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Fate and behavior of inorganic constituents of RDF in a two stage fluid bed-plasma gasification plant

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HIGHLIGHTS

- An examination of residues from a two-stage waste thermal treatment is presented.
- Sulphur and chlorine are partially retained in the first stage.
- Alkali metals are partially inactivated by reactions with the mineral matter of RDF.
- 90% of ash-type components in RDF are recovered as a stable vitrified product.

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ABSTRACT

To accelerate progress in the industrial use of RDF as an alternative fuel in gasification plants, the problems associated with hazardous solid residues and ash deposition must be resolved. The practical approach to reduce these problems must be aimed at preventing the accumulation of fly ash/condensable vapours on heat transfer surface areas while minimising the amount of residual materials that have to be treated before the disposal. One such approach is adopted in an advanced two-stage thermal process which incorporates a plasma processing stage for conditioning the gas generated from a primary waste gasification unit, primarily for the treatment of household and industrial wastes. This paper presents a comprehensive examination of ashes sampled under different operational conditions and in different locations of a two-stage fluid bed-plasma demonstration plant. A demonstration test miming the normal commercial operation was conducted over 44 h of operation with RDF from a standard UK municipal solid waste. The results are presented according to solid samples composition, gas composition, and further specific data (e.g., enrichment factor, XRD analysis, leaching test, etc.). An investigation on pollutant removal from the hot syngas, focusing on the partitioning and chemistry of sulphur and chlorine along with other relevant components, is also carried out. Experimental trials revealed a reduced extent of alkali and metals availability in the gas phase, i.e. a minor deposit forming potential into downstream equipment. From 85% to 91% of the fly ash was captured and vitrified within the plasma converter and made non-leachable with respect to non-volatile heavy metals, allowing for near complete landfill diversion.

1. Introduction

Since the 1980s, solid wastes have been processed for energy recovery (now known as Waste-to-Energy or WtE). It has matured into a safe and effective technology reliably reducing waste that would otherwise be landfilled, and instead producing valuable energy resources. Waste gasification, for example, has attracted considerable interest amongst thermal treatments, since the syngas created by this process can be utilised in a range of applications including power and heat generation, and for fuel and chemical production [1]. Refuse derived fuels (RDF) provide solutions to the disposal of non-recyclable waste fractions, and can be used as a direct substitute for primary fossil fuels in gasification. The materials have been used for providing heat and power to a diverse range of industries from paper mills to cement productions to power generators [2,3]. RDF is produced by shredding and dehydrating wastes, including municipal and industrial waste, commercial waste, construction and demolition waste, sewage sludge, etc. As such, RDF can contain a range of plastics, fiber,

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textiles, putrescible materials, rubber, metallic components and dusts, some of which are considered hazardous in nature.

With more than 30 commercial units in operation worldwide, fluid bed gasifiers (FBG) are frequently employed in RDF conversion technologies due to their ability to handle relatively coarse and chemically heterogeneous materials [1,4]. Most of these plants utilise the FBG coupled with a melting system, with the gasification process working in effect as a pre-treatment for the successive stages of gas combustion and ash melting. This configuration offers the advantages of reduced amounts of pollutants, less final ash disposal and small volumes of exhaust gases when compared to conventional incineration plants. In addition, the production of vitrified slag can be recycled as supplementary asphalt of road paving material [4]. By contrast, the use of stand-alone FBGs for syngas production at industrial scale, where the syngas is first cleaned and then sent for final utilisation, is still at early stage of development. The major technical problems faced by stand-alone FBGs are intrinsically related to the composition and physical properties of RDF. The high quantity of fly ash and volatile material in RDF can provide a decrease in thermal output, create high ash clinkering, and increase emission of tars and pollutant gases such as H_2S and HCl. Furthermore, the large quantities of gases and vapours leaving the solid matrix can entrain organic and inorganic material, even if the material itself is non-volatile, thus producing a large amount of residues downstream. As a result, the combination of high velocities in FBG and high volatile matter in RDF indicates a potential for creating significant inorganic vapours and fly ash deposition problems during gasification, with the severity varying significantly with the different nature of the feedstock [5]. Waste composition, for example, has been observed to affect the partitioning of toxic elements such as Pb and Zn; volatilisation of which increase with increasing amount of Cl in the waste [6]. In RDF, Cl is generally present as inorganic chlorine (NaCl and KCl) and organic chlorine (dense plastics, PVC), in about equal amounts (0.1–1 wt.%). Organic chlorine compounds have a low binding energy (PVC 397 kJ/mol), compared to inorganic chloride salts (NaCl 787 kJ/mol, KCl 717 kJ/mol). For this reason, in RDF gasification, plastics start to release HCl at 300 °C and decompose almost completely at 550 °C, whereas NaCl and KCl start volatilising at 800 °C with most chlorine remaining in the sand bed [7]. Other components, such as sulphur, have been proven to have an important effect to improve the conversion rate of NaCl to HCl and prevent chlorine from being bound in surface deposits [8]. Like chlorine, sulphur exists in wastes both within organic structures and inorganic salts (sulphates principally). Previous studies have shown that *in situ* sulphur and chlorine capture by the bed inventory has the potential to decrease the risk of corrosion and alkali deposits in the downstream units [9]. This process refers to as chlorine and sulphur self-retention (CSR-SSR), and occurs in FBG as a result of the reactions between the mineral matter in the bed inventory (e.g. RDF ash and bed particles) and the acid compounds evolved during gasification. Knudsen et al. [10] found that silica (SiO_2) plays an important role in sulphur and chlorine release at temperatures above 700–800 °C, with an abrupt increase in S-release at temperatures above 700 °C noted for Si-rich RDF (i.e. ‘rich’ relative to K and Ca). The role of ash in S-capture, with K_2SO_4 and $CaSO_4$ salts being important sequestered species, is also reported [10,11]. Consequently, the emission of many pollutants (HCl, H_2S, volatile metals, etc.) are significantly affected by the reaction of sulphides and chlorides (present in the feedstock) with heavy, alkali, and alkaline earth metals. Alkali metals, for example, are commonly associated with fouling deposits in gasification plants, resulting from the vaporisation and subsequent condensation on heat transfer surfaces that can trap fly ash particles and elutriated material. In addition, the alkalis are fluxing agents that can form low melting point eutectics in the thermal process, limiting the temperature of operation of the gasifier to around 800–850 °C, in order to avoid agglomeration and ultimately de-fluidisation of the bed [12]. This has a direct influence on the quality of syngas that is generated. At a temperature of 800 °C, high levels of problematic tars are generated. Unless the tars are removed or destroyed, they limit downstream processing options and conversion efficiency [13]. Several physical approaches for tar and particulate reduction outside of the gasification stage have been reported in the literature, and are compared in Table 1 A high temperature stage for removal of particulates is generally convenient since, at temperatures lower than 400 °C, tar condensation can produce heavier plugging and fouling problems of gas cleaning equipment. However, not all technologies have been proven efficient in terms of contaminants removal, economically feasible, and environmentally sound. Hot barrier filters, for example, are not suitable for tar removal at large scale, due to the high maintenance requirements. Other cleaning units, such as cyclones, may remove coarse particulates and a small portion of condensables, but leave the problem of fines and tar removal unchanged [13]. Tar and fine particulates can also be removed by wet scrubbers, although the recycling/reuse of the waste streams produced, introduces new technical obstacles and environmental issues [14]. The dominant effect is expected to be a higher dust loading when operating with waste materials, which could adversely affect the scrubber operation and create an additional hazardous waste stream. The operation on RDF may also introduce a change in tar loading and composition, which could require design changes.

Another class of contaminants present in waste residues consist of heavy metals, i.e. those elements with a density of approx. 5000 kg/m^3 or higher, such as Cd, Pb, Hg, Zn and Cu. They occur normally in RDF, being originated from small residual metal pieces, solder, plasticisers and paints present in waste-derived fuels. These elements may pose a threat to the environment or to human health by dispersion in the atmosphere or leaching from the solid residues [15]. Thus, it is important to know their behavior in the thermal process for the selection of an efficient gas cleaning methodology. Depending on many factors (e.g. nature of the incoming material, oxidative conditions, etc.), heavy metals redistribute among the various ash types and the gas phase. Some (Cr, Ce, Cs, Eu, Fe, Mg, Sr, Th and Ti), historically referred to as Class I metals [16], do not volatilise during gasification and distribute more or less equally amongst bed material and fly ashes. Class II elements (mainly Ba, Co, Cu, Ni, P, U, V, As, Cd, Mo, Pb, Sb) may be vaporised at high temperatures but are found mainly in the fly ashes after condensation on particulates downstream of the process [16,17]. A further problematic issue for the fluid bed waste gasification industry today relates to the management of these contaminated residues, as they require some form of physico-chemical treatment before either disposal or reuse is permitted. The consequential increase in costs to remove/dispose these deposits can eliminate the benefit of gate fees attributable to treating RDF. This has been the primary cause of waste gasification developments failing over the last 30 years [18] and has prevented their commercial adoption for production of syngas suitable for transformation into a fuel gas, such as substitute natural gas (SNG) or hydrogen. Therefore, there been a significant effort to develop technologies that can produce a good quality syngas, while minimising the amount of residual materials that have to be treated before the disposal.

Results have been variable but several systems appear to be promising; one possible approach involves the combination of a primary waste treatment unit (e.g. FBG) and a high temperature refining stage, such as an ash melting furnace or a plasma converter. Forerunners of this approach are Ebara in Japan and APP in UK [19]. The high temperature in the second stage breaks down tar and char enhancing the quality of the syngas, and vitrifies the ashes generated from the separate FBG, which would otherwise pose