Performance analysis of RDF gasification in a two stage fluidized bed–plasma process

M. Materazzi [a,b], P. Lettieri [b,*], R. Taylor [a], C. Chapman [a,*]

[a] Advanced Plasma Power Ltd., Swindon, Wiltshire SN3 4DE, United Kingdom
[b] University College London, London WC1E 7JE, United Kingdom

ARTICLE INFO

ABSTRACT

The major technical problems faced by stand-alone fluidized bed gasifiers (FBG) for waste-to gas applications are intrinsically related to the composition and physical properties of waste materials, such as RDF. The high quantity of ash and volatile material in RDF can provide a decrease in thermal output, create high ash clinkering, and increase emission of tars and CO_2, thus affecting the operability for clean syngas generation at industrial scale. By contrast, a two-stage process which separates primary gasification and selective tar and ash conversion would be inherently more forgiving and stable. This can be achieved with the use of a separate plasma converter, which has been successfully used in conjunction with conventional thermal treatment units, for the ability to 'polish' the producer gas by organic contaminants and collect the inorganic fraction in a molten (and inert) state. This research focused on the performance analysis of a two-stage fluid bed gasification–plasma process to transform solid waste into clean syngas. Thermodynamic assessment using the two-stage equilibrium method was carried out to determine optimum conditions for the gasification of RDF and to understand the limitations and influence of the second stage on the process performance (gas heating value, cold gas efficiency, carbon conversion efficiency), along with other parameters. Comparison with a different thermal refining stage, i.e. thermal cracking (via partial oxidation) was also performed. The analysis is supported by experimental data from a pilot plant.

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1. Introduction

As global waste levels raise and fossil fuel and raw material reserves decline, the world is facing a growing resource crisis. A major task for global community in the next decades will be to develop means of securing dependable sources of renewable energy and also to greatly reduce the amount of materials obtained from virgin reserves. The combination of renewable energy requirements and diversion of materials from landfills has led to a focus on the use of waste materials as sources of renewable energy. In this context, there is considerable interest in new ways to dispose of waste using advanced thermal conversion technologies. Waste gasification, latest addition to Waste-to-Energy technologies, converts solid wastes into green electricity or clean gaseous fuel known as synthesis gas (or syngas). This promising technology has received increasing attention in the past two decades due to the growing demand for clean fuels and chemical feedstocks, as well as the need for reducing dependency on fossil fuels, lowering greenhouse gas emissions and disposing of existing wastes (Juniper, 2001; LAEC, 2009).

Most of the gasification systems from waste are based on high-temperature techniques that use oxygen as a source of heat or as partial oxidation agent. Oxygen-based gasification offers advantages over air-based gasification such as reduced capital costs or similar operating costs combined with the potential to use the higher calorific value syngas in high-efficiency power generation systems, greatly enhancing revenue creation potential (Chapman et al., 2014). Among all waste gasification technologies, fluidized bed reactors are the most promising, for a number of

reasons (Basu and Kaushal, 2009). In particular, the enhanced flow mixing between reactants, the nearly constant temperature and the great operating flexibility of fluidized bed reactors make it possible to utilize different types of feedstock, including biomass and solid wastes. These gasifiers usually work as "partial combustors", and a portion of the carbon present in the fuel is combusted to support pyrolysis and gasification reactions. Because of the relatively low temperature used to prevent agglomeration and sintering of ashes and bed material, the gas that is produced by a standard fluid bed gasifier (FBG) has tars and other condensable organic species that are technically difficult and costly to remove. Furthermore, the bottom ash/char that is generated in the gasifier or pyrolysis fluid bed reactor may contain high levels of carbon, heavy metals and organic pollutants which lower the conversion efficiency of the process and limit any secondary usage (Dayton et al., 1999). Nowadays, tar generation and ash disposal represent the strongest barrier for use of stand-alone FBGs for waste to syngas applications. *Allothermal* FBGs have been proven to decrease the amount of tar produced, while avoiding dilution of the syngas with products of combustion. Such processes make use of external heat sources (separate combustion chambers or plasma torches) to pyrolyse and crack the input material. Typical examples of FBGs combined with a combustion system are given by internally circulated fluidized beds, dual fluidized beds and heat pipe reformers (Xiao et al., 2010; Kern et al., 2013; Karellas et al., 2008). All these technologies are originally developed for operation on pure biomass. However, the translation of the systems to operation on waste is the issue which represents the most significant technical difficulty, and from this cascade particular concerns regarding the ability to achieve long term stable operation. These concerns arise out of the inherent design of the systems which do not seem well suited to heterogeneous feedstock in terms of morphology and chemistry particularly with a low fixed carbon, and high ash and tramp material levels typical of wastes. To date, there is limited publically available documented evidence of operation of these reactors on wastes. Vreugdenhil (2010) reports an alkali distribution assessment in allothermal FBG which covers straw and refuse derived fuel (RDF). However, the gasifier only operated successfully on a blend of 60 wt% RDF and 40 wt% beech wood (pellet) and not pure waste.

The use of plasma has increasingly been applied with pure waste treatment for its ability to completely decompose the input waste material into a tar-free synthetic gas and an inert, environmentally stable, vitreous material known as slag. The principal advantages that plasma offers to thermal conversion processes, besides the already mentioned tar/ash related issues absence, are a smaller installation size for a given waste throughput, and the use of electricity as energy source, characteristics which permit the technology to treat a wide range of heterogeneous and low calorific value materials including various hazardous waste, such as PCBs, medical waste, and low-level radioactive wastes (Kim et al., 2003; Nema and Ganeshprasad, 2002). Its efficient application in the treatment of general waste in a single stage is still under debate though, due to the power required to convert the solid waste to a gas. The relevant literature reports approximately 800 kW h of electricity consumed per ton of municipal solid waste (MSW), corresponding to approximately 2000 kW h of primary energy (assuming an average efficiency of 40% for electricity generation) which is close to the total energy contained in one ton of MSW (i.e. 2500 kW h) (Helsen and Bosmans, 2010). Only additions of combustion heat supplied by the waste feedstock or a fuel additive make the process suited to large waste streams.

These considerations led to the development of multiple-stage processes, where the plasma is used as a post-processing stage for conditioning the product streams generated from the primary gasification unit (e.g. FBG or rotary kiln). With this configuration,

the majority of the energy input to the process is derived from the controlled oxidation reactions of the solid fuel at the gasifiers, which greatly limits the plasma arc electrical power demand which constitutes only a minor fraction of the total energy content of the fuel to the process.

The absence of tars in the product gas resulting from plasma cracking at 1100–1200 °C may be due either to their decomposition, as they are unstable at that temperature, or due to plasma-enhanced conversion to CO and H_2 by reaction with oxygen radicals originating during plasma gasification. This process can be further enhanced by injecting a limited amount of CO_2 or O_2 as secondary streams into the second stage (Materazzi et al., 2014). As a result, in the process of the second stage plasma gasification as well as thermal cracking, tar and other condensable liquors are totally converted to gaseous products (Milne and Evans, 1998).

This study focused on the thermodynamic assets of using a two-stage process for RDF gasification over the conventional single fluid bed approach. The feedstock consists of a RDF produced from a combination of residual municipal, commercial and industrial wastes. The experimental analysis will identify the relevant parameters in the design and operation of a second stage plasma converter and compare single stage fluid beds with two-stage systems. The use of a thermal cracking stage in substitution of the plasma converter is also assessed, and comparison of the thermodynamic parameters for the two technologies will determine if there are meaningful differences among them.

2. Single vs two-stage gasification

2.1. RDF gasification steps

RDF contains high quantity of biodegradable material as well as plastics and provides solutions to the disposal of non-recyclable waste fractions, for it can be used as a direct substitute for primary fossil fuels in gasification. The physico-chemical processes taking place between the gasification agents and RDF, yielding syngas, are complex and are influenced by varying feed composition, process design and operating conditions. Nonetheless, the gasification process may be considered as a sequence of distinct conversion mechanisms (Table 1). Initially, RDF entering a gasifier is heated, to temperatures of 100–150 °C, and dried with heat received through heat transfer from other parts of the gasifier. The rate of drying depends upon the temperature, velocity of the gas, as well as the external surface area of the feed material (presented as pellets or shredded material), the internal diffusivity of moisture and

Table 1
Conversion steps and characteristic parameters in gasification (Basu and Kaushal, 2009).

	Primary conversion	Secondary conversion
Time (ms)	1–1000	1000–10000
Temperature (°C)	150–700	700–1200
Phenomena involved	• Rapid heating and drying • Pyrolysis • Comminution of solid particles • Partial oxidation of primary volatiles and char • Decomposition of primary tars • Water–gas reaction • Ash detachment	• Hydrogasification • Water–gas shift • CO_2 gasification • Tar cracking • Steam reforming • Boudouard reaction • Ash inertization (melting at $T > 1000$ °C)
Main products	Mixed oxygenates, olefins, aromatics, C_xH_y, CH_4, PAHs, H_2, CO, CO_2, H_2O, char + ash	H_2, CO, CO_2, H_2O, ash/slag

the nature of bonding of moisture to that material. For example, very rapid drying in RDF is promoted by the nature of the waste having higher levels of plastic, which tend to carry free moisture and dry easily; conversely, low vegetable and putrescible material has bound moisture and takes longer to dry. At this stage, no chemical reactions occur but the material, especially if rich in light plastics, may be subject to physical shrinkage and compression (Basu and Kaushal, 2009).

The next and first actual conversion step, is usually referred to as pyrolysis (or thermal devolatilization), wherein water vapor, organic liquids and non-condensable gases, such as CO, H_2, CO_2, are separated from the solid carbon (i.e. fixed carbon) and ash content of the fuel. The vapor/liquid product comprises mostly of polyaromatic hydrocarbons (PAHs) and tar (i.e. dark, oily, viscous material, consisting mainly of heavy organic and mixed oxygenates). Subsequently, the volatiles and char undergo a second gasification step and they modify their composition due to the occurrence of several reactions becoming the final syngas. A further stage (sometimes referred to as tertiary conversion) may be identified in syngas upgrading at high temperatures due to hydrocarbons cracking (Milne and Evans, 1998). Most of these reactions are endothermic (e.g. steam reforming, hydrogasification, etc.) and require a consistent amount of energy to proceed. In *autothermal* reactors, this quantity of energy comes from the exothermic oxidative reactions which occur simultaneously.

The distinction between primary and secondary conversion is based on the different times of conversion of the various processes. Experimental studies have shown that as a result of the rapid heating of the fuel, 90% of devolatilization takes place in a matter of milliseconds, whereas the reminder of gasification processes (mainly heterogeneous reactions) take one or two orders of magnitude longer time (Gomez-Barea et al., 2010). In this sense, char gasification is the most important and critical of all reactions. Though char from RDF usually constitutes a minor fraction of the fuel, its conversion kinetics has a major effect on the performance of a gasifier, for it is the slowest of conversion processes (Gomez-Barea et al., 2010; Timmer, 2008; Higman and van der Burgt, 2008). In fact, due to the porous nature of char, it is not always possible to achieve complete chemical control of the reaction because the diffusion within the pores limits the overall rate of reaction. When this happens, both processes, chemical reaction and pore diffusion, exert an influence on the progress of reaction, which in turn limits the conversion into valuable syngas. The extent of diffusion resistance can be reduced by properly reducing the particle diameter (to less than 1 mm) and/or by increasing the process temperature, as it is done for example in entrained flow gasification. However, the difficulty in pulverized the feedstock makes this technology very unsuitable for general waste processing (Ciferno and Marano, 2002). From this general concept originates the idea of dividing the gasification process in two different reactor design arrangements, namely 'single-stage' and 'multi-stage' groups.

2.2. Single stage FBG process

Fluid bed systems are the most employed in single stage processes for their homogeneous temperature, good flow mixing inside the reactor, rapid heating of the feedstock, and the possibility of including catalyst in the bed inventory to enhance the reforming reactions (Arena, 2012). The expanded bed creates a large mass of hot material that is able to absorb and mitigate any fluctuation in fuel conditions. This "flywheel effect" is better suited to minimize spikes in emissions due to the wide fuel variability when working with RDF, since small differences in fractions of certain 'key components', plastics in particular, may cause relevant changes in the gasification product yields.

The aim of a 'single-stage' FBG is to convert organic substances entirely in one reactor. Depending on the type of feeding, the solid fuel is injected into or onto the heated fluidized particles, together with oxygen, which is delivered by a fan (or blower) through the distributor plate and upwards through the bed particles. Steam can also be added to the process to aid conversion. The high levels of volatiles, especially plastics in RDF are likely to lead to rapid devolatilisation on contact with the hot bed material. As the RDF particles devolatize, mixed oxygenates and other volatiles undergo gas-phase reaction with the most reactive species in the ambient gas, that is, oxygen. Thus, it is the oxygen that supplies the required heat by reacting with the reactive volatiles (Albal et al., 1989). The conversion of char and tar in FBGs relies on a number of physical conditions including temperature, heating rate, residence time and degree of dispersion of the particles in the bed. The RDF conversion scheme is presented in Fig. 1, where it is shown the transition as a function of process temperature from primary products to the ideal clean syngas.

Most RDFs are characterized by high moisture and volatile content, and a porous-fragile structure (Ravelli et al., 2008). These features reflect the propensity of such fuel to give rise to large quantities of tars evolved and a multitude of fine fragments of carbon and fly-ash particles. Because of high reactivity, the fine char and tars conversion occurs mostly via thermal cracking and direct combustion, and are thermodynamically favoured by high temperature. Besides, raising the temperature to certain levels generally enhances the kinetics of slow reactions, producing higher yields of synthesis gas. Temperature in autothermal FBGs is controlled by the oxidant flow which sustains the exothermic oxidation reactions. However, when the optimal equivalence ratio (the actual oxygen fuel ratio/the oxygen fuel ratio for complete combustion) is exceeded, more fuel gas is burned to CO_2 and H_2O and the heat release increases at the cost of product gas, lowering the chemical energy in the gas. This effect is more evident when high quantities of moisture and ash are present in the initial RDF and the oxidant supply rate must be enhanced to generate sufficient heat to sustain the gasification reaction. Furthermore, working at high temperatures increases the melting danger of various mineral phases in the system, and promotes coalescence of solid particles. Alkali-induced agglomeration and defluidization of the bed may cause severe operational problems and can be detrimental to the overall process. For these technical constraints, FBGs tend to produce a syngas containing high levels of condensable organics and gaseous hydrocarbon species which can preclude the direct use of syngas in high-efficiency power generation equipment. The use of catalysts *in situ* (as FBG bed additives) to reduce tar content has been reported by many researchers (Bridgwater, 1994; Corella et al., 2002; Rapagna et al., 2000; Arena and Di Gregorio, 2014), although problems still persist. Dolomite, for example, is a soft material and hence gets easily eroded, thus producing problems of carry-over of fines (Milne and Evans, 1998). Moreover, the extent of tar reduction that can be attained by this method is limited by the high level of ash contained in RDF, which dilute the efficacy of the added catalyst. Much effort has been expended on developing technologies to remove these problematic tars, including physical removal, partial oxidation and chemical adsorption (Devi et al., 2003). However, the method must be efficient in terms of tar removal, economically feasible, environmentally acceptable, but more importantly, it should not affect the formation of useful gaseous products (i.e. CO and H_2). As such, the ideal process should specifically aim at the efficient conversion of carbon content in the gasification process itself, rather than remove tar and char from the gas with consequent loss of potential valuable syngas. Decomposition of tars, via additional reforming stages or thermal/catalytic cracking, is therefore a better alternative when compared to other removal methods based on condensation or
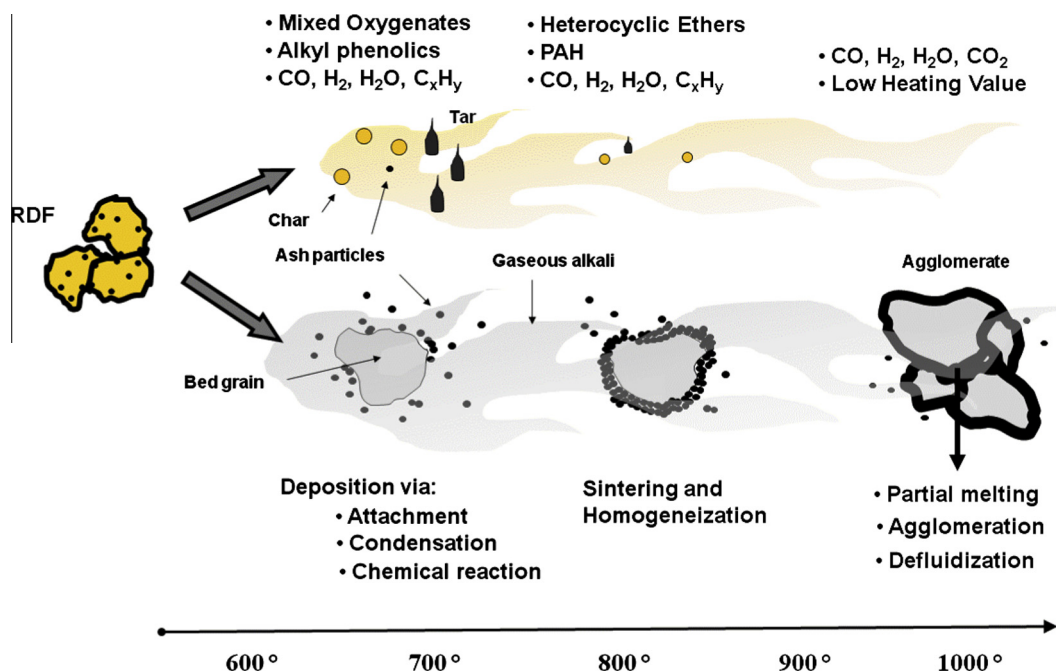
Fig. 1. RDF maturation scheme and influence of temperature change in a single stage FBG.

filtration. On the other hand, the syngas produced by single-stage FBG can be used 'as it is' only if the requirements placed on product gas quality are low (e.g. syngas combustion, etc.).

2.3. Two stage FBG–plasma process

The two-stage concept design physically separates the principal unit operations of pyrolysis-preliminary gasification zone from the final conversion zone, involving two different levels of heat intakes. Most of this type of advanced thermal processes eliminates char and tar gasification as a limiting process steps and, consequently, the efficiency of the process depends on the ability of the system to provide longer residence time whilst making a more efficient use of the oxygen required to increase the temperature. The influence of gasification temperature and residence time on a typical tar component is illustrated in Fig. 2, where naphthalene cracking is simulated in a 1-D thermal stage.

From Fig. 2 it is evident the major role that temperature and residence time have to control the conversion of heavy PAH
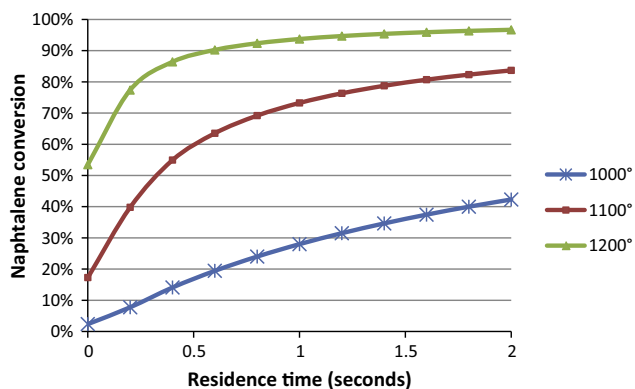

Fig. 2. Reactivity of Naphthalene for thermal conversion in a plug flog reactor. Curves are calculated from the kinetic data of Jess (1996) with a constant volume rate of producer gas.

compounds after their formation in the FBG. With increasing these two factors, tars are increasingly converted in consecutive reactions to non condensable gases. The result is a higher yield of synthesis gas than is possible by single stage partial oxidation. Most such processes have been based on two sequential reactors where this can be achieved more easily. Furthermore, the separation and control of the unit operations allow independent optimization of each operation (Materazzi et al., 2013).

A separate thermal cracking stage, which uses oxygen to reach high temperatures, has been previously used associated with FBGs, to reduce tar content and accelerate char reactions. Examples are found in the Thermoselect and Noell dust cloud gasification processes and in the large-scale Creusot-Loire two-stage plant, which was built in the mid-1980s and is still in use (Vreugdenhil and Zwart, 2009). New advanced technologies have been deployed for handling the post-FBG fumes, including thermal plasma, microwaves, etc. (Fourcault et al., 2010; Xie et al., 2014). Most of them, as it is the case for thermal plasma, also operate at very high temperatures. The main benefits are that almost complete tar conversion is achieved (the tar contents at the output of a gasification stage by thermal plasma are 1000 time less than that obtained by autothermal fluidized bed) and that temperature, speed of the process and rate of heat transfer can be controlled to change the composition of the products. In particular, the water gas shift reaction, which drives the hydrogen to carbon monoxide ratio of the syngas, can be controlled via a modification of the external energy into the reaction system. These results can be very interesting for applications of synthesis gas in second generation biofuel that require tar concentration below 0.1 mg m^{-3} and high content of H_2 (Bosmans et al., 2013).

Advanced Plasma Power (UK) developed a two stage process (the Gasplasma process) which combines fluid bed gasification with plasma technology (Fig. 3).

The first stage is a bubbling fluidized bed gasifier operated in temperature range between 650° and 800 °C, where the intense gas/solids contacting ensures the high heat transfer and reaction rates required to efficiently gasify the waste fuel. The raw syngas produced is normally laden with solid, condensable and gaseous
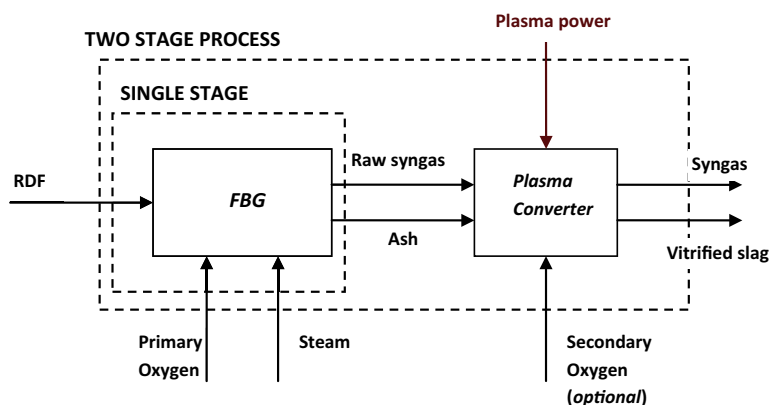
Fig. 3. Schematic of a two-stage fluid bed–plasma thermal process (Materazzi et al., 2013).

contaminants which preclude any practical use in modern energy production devices. The second stage is a direct current (DC) plasma converter that 'polishes' the producer gas by organic contaminants and collects the inorganic fraction in a molten (and inert) slag. This slag is formed by the melting ash particles that continuously separate from the gas stream. Additional solids (oversize material) from the FBG bottom ash may be fed into the furnace to form more slag. Unlike some other gasification technologies, there is no need of intermediate fuel gas cleanup between the gasifier and the ash melting plasma converter. The plasma power is controlled to provide a uniform syngas temperature (~1200 °C) and destruction of the residual tars and chars contained within the crude syngas. Downstream of the plasma converter, the syngas can be directed straight to a solid oxide fuel cell (SOFC) stack for power generation, or cooled to around 200 °C in a steam boiler prior to cleaning treatment to remove any residual particulates and acid gas contaminants. The refined gas can be then used for power generation (gas engines or gas turbines), for conversion to a liquid fuel, or used as a chemical precursor.

The main advantage of coupling FBG and plasma technologies is that the oxidant addition rate and power input in the two-stage process can be controlled independently while, unlike single stage FBGs, the gasification stability is not dependent on the gas evolved from the fuel itself. The energy input from plasma is readily controllable and (unlike oxidizing systems) is independent of the process chemistry, generating low off-gas volumes, reducing the size, complexity and the associated capital and operating cost of the downstream gas cleaning equipment and rendering the process flexible to changes in the RDF characteristics, typical of waste materials (Bosmans et al., 2013). The tar and ash removal by plasma methods is one of the most concern topics for current scientific research and numerous treatment methods regularly emerge from the scientific community and are reported to be very effective in tar reduction and ash disposal but still need to be optimized to be economically viable and used industrially.

3. Process modelling and validation

3.1. Equilibrium approach

Modelling a two-stage plasma assisted process can provide guidance on the optimization of the gasification parameters, so that one can find the best operation conditions between the two stages. At this level of analysis, the process is treated from a purely thermodynamic point of view, and therefore the results are applicable to both stages, namely, single stage FBG and plasma converter. For a given set of inlet conditions (feed composition and

oxidant flowrates), the exit conditions are computed assuming thermodynamic equilibrium. Although a literature analysis has shown that, generally, equilibrium models fail in matching experimental results from FBGs, where the reactor temperature is below 800 °C, these models give good correlation at elevated temperatures (above 1000 °C) that occur on advanced thermal processes, yielding predictions in close accord with experimental observation (Materazzi et al., 2013). Furthermore, the synergy between high operating temperature and long residence time in a two-stage process makes the system suitable for equilibrium analysis. The results here presented are derived from the two-stage equilibrium model reported in a previously published paper (Materazzi et al., 2013).

Conditions here vary essentially for the additional term in the energy balance, due to the plasma heating effect, and the secondary oxygen feed, which both increase the sensible heat contained in the product gas. This latter case is useful to compare results between the plasma converter and a generic thermal cracker stage, where only oxygen is used to provide the heat. The following assumptions are used to validate the model:

– The material properties like temperature (of gas phase and solid phase), gas composition and solid composition in each stage is expressed by "mean" values, which are calculated from the mass and energy balance.
– The plasma field does not affect either the rates of reactions, or the basic pathways of a chemical mechanism that would be observed in a generic thermal cracking process.
– The energy input in the plasma converter increases with its throughput, which is proportional to the cube of the reactor diameter. The heat loss by sidewall heat fluxes are dominated by radiation from the hot, molten bath, which is proportional to the square of the diameter. The energy duty of the plasma converter is, therefore, strongly scale dependant.
– Oversize material generated within the bed is fed to the plasma converter – diversion of this material would significantly reduce parasitic load in the second stage (either in plasma or thermal cracking mode).
– The temperature of slag flowing out of the furnace is calculated from energy balance by setting an appropriate temperature difference between the gas and slag of approximately 300 °C. No chemical reaction was considered in the melting process.

3.2. Experimental apparatus and materials

In order to validate the simulation results, two different RDF gasification experimental data from a previously published work

(Materazzi et al., 2014) were used. The prepared waste used for the experiments (described in Table 2) came from a number of waste treatment facilities in floc form, in a density range of 150–250 kg/m^3 and particle size between 10 and 25 mm.

Table 2 presents the experimentally derived proximate analysis (wet basis), ultimate analysis (wet basis) gross calorific value (GCV) and net calorific value (NCV) of two wastes used. In Case 2, the RDF is prepared from blends of 50% industrial waste and 50% municipal solid waste (MSW), whereas in Case 1 it is prepared from MSW only. The tests were performed in the APP demonstration plant in Swindon (UK), which is a reduced capacity version of a commercial fluid bed–plasma plant. It comprises a FBG designed for steam/oxygen gasification closely coupled to a single carbon electrode plasma converter (PC), as shown in Fig. 4.

The waste feed was metered into the FBG of mullite sand under controlled conditions, using a variable speed screw feeder at rates of 40–60 kg/h. The pilot DC plasma converter can operate at currents between 600 A and 1000 A and arc powers of 50–250 kW. The crude syngas produced in the FBG enters the side of the converter chamber above the slag level and circulates around the periphery of the chamber allowing the gas to increase in temperature (~1200 °C) while receiving maximum exposure to the intense ultra violet light from the plasma arc, aiding cracking of tar substances. In addition, the converter is arranged in such a way as to capture the particulate materials entrained in the gas flow from the FBG and convert these into slag, which is tapped periodically from the base of the PC. Downstream of the PC, the syngas is cooled down to below 200 °C in a steam boiler prior to a very basic treatment to remove any residual particulates and acid gas contaminants (mostly, HCl and H$_2$S). This includes a dry filter (incorporating a ceramic filter unit with sodium bicarbonate dosing and activated carbon) followed by a wet scrubber. In the demonstration plant, the refined gas (LHV = 10–14 MJ/N m^3) is directed to a gas engine for production of power before the oxidized gases are released to atmosphere. For the purpose of this study, the syngas composition was continuously measured along the plant using a Gasmet Fourier Transform Infra-Red (FTIR) Analyser, supplied by Quantitech. The magnitude of the error associated with the measurement of the gas composition is below 1%. Additional CO/CO$_2$ IR monitoring using is undertaken utilizing a XEntra 4210 analyser provided by Servomex (Crowborough, UK). The calorific value of the gas and its Wobbe index is monitored using a CWD 2005 Calorimeter supplied by Union (Karlsruhe, Germany). Near the end of the trials, about 65 kg of slag (corresponding to approximately 12 h of operation) were tapped from the plasma converter, and later sampled in order to assess the mass accumulated and its composition.

The full and more detailed description of the apparatus and plant operation for this test, as well as slag characterization and material recovery description, have been already published (Materazzi et al., 2014, 2015a) and not reported in this paper.

4. Results and discussion

4.1. Gas composition

Fig. 5 shows the comparison between experimental and model predicted gas compositions for some of the modelled species. A compatibility test with the water gas shift (WGS) equilibrium at 1200 °C was also performed for the second stage, i.e. plasma converter. The only components present at concentrations higher than 10^{-4} mol% at equilibrium beyond 700 °C are CO, CO$_2$, CH$_4$, H$_2$, N$_2$, and H$_2$O. For the sake of simplicity, all the hydrocarbons (including methane and residual tar components) measured data were enclosed in the label VOC (Volatile Organic Carbon).

As noted in previous works, the gas stream exiting the single FBG shows a marked divergence from the predicted thermodynamic equilibrium conditions, whereas a very satisfactory agreement is found for the 2-stage process (Materazzi et al., 2014, 2013). The reason for the discrepancy between the observed and predicted gas composition results on the first stage is mainly attributed to the unsuccessful estimation of hydrocarbon content by the model. The experimental gasifier exit gas composition revealed that up to ~11% methane and other volatile organics were present in the measured data, while almost no organic carbon presence was detected downstream the PC (Table 3). This is due to the ability of the plasma to effectively crack and reform tars and VOC compounds, as largely reported in the published literature (Materazzi et al., 2014, 2015b).

Of relevance, the measured steam, and CO$_2$ content is also very high in the FBG. The reason for this can be reasonably linked with the feedstock nature and composition, and the complex gasification dynamic within the fluid bed gasifier. As stated in Section 2.2, the FBG system is autothermal, in the sense that it usually relies on a fraction of the input char, being 'fixed carbon', that reacts with the oxygen through the bed and provides sufficient heat to sustain the endothermic reactions that produce H$_2$ and CO. However, reactor operations resulting in lack of contact between char/oxygen and an unfavorable consumption of oxygen by the devolatilisation gases are frequently observed in large scale FBGs (Gómez-Barea and Leckner, 2010). These issues are particularly exacerbated when operating on RDF, due to the much lower fixed carbon content and much higher volatile content compared to other fuels, such as biomass or coal. Crucially, the higher levels of volatiles reduce the delivery of 'fuel' char into the bed, and more devolatilised products, in which tar is the less reactive, react with oxygen producing CO$_2$ and H$_2$O. This effect is even more evident when high quantities of moisture and ash are present in the feedstock material (Case 2) and the oxidant supply rate must be enhanced to generate sufficient heat to sustain the gasification reaction.

On the contrary, the syngas from the plasma converter appears to be much richer in the primary syngas constituents (i.e. H$_2$ and CO). Such shift in gas composition is strongly indicative of increasingly favorable conditions for the water gas shift (WGS) reaction in the plasma converter, in accordance with:

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad (WGS)$$
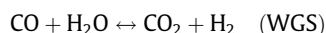
The good matching between the model and WGS predictions out of the two-stage process confirms the dominance of the latter in determining the gas composition at high temperatures.

Table 2
Proximate and ultimate analyses of solid wastes used (as received).

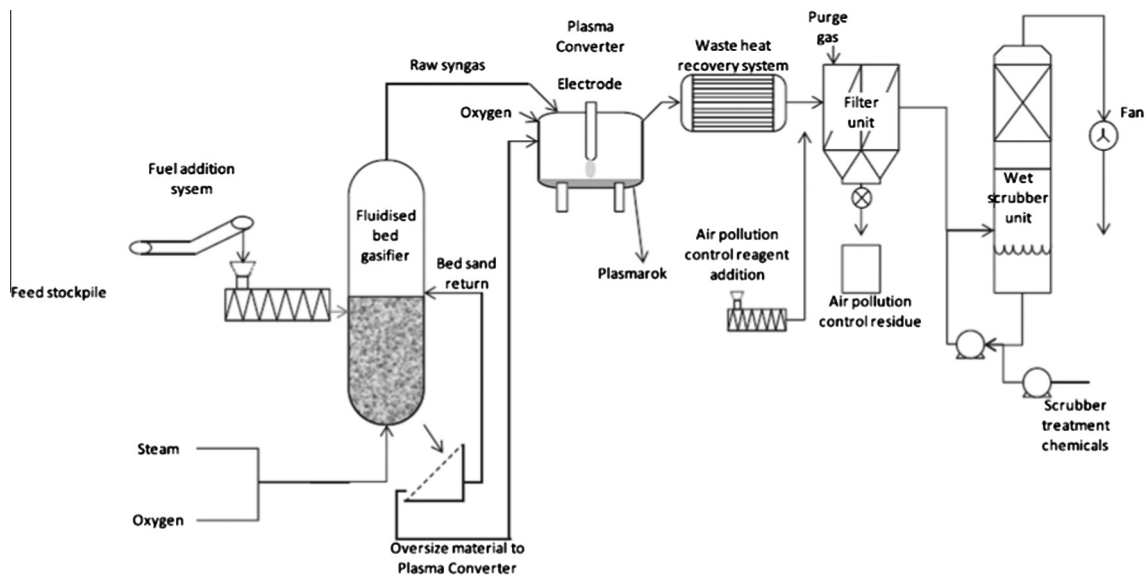|	Case 1	Case 2
Description		
Proximate analysis, % (w/w)		
Fixed carbon	6.4	12.2
Volatile matter	59.6	50.2
Ash	19.1	23.2
Moisture	14.9	14.4
Ultimate analysis, % (w/w)		
C	41.0	47.0
H	5.7	6.3
O	17.5	6.9
N	1.2	1.7
S	0.2	0.1
Cl	0.4	0.3
NCV, MJ/kg (dry basis)	19.99	24.18
GCV, MJ/kg (dry basis)	21.47	25.80

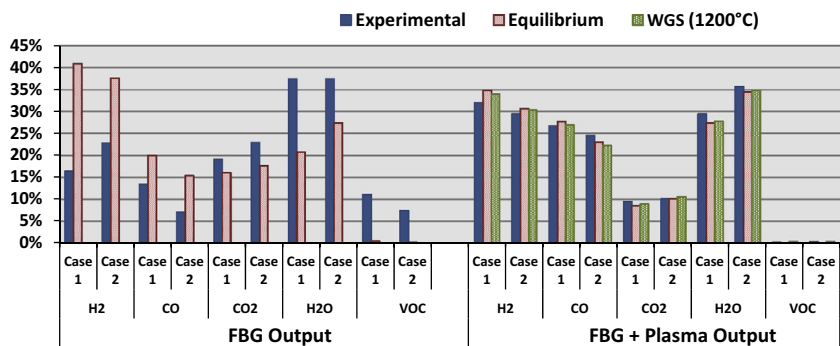**Fig. 4.** Schematic of the Gasplasma pilot plant.

Fig. 5. Comparison of molar gas composition predicted by the equilibrium model with experiment data from FBG gasifier (left); the equilibrium and Water Gas Shift equilibrium models with experiment data from FBG + Plasma converter (right).

Table 3
Comparison between experimental values detected pre and post-plasma, along with equilibrium model predictions for Case 1 RDF (Materazzi et al., 2014).

		FBG	FBG + PC		Conversion[*] (%)
		Experimental	Experimental	Theoretical	
VOCs					
Methane	vol%	11.15	0.15	0.00	98.0
Acetylene	ppmv	680	36.9	0.00	95.0
Ethylene	ppmv	1100	52.6	0.00	95.0
Naphthalene	ppmv	1000	52	0.00	95.0
Toluene	ppmv	21,000	130	0.00	99.9
Benzene	ppmv	12,000	13.22	0.00	99.9
Tars					
Phenol	mg/Nm^3	31.875	<0.625	–	>98.04
3/4-Methylphenol	mg/Nm^3	17.5	<0.625	–	>96.43
2,4-Dimethylphenol	mg/Nm^3	0.6875	<0.0625	–	>90.91
Acenaphthylene	mg/Nm^3	17.5	<2.625	–	>85.00
Acenaphthene	mg/Nm^3	0.875	<0.0625	–	>92.86
Dibenzofuran	mg/Nm^3	0.875	<0.0625	–	>92.86
fluorene	mg/Nm^3	6.875	<0.0625	–	>99.09
Phenanthrene	mg/Nm^3	19.375	<3.0625	–	>84.19
Anthracene	mg/Nm^3	6	<0.8125	–	>86.46
Pyrene	mg/Nm^3	13.75	<1.5	–	>89.09

[*] Based on experimental values.

4.2. Carbon conversion efficiency

The suitability of the examined model relies on the premise that the first stage operates beyond the carbon boundary point, i.e. 100% of solid carbon is completely gasified (Materazzi et al., 2013). In reality, the conversion of char, whose kinetic represents the rate limiting step of gasification processes, is related to the effective time of exposure with the hot gas, which in turn depends on the local conditions in the gasification stage. Although in a bubbling fluidized bed, flow mixing is generally highly favored, entrainment of finer char particles during the first stage may be severe, thus limiting the carbon conversion efficiency (CCE). This can be determined from the following equation, in which the total carbon content of the gas resulting from the gasification reaction is given as a fraction of the total carbon content of the RDF used in the process:

$$\mathrm{CCE} = \frac{\textit{Sum of mass of carbon contained in the gas phase components}}{\textit{Mass of fuel fed to system} \times \textit{Carbon content of feed}}$$
$$= \frac{\sum_i M_i \times C_{\mathrm{gas},i}}{M_{\mathrm{RDF}} \times C_{\mathrm{RDF}}}$$

where $C_{\mathrm{gas},i}$ is the carbon content of the ith gas component, and C_{RDF} is the carbon content of RDF.

Waste gasification studies have shown that relatively high unburnt carbon and hydrocarbon contents may be found in the ash residues, limiting to some extent the carbon conversion efficiency (Wu et al., 2014). For example, a carbon conversion efficiency of 80–92% is reported for MSW gasification in a FBG operating at 700–800 °C (Kwon et al., 2010). This is usually expressed by a loss on ignition index (LOI) in the ashes as high as 25% (dry basis wt%) and Total Organic Carbon (TOC) of 3–5%, indicating that a significant portion of carbon is retained in the solid residues, or lost with tars emission (Wu et al., 2014). The second stage plays a critical role in this sense; the furnace geometry is intended to produce a slow cyclonic action to avoid short circuiting of particles, which receive maximum exposure to the intense ultra violet light within the converter. Therefore, carbon associated with fly ash (fine char) and bottom ash fractions (coarse char) is recovered within the second stage, where ash components are vitrified releasing bound carbon, which reacts to produce further calorific syngas components, leading to high CCE. The main indicators for combustible and unburned carbon in the slag samples, along with the carbon conversion efficiencies of the overall process, are reported in Table 4.

Testing of the slag samples against organic parameters showed near zero values, being in compliance with model predictions. Total Organic Carbon (TOC) was below 1% in weight in both samples, and loss on ignition indexes were below detection limits. As stated before, these very low values are due to the combination of high temperature, turbulence, and residence time attained in the plasma converter, which results in the conversion of residual carbon to gas-phase carbon-containing species, e.g. CO and CO_2. For the two RDF materials considered in this study, carbon conversion efficiency is seemingly independent of the feed type, with both efficiencies higher than 96%.

4.3. Energy conversion efficiency

The Cold Gas Energy Conversion Efficiency (ECE) can be defined as the ratio of the energy contained within the gaseous product of the gasification reaction to the energy content of the fuel added to the system. Thus,

$$\mathrm{ECE} = \frac{\textit{Sum of calorific contents of gas phase components}}{\textit{Calorific content of the fuel fed to the system}}$$
$$= \frac{\sum_i M_i \times \mathrm{LHV}_i}{M_{\mathrm{RDF}} \times \mathrm{NCV}_{\mathrm{RDF}}}$$

where M_i is the mass flow rate of the ith gas component, and LHV_i is the net calorific value of the ith gas component. ECE values for the two cases are reported in Table 5, along with CGE_m (see Section 4.3), CO/CO_2 and H_2/CO ratios and heating values of the clean syngas.

While using a fixed energy input rate to the process of 1000 MJ/h (a figure equating to around 40–60 kg/h of feed input in the demonstration plant) and using the different feeds reported in Table 2, energy conversion efficiencies of 85–89.2% were predicted, in good agreement with measured values. These values compare well with published efficiencies for RDF gasification of 73% (Rao et al., 2004; Mamphweli and Meyer, 2010). Furthermore, the clean gas (especially in Case 2) has a very high quantity of H_2 with respect to other components. Therefore, it is particularly suitable for use in energy systems and as a chemical or biochemical precursor for the production of chemical substances and liquid fuels (Ciferno and Marano, 2002).

Of interest, the difference in syngas quality between Case 1 and Case 2 is not very significant despite the different residual ash (inert) loading of the feed. In fact, in a single stage FBG, increasing ash load normally reduces energy conversion efficiency. This is due to the need for additional oxygen to raise the temperature of the increasing ash materials retained in the fluidized bed to the system operating temperature. Whilst some of this oxygen would be consumed by oxidation of ash components, the vast majority would be used for combustion of feed to produce H_2O and CO_2 which do not contribute to the syngas calorific value. However, this approach does not hold true for a two-stage approach, where a variation in RDF with different moisture/ash loading does not necessarily require adjustment of process oxygen to achieve desired bed temperature, since the conversion can be completed in the second stage by the aid of the plasma.

4.4. Cold gas efficiency

In order to evaluate whether the higher flexibility in the FBG positively compensates for the plasma power demand in the

Table 4
Residual carbon analysis for Case 1 and Case 2 slag samples (Materazzi et al., 2014).

	Experimental					Theoretical
	DOC mg/kg	TDS mg/kg	TOC w/w%	LOI %	CCE %	CCE %
Case 1	3.8	50	<0.98	<0.2	96.9	100
Case 2	8.8	86	<0.66	<0.2	97.4	100

Table 5
Comparison of experimental and model predicted performance parameters.

	Case 1		Case 2	
	Experimental	Theoretical	Experimental	Theoretical
Process conditions				
FBG temperature, °C	770	765	720	710
PC temperature, °C	1200	1200	1250	1250
ER	0.37	0.37	0.35	0.35
Clean syngas[a]				
CO/CO_2	1.61	1.56	1.71	1.75
H_2/CO	1.62	1.55	2.3	2.38
LHV, MJ/kg	11.9	11.6	10.7	11
ECE, %	86.2	85	88.9	89.2
$CGEm$, %	78.2	82.2	77.3	81.9

[a] Values refer to clean syngas (Argon free), as received from gas cleaning section.

second stage, the relationship among plasma power and heating value variation should be considered at the same time.

One particular factor that has a significant effect on the balance between the plasma requirements and the heat lost is the effect of scale-up from pilot scale to full industrial size plant. In fact, the assumption of energy balance of the plasma being dominated by Joule heating and radiative transfer implies that the parasitic loads of the converter are inversely proportional to the size of the unit. Larger scale furnaces typically have larger heat fluxes but lower total losses due to the reduced surface to volume ratio (Barcza, 1986). For this reason, as reactor scale increases, the energy efficiency of the two-stage system becomes more predictable, i.e. heat losses are less significant.

For this purpose, the Cold Gas Energy Conversion Efficiency can be modified (CGE_m) and applied to a full scale two-stage gasification process as follow:

$$CGE_m = \frac{\sum_i M_i \times LHV_i}{(M_{RDF} \times NCV_{RDF}) + W_{power}}$$

where W_{power} is the power of plasma supplied in the second stage, normalized for a full scale system (100 ktpa of RDF) on account of the disproportionally high inherent thermal losses (heat losses per unit surface area) of the small pilot plasma unit. Table 5 shows the CGE_m being stable between 77% and 78%. Interestingly, the majority of the energy input to the process is derived from the controlled oxidation reactions of the solid fuel in the FBG, which greatly reduces the plasma arc electrical power demand to less than 10% of the total energy content of the fuel to the process. These values can be further improved by increasing the throughput and diverting part of the inert solid input (metals, glasses, etc.) to the material recovery section. The additional energy input has the main role of melting the ash particles and solid addition from the FBG. Nevertheless, part of the plasma energy turns into the sensible heat of the syngas, thus affecting the equilibrium of the whole gasification process. When the power of plasma increases, no doubt the temperature and the quality of the gas increase accordingly (Fig. 6). In fact, due to the increase of temperature, the tar cracking and methane reforming reactions are prompted, so to produce more CO and H_2 and increase the LHV.

This twofold role of plasma produces a self-compensating effect in determining the CGE_m, as shown in Fig. 7. When the W_{power} value increases from 0 to 0.4 kW/N m^3 of syngas (i.e. temperature increases from 750 to 1300 °C), the CGE_m of the process increases slightly from 0.815 to 0.820. If on the one hand, an increase in W_{power} should in fact lower the CGE_m, on the other hand plasma action plays a crucial role in the process of conversion of tars and char to CO and H_2, enhancing significantly the gas heating value, and thus the CGE_m of the process.
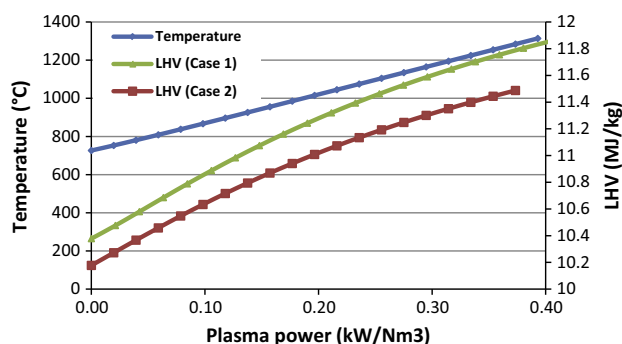

Fig. 6. Effect of the plasma power (measured as kW per N m^3 of syngas reformed) on temperature and syngas LHV.
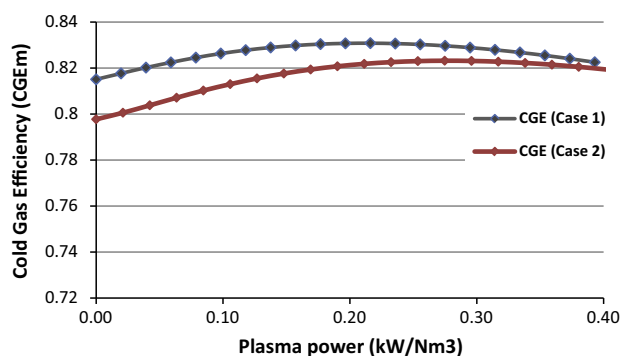

Fig. 7. Effect of the plasma power (kW per N m^3 of syngas treated) on cold gas efficiency.

These results are in agreement with previous experimental results with different feedstocks (Materazzi et al., 2013). Similarly to the effect of temperature, it is believed that the slight increase of CGE_m with increasing plasma power is mainly due to favoured char gasification and tar cracking by enhanced reaction kinetics. If the value of power exceeds 0.4 kW/N m^3 (i.e. gas temperature exceeding 1300–1400 °C), the negative effects of parasitic loads become more significant, so CGE_m would start to decrease.

4.5. Plasma vs secondary oxygen

In a thermal refining stage, the energy needed for gas heating up, tar cracking and ash vitrification can be produced from an external source (e.g. plasma), or from the injection of limited amount of secondary oxygen (e.g. thermal cracker). In the latter case, the heat released in the exothermic reactions provides the thermal energy for the primary reforming reactions to proceed very rapidly.

The amount of secondary oxygen is normally limited by the equivalence ratio (ER), which for traditional gasification cannot exceed the value of 0.4–0.5 (Basu and Kaushal, 2009; Materazzi et al., 2013). Higher values of ER would determine the combustion of part of the syngas and the consequent reduction of syngas LHV.

At this point of the analysis, it is worthwhile to compare the plasma converter with a conventional thermal cracker, and see if there are meaningful differences among these two technologies.

The amount of secondary oxygen input in a two-stage process can be expressed by the oxygen inlet ratio (OIR), which is defined as:

$$OIR = \frac{O_2 \ inlet \ at \ the \ second \ stage}{O_2 \ inlet \ at \ the \ first \ stage(FBG)} (w/w)$$

The first gasification step is normally run at optimal ER. This then sets the lower limit on the amount of oxygen required in the FBG. Simulations of different oxygen flow rate at the second stage were instead carried out to study the influence of additional oxygen on the cold gas efficiency of a two-stage process, for the same temperature increment observed in the previous section. This was seen to occur when oxygen inlet at the second stage varies from 0 to 0.36 times the oxygen inlet at the first stage (which is maintained constant).

The influence of oxygen inlet ratio on gasification temperature and syngas quality is shown in Fig. 8. With the increase of oxygen ratio, the second stage temperature increases from 710 °C to about 1350 °C, as much as the increase produced by plasma in the previous case (Fig. 6). However, in this case the rise in temperature does not translate into a better syngas quality. The LHV is significantly affected by the extent of exothermic reactions, i.e. by the time
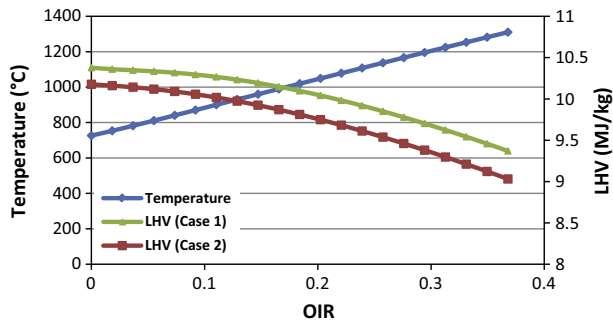
Fig. 8. Effect of oxygen partition ratio on temperature and syngas LHV.

the system reaches the high temperature required for ash vitrification and tar reforming, more gas has reacted to form H_2O and CO_2.

This also reflected into the CGE, which is drastically reduced by virtue of the low LHV having a predominant role. Fig. 9 compares the variation of CGE_m for a plasma converter and for a thermal cracker – with varying the plasma power and OIR respectively – for the same temperature range (710–1350 °C). It is found that when the plasma input increases from 0 to 0.4 kW/N m^3, the CGE_m is mostly unvaried, with values approaching 0.820. For the same temperature rise (corresponding to an increase of OIR from 0 to 0.36), the CGE_m of a thermal cracking stage decreases from 0.815 to 0.785.

It is clear that the energy efficiency for the two-stage process is strongly penalized when altering the gasification extent by increasing the oxidant inlet at the second stage, whereas it is favoured when using an external source like plasma.

However, this is a purely theoretical conclusion, based on thermodynamic equilibrium and 100% carbon conversion, which does not imply that a pure plasma powered system is always the best option. In practice, a combination of plasma input and secondary oxygen is usually the preferred solution. Tars, aromatic compounds and the remaining char can undergo partial oxidation by precisely controlling the amount of the secondary oxygen inlet fed into the plasma converter (OIR = 0.1–0.15). The heat released in the exothermic reactions provides additional thermal energy for the primary gasification reaction to proceed very rapidly, reducing the heating power required by the plasma electrode to melt the ashes.

Furthermore, additive such as oxygen and/or steam can alter the kinetic paths of plasma reactions, participating in oxidative decomposition of soot precursors, and extending the time-scale of the reactions (Materazzi et al., 2014; Lee et al., 2013).
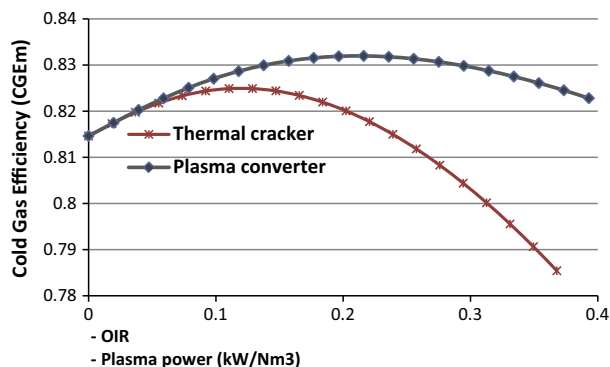
5. Conclusions

This research focused on a novel two stage fluid bed gasification–plasma converter technology to transform solid waste into clean syngas at a commercial scale. The overall aim of this research was to investigate the performance of the process, focusing on the syngas composition, carbon conversion efficiency and energy conversion efficiency, along with other relevant parameters. Comparison with other thermal refining stages, such as thermal cracking (via partial oxidation) was also performed. Analysis, including thermodynamic modelling, was supported by experimental data.

The known deficiencies of a single stage FBG process, have led to the theoretical prediction of the gas composition at the exit of the first stage deviating significantly from the values derived from the trials. From a practical point of view, this is of no consequence, as the equilibrium condition for the bulk gas species is always attained for the two-stage process, which gives a very satisfactory agreement. The study effectively demonstrated that the two-stage gasification system significantly reduces the concentration of condensable tars in the syngas, improving the gas yield of the system and the carbon conversion efficiency which is crucial in other single stage systems.

Testing of the slag samples against organic parameters showed near zero values, being in compliance with model predictions. These very low values are due to the combination of high temperature, turbulence, and residence time attained in the plasma converter, which results in the conversion of residual carbon to CO. For the two RDF materials considered in this study, carbon conversion efficiency is seemingly independent of the feed type, with both efficiencies higher than 96%.

Simulations of different oxygen flow rate were carried out to study the influence of additional oxygen on the cold gas efficiency of a two-stage process, at the same temperature range observed in a pure plasma stage. The LHV of the syngas is significantly affected by the extent of exothermic reactions, i.e. by the time the system reaches the high temperature required for ash vitrification and tar reforming, more gas has reacted to form H_2O and CO_2. On the contrary, by using plasma to increase the temperature, cold gas efficiency remains unvaried, with values as high as 0.820. This thermodynamic analysis shows that the energy efficiency for the two-stage process is strongly penalized when altering the gasification extent by increasing the oxidant inlet at the second stage, whereas it is favoured when using an external source like plasma.

Fig. 9. Effect of oxygen inlet ratio and plasma power on overall process performance (CGE).

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