Full Length Article

Thermo-conversion of Solid Recovered Fuels under inert and oxidative atmospheres: Gas composition and chlorine distribution

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ABSTRACT

The interest in thermo-conversion of Solid Recovered Fuels (SRFs) processes for syngas production has increased in the last decades. However, the monitoring and control of trace contaminants in SRFs such as chlorine in syngas still meet difficulties. The aim of this study is to determine the gas composition and to track the chlorine content in the products from the pyrolysis and oxidation of SRFs. Two types of SRFs from two different industrial sites in France were chosen for this study. The first one, SRF1, was chosen for its low chlorine content (0.3 wt% of Cl) comparing with the second one, SRF2 (1.1 wt% of Cl). SRF1 with low chlorine content showed that the most of Cl was transferred into the gas phase during thermo-conversion process. SRF2 with high chlorine content showed more NaCl in the residual solids after the reactions than its initial inorganic chlorine content.

1. Introduction

In 2012, the EU-28 generated 2 414.4 million tonnes of non-hazardous waste and 100.7 million tonnes of hazardous waste. Germany, France and the United Kingdom made up a 39% share of total EU-28 waste generation. More than 45% of the waste treated was subject to recovery, other than energy recovery, and almost half, more than 48%, was subject to disposal operations other than incineration, mostly landfilling [1].

The EU aims to minimize disposal methods that do not contribute to a valorisation of MSW such as landfilling. Thus, a waste recovery option that offers business opportunities for the waste management companies is to produce the so-called Solid Recovered Fuels (SRF). Referring to the standard EN 15357 [2], Solid Recovered Fuels or SRFs are "solid fuels prepared from non-hazardous waste to be utilised for energy recovery in incineration or co-incineration plants and meeting the classification and specification requirements laid down in EN 15359" [3]. SRFs offer the opportunity to produce energy from processed fractions of MSW that cannot be recycled, which is an acceptable waste recovery option. In 2012, the remaining waste, that was not recovered nor landfilled, was incinerated with energy recovery (4% of waste) and without energy recovery (2% of waste) [1].

In the case of energy recovery, SRFs can thus contribute to the preservation of natural resources as they can substitute fossils fuels. Another major benefit of SRFs is their biogenic contents of the initial waste stream (wood, paper, cardboard…), a carbon dioxide (CO_2) neutral. This biogenic fraction varies with regions and economics and it can be estimated by the determination of biomass content using the standard EN 15440 [4]. Many studies [5–8] showed that SRFs derived from MSW have a high biogenic fraction (50–70%).

For thermochemical conversion processes (incineration, co-combustion, pyrolysis and gasification), there is a big debate about the best technology dealing with biomass and waste. To answer this question, Life Cycle Assessment (LCA) has been used extensively these last decade to study the environmental loads of thermal Waste-to-Energy (WtE) technologies [14]. LCA makes it possible to compare the different technologies, to choose the most adapted thermo-conversion process based on energy, environment and economy criteria. Arena et al. [15] found that combustion and gasification WtE technologies had sustainable environmental performances, but the combustion unit was better for most of the selected impact categories. In contrary, Consonni and Vigano [16] showed that waste gasification has lower generation of some pollutants comparing to conventional WtE. The energy performances of combustion and gasification were very similar.

The gasification of different wastes, including SRFs, has been studied in detail by other authors [9,10,17,18]. Some of these studies have also investigated the influence of process conditions on syngas quality [10,19,20]. By far, the most case-studies assessed combustion and gasification, while relatively few studies focused on waste pyrolysis. From these few studies, pyrolysis characteristic of SRFs were studied at laboratory scale using a thermogravimetric analyser [21,22] or using a fixed bed reactor [23]. In the both cases, tests were performed in non-isothermal conditions: the SRFs samples were heated from room temperature to a fixed high temperature at a constant heating rate

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(between 1 and 20 °C/min). Those researchers have focused on the behaviour of SRFs samples from a pure thermogravimetric point of view which involves weight loss as a function of temperature of the sample. It is observed that the volatiles from plastics generally start to evolve at a higher temperature range (300–500 °C) as compared to those from biomass or coals (200–400 °C) [24]. Considering the product yields, the results showed that both light and heavy liquid fractions increased with the presence of plastic material in the waste [25]. They supposed that the olefinic products from plastics thermal conversion react with some products from the biomass depolymerisation to result in the formation of light liquids.

Nevertheless, due to their nature or preparation method, SRFs can contain high levels of chlorine, sulphur, and heavy metals. For thermal processes, they cause fouling, corrosion of pipes and down-stream units, besides poisoning of catalysts [9]. Referring to EN 15508 [8], the technological criterion for SRFs is chlorine content. The chlorine nature in SRF is dual, organic from chlorinated polymers (e.g., PVC) and inorganic, for instance salts (NaCl and/or KCl) from food waste [6,7,11]. In general, the Cl content should be below 0.5 wt% or 1.0 wt% depending on the application.

Worldwide, in term of polymer consumption, polyvinyl chloride (PVC) is ranked second behind polyethylene [12]. Thus, PVC is omnipresent in SRFs composition and they will affect the thermo-conversion and gas composition. Around a half of the chlorine in municipal solid waste (MSW) comes from PVC, which means a half of the HCl in the combustion gases from MSW incinerators [13]. In addition to the formation of HCl, other forms of chlorine such as chlorides of Na, K, Zn, Pb, Sn, Sb, Fe, and other elements in the gas phase can cause high temperature corrosion of incinerators and reactors. To minimize the costly chlorine-associated problems, it is important to study the chlorine concentration in waste, chlorine species and thermal behaviour of chlorine [11].

In this study, we will focus on the fate of chlorine during SRFs pyrolysis and oxidation in an isothermal furnace. The operational conditions of the isothermal furnace, used in this study, imitate the industrial scale operation conditions. The main objective of this study is to determine gas composition and to track the chlorine content during pyrolysis and oxidation for both SRFs.

2. Materials and methods

2.1. Samples preparation and characterization

Two types of SRFs from two industrial producers in France were chosen for this study. During the preparation of the first one (SRF1), an optical detector was used in order to minimize its chlorine content. The second one (SRF2) was prepared without optical detector, and contains obviously more chlorine than that in the first SRF.

Before the characterization and thermo-conversion tests, the two SRFs samples were dried and ground under 1 mm using a rotary cutting mill equipped with a 1 mm sieve (Fig. 1).

The proximate analyses of the two SRFs were carried out according

Fig. 1. Illustration of SRF sample for laboratory analysis and experiments.

to the EN 15402 [26] for volatile matter and EN 15403 [27] for ash content. The fixed carbon was deduced by difference.

The elemental composition of the samples was carried out according to:

- EN 15407 [28] for the determination of carbon (C), hydrogen (H) and nitrogen (N) content, with a CHN analyser Flash 2000.
- EN 15408 [29] for Sulphur (S) and chlorine (Cl) content. This method consists of an oxygen combustion procedure of the sample in a bomb. Sulphur and chlorine compounds are converted respectively to chloride and sulphate which are absorbed and dissolved in an absorption solution (KOH 0.2 ml/l solution). After each sample's combustion in the calorimetric bomb IKA C500, the bomb was washed out to recover the solution, which were subsequently analysed by ionic chromatography to determine S and Cl contents.
- EN 15410 [30] for the determination of the content of major and trace elements. The method consists of using an inductively coupled plasma-optical emission spectrometer (ICP-OES). Before analysis, the SRFs samples were digested at 220 °C with an adapted acid mixture using a special closed reactor. The dissolution conditions were optimized to dissolve completely these SRFs samples. The most adapted acid mixture was: sulfuric (3 ml), nitric (3 ml), hydrofluoric (1 ml) and hydrogen peroxide (3 ml), with a SRF sample of about 200 mg.

The calorific value was measured following the standard EN 15400 [31], using the calorimetric bomb IKA C500.

Table 1 depicts the results for the characterization of the two SRFs samples. The data of the proximate analysis, C, H, N, O, S, Cl and the LHV are the average of at least triplicate analyses, and the data for the other major and trace elements are the average of at least 5 analyses.

Table 1
Proximate and ultimate analyses of of SRF1 and SRF2.

Parameters		SRF 1	SRF 2
Moisture content (wt%, w.b.)		7.3 ± 0.2	8.3 ± 0.2
Proximate analysis (wt%, d.b.)	Volatiles	73.3 ± 0.1	74.8 ± 0.5
	Fixed carbon[*]	9.4 ± 0.3	7.5 ± 0.7
	Ash	17.3 ± 0.3	17.7 ± 0.2
Elemental composition (wt%, d.b.)	C	46.20 ± 0.82	49.90 ± 0.67
	H	6.20 ± 0.42	6.63 ± 0.35
	N	0.60 ± 0.04	0.66 ± 0.01
	S	0.10 ± 0.02	0.51 ± 0.10
	Cl	0.30 ± 0.20	1.09 ± 0.15
	Al	0.99 ± 0.51	0.18 ± 0.05
	Ca	3.35 ± 0.59	1.14 ± 0.37
	Fe	0.24 ± 0.06	0.18 ± 0.01
	K	0.14 ± 0.06	0.12 ± 0.03
	Mg	0.22 ± 0.10	0.21 ± 0.01
	Na	0.46 ± 0.01	0.47 ± 0.01
	P	0.15 ± 0.02	0.09 ± 0.04
	Si	1.00 ± 0.03	1.19 ± 0.11
	Sn	0.08 ± 0.02	0.10 ± 0.01
	Ti	0.14 ± 0.01	0.24 ± 0.06
	Zn	0.03 ± 0.01	0.23 ± 0.07
Trace elements (mg/kg, d.b.)	As	39.0 ± 23.3	26.1 ± 14.0
	Cd	13.6 ± 10.6	5.6 ± 1.4
	Co	9.2 ± 6.4	10.2 ± 8.0
	Cr	77.0 ± 5.8	126.4 ± 19.8
	Cu	45.0 ± 10.8	610.2 ± 105.6
	Mn	78.4 ± 5.4	97.5 ± 48.8
	Ni	46.7 ± 30.4	49 ± 11.6
	Pb	27.7 ± 30.9	1.4 ± 1.2
	Sb	45.7 ± 7.1	28.8 ± 4.8
	Tl	1.0 ± 8.7	1.5 ± 0.5
	V	28.9 ± 3.5	89.1 ± 12.6
	Hg	0.10 ± 0.01	0.74 ± 0.03
LHV (MJ/kg, d.b.)		23.2 ± 0.2	22.6 ± 0.3

[*] By difference; w.b.: wet basis, d.b.: dry basis.