Two stage fluid bed-plasma gasification process for solid waste valorisation: Technical review and preliminary thermodynamic modelling of sulphur emissions

Shane Morrin [a,b], Paola Lettieri [a], Chris Chapman [b,*], Luca Mazzei [a]

[a] *Department of Chemical Engineering, University College London, London, WC1E 7JE, Great Britain, United Kingdom*
[b] *Advanced Plasma Power, South Marston Business park, Swindon, SN3 4DE, Great Britain, United Kingdom*

ABSTRACT

Gasification of solid waste for energy has significant potential given an abundant feed supply and strong policy drivers. Nonetheless, significant ambiguities in the knowledge base are apparent. Consequently this study investigates sulphur mechanisms within a novel two stage fluid bed-plasma gasification process. This paper includes a detailed review of gasification and plasma fundamentals in relation to the specific process, along with insight on MSW based feedstock properties and sulphur pollutant therein. As a first step to understanding sulphur partitioning and speciation within the process, thermodynamic modelling of the fluid bed stage has been performed. Preliminary findings, supported by plant experience, indicate the prominence of solid phase sulphur species (as opposed to H_2S) – Na and K based species in particular. Work is underway to further investigate and validate this.

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1. Introduction

There are numerous materials with an organic content (including fossil fuels, biomass and solid waste) which may be suitable for gasification or other thermochemical processes.[1] To date, however, most development has been on fossil fuels, with biomass and then solid waste lagging (Childress, 2008). Nonetheless, recent policy to tackle resource conservation and climate change has given waste gasification renewed impetus.

Gasification of either fossil or biomass based materials can play a central role within an integrated refinery (IChemE, 2010). Syngas has many potential uses. In fact, power generation represents just ∼20% globally, with the remaining capacity divided largely between chemicals and Fischer–Tropsch fuels (Childress, 2008; Young, 2010).

This study focuses on a novel two stage fluid bed gasification – plasma converter technology to transform solid waste into energy at a commercial scale. The feedstock consists of a refuse derive fuel (RDF) produced from a combination of residual municipal and commercial waste. The aim of this research is to investigate pollutant removal from the hot syngas, focusing on the partitioning and chemistry of sulphur along with other relevant components. Analysis, including thermodynamic modelling, is supported by experimental data from a demonstration plant.

The following ' 2 provides technical insight on the fundamentals of gasification and plasma in relation to above process, as well as municipal solid waste (MSW) based feed and sulphur therein. Section 3 builds on this, illustrating the thermodynamic modelling approach. This leads to the presentation of preliminary model findings in Section 4, followed by the overall conclusions in Section 5.

2. Review

2.1. Technology principles

2.1.1. Gasification

Gasification is the thermochemical conversion of organic matter (i.e. carbonaceous) by partial oxidation (i.e. substoïchiometric) into a gaseous product (i.e. synthesis gas or syngas) (Ciferno and Marano, 2002). This syngas may be used directly for combustion or synthesised into fuels or chemicals. The main syngas components are H_2 and CO, with lower concentrations of CO_2, H_2O, CH_4, higher hydrocarbons and N_2. Reactions take place at elevated temperatures (500–1400 °C) and a range of pressures (from atmospheric to 33 bar). The gasifying medium used may be air, pure oxygen, steam or a mixture of these. Gasification chemistry is complex (influenced by varying feed, process design and operating conditions); however, it may be considered as a simplified two step process namely, pyrolysis followed by gasification (Fig. 1).

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[1] Abbreviations: dry recyclables (DR); model simulation (sim); bubbling fluidised bed (BFB); and net electrical efficiency (NEE).

* Corresponding author. Address: Advanced Plasma Power (APP), Unit B2 Marston Gate, South Marston business park, Swindon, Great Britain, SN3 4DE, United Kingdom. Tel.: +44 1793 238 523; fax: +44 1793 828 287.

E-mail addresses: shane.morrin@ucl.ac.uk (S. Morrin), p.lettieri@ucl.ac.uk (P. Lettieri), chris.chapman@app-uk.com (C. Chapman), l.mazzei@ucl.ac.uk (L. Mazzei).
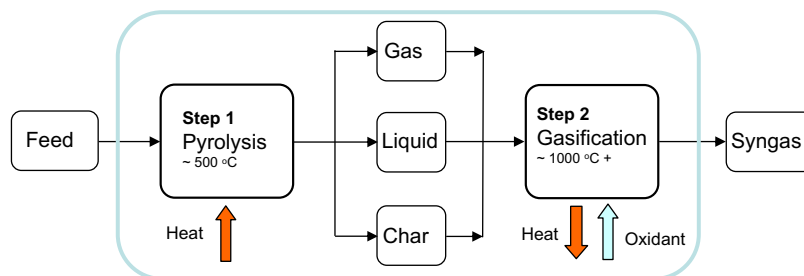
Fig. 1. Gasification steps (Adapted from Ciferno and Marano, 2002).

Pyrolysis (i.e. devolatilisation) is the decomposition of the feedstock by heat in the absence of oxygen. This is the first step in gasification wherein water vapour, organic liquids and noncondensable gases are separated from the solid carbon (i.e. char) content of the fuel. The process is slightly endothermic, producing 75–90% volatile materials (for biomass) in the form of gaseous and liquid (i.e. condensable vapours including tar) hydrocarbons. The relative yield of gas, condensable vapours and residual char depends largely on the rate of heating and final temperature. Pyrolysis is initiated at around 230 °C when thermally unstable feed constituents (for example, lignin in biomass and volatiles in coal) break down and evaporate with other volatile constituents. The other pyrolysis processes begin slowly at ∼350 °C. Above 700 °C these become almost instantaneous. The product gasses tend to be light (including H_2, CO, CO_2, H_2O and CH_4) with a low heating value (∼3.5–9 MJ/m^3). The vapour/liquid product comprises mostly of polyaromatic hydrocarbons (PAHs) and tar (i.e. a dark, sticky viscous, corrosive liquid composed of heavy organic and inorganic molecules).

During the subsequent gasification step (i.e. the second step in the overall gasification process) the volatile hydrocarbons and char are converted into syngas (Table 1) (Ciferno and Marano, 2002). The most important reduction reactions are the water–gas (Eq. 6) and Boudouard (Eq. 7) reactions (Knoef, 2005). These reactions are reversible, heterogeneous and endothermic, resulting in higher CO and H_2 gas volumes (at higher temperature and lower pressure).

2.1.2. Plasma

Plasma refers to any gas of which at least a percentage of its atoms or molecules is partially or totally ionized (Moustakas et al., 2005). The energy required can be thermal, electrical or electromagnetic. Plasma forms when a sustained electrical arc is generated by the passage of electric current (continuous, alternate or high frequency) through a gas. Electrical resistivity across the system creates massive localised heat. This strips electrons from the gas molecules resulting in an ionised gas stream, or plasma (Gomez et al., 2009).

Compared to most gases even at elevated temperatures and pressures, the chemical reactivity and quenching rate characteristic of plasma is far greater (Moustakas et al., 2005). This is due to the high temperatures and presence of highly reactive atomic and ionic species. As a result, any organic molecules in the vicinity break down due to the high temperature conditions forming a synthetic gas (Lemmens et al., 2007). At the same time, fusion of inorganic components (glass, metals, silicates and heavy metals) occurs, forming a molten slag (and metal phases) which vitrifies on cooling. In this respect the role of the plasma is often not direct – for example, transferring energy to a metal bath at the base of the holding vessel which in turn radiates heat throughout its interior.

Depending on the energy source used and the conditions under which the plasma is generated, two main groups of plasmas can be distinguished: high temperature or fusion plasmas, and low temperature plasmas or gas discharges (Table 2) (Helsen and Bosmans, 2010). Low temperature plasmas are the most used in industrial processes (Gomez et al., 2009). In turn, there are two types within this subset, namely cold and thermal plasmas (Iron and Steel Society, 1987). Cold plasmas are characterised by a non-equilibrium state. Thermal plasmas, which are immediately relevant to this study, achieve a quasi-equilibrium state, characterised by high electron density and low electron energy. Temperatures between 2000 and 30,000 °C may be reached, dissipating sharply moving away from the core (Moustakas et al., 2005).

Most thermal plasmas are generated by either radio-frequency induction (RFI) discharge or an electric arc, created by a plasma torch (Helsen and Bosmans, 2010). Two types of plasma arc torches exist, namely: the transferred; and non-transferred. The transferred torch (i.e. as used in this study) creates an electric arc between its tip and a metal bath or the conductive lining of the reactor wall. Transferred arc reactors offer high heat fluxes, advantageous for solids melting (Heberlein and Murphy, 2008). In the non-transferred torch configuration, the arc is produced within the torch itself. The plasma gas is fed into the torch, heated, and then exits through the tip of the torch.

Owing to their high temperature, reactivity and quenching rates, thermal plasmas have potential in a variety of chemical processes, making them popular in industry. This includes thermochemical treatment of waste – rapidly initiating decomposition, evaporation, pyrolysis and oxidation reactions (Moustakas et al., 2005; Gomez et al., 2009).

The use of plasma-based systems for waste management is a relatively new concept (Helsen and Bosmans, 2010). Applications may be categorised as follows: plasma pyrolysis; gasification; compaction and vitrification; or a combinations of these. Plasma-based waste treatment systems tend to incorporate transferred arc reactors since they offer high heat fluxes (Heberlein and Murphy, 2008). This facilitates decontamination in combination with volume reduction and immobilisation of inorganic contaminants, features typical of solid waste.

Plasma, incorporated with conventional gasification, enables the use of low-energy fuels which may otherwise have difficulty

Table 1
Main reactions during the second gasification step[a].

Type/Label	Reactions	Energy (kJ/mol)	Equation
Exothermic			
Combustion	{volatiles/char} $C + O_2 \rightarrow CO_2$	−393.8	1
Partial oxidation	{volatiles/char} $C + O_2 \rightarrow CO$	−123.1	2
Methanation	{volatiles/char} $C + H_2 \rightarrow CH_4$	−74.9	3
Water–gas shift	$CO + H_2O \rightarrow CO_2 + H_2$	−40.9	4
CO methanation	$CO + 3H_2 \rightarrow CH_4 + H_2O$	−217.0	5
Endothermic			
Water–gas/ steam-carbon	{volatiles/char} $C + H_2O \rightarrow CO + H_2$	118.4	6
Boudouard	{volatiles/char} $C + CO_2 \rightarrow 2CO$	159.9	7

[a] Adapted from Ciferno and Marano (2002), Knoef (2005), and Basu (2006).

Table 2
Summary comparison of plasma types and key features.

Plasma group		Species state within plasma	Features
High temperature		Thermodynamic equilibrium	
Low temperature	Cold	Non-thermodynamic equilibrium	High chemical reactivity
	Thermal	Quasi thermodynamic equilibrium	High quenching rates
			Types:
			• Radio frequency induction (RFI)
			• Transferred, non-transferred
			Temperature range: 2000–30,000 °C

sustaining reactions. This is normally performed in either a one or two stage process format. In the one stage format, pyrolysis or gasification is sustained by applying a thermal plasma directly onto the waste material. All of the energy required for decomposition comes from the plasma (van Oost et al., 2009). This allows for control of temperature independent of fluctuations in the feed quality along with better control of the syngas composition – increasing its heat capacity and reducing contamination (Lemmens et al., 2007). A variation of this single stage approach is for the plasma to provide part of the heat required for processing, with the remainder supplied by the waste feedstock or a fuel additive (Helsen and Bosmans, 2010). Examples of technology development include Westinghouse in Madison, USA and Europlasma in Morcenx, France.

The two stage format has quite a different concept. The first stage incorporates a conventional gasifier. A second plasma stage is then used to refine the syngas. Forerunners in this approach are Advanced Plasma Power (APP) in the UK and Plasco Energy Group Inc., Canada. Using two stages increases throughput, since plasma decomposition of solid waste in a single stage is much slower than refining tars and chars in the synthesis gas. It is also proposed that control of volatile organic compounds (VOCs) and tars in the syngas is improved along with conversion efficiency. In comparison, direct pyrolysis or gasification in a single stage has a higher electricity requirement (in some instances equating to the energy content of the feedstock). For this reason, the single-stage format is more appropriate in handling small difficult-to-treat process streams (for example, hazardous or medical waste). Consequently, the two-stage process is suited to larger waste streams.

2.1.3. Two stage process

This study focuses on a two stage fluid bed gasifier – plasma converter process developed by APP (Fig. 2). These key stages are incorporated into the overall process including: fuel preparation; fluid bed gasifier; plasma converter; gas cleaning; and power generation (APP, 2008). The thermal processing stages operate under slightly negative pressure. A nominal input feed of 90,000 tonnes p.a. RDF produces 16–21 MW$_e$ gross for export (APP, 2010a).

Untreated municipal or commercial waste is first mechanically processed in a materials recycling facility (MRF) at the front end. This is done to homogenise the material and remove moisture, recyclables (for example, metals and dense plastics) and reject materials (for example, oversize and inerts). A 150,000 tonnes input feed produces an output of ~90,000 tonnes RDF with a moisture content of 10–17%, 10–20% ash content and 12–16 MJ/kg calorific value (CV) (APP, 2010a).

The RDF is then metered into a bubbling fluidised bed (BFB) gasifier above a bed of coarse mullite sand. An updraft of steam and oxygen helps fluidise the bed – RDF mix, whilst supporting gasification reactions. The bed operates at ~850 °C. The volatile organic compounds and the fixed carbon content of the RDF are converted into a crude syngas contaminated with tarry particulates and solid chars.

The syngas passes from the top of the BFB into the plasma converter above its slag level. The centrifugal design of the converter
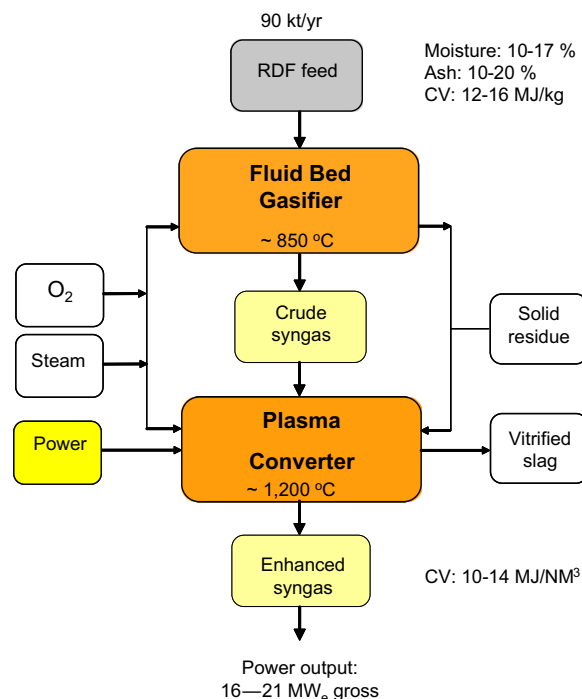

Fig. 2. APP process: Key stages and operating parameters.

encourages particulates to drop out of the syngas. Intense heat and ultraviolet (UV) radiation from a single carbon plasma electrode crack the complex organics (i.e. tars and chars) in the syngas. This is aided by a supply of oxygen and steam. At the same time, ash and inorganic material are retained in the molten slag. The fuel gas exits the converter at 1000–1200 °C comprising mostly of H_2, CO and CO_2.

The syngas is then cooled (from 1200 to 200 °C) using a steam boiler. The steam produced is used within the process and also to generate electricity using a steam turbine. From here the syngas passes through a gas cleaning system to remove particulates, vapour phase metals and acid gases (mostly, Cl⁻ and S⁻ based). This system includes a dry filter (incorporating a ceramic filter unit with sodium bicarbonate dosing) followed by a wet scrubber. The clean syngas (CV = 10 – 14 MJ/NM³) is dewatered before being combusted in a series of gas engines to produce electricity (APP, 2010a). The hot engine exhaust also generates steam for use in the process. Abatement equipment on the exhaust (including a catalytic converter) ensures that emissions comply with the European Industrial Emissions Directive (IED).

Depending on the RDF's CV, the output for the APP process is predicted to be in the range 0.95–1.27 MWh/t RDF with a net electrical efficiency (NEE) of 23–30%. With reference to operating data for incinerators in the UK, a range of 446–564 kWh/t is reported in terms of average and best performance respectively (Tolvik, 2011). This equates to an NEE of 17–22%, assuming a CV of 9.2 MJ/kg. The

outlook for modern European incinerators is similar, with electricity production at 550 kW/t on average (Santec, 2010).

APP's demonstration plant incorporates the main process units described above, including: a BFB; plasma converter; heat recovery unit; dry filter/scrubber; wet scrubber; and gas engine (Fig. 3). Depending on bulk density, heating value and other feed properties, the plant may handle 40–100 kg/h of RDF, supported by oxygen and steam gasifying media. The process is centrally controlled and monitored by way of a Supervisory Control and Data Acquisition (SCADA) computer interface. Syngas monitoring is performed inline using a Fourier Transform Infrared (FTIR) spectrometer (to identify gaseous oxides, N-species, CH-species, SO_2 and HCl) and infrared paramagnetic cell (to identify CO, CO_2, O_2).

2.2. Feed composition

2.2.1. Overview

As noted, a wide range of materials with an organic content may be suitable for gasification. The composition of the feedstock, and properties therein, has a major bearing on the performance of a gasifier or other thermal process in terms of plant availability, energy conversion efficiency and environmental emissions. Consequently, these factors are integral to the design (Kaiser, 1966; Kathiravale et al., 2003). This is especially true for a heterogeneous MSW-type feed. In turn, Niessen (2002) proposes that this is even more important for solid waste materials than for liquids or gases due to their tendency for high ash and the presence of contaminants.

An important aspect to understanding the gasifier feedstock is to break it down into its components – both on a macro 'material' level and subsequent 'micro' element level. Important material

Fig. 3. APP demonstration plant.

composition studies in the UK include Defra (2010) for England and WRAP (2010) for Wales. Focusing on the WRAP (2010) data, analysis was performed for this study to assess the impact of recycling on the biomass and energy content of the residual waste fraction (i.e. the fraction most relevant to thermal treatment) (Table 3). Total MSW recycling was increased from 37.4% (labelled the 'original') to 74.0% (labelled 'dry recyclables (DR) max'). Of interest, increasing the recycling rate (i.e. to DR max) appears to improve the residual waste's HV (i.e. from 10.3 to 12.2 MJ/kg). In agreement with US DOE (2007), this is due to a lower ratio of biomass to non-biomass materials.

Material composition data may be further refined, considering various aspects of proximate and ultimate analysis. The arising of various elements in the global MSW feed, including sulphur, will depend on the elemental content associated with each component material and in turn their relative arising in the global feed. The functionality and interaction of different elemental components is also important – influencing the partitioning and speciation during thermal processing (Section 2.2.2).

With regards to process design and simulation, the accuracy of the model output ultimately depends on the quality of input data as well as the model's own internal database (Section 2.3). Such proximate and ultimate analysis data may be obtained from lab analysis or from reported sources. There are, however, significant gaps in the data reported for MSW component materials (Chester et al., 2008). The most comprehensive data source identified for use in this study was that of UK DOE (1995).

2.2.2. Sulphur

It is reported that most feed-bound sulphur is released as H_2S under reducing gasification conditions, both for biomass (Kuramochi and Kawamoto, 2005) and coal (Álvarez-Rodríguez and Clemente-Jul, 2008; Jazbec et al., 2004; Nakazato et al., 2003). The release of sulphur compounds may lead to issues including equipment corrosion, turbine damage, catalyst deactivation or fuel cell damage. To prevent this, up and/or down-stream abatement techniques need to be employed.

Unless H_2S and any other sulphur compounds are removed from syngas, they will be converted to SO_2 during combustion. Sulphur dioxide in turn contributes to acid rain (often impacting long distances from source) along with more immediate process and occupational issues. In addition to a range of national and international agreements, the IED sets specific limits for SO_2, namely: daily average (50 mg/m^3); and half-hourly average (200 mg/m^3 (100%) and 50 mg/m^3 (97%)).

Owing to its heterogeneous and varying material content, MSW may present a range of sulphur concentrations (for example, 0.60–0.10 wt.% for RDF in Italy) (Yassin et al., 2009; Borgianni et al., 2002, respectively). Biomass also has a varied makeup, albeit to a lesser extent. In turn, its sulphur content tends to be lower (for example, 0.04–0.25 wt.%) (van der Drift et al., 2001). In contrast, coal has a more consistent composition, with a low to high sulphur content range depending on rank (for example, 0.3–5.0 wt.% (Jazbec et al., 2004)).

Information on other feed constituents is also important since these can interact and impact on sulphur emissions during thermal processing. For instance, during the gasification of biomass and other materials, the formation of halides and sulphides with metals (i.e. heavy, alakali and alkaline earth metals) can help reduce HCl and H_2S emissions (Kuramochi and Kawamoto, 2005).

The propensity of sulphur to be released and combined into different products during gasification also depends on its molecular form and association with constituents in the feed (i.e. its functionality). Not with standing, Zevenhoven et al. (2001) note that the inorganic content of biomass behaves in a very different manner to that of coal. It is also noted that inorganic elements may bind

Table 3
Residual MSW in Wales (2008 / 09)[a], original fraction and fraction after maximum recycling: Contribution of biomass and other to total GCV$_{ar}$.

Contribution	Original Residual Waste			Residual Waste after max DR[e]		
	Combustible Content [c]	Total GCV$_{ar}$[d]		Combustible Content	Total GCV$_{ar}$[d]	
	(wt.%)	(MJ/kg)	(%)	(wt.%)	(MJ/kg)	(%)
Biomass [b]	63.06	5.29	51.54	48.26	4.74	38.80
Other combustibles	21.65	4.97	48.46	33.59	7.48	61.20
Total	84.71	10.26	100.00	81.85	12.22	100.00

[a] Analysis based on composition data from WRAP (2010).
[b] Biomass content estimated as per the Environment Agency regulations (WRAP, 2010).
[c] Combustible content estimated for each material.
[d] Heating value (HV) calculations based on data in Tchobanoglous et al. (1993).
[e] Dry recyclables refers to both materials collected for recycling and materials for composting in an as received condition.

to the organic matrix of the fuel. This review indicates that research on sulphur functionality is lacking for biomass and MSW in particular. In contrast, there is a substantial body of work for coal including Khan (1989).

Research on MSW gasification in general is lacking (He et al., 2009). In this respect, up to quite recently experimental data on sulphur emissions during biomass gasification has also been limited (Kuramochi and Kawamoto, 2005). The same study found that nearly all feed-sulphur became H$_2$S during gasification. Using an equilibrium model, it was found that H$_2$S emissions were proportional to the sulphur content of the feed especially at high temperatures (1023–1123 K). At lower temperatures, this was less apparent, perhaps due to interaction with metal compounds (forming sulphides, for example). Once again, research on coal gasification is abundant in contrast, with H$_2$S being most prominent (~90%) (Jazbec et al., 2004). The organic sulphur content of coal strongly influences the sulphur content of the tar or gases (Khan, 1989). Pyritic sulphur, on the other hand, largely determines the sulphur content of char.

With regard to sulphur partitioning during gasification, research appears to be more developed for biomass than for MSW. As with other materials, the partitioning of sulphur (and other inorganic elements) depends on gasification stage, temperature and the association of fuel elements (Zevenhoven et al., 2001). However, as mentioned, behaviour in biomass is different to that in coal.

In addition to being aware of the sulphur content of a fuel, in order to predict partitioning and emissions, understanding the interaction and behaviour of other constituents is very important (Kuramochi and Kawamoto, 2005). For instance, the formation of halides and sulphides with heavy, alkali, and alkaline earth metals can reduce H$_2$S (and HCl) emissions. This process depends on temperature, therefore it is necessary to predict the phase distributions of metals and sulphur at various temperatures.

Given the abundance of research on coal, it is worth while noting where parallels may be drawn in relation to biomass and MSW. For instance, Jazbec et al. (2004) note that the extent of gasification (i.e. during devolatilisation) and in turn sulphur liberation depends on several parameters including coal type, heating rate, temperature, reactor configuration, bed height, pressure, and soak-time at the pyrolysis temperature (Khan, 1989). Additional variables include the form of sulphur in the feed (for example, inorganic versus organic), intimacy between minerals and the primary products of devolatilisation. It is also noted that the indigenous mineral content of the feed (particularly calcium, sodium, or iron compounds) may react and fix sulphur species within the solids during devolatilisation.

A range of different H$_2$S sorbent materials were identified during this review. Materials reported to be effective include calcite and olivine (Pecho et al., 2008), CaO and Fe$_2$O$_3$ (effective under mild pyrolysis conditions (Khan, 1989)). By far the most effective sorbents were limestone and dolomite. Calcined and fine grained limestone functioned well (Nakazato et al., 2003; Yrjas et al., 1996; Khan, 1989). However, dolomite in various forms (calcined, uncalcined and hydrated calcined) proved most versatile (Álvarez-Rodríguez and Clemente-Jul, 2008; Yrjas et al., 1996; Khan, 1989).

From the above review a number of ambiguities in the research base are apparent. Studies on coal gasification and sulphur are abundant. Biomass based work, however, is far less common. In turn, little if any research on MSW was identified. This includes the absence of reported knowledge with respect to sulphur partitioning and speciation. The functionality of sulphur in the different feedstocks follows a similar trend. The heterogeneous nature of MSW poses a particular quandary in this respect. Most of the research identified was also limited to a bench scale or computer simulation. Appropriate research based on pilot, demonstration or larger plant was not identified. The innovative basis of this study lies in addressing the above ambiguities in the context of APP's novel fluid bed gasifier – plasma converter technology.

2.3. Modelling

As mentioned, the partitioning of different species depends on gasification stage, temperature and association with other fuel elements amongst other factors. The conventional approach to predicting gasification emissions is based on the use of thermodynamic and/or kinetic models (Kuramochi and Kawamoto, 2005). Of the studies reviewed in relation to sulphur, three followed a thermodynamic approach (Kuramochi and Kawamoto, 2005; Delay et al., 2001; and Zevenhoven et al., 2001) and one both thermodynamic and kinetic (Jazbec et al., 2004).

Thermodynamic equilibrium calculation models may be used to predict the equilibrium composition (i.e. distributed between gas and solid phases) of multi-component reacting system across a range of temperatures and pressures (Kuramochi and Kawamoto, 2005). This is a common approach based on established thermodynamic principles (Zevenhoven et al., 2001). Equilibrium modelling considers the gasifier as an equilibrium reactor. This generates comprehensive information about the overall system as well as a first description on more specific complex areas. While this is useful when kinetic data is lacking, there are limitations since the approach assumes an infinite reaction time and perfect mixing. In practice, residence times may vary depending on individual constituents as well as plant operation and design. Reaction rates will also vary. Furthermore, mass transfer between phases can be slower than the reactions themselves.

Two equilibrium calculation methods are introduced by Kuramochi and Kawamoto (2005). The first involves mass balance calculation and equilibrium equations. The second, often referred to as the Gibbs Energy minimisation method, is based on the principle that the total Gibbs Energy of a system is at its lowest value when at equilibrium. This approach is believed to be more versatile and also more capable with respect computation.

The equilibrium calculations include the reactions expected between the elements associated with the feed material (Zevenhoven et al., 2001). It is noted that, prior to commencing any modelling work, it is necessary to decide which elements, species and phases are to be considered. Model performance and accuracy is strongly dependent on the quality of input data. Therefore, once thermodynamic data sources have been identified, these must be evaluated critically.

Commercially available software based on Gibbs energy minimisation includes FACT and HSC Chemistry (Kuramochi and Kawamoto, 2005; Delay et al., 2001). These can be used to investigate equilibrium gas chemistry or, in the case of Zevenhoven et al. (2001), ash chemistry amongst other phenomena.

3. Materials and methods

3.1. Background

With reference to the overall project aim (Section 1), the following section looks at estimating the equilibrium distribution of sulphur and other major species between the gas and solid phase at the fluid bed gasifier stage of the APP process. This approach is in line with work done by Kuramochi and Kawamoto (2005) and Delay et al. (2001). Findings are based on modelling performed by the authors using HSC Chemistry®5.1 (as referenced by Kuramochi and Kawamoto (2005) and Lohsoontorn et al. (2008)). As mentioned, thermodynamic equilibrium modelling provides a good approximation of complex systems (Zevenhoven et al., 2001).

For a given specified system, HSC will calculate its thermodynamic equilibrium composition based on Gibbs energy minimisation (Section 2.3). The software is supported by a thermochemical database containing enthalpy (H), entropy (S) and heat capacity (Cp) information for more than 1700 chemical compounds (HSC, 2002). This enables the simulation of chemical reactions and processes on a thermochemical basis. Amongst other things, the effects of different variables on the chemical system at equilibrium may be studied. So long as the inputs and system variables are specified, HSC can theoretically predict the resultant products for most chemical processes. There are limitations, however, since the HSC model does not account for the kinetics (i.e. rates) of chemical reactions nor nonideality of solutions.

3.2. Methodology

The model was set up by specifying the material inputs (including: feed composition in terms of its elemental and compound make up; and steam and oxygen addition) and fluid bed gasifier system variables. The input feed consists of RDF, the composition of which is presented in Table 4. A temperature range of 700–900 °C was chosen (i.e. in line with the fluid bed operating temperature), increasing at 50 °C intervals.

To begin with, a list including both the system input species (i.e. reactants) and proposed output species needs to be specified on the model's input interface. This includes the proposed phase distribution of species. The selection of output species draws from an understanding of gasification and thermodynamic principles, literature findings and plant experience in addition to the model's internal database.

An iterative approach was used to develop the species list. Initially the list was expanded to identify any other potentially viable species (in particular those associated with sulphur and/or chlorine). After running the simulation and reviewing the results, any insignificant species (i.e. 10^{-5} kmol) were removed. This resulted in a 'baseline' list, used again in later analyses.

Analysis was then performed in relation to sulphur. Using the baseline list as a datum, the sulphur content of the feed was adjusted ranging from a minimum of 0.001 kmol to a maximum 2.50 kmol. For each incremental step (labelled simulation ('sim') 1–9), the output data obtained was recorded for later analysis (Table 5). This approach is similar to that outlined by Kuramochi and Kawamoto (2005).

Table 4
Specification of the RDF feed to the fluid bed stage.

Ultimate analysis	(% w/w)	Proximate analysis	(% w/w)
C	43.0	Fixed carbon	11.6
H	5.6	Volatile matter	64.8
O	26.6	Moisture	11.5
N	0.61	Ash	12.1
S	0.25		
Cl	0.34		

Table 5
HSC input and output data: Sulphur species only, fluid bed stage, equilibrium composition at 800 °C.

	Sim 1	Sim 2	Sim 3	Sim 4	Sim 5	Sim6	Sim 7	Sim 8	Sim 9
	min S				baseline				max S
Input	kmol	kmol	kmol	Kmol	kmol	kmol	kmol	kmol	kmol
S-input	0.001	0.2	0.4	0.6	0.722	1.00	1.50	2	2.5
Output	mol.%	mol.%	mol.%	mol.%	mol.%	mol.%	mol.%	mol.%	mol.%
Gas phase									
S	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.02	0.03
COS(g)	0.00	0.00	0.00	0.00	0.00	0.01	0.04	0.07	0.09
H$_2$S(g)	0.00	0.00	0.01	0.02	0.04	0.22	1.23	2.14	2.90
Sub total	0.00	0.00	0.01	0.02	0.04	0.23	1.28	2.23	3.02
Solid phase									
CaS	0.00	0.00	0.00	0.00	0.01	0.03	0.18	0.31	0.42
NaS	0.01	0.05	0.15	0.43	0.80	4.20	21.71	34.59	42.68
FeS	0.00	0.01	0.02	0.05	0.10	0.58	3.20	5.39	7.06
K$_2$S	99.94	99.78	99.33	98.03	96.21	91.26	69.93	53.90	43.48
MgS	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
ZnS	0.00	0.00	0.01	0.02	0.05	0.25	1.14	1.53	1.62
Cu$_2$S	0.04	0.15	0.48	1.44	2.78	3.38	2.25	1.69	1.35
PbS	0.00	0.00	0.00	0.01	0.01	0.08	0.31	0.37	0.36
Sub total	100.00	100.00	99.99	99.98	99.96	99.77	98.72	97.77	96.98
Grand total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

4. Results and discussion

The output data from the above preliminary analysis has been arranged to focus on output sulphur species presented as mol% against the quantity of sulphur in the input feed.

Trends for the solid and gas phase remain largely consistent across the 700–900 °C temperature range (Fig. 4). Interestingly, the results indicate that sulphur species are more prominent in the solid phase, representing some 90% of the total across the temperature range. Although this is in agreement with APP plant experience, it contrasts with other researchers who specify that gaseous H_2S is the main sulphur species (APP, 2010b) (Section 2.2.2). Sodium and potassium are the main sulphur 'getters' – representing over 85% of the total across the range – with K_2S most prominent at lower input [S], replaced by NaS with increasing input [S]. All of the other solid phase species are less significant, the most prominent being FeS which peaks at 7.84%. Consequently, predicted gas phase sulphur (represented by S, COS and H_2S) is at a similarly low level.

On a logarithmic scale, it can be seen that most solid phase species trend consistently upwards with increasing temperature and input [S] (Fig. 5). Furthermore, as input [S] is increased, the influence of temperature appears to become less pronounced for species such as K_2S, NaS and FeS.

Sulphur species are again shown to be less prominent in the gas phase across the temperature range. Nonetheless, H_2S is prominent in the gas phase, with concentrations one or two orders of magnitude above COS or S, respectively. Temperature appears to have a strong influence, with species concentrations trending upwards consistently. A marked increase in species concentrations after Sim 6, H_2S in particular, may be attributed to a step rise in the input [S].

Contrasting the solid and gas phase species trends, temperature appears to have more influence over the gas phase species. This may be due to homogeneous reactions being more prevalent. There is also more 'noise' evident amongst the trends for the solid phase. The potential prevalence of heterogeneous reactions may help to explain this.

Given that output sulphur species consume just a fraction of the metals input, such reactions may be expected to continue beyond the operating range examined here. This will be assessed through further simulation, looking at a broader range of input [S] and temperatures. This and adjusting the metals content of the feedstock, along with other process variables (for example, varying the reducing conditions by adjusting oxygen and steam addition) also ties in with identifying conditions where H_2S may become prominent. With respect to the prominence of Na and K species, work is in progress to further clarify and validate this, paying attention to Ellingham diagrams and other thermodynamic guides. The influence of varying Na and K concentrations in addition to Si and Al (i.e. ash forming constituents) will also be examined, with reference to studies by Kuramochi and Kawamoto (2005) and Wei et al. (2004) amongst others. Examining the influence of different sulphur functionalities (for example, organic and inorganic species as opposed to elemental sulphur) is also of interest. The role played by chlorides is another area, given their propensity for metals. Similar analysis will be performed on the plasma converter stage.

As mentioned, the findings presented here are quite preliminary, with model results being indicative only. Further analysis in line with that mentioned above, including a sensitivity analysis, in addition to the use of real process data, will help provide validation. In this respect, work is in underway to perform a detailed sul-
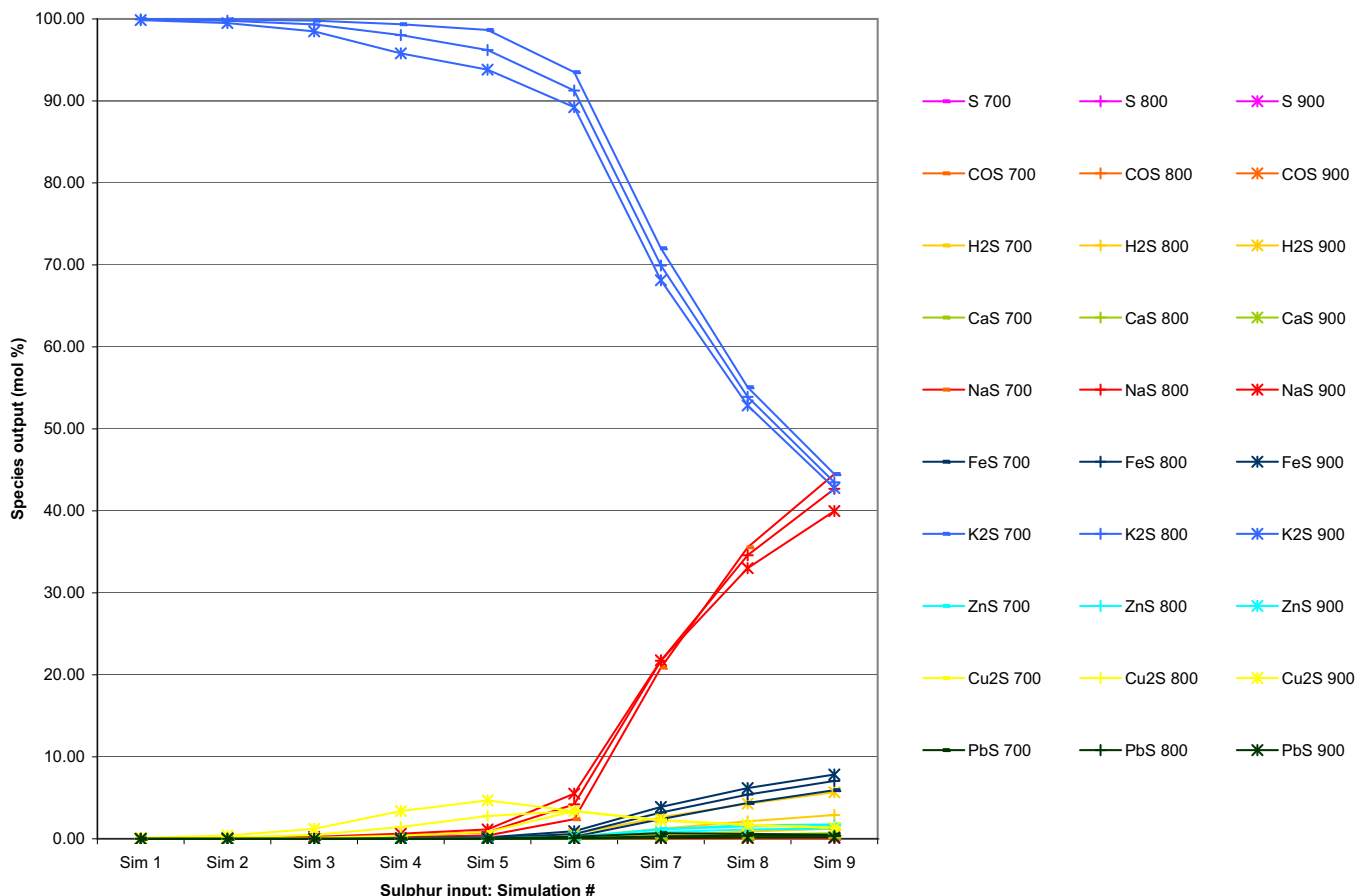

Fig. 4. HSC output data, fluid bed stage: Sulphur species only, equilibrium composition at 700–900 °C (mol%, ordinary scale).
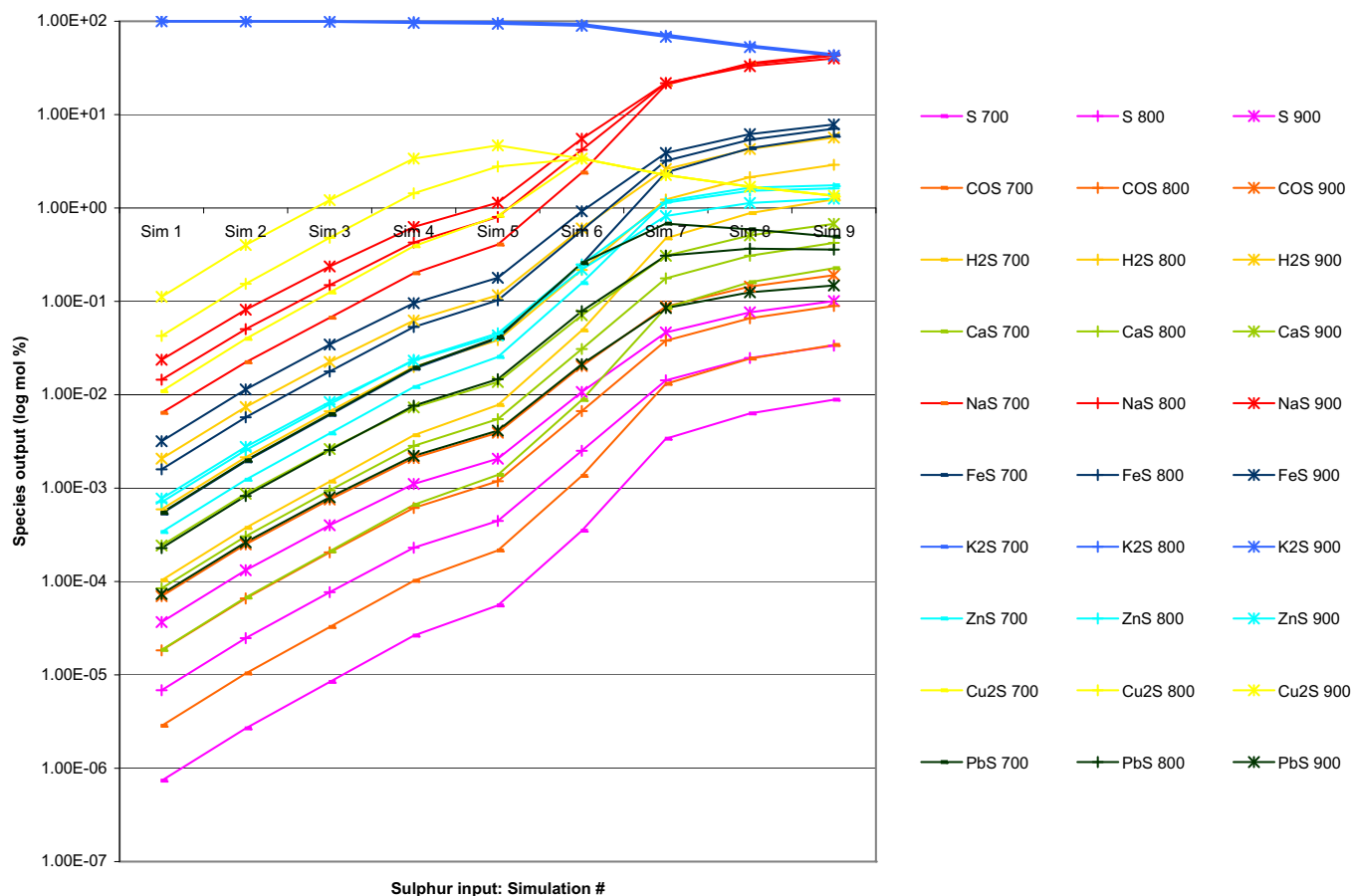
Fig. 5. HSC output data, fluid bed stage: Sulphur species only, equilibrium composition at 700–900 °C (mol%, logarithmic scale).

phur balance study (including phase distribution and speciation) on the APP demonstration plant.

A significant amount of work remains in order to understand the chemistry and mechanisms associated with sulphur (along with influential species such as chlorides and metals) in the fluid bed and plasma stages. This is being approached by three work routes, namely: plant/process; modelling; and other desk study. Plant/process work refers to experiments performed as well as process samples and data obtained from process runs. This includes physical analysis of the feedstock and collected samples. Modelling will progress building on existing HSC analysis. In turn, development of a more first principles based model is being considered. Plant data is important in this respect with regards to validation. 'Other desk study' includes understanding sulphur functionality in the feedstock along with analysis and ongoing literature review.

5. Conclusions

This paper introduces gasification and plasma principles with reference to an innovative two stage process generating energy from an MSW based feed. This informs the overall research aim to understand sulphur speciation and partitioning therein.

From the review it is apparent that gasification of solid waste has significant potential. Nonetheless, ambiguities in the knowledge base are quite evident. Most research is at lab scale or model based, with reports on MSW gasification, or the role of sulphur therein, lacking.

To gain an initial understanding of the process, thermodynamic analysis of the fluid bed gasification stage has been performed. Pre-

liminary model findings, supported by plant experience, indicate the prominence of solid phase sulphur species (as opposed to H_2S) – Na and K based species in particular. Work is underway to further investigate and validate this, with reference to phase diagrams, additional modelling and real process data.

This ties in with longer term plans to understand the chemistry and mechanisms associated with sulphur throughout the two stage fluid bed – plasma process. This is being approached by way of plant experiment and process data, thermodynamic modelling and ongoing desk study.

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