an organic form, namely plastics [e.g. PVC]. It produces toxic gases [e.g. HCl] at a later stage inside boilers, and through the 'Deacon' reaction Cl molecules and radicals participate in the formation of organic contaminants such as chlorobenzenes [CBs], chlorophenols [CPs], polychlorinated biphenyls [PCBs] and PCDD/Fs. Extended literature is available regarding Cl behaviour, mass balance and partitioning issues in waste derived fuels incineration, and a few characteristics can be identified as common in most of these contributions:

- Artificial feedstock is used as test material (Wey M.Y., Chen J.C. & al. 2006; Wey M.Y. Ou W.Y. & al. 2001; Chiang K.Y., Wang K.S. & al. 1997; Wey M.Y., Liu K.Y & al. 2008). This strategy ensures the necessary knowledge of the waste fuel composition. Furthermore the experimental work is simplified by the avoidance of complicated sub-sampling procedures. The trade-off in this case is to overlook the effects that heterogenous waste feedstock can have in the Cl behaviour; e.g. different metals, or metal chlorides, namely copper and iron can have a catalytic effect on the organochlorides formation process (Gilardoni S., Permo P. & al. 2004; Liu K.Y., Pan W.P. & al. 2000; Wikstrom E., Ryan S. & al. 2003).
- Bench scale examination (Hilber T., Martensen M. & al. 2007; Chiang K.Y., Wang K.S. & al. 1997; Watanabe N., Yamamoto M. & al. 2004; Liu G. Q., Itaya Y. & al. 2001; Guo X.F., Yang X.L. & al. 2001). In most

experimental works the apparatus is characterised by its small scale and the feedstock test quantity does not exceed a few grams. The advantage of this approach is usually very good control over the experimental conditions, and the reproducibility of results. However, valuable information about the kinetics of the process and/ or the memory effect influencing the generation of organochlorides is not examined.

- Chlorine behaviour is investigated either from an organic or an inorganic point of view.

In this work the concept of the 'chlorine class', based on the SRF classification system, is utilized in a medium experimental scale in an effort to bridge the abovementioned trade-offs and to meet the following objectives:

- The test of the behaviour of an actual 'Cl class 2' SRF in fluidized bed combustion [FBC] and the demonstration of the experience gained from the recently developed relevant standards.
- The production of a Cl mass balance and transfer coefficients at a pilot scale FBC.
- The presentation of holistic data regarding the organic and inorganic Cl load in the FBC by-products: the organochloride load in the flue gases and the fly ash is determined using penta-chlorobenzene [Cl_5BZs] as an indicator due to good correlation with the international toxic equivalent [I-TEQ] values [I-TEQ of PCDDs/ PCDFs] = [Cl_5BZs], $r^2 = 0.84$ (Kato & Urano, 2001a), while for the inorganic, gaseous HCl, and water soluble chlorides in the solid phase residues are chosen as more representative for the mass balance needs.

3. MATERIALS AND METHODS

3.1 Feedstock properties and sampling procedure

Solid recovered fuel derived from East London's Waste Authority, as processed by a private contractor in a sequential separation, shredding, and aerobically biodrying MBT process, classified as a "NCV 3; Cl 2; Hg 1" class SRF was the feedstock for the trial. A batch of 100kg was sampled from the MBT plant and it was later sub-sampled as a 'static pile' according to the relevant standard (CEN/TS 15442, 2006). Twenty four piles of equal volume were created, after homogenisation by mixing, and an equal number of increments, with an arbitrary mass of 100g each was collected by sub-sampling 33g from the top, the middle and the bottom of each pile. The resulting 2.4 kg lab sample was shredded to <4 mm, and by mixing and quartering (CEN/ TS 15413, 2006) was further reduced to 300g. Three replicates of 100 g were produced, shredded to 0.5mm, and 1g from each replicate was finally tested for Cl content using the oxygen bomb method (CEN/ TS 15408, 2006) and was found at 0.4 ± 0.02 %wt dm. Figure 1 illustrates the sampling plan .

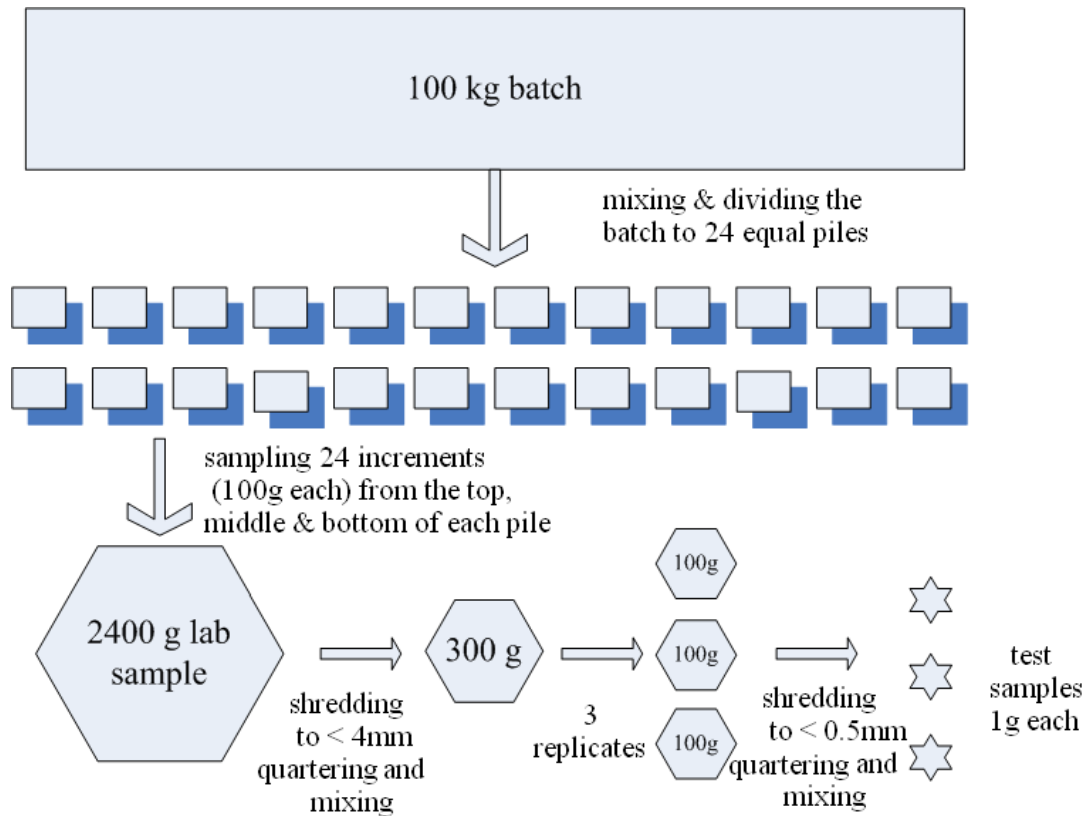


Figure 1. SRF sampling plan

3.2 Fluidized bed combustion rig operating conditions

The 50kW fluidized bed combustor [Figure 2] used for the trial consisted of a screw feeding hopper, the main bed chamber (dimensions 173*30*30 cm), a secondary combustion chamber that leads to a vertical ash deposit/ combustion system, a water cooling tower, a cyclone and an exhaust fan prior to the stack. The rig was monitored by 19 thermocouples, CO, CO₂, and O₂ online gas monitoring systems, HCl and gaseous chlorobenzenes capturing bubblers. The bed area was filled with 30.2 kg of silica sand [particle size 1.00 – 0.5 mm, 16/30 grade, density 1,556 g/l, bed static dimensions= 30*30*15.35 cm]. The FBC was vacuum cleaned the day before the experiment for the removal of residual ash and particles from previous trials. Furthermore, it operated overnight, burning natural gas resulting in a bed temperature of 460 °C for the elimination of organic species. The supply of primary and secondary air and natural gas before the SRF feeding was 450, 600 and 11.5 l/min respectively. The SRF incoming flow varied throughout the trial with a mean value of 117g/min and a lambda [λ] coefficient equal to 1,6. The duration of the test was 300 minutes and the bed temperature was at 800 ± 20 °C.

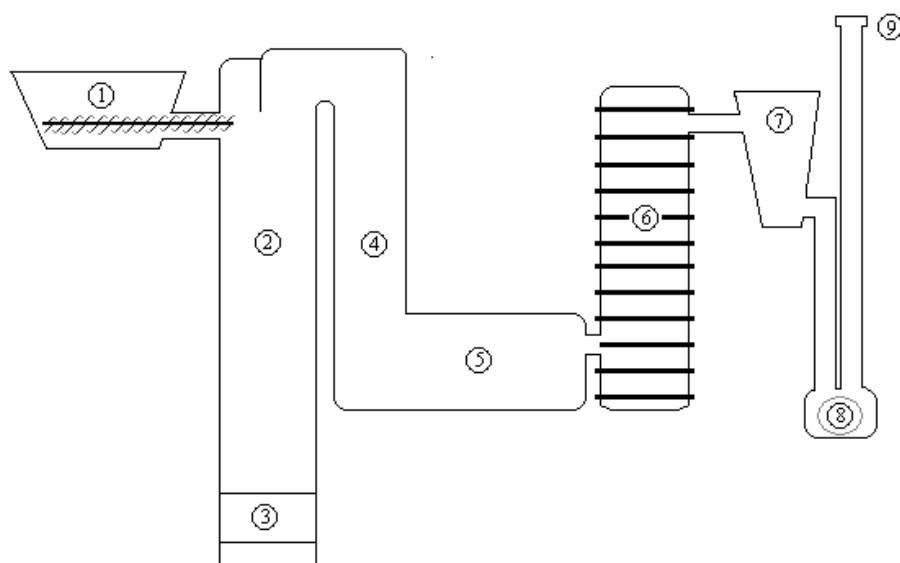


Figure 2. Fluidized Bed Combustor- 1: screw feeding hopper, 2: FB chamber, 3: bed area, 4: vertical secondary chamber, 5: horizontal secondary chamber, 6: water cooling tower, 7: cyclone, 8: exhaust fan, 9: stack

3.3 Sampling and analysis

3.3.1 Organics

The airborne chlorobenzenes were captured using the apparatus presented in Figure 3. The sampling train, as described in the literature (Kato & Urano, 2001b) is a modified standard (BS EN 1948, 2006) rig, and has a proven efficiency >85% for Cl₅BZs recovery. The detection and quantification of the chlorobenzenes was done by GC/MS analysis.

The fly ash, spiked with 800 ng of 1,3,5- tribromobenzene [extraction efficiency internal standard], was digested with 2M HCl to assist the chlorobenzenes extraction with Soxhlet and 175 ml toluene for 20 hours. The extract was concentrated to about 10 ml using rotary evaporation, cleaned through a multilayer silica gel column [sodium sulphate, 10% silver nitrate, 20% sulphuric acid, 40% sulphuric acid, 40% potassium hydroxide] and eluted twice the height of the column with hexane. The eluate was further evaporated using a nitrogen flow to <1 ml and transferred using micro syringes to vials for GC/MS analysis. The extracts were spiked again with 1 µl of 1,2- dichlorobenzene-d₄ prior to injection. The GC/MS parameters are presented in Table 1. The extraction method from the specific matrix was a combination of methods for PCDD/F's and CB's extraction, found in the literature (He P.J., Zhang H. & al. 2004; Sun Y., Takaoka M. et al. 2006)

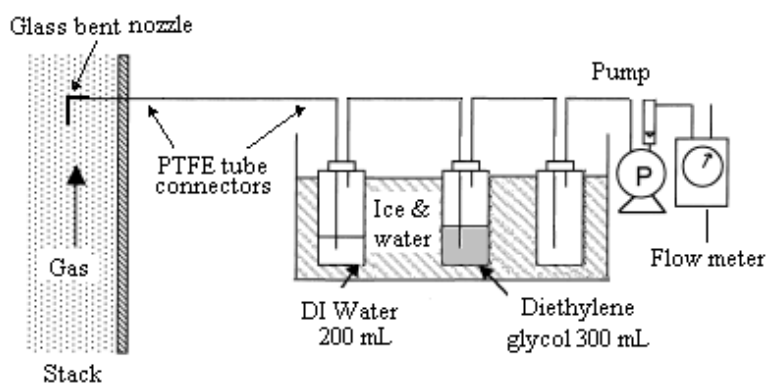


Figure 3. Chlorobenzenes sampling train

Table 1. GC/MS analysis parameters

GC/MS Instrument	Perkin Elmer- Autosystem XL/ Turbo Mass Gold
Column	Rtx® - 1MS (fused silica), Thames- Restek, UK Ltd., Length: 15m, ID: 0.25mm, IL :0.25 μ m
Oven temperature ramp	50 °C – 30 °C/min - 130 °C- 15 °C/min- 330 °C- hold 6 min
Injection temperature, type, volume	330 °C, split , 2 μ l
Carrier gas flow, pressure	He 2ml/ min, 50 kPa (3.1 min)- 40 kPa/min- 150 kPa
Ionisation method	(70 eV)

3.3.2 Inorganic

The resulting 35.4 kg of mixed silica sand and bed ash were carefully collected, placed in polypropylene plastic [PP] bags and latter emptied and washed in a tank with 17.6 l of DI water. The tank was continuously mixed for a day and 5 replicate samples were taken, centrifuged and filtrated. The horizontal chamber and cyclone ash were vacuum cleaned and collected separately in clean pre- weighted vacuum bags; their net mass was 2,211 and 465 g respectively. Three replicates of each fly ash type (horizontal and cyclone) were tested for total chlorine using the oxygen flask method. Furthermore, six replicates of half gram of each ash type was diluted in 250 ml of DI water and agitated for three hours followed by centrifugion and decanting. The filtered liquid was stored in PP bottles, at 4 °C for chloride anions analysis through ion chromatography (Dionex, UK- Ion Chromatographer, column: Ion Pac As9- HC 4*250 mm) while the HCl capturing solution was analysed by volumetric titration with silver nitrate.

4. RESULTS AND DISCUSSION

The chlorine mass balance, considering the water soluble chlorides in the gas and solid by- products, closes at 92.8%. The remaining 7.2% represents the organically bonded Cl species and any losses in the collection or capturing of the ashes and flue gases respectively. From the original Cl in the SRF feedstock, 18.3% was found at the bed area, 28.7% in the horizontal chamber ash, 17.2% in the cyclone ash and 29%

volatilised as HCl. The mass balance has been calculated according to Equation 1:

$$C_{in} = C_b + C_h + C_c + C_g \quad (1)$$

Where: C_{in} , is the total Cl in the input; C_b , is the Cl found in the bed ash; C_h , is the Cl of the horizontal chamber ash; C_c , is the Cl of the cyclone ash; and C_g , the Cl volatilized as HCl. Table 2 summarises the data on the transfer coefficients and the organochlorides load of the tested SRF.

The measurement and expression of the Cl content in the bed ash presented a few peculiarities. The ash could not be distributed and homogenized with the silica bed particles, resulting in big deviations in the originally sampled replicates. Furthermore, an amount of unburned particles, mainly glasses and ceramics, were found, as expected in the bed ash, and the expression of the results of the Cl content on a w/w basis would be meaningless. The emptying of the whole bed to a tank full of DI water and the measurement of the total water soluble chlorine seems to overcome this problem.

The chlorine mass balance presents certain challenges regarding the partitioning of organically bonded and inorganic species. There is an amount of Cl, for example in the cyclone ash, that is either bonded to organic molecules, or to inorganic salts physically trapped in the ash matrix, but still insoluble in water. A similar issue has been discussed for coal fuels (Cox J., Larson A.E. & al, 1984). Furthermore a detailed measurement of the organically bonded chlorine would require extensive identification and quantification of trace species [e.g. PCDD/Fs consist of 210 isomers].

Finally the results are in general agreement with other figures in the literature that examine the Cl mass balance in FBC (Hilber T., Thorwarth, H. & al. 2007). In comparison with data from other rigs used to measure the volatility of Cl in waste, e.g. quartz moving furnace (Liu G.Q., Itaya Y. & al. 2001), the figures in this experiment present lower HCl values. This fact suggests that the results are process specific.

Table 2

Inorganic Cl transfer coefficients and organochlorides load

Inorganic chlorine partitioning			
Output	Mean – water soluble Cl	St. Dev.	% of Cl input
Bed ash	22.35 g- total	4	18.4
Horizontal chamber ash	15.5 mg/g of ash	0.36	28.2
Cyclone ash	44.8 mg/g of ash	0.9	17.2
Flue gases- HCl	35.25 g- total	-	29
Organochloride load			
Output	Cl ₅ BZs		
Cyclone ash	6.9 ng/ g of ash	1.4	
Flue gases	4.4 µg/ m ³	0.3	

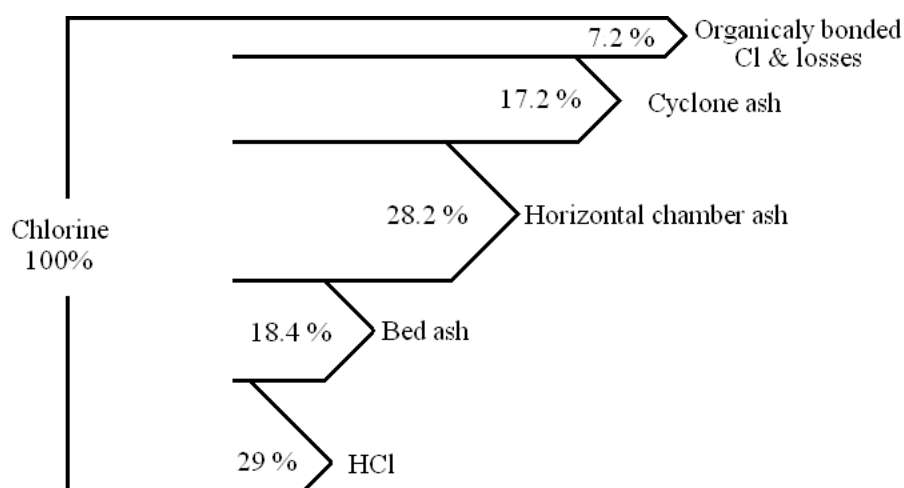


Figure 3. Shankey diagram- Cl mass balance

5. CONCLUSIONS

Detailed chlorine transfer coefficients have been developed for a 'chlorine- class 2' SRF in a pilot scale FBC. A general remark is that approximately one third of the chlorine in the SRF is volatilized in the process. Furthermore, the organochloride pollutants load in the flue gases and the fly ash, expressed as penta-chlorobenzene has been determined. Figure 3 illustrates the transfer coefficients in a Shankey diagram. The results, although rig and feedstock specific, can be considered as a guide for issues related to the utilization of SRF in similar processes, such as fine tuning of gas cleaning suites, and as a contribution to the technical literature/ confidence for the utilization of SRF in energy recovery processes.

ACKNOWLEDGEMENTS

The project has been supported by ENTRUST, Shanks Group plc and Grantscape Ltd. Furthermore, the management and employees of Shanks Group plc provided valuable help in the SRF sampling procedures. Knight Energy Services laboratories are also acknowledged for their kind support in providing the oxygen bomb analysis.

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Demonstration Of Experience Gained From The Gasification Of East London's Solid Recovered Fuel In A Spout Bed Rector

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Abstract

Thermal treatment is considered a valuable option for the recovery of the energy content of wastes within the waste management hierarchy. Recent developments in the field, indicate that the utilization of the combustible output fractions of mechanical- biological treatment (MBT) plants like solid recovered fuels (SRF) in new technologies, like gasification can contribute towards 'zero waste' strategies. In this work the Cl mass balance in gasification is investigated. The results indicate that lower temperatures and reducing conditions under gasification can retain chlorine and heavy metals in the generated solid residues. Thus, gasification can potentially be a safer process than combustion in terms of gaseous pollutants generation.

Keywords: RDF, gasification residues, transfer coefficients, tar

1. INTRODUCTION

Thermal treatment is considered a valuable option for the recovery of the energy content of wastes. Recent data (Defra, 2009) indicate that EU countries like Denmark, Netherlands, Belgium, Sweden, Luxemburg, Germany, France and Portugal, incinerate more than 20% of their generated municipal solid waste, while the equivalent percentage in the USA is ca. 17.2 % (Themelis et al., 2002). Besides incineration, other technologies that utilize starved oxygen environments, like gasification and pyrolysis, have met commercial success in Europe and Asia

(Heerman et al., 2003). These technologies are often advocated to have certain advantages in comparison to traditional incineration; reduced pollutants generation, higher energy efficiencies, and tolerance to corrosion phenomena are only a few (Malkow, 2004).

The developments in the field of thermal treatment are signposted by changes in waste derived fuels as well. After the universal acceptance of the waste management hierarchy, a shift from mass grate technologies towards utilization of the combustible output fractions of MBT plants is expected. These developments are supported by efforts for the standardization of solid recovered fuels (CEN/ TS 15359, 2006) in terms of calorific value, trace metals and chlorine content to address the economic, emissions, and technological issues arising from the utilization of waste fuels in energy recovery processes.

Solid recovered fuels, according to the abovementioned standard, are distinguished from the classical term of refuse derived fuel (RDF); the initial acceptance criterion is a non-hazardous waste source and the final criterion is the classification according to the following properties:

- The mean for net calorific value
- The mean value of chlorine content
- The mean and 80th percentile values for mercury content

Each property is divided in five classes with limit values and the combination of the properties classes makes up the class code for each SRF. Therefore, the statistical safe knowledge of the abovementioned properties through quality assurance and control protocols (QA/QC) can create homogeneous data for comparisons among different SRF classes, and different thermal treatment techniques.

This work focuses on the chlorine mass balance, and its partitioning in SRF gasification by-products. Waste derived chlorine enters thermal treatment processes either in an inorganic form, namely salts (e.g. NaCl, KCl) in food residues and other organic waste, or in an organic form (e.g. plastics like PVC). It produces toxic gases (e.g. HCl) inside boilers, and through the ‘Deacon’ reaction Cl molecules and radicals participate in the formation of organic contaminants such as chlorobenzenes, chlorophenols, PCBs and dioxins (Wikstrom et al., 2003; Wey et al., 2008; Arena et al., 2009). Furthermore, HCl and Cl molecules, or radicals trigger corrosion phenomena inside boilers (Fordham et al., 2002; Sroda et al., 2006).

Extended literature is available regarding Cl behaviour, in waste derived fuels thermal treatment, and a few characteristics can be identified as common in most of these contributions:

- Artificial feedstock, or single stream waste is used as test material (Wikstrom et al., 1996; Liu et al., 2001; Corella et al., 2008; Song et al., 2009). This strategy ensures the necessary knowledge of the waste fuel composition, and the experimental work is simplified by the avoidance of complicated sub-sampling procedures.
- Bench scale examination (Bjorkman and Stromberg, 1997; Borgianni et al.,

2002; Song et al., 2009). In most experimental works the apparatus is characterised by its small scale and the feedstock test quantity does not exceed a few grams. The advantage of this approach is usually very good control over the experimental conditions, and the reproducibility of results.

The trade-off in these cases is to overlook the effects that heterogeneous waste feedstock can have in the Cl behaviour; e.g. different metals, or metal chlorides, namely copper and iron can have a catalytic effect that affects Cl partitioning. Moreover, small test quantities, or batch tests give data that might ignore reactions downstream the main reaction chamber in large scale processes (e.g. memory effect, or interactions with other by- products).

In our work, the ‘in vivo’ Cl mass balance in gasification is investigated. The use of SRF as feedstock, the scale of the experimental rig, and steady state conditions, throughout the trial aim to the generation of Cl transfer coefficients that correspond to full scale processes. Furthermore, the concentration of heavy metals in the solid residues is investigated and comparisons with literature values are performed.

2. MATERIALS AND METHODS

2.1 SRF feedstock

SRF derived from East London’s Waste Authority, as processed by a private contractor in a sequential, shredding, aerobically bio-drying, and separation MBT process, classified as a “NCV 3; Cl 2; Hg 1” class SRF was the feedstock for the trial. Figure 1, illustrates the arrangement and the materials balance of the MBT- SRF plant, and Table 1 summarises the proximate and ultimate analysis of the feedstock.

Table 1

SRF properties

Proximate analysis		Ultimate analysis (%wt dm)	
Moisture content (%wt ar)	13.2 ± 1.5	C	47.4 ± 4.2
Ash content (%wt ar)	13.7 ± 2	H	5.7 ± 2.9
NCV (MJ/kg)	17 ± 3	N	0.8 ± 0.3
		S	0.1 ± 0.02
		Cl	0.5 ± 0.02
		O*	45.1*

* By difference

A batch of 100kg was sampled from the MBT plant and it was later sub-sampled as a static pile, according to the relevant standard (CEN/TS 15442, 2006) for the detailed investigation of proximate characteristics and chlorine content. The remaining data on ultimate analysis (Table 1) were provided by the SRF producer based on routine QA/QC analysis. Based on the ultimate analysis, and the assumption that SRF comprises mostly out of lignocellulose materials (Bangala et al., 1997), an approximate theoretical formula was estimated ($C_6 H_9 O_4$) for the feedstock. This approach, as indicated in literature (Themelis et al., 2002), can simplify the

stoichiometric calculations for heterogeneous materials. Finally the feedstock was shredded to dimensions <8mm and dried for 48 hours at 40 °C before the experiment.

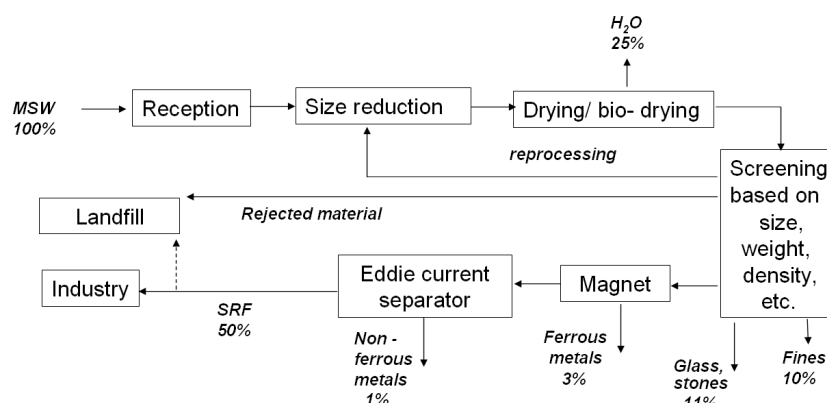


Figure 1. Simplified arrangement and mass balance of East London's MBT- SRF production plant, adapted from Gascoyne, 2008

2.2 Gasification experiment

Experience throughout various trials in the gasifier, highlighted the importance of the feeding system for fuels with similar properties. SRF is characterised by physical (and chemical) heterogeneity, and is a material with a rather low bulk density, thus feeding it in reactors at steady state conditions, can present challenges (e.g. bridging effect). After numerous tests with various feeding systems, the combination presented in Figure 2, (continuous stirred feeding hopper- SRF Venturi entraining system) managed to address the above-mentioned problems without any compromise in stoichiometry.

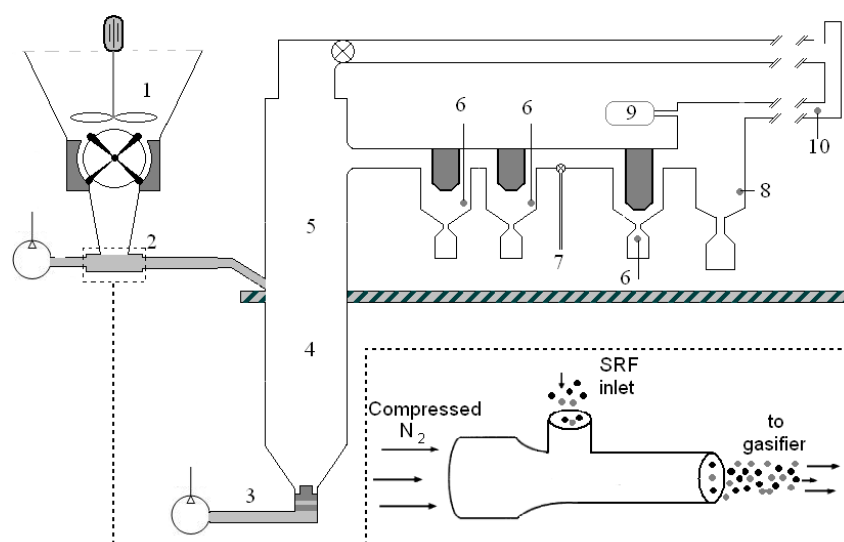


Figure 2: Schematic of spout bed gasifier and Venturi details. 1.Feeding hopper, 2. SRF Venturi entraining system, 3. Fluidisation air mix inlet, 4. Combustion zone, 5. Gasification zone, 6. Tar and ash traps, 7. Syn-gas sampling point, 8. Cyclone, 9. Flare, 10. Flue gases sampling point

The gasification took place in a spout bed gasifier (Figure 2), with main chamber dimensions 25*150 cm. The rig was preheated with ceramic electric heaters and a feeding rate of 3,3 kg/ hour was achieved through the pneumatic feeding system. The lamda coefficient was variable during the trial, and ranged between 0.25- 0.4 aiming to the equilibration of endothermic and exothermic reactions, in terms of temperature. The trial lasted 30 minutes and the average temperature was at 700 °C. The fluidisation conditions were continuously monitored through pressure gauges at the main bed area (Figure 2- sections 3-4) and the pressure ranged between 0.5- 0.8 bars.

2.3 Analysis

After the experiment the rig was allowed to cool down for 24 hours and it was disassembled. The bed material was collected in a tank with deionised water and six replicate samples were taken, centrifuged and filtrated. The tars- ashes were collected using vacuum from the particles traps. Six replicates of one gram each from each trap were analysed for total Cl, using the oxygen bomb method (ASTM, 1991) and ion chromatography (Dionex, UK- Ion Chromatographer, column: Ion Pac As9- HC 4*250 mm).

A hydrofluoric-free digestion method was used for the examination of the residues' metals content. The method was tested for its recovery, using a certified reference material (CRM) (BCR- 176R, JRC, IRM), and gave comparable results with aqua regia digestion (BSI, 1995). For the majority of metals the recovery was between 70-90%, except from chromium that had a recovery of 19- 30%.

An Anton Parr Multiwave 3000 microwave oven unit was utilised for the microwave assisted digestion (MWAD) using 400 ±1 mg of test material, 5 ml of concentrated (15.8 M) nitric acid, and another 3ml of hydrogen peroxide (100 volumes). The following MWAD programme was applied: 20 minutes for the instrument to reach 18 bar and 190 °C, where held for 20 minutes and finally another 20 minutes for the vessels to cool down. The mixture was then filtered using 0.45µm Whatman cellulose filter papers and diluted with ultra pure water, to a fixed volume of 100 ml. All chemicals were trace analysis grade and purchased from Fischer Scientific UK. The quantification was achieved through a graphite furnace/ flame- atomic absorption spectrometer (GF/F-AAS) A-Analyst 800 Perkin Elmer instrument, equipped with an air/ acetylene flame and an AS-90 autosampler.

3. RESULTS AND DISCUSSION

The gasification experiment volatilised ca. 75 wt % of the material. The remaining 25% was distributed between ashes and tars, at ratios of 14% and 11% respectively. Furthermore, bulk density tests in the SRF and the produced residues revealed a volume reduction greater than 90%. Due to the set up of the experimental rig, these residues were collected, and thus analysed as a homogeneous product.

3.1 Behaviour of Chlorine

As illustrated in Figure 3, the majority of chlorine in the feedstock ends up in the solid residues. The quantity of Cl found in the bed material was minor (<1%). Almost 84% of Cl that entered the gasifier was converted to solid organic products of incomplete combustion e.g. chlorophenols, chlorobenzenes, etc. and salts in the tar and ashes. A very interesting outcome is that the amount of chlorine that volatilised as HCl in the process was only 5%. This figure is 5-6 times lower when compared to tests using the same feedstock, in similar rigs, under excess oxygen environments (Balampanis et al., 2008). This finding is of particular importance as it verifies that gasification can potentially be a safer process than combustion in terms of gaseous organochlorides generation.

Various explanations can be given for the low HCl levels. The gasification reactions are roughly endothermic, thus an amount of energy is absorbed in the process. That leads to lower temperatures inside the upper part of the reactor that can retain Cl in the feedstock from passing to the gaseous phase. This can obstruct the volatilisation of inorganic Cl species that volatilise at higher temperatures than organically bonded Cl (e.g. PVC).

In addition to that, experimental studies using coal and biomass (Kuramochi et al., 2005; Takeda et al., 2006) have shown that the evolved HCl can react further with metal impurities, alkali metals, or active carbon structures within the produced tars-ashes to be further retained in the gasification solid residues. That hypothesis is confirmed in our case, where the Cl content within the residues increased downstream the reactor, proportionally to the particles' residence time, as illustrated in Figure 4.

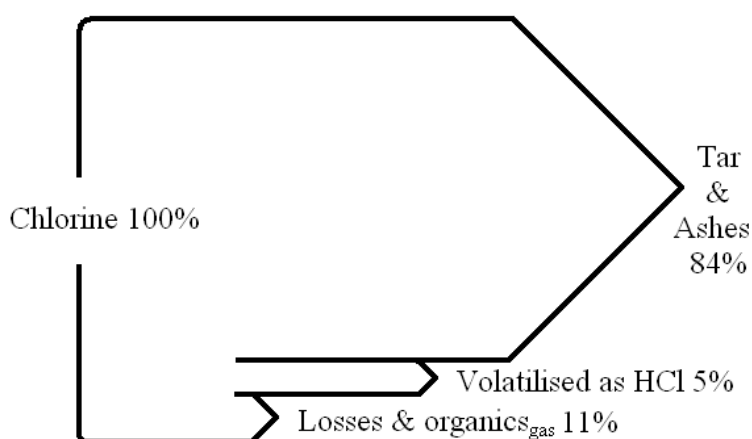


Figure 3. Sankey diagram of Cl mass balance

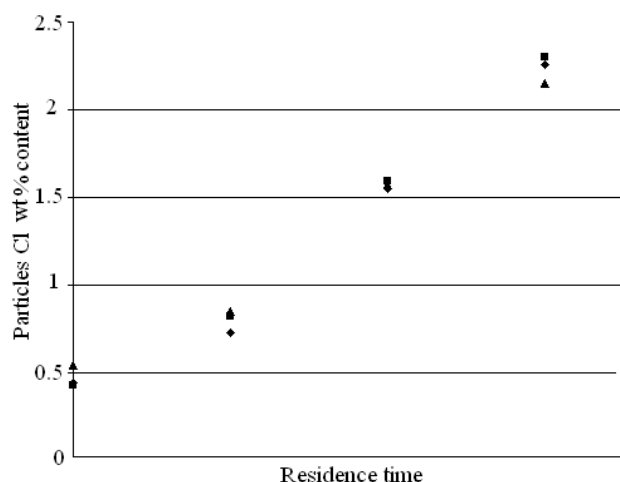


Figure 4. Chlorine content of ashes-tars as a function of particles' residence time

3.2 Behaviour of heavy metals

The concentrations (range, mean, first and third quartiles) of various metals in the gasification solid residues are illustrated in Figure 5. Copper ranged between 0.37- 1.57 mg/g, cadmium ranged between 2.7- 54.5 $\mu\text{g/g}$, nickel ranged between 0.3- 0.63 mg/g, zinc ranged between 0.62- 1.5 mg/g, lead ranged between 0.32- 0.63 mg/g, and chromium ranged between 1.6- 2.2 mg/g. Given chromium's low recovery on the CRM, its actual concentration in the residues should be expected to be 3-4 times higher than the one presented here.

Except from cadmium, which is the most volatile of the examined metals, the concentration of metals in the gasification residues is considered relatively high. An interesting comment can be made when these values are compared with the ones from combustion residues, like fly ash, from literature (Amutha Rani et al., 2008; Quina et al., 2008). While Pb, and Zn are in the lower reported ranges, Cu, Ni, Cd, and Cr range at the same, or higher levels than conventional incineration derived fly ash. Thus, lower temperatures and reducing conditions (the same reasons than retain Cl in the solid phase) can play a role in the phase distribution of heavy metals as well, as reported elsewhere (Malkow, 2004).

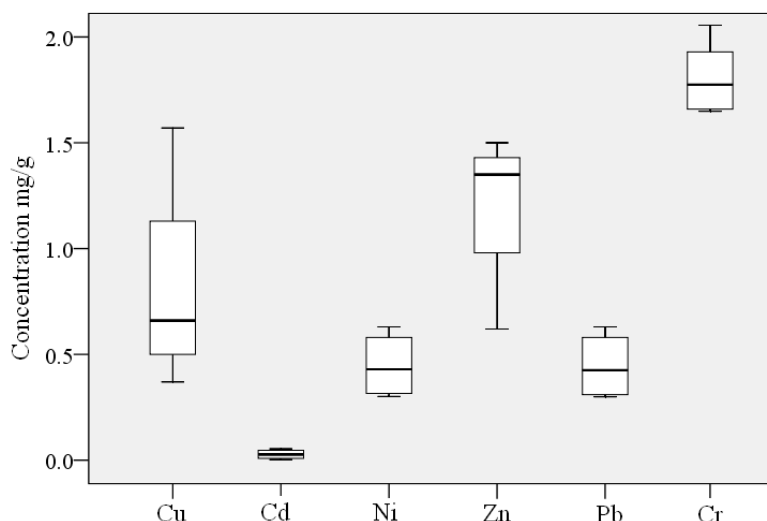


Figure 5. Concentration of various heavy metals in gasification tar- ash

It is therefore evident that gasification of SRF might have advantages in terms of impurities in the flue gases (and subsequent benefits for the design of smaller capacity air pollution control units), but these are concentrated in the solid residues. These residues should require further treatment before final disposal to avoid leaching of metals and other toxics in the environment.

4. CONCLUSIONS

SRF derived from East London's Waste Authority was tested in a spout bed gasifier under steady state conditions and the following conclusions can be made:

- The continuous feeding of SRF might present problems in thermal rigs for reasons related to bridging effects and stoichiometry. The employment of pneumatic systems like Venturi nozzles can address these problems.
- Gasification of SRF can contribute to 'zero waste' strategies, through enhanced energy recovery and mass and volume reduction that reach 75% and 90%, respectively.
- Transfer coefficients indicate that 84% of the incoming Cl ends up in the solid residues, and only 5% volatilises as HCl. Thus, gasification can potentially be a safer process than combustion in terms of gaseous organochlorides generation, as it retains most Cl in non volatile phases.
- Lower temperatures and reducing conditions under gasification can retain heavy metals in the generated solid residues. This might have advantages in terms of gaseous pollutants abatement, but the stabilisation of the generated residues should be taken into account prior to final disposal.

The results are expected to build technical confidence for the commercial utilisation of SRF in similar energy recovery processes.

5. ACKNOWLEDGEMENTS

The project has been supported by ENTRUST, Shanks Group plc and Grantscape Ltd.

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