Municipal Solid Waste Cofiring in Coal Power Plants: Combustion Performance

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Additional information is available at the end of the chapter

Abstract

The combustion of fuel derived from municipal solid waste is a promising cheap retrofitting technique for coal power plants, having the added benefit of reducing the volume of waste disposal in landfills. co-combustion of waste-derived fuel (WDF) and coal, rather than switching to WDF combustion alone in dedicated power plants, allows power plant operators to be flexible toward variations in the WDF supply. Substituting part of the coal feed by processed high calorific value waste could reduce the NO_x, SO_2, and CO_2 emissions of coal power plants. However, the alkaline content of WDF and its potentially harmful interactions with the coal ash, as well as adverse effects from the presence of chlorine in the waste, are important drawbacks to waste-derived fuel use in large-scale power plants. This chapter reviews these points and gives a centralized review of co-combustion experiments reported in the literature. Finally, this chapter underlines the importance of lab-scale experiments previous to any large-scale application and introduces the idea of combining waste and additives dedicated to the capture of targeted pollutants.

Keywords: waste, coal, power plant, emissions, RDF

1. Introduction

Worldwide, around 1.3 billion tons of MSW (municipal solid waste) are generated every year, an amount that is expected to grow to 2.2 billion tons of MSW per year by 2025 [1]. A large fraction of MSW is disposed in landfills, which may lead to groundwater contamination by leachates and atmospheric emission of biogas, a mixture of CH_4 and CO_2 generated by biological processes related to MSW decay. In order to avoid these environmental disturbances,

governments lean toward banning landfill sites and encouraging development of alternative waste treatments.

Many of the components of MSW currently sent to landfill, such as paper, cardboard, textiles, wood, and plastics, are not hazardous and have high caloric content. For example, the composition of the MSW landfilled in 2013 in the United States is given in **Figure 1**. Instead of being disposed in a landfill, these components could be recovered and treated to produce waste-derived fuels (WDFs) for use as an energy source.

Based on financial, environmental, social, and management considerations, the waste management sector defined a "waste management hierarchy," classifying the different waste management options, presented in **Figure 2**. This concept, which appeared in the early 1970s, was formalized in the 2008 European Commission Waste Framework Directive [3]. From a sustainability point of view, waste reduction, reuse, recycling, and recovering are preferred— all these options decreasing the quantity of waste to be disposed of [1]. Unfortunately, not all waste streams can be diverted to such end and final wastes are always produced. Furthermore, even though some materials can have an increased lifetime, they generally end up degraded and in a state where their reutilization is impossible. Finally, some wastes, especially if they are made of mixed materials, are so that their recycling is really costly or is associated with a quite high energy demand or pollutant production and therefore is unrealistic [4]. For these wastes, energy recovery through co-combustion is an option of great interest.

Currently, coal combustion accounts for around 40% of the world's electricity generation [5] despite the fact that coal combustion is a major source of NO_x and SO_2 emissions. These emissions are precursors for acid rain, and therefore sensible environmental policy suggests that they be curtailed. Cheap retrofitting techniques are needed to permit existing infrastructure to continue to operate without contributing to the incidence of acid rain.
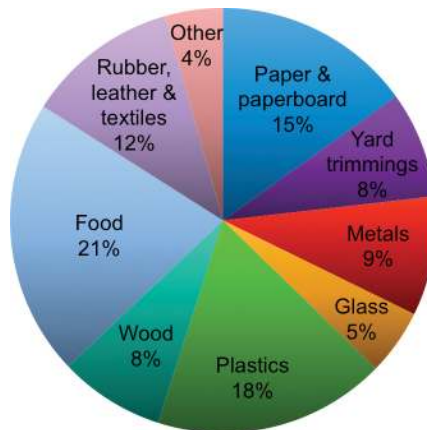

Figure 1. Total MSW discards (by material) in the United States in 2013 [2].

Since municipal solid waste generally has negligible sulfur content and lower nitrogen content than coal, substituting part of the coal with waste-derived fuel might be beneficial to the environmental performance of coal power plants. Furthermore, since the coal power plants electric efficiency is usually 10–20% superior to that of incinerators [6], burning MSW in coal power plants can lead to higher waste utilization efficiency than in dedicated incineration plants. Also, MSW contains a renewable fraction and can therefore helps reducing the amount of fossil CO_2 generated by coal power plants. This is somewhat mitigated by the higher chlorine and alkaline content of WDF compared with coal, which may contribute to corrosion and ash deposition issues. Consequently, the co-combustion of coal and WDF has to be studied before a large-scale utilization of WDF in power plants. This chapter will discuss the production of WDF as well as the effect of its cofiring in coal power plants in terms of CO_2, NO_x, and SO_2 emissions. The ashes behavior and the fate of chlorine in the combustors will also be covered. This chapter therefore summarizes the benefits and limitations related to WDF co-combustion in existing coal power plants.

2. Fuels derived from waste, a large ensemble

Due to their inhomogeneity, their high moisture content and fraction of incombustibles, municipal solid wastes cannot be fired in large-scale coal power plants unless they are transformed in a more homogeneous and calorific feedstock, broadly called waste derived fuels (WDFs). Unfortunately, the fuels that can be derived from MSW are almost as diversified as the MSW themselves.

Depending on the characteristics and the type of wastes used for the production of the WDF, it is common to differentiate solid recovered fuel (SRF) from refuse-derived fuel (RDF). Generally, SRF is more homogeneous, less contaminated, and have a higher calorific content than RDF that is more generic. In Europe, to overcome the ambiguous situation regarding fuel quality, the European Commission has given mandate to CEN/Technical Committee (TC) 343 to prepare a document classifying solid recovered fuels [7]. Different SRF qualities based on three criteria that are the net calorific value (serving as the economic indicator), the chlorine content (as the technological indicator), and the mercury content (as the environmental key
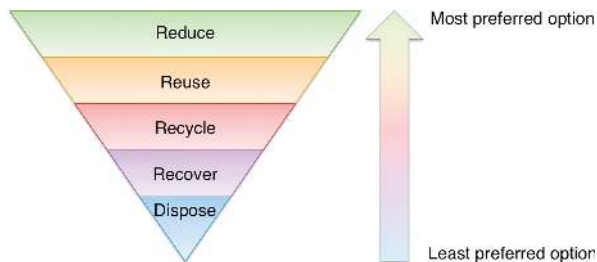

Figure 2. Waste management hierarchy.

parameter) have been defined [8]. Readers are advised to refer to the CEN/TC 343 published standards for more information.

On top of RDF and SRF, there has been mention of process engineered fuel (PEF), engineered fuel (EF), refuse plastic fuel (RPF), generally made of more than 60% of plastic waste [9], and packaging-derived fuel (PDF). These fuels are usually of higher quality than RDF and SRF as they are made of source-separated processed dry combustible fraction, which cannot be used for recycling [10, 11]. Also, they are of predictable and consistent quality, which is critical to ensure their market security. Finally, they are not considered as waste but as a marketable product that has to meet strict end-user requirements [12].

Numerous processes have been implemented to produce WDF from MSW. These processes generally consist of sorting and mechanical separation of the waste, size reduction (shredding, chipping, and milling), separation and screening, blending as well as drying and densification [13–15]. All these steps are used to increase the homogeneity and the heating value of the final WDF, improving their in-situ handling and feeding. An example of WDF production chain is given in **Figure 3**.
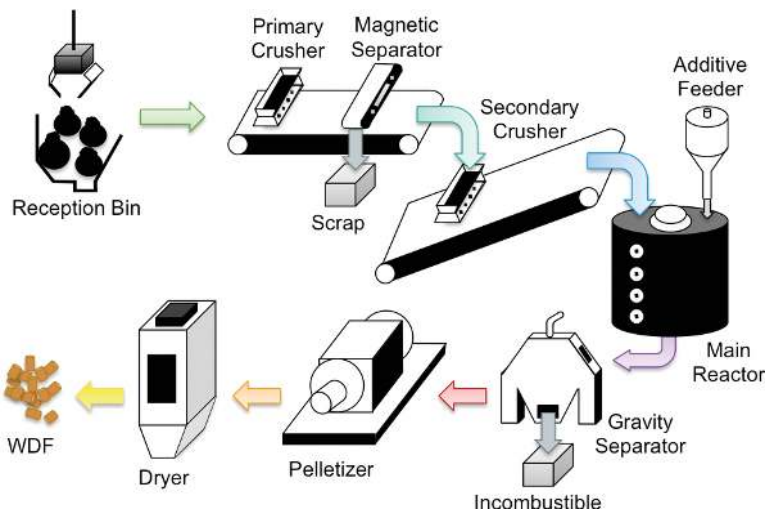

Figure 3. Production of WDF, inspired from [16].

WDF production generally involves a source-separation step where the organic fraction (food residues, yard trimmings, etc.) is removed. One of the best-established and less expensive processes is the mechanical biological treatment (MBT). In an MBT plant, the metals and inert materials are removed, the organic fraction is screened out, and the high-calorific fraction is separated. The organic fraction is further stabilized using composting processes, either with or without a digestion phase, producing compost and biogas. The high-calorific fraction, on the other hand, is further processed into waste-derived fuel, as described above [11]. Extensive mechanical treatment (MT) processes can also be used to produce WDF [7].

Even though the majority of the technologies involves the removal of the organic fraction some, such as the dry stabilization process, produce WDF containing the organic fraction. In this process, the residual waste, after separating out metals and inert materials, is dried through a composting process leaving the residual mass with a higher calorific value [11]. The high-calorific output of this process, developed in Germany, has the trade name of "Trockenstabilat". WDF containing the stabilized organic fraction are however not the norm, and will therefore not be studied in the rest of the chapter.

The high-calorific fraction of the waste, used as WDF, can generally be separated into a biogenic fraction and a plastic fraction. The biogenic or fibers fraction refers to the textiles, wood pieces, papers, and cardboards found in the MSW. Papers range from newspaper to glossy magazine sheets and can contain multiple chemicals as a large variety of additives are used during their fabrication, whether it is as pigment, binder, filler, or else. As an example, some of the pigments that can be used are clay (kaolin), calcium carbonate, titan oxide, satin white ($3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 3H_2O$), barium sulfate, talc, and aluminum hydroxide [17]. Calcium carbonate can further be used as filler, and therefore may account for up to 15% of the paper content.

The plastic fraction, majorly derived from oil, also regroups a wide variety of materials. The more common plastics found in MSW are polyethylene (PE), polypropylene (PP), polystyrene (PS), and polyvinyl chloride (PVC) [14]. While the biogenic fraction has a high ash content, the plastic fraction generally contains chlorine, both raising processing and environmental concerns [18].

Finally, multimaterial pieces can also be found in the high-calorific fraction of MSW, such as cardboard drink containers or Tetrapack™, combining both paperboard and plastic, with or without aluminum foil.

Once produced, the waste-derived fuels can be used for the electricity production combined with coal or natural gas in thermal power plants, for their energetic content in industrial processes (e.g., cement kilns and blast furnace) or for their material properties also in various industrial processes (e.g., asphalt production) [19]. Due to the large number and poor environmental performance of coal power plants and the importance of developing cheap retrofitting technology to improve this performance, only the utilization of WDF in coal power plant will be studied in this chapter.

During co-combustion studies, proportions of each of the combustible can be expressed in terms of weight fraction or energetic (also called thermal) fraction [20]. Energetic fractions are evaluated according to:

$$x_{WDF}^e = \frac{W_{WDF} \, LHV_{WDF}}{W_{WDF} \, LHV_{WDF} + W_c \, LHV_c} \tag{1}$$

with W the mass flow (kg/h) of the WDF and of the coal (c), and LHV the lower heating value (kJ/kg). The mass fractions, on the other hand, are evaluated as follows:

$$x_{WDF}^{wt} = \frac{W_{WDF}}{W_{WDF} + W_c} \qquad (2)$$

It should be mentioned that a large number of research projects currently focus on oxycombustion of coal and waste, which facilitates CO_2 sequestration from the flue gas [21–23]. However, the costs related to such technology still remain a major obstacle to any commercial application [24]. The rest of this chapter will therefore only focus on the benefits and limitations related to WDF co-combustion in existing coal power plants.

3. Effect of WDF co-combustion on CO_2 emissions

Because WDF contain products derived from biogenic sources (e.g., paper), "fossil CO_2" emissions are reduced when WDF is cocombusted with coal [25]. Indeed, biogenic sources capture the same amount of CO_2 during their lifecycle than what is emitted during their combustion [26]. Furthermore, methane being a greenhouse gas 25 times more damageable than CO_2 in terms of global warming [27], the beneficial effect of waste co-combustion in terms of greenhouse gas emission is even greater if are taken into account the avoided methane emissions associated with their disposal in landfills. Therefore, in the European Union, for example, diversion of MSW from landfilling to composting, recycling, and energy recovery could produce a reduction from 40 to over 100 Mt CO_2-equivalent per year [28].

In order to evaluate the fossil CO_2 emissions that could be avoided through WDF cocombustion, one needs to know the carbon and water content, the calorific value, and the biogenic fraction of the fuel [9]. Characteristics of varied WDF found in the literature are given in **Table 1**.

What can be seen from **Table 1** is that WDF with a wide range of carbon content (from 34 to 69%) and of heating value (from 13 to 27 MJ/kg) can be produced. As for the biogenic content, it is rarely known, especially for RDF. Furthermore, fossil CO_2 emissions avoided will depend on the coal characteristics, which also vary widely.

Anyhow, for example in [10], the authors evaluated that the emission of fossil CO_2 associated with lignite combustion is around 955 g/kg, whereas that of an SRF with a biogenic content of 67% is $(1–0.67) \times 1067 = 352$ g/kg. Lignite and SRF having comparable calorific content, for a 15 wt% cofiring ratio, emission of 90.5 g of fossil CO_2 are avoided per kilogram of feedstock burned. Taking, for example, REW's BoA 2 and 3 boilers, which are fed with lignite at a rate of 820 t/h [29], fossil CO_2 savings of around 74.2 t/h could be obtained through WDF co-combustion, which sum up to 1781 t of fossil-CO_2 avoided per day in one boiler.

Since WDF co-utilization in existing thermal plants usually requires low additional investments and, as was described in this section, since WDF are partially renewable, co-combustion of WDF could allow the production of partly renewable electricity at low cost. Furthermore, in comparison with pure WDF combustion systems, the potential variability of the cofiring ratio allows energy producers to be adaptable toward fluctuations in WDF availability.

Even though CO_2 emissions are in the heart of nowadays concerns, other pollutants such as NO_x and SO_2 still remain critical in coal power plants. The effect of WDF co-combustion on their emissions is discussed in the following two sections.

Fuel name	Ref	Dp	Proximate analysis, wt%				Ultimate analysis, wt%					Trace elements, wt%			HHV	LHV	Fib. %
		mm	WC	VM	FC	Ash	C	H	N	O	S	Cl	Ca	Na	MJ/kg		
EF	[12]	1–8	6.8	67.5	10.1	15.6	39.0	5.8	0.7	37.7	0.1	–	–	–	15.9	–	30
EF	[29]	0.1–0.4	1.0	82.5	14.1	2.4	55.6	7.7	0.22	32.9	0.20	0.047	1.72	<1	23.7	–	80
EF	[29]	0.1–0.4	1.4	84.2	12.0	2.4	58.9	8.5	0.22	28.3	0.17	0.062	1.65	<1	26.6	–	70
EF	[29]	0.1–0.4	2.8	85.3	10.9	1.0	52.0	7.0	0.23	36.7	0.25	0.039	1.60	<1	22.0	–	90
SRF	[6]	0.164	5.20	72.1	7.1	5.7	58.0	6.6	1.00	27.4	0.42	0.28	0.67	0.11	–	20.9	–
SRF	[7]	18	3.0	79.6	6.3	11.1	40.5	5.3	0.03	–	0.07	0.02	–	0.025	22.7	21.4	78
SRF	[28]	–	18.3	–	–	7.5	54.9	7.6	0.79	29.1	0.15	0.46	1.78	0.196	–	18.8	–
SRF	[28]	–	18.1	–	–	7.5	55.1	7.6	0.48	29.1	0.15	0.44	1.91	0.186	–	18.8	–
SRF	[30]	0.5–1.3	28.1	56.0	6.4	9.7	60.1	8.4	0.98	30.3	0.21	–	–	–	–	14.8	75
RDF	[7]	18	30.4	46.1	8.3	16.2	28.1	3.4	0.98	–	0.32	0.25	–	0.536	14.8	13.2	–
RDF	[13]	15	5.4	71.6	10.8	12.2	40.4	5.7	0.92	36.1	0	0.85	0	–	–	–	–
RDF	[24]	0.12	2.6	80.2	2.8	14.4	44	6.8	1.0	31.1	0.06	–	–	–	26.9	25.1	–
RDF	[31]	–	3.7	67.6	9.8	18.9	61.2	8.2	1.3	26.6	0.2	2.5	–	–	22.3	20.8	–
RDF	[31]	9.5	1.7	73.6	7.0	17.7	69.1	7.4	1.9	19.6	0.3	1.7	–	–	24.6	23.3	–
RDF	[31]	–	19.7	49.1	10.8	20.4	57.4	3.8	–	36.8	0.2	1.8	–	–	13.9	12.6	–
RDF	[32]	–	3.0	70.8	13.0	13.0	49.7	7.0	0.82	25.2	0.15	1.15	–	–	–	21.1	–
RDF	[33]	3–6	1.8	75.1	9.6	13.5	49.4	6.9	0.8	28.4	0.3	0.5	–	–	–	21.1	–
RDF	[34]	–	4.5	81.2	8.0	6.4	46.0	6.4	0.25	34.6	1.08	0.85	–	–	–	23.9	–
RDF	[35]	21.5	0	67.6	9.7	22.7	59.0	9.6	0.61	30.9	0.01	–	–	–	–	12.3	–
RDF	[36]	15–50	1.6	62.3	5.1	31.0	39.2	5.1	0.11	24.0	0.08	0.79	–	–	–	17.5	–
RDF	[37]	–	7.83	70.6	12.8	8.7	41.7	5.6	0.80	35.3	0.09	0.14	1.35	–	–	16.4	–
RDF	[38]	15	0	73.5	9.4	17.2	57.2	9.1	0.21	14.4	0.26	–	–	–	–	24.1	–
RDF	[39]	–	18.8	55.3	13.5	12.4	34.0	4.2	0.54	29.7	0.22	0.123	–	–	13.0	–	–
RDF	[40]	0.1	1.48	70.7	11.2	16.6	43.5	5.8	0.9	32.6	0.6	–	–	–	–	–	–
HT MSW	[41]	1.5	0	75.2	23.8	1.09	56.9	7.3	0.97	32.6	0.08	1.09	0.1	0.67	19.1	–	–

EF, engineered fuel; SRF, solid recovered fuel; RDF, refuse derived fuel; HT MSW, hydrothermally treated municipal solid waste.

Table 1. Examples of WDF characteristics.

4. Effect of WDF co-combustion on NO_x emissions

During combustion processes, nitrogen oxides, collectively termed NO_x, are formed either from fixation of N_2 in the combustion air or from oxidation of nitrogen chemically bound in the fuel [30]. A schematic representation of the different NO formation paths is given in **Figure 4**. Thermal-NO refers to NO formed by oxidation of atmospheric nitrogen at high temperature, whereas prompt-NO is formed by reactions of atmospheric nitrogen with hydrocarbon radicals in fuel-rich regions of flames. Finally, fuel-NO refers to NO formed by oxidation of the nitrogen bound in the fuel. Due to the relatively high nitrogen content of coal, the latter is the largest source of NO_x in coal-fired systems [31]. On the other hand, NO can be reduced to N_2 by heterogeneous reaction with carbonaceous surfaces, and therefore can be reduced by reaction with char and soot particles [32]. The amount of NO_x emitted is therefore closely dependent on the combustion environment but also on the fuel composition.
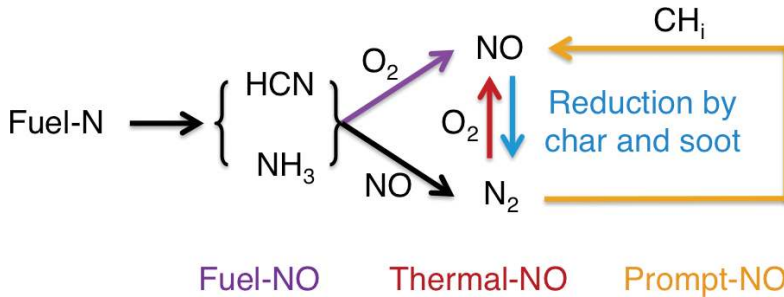

Figure 4. Schematic representation of NO formation in coal combustion system.

Largely, all combustion processes lead to the formation of NO_x, emitted mostly as nitric oxide (NO) with smaller amounts of nitrogen dioxide (NO_2). Nitrous oxide (N_2O) emissions can be significant in fluidized bed combustion, but are negligible in most combustion systems [30].

During co-combustion tests of WDF in fluidized bed combustors (FBCs), authors reported a reduction in NO_x emissions [12, 33–35]. They explain these reduced emissions by the lower nitrogen content of WDF compared with coal, up to 10 times less [30], but also by the nature of the nitrogenous groups in the waste material. Indeed, the main nitrogen compounds of WDF are simple proteins known to release NH_3, which is then decomposed to NH_2, NH radicals forming N_2 after reacting with NO [34]. However, with the increase in cofiring ratio (>30%), increases in NO_x emissions have been recorded [13, 33]. The authors suggest that since less coal is fed to the FBC, availability of unburned carbon is reduced, decreasing the extent of NO reduction by char.

Reductions in NO_x emissions was also recorded during cofiring tests in a cyclone fired combustor [36], as well as in entrained flow reactors (EFRs) [6, 37]. In EFR, contrary to FBC, increased cofiring ratio led to increasing NO_x reductions. The conversion of fuel nitrogen into NO seemed therefore to decrease with increasing share of WDF. This is likely related to the

high volatile content of WDF (as can be seen in **Table 1**), which might generate a reduction zone with lower excess air ratio near the burner [6]. This lower oxygen concentration may inhibit the conversion of fuel nitrogen to NO resulting in reduced NO formation. In addition, since the formation of thermal NO may not be negligible in the EFR, co-combustion of coal and WDF may result in a lower flame temperature compared with coal alone, thus leading to a reduced formation of thermal-NO.

Because NO_x emissions are closely related to the combustion environment, it is critical to maintain a stable and homogeneous solid feed-rate. However, several studies reported difficulties in achieving a steady mass flow rate of WDF to the combustor [12, 34, 36, 37]. This could be due to its inhomogeneity or its "fluffiness". Therefore, for large-scale utilization of WDF, attention should be brought to the optimization of the feeding system. Increasing the carrier gas flow rate, adding a dedicated burner, and working at low cofeeding ratio can help reduce these feeding fluctuations. Finally, producing a homogeneous WDF in terms of particle size and composition, with physical properties as close as possible to that of the injected coal, is advised in order to experience smooth operation of the boiler with reduced NO_x emissions.

5. Effect of WDF co-combustion on SO_2 emissions

Whether a fluidized bed combustor, a cyclone fired combustor, or an entrained flow reactor was used, increasing the WDF cofiring ratio led to a decrease in SO_2 emissions [6, 12, 33–36, 38]. Two main explanations can be found regarding the decrease in SO_2 emissions. The first
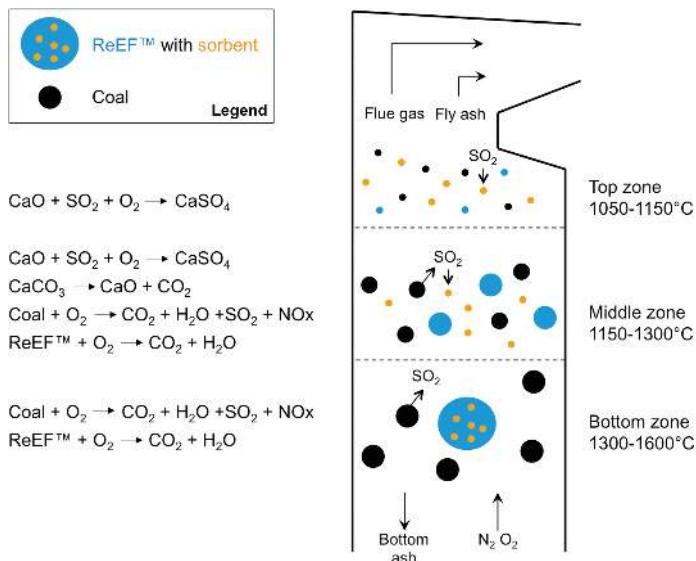

Figure 5. Expected behavior of a WDF combined with alkaline sorbent in a pulverized fuel combustion environment, inspired from [42].

one is the reduced sulfur content of the WDF compared with coal. The second one, corroborated by an increased sulfate content in the bottom and fly ash, is the absorption of SO_2 by alkaline oxides, and more precisely calcium. With the higher calcium content of the WDF compared with coal, a sulfur self-retention process can occur according to the following overall reaction [39]:

$$CaO + SO_2 + 0.5\,O_2 \rightarrow CaSO_4 + heat \tag{3}$$
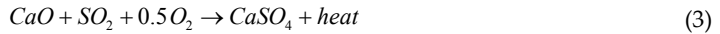
i.e. decreasing the concentration of SO_2 in the flue gas.

To further take advantage of such phenomenon, Accordant Energy LLC®, formerly known as ReCommunity Inc., developed a novel WDF, called ReEF™ or ReEngineered Feedstock™, to which air-emission control sorbents (e.g., calcium-, sodium-, halide-based and DeNOx reagents) are physically bound [40, 41]. Due to the combined effect of a lower sulfur content in the solid feed, SO_2 capture by the sorbents and transport of small sorbent particles by larger waste particles, SO_2 emissions can be greatly reduced. A schematic representation of this novel technology's behavior is given in **Figure 5**.

In pulverized coal boiler, the ReEF™ is designed so that as the solid feed and the reactant gas enter the bottom of the reactor, the fibers and plastics undergo endothermic pyrolysis, and protect inorganic sorbents from exposure to high temperature, thus minimizing sintering. At this level in the reactor, the coal burns and releases SO_2. When ReEF™ fragments travel upward and are combusted, sorbents are released and can capture the SO_2 present in the flue gas. At the same time, any remaining residues continue to combust. Finally, in the top zone, also called the convection zone, sorbents desulfurize the flue gas to the point when complete burnout and conversion are achieved. This way, optimal ReEF™ design minimizes sintering of the sorbent early in the reactor while maximizing gas absorption later at lower temperatures before exiting as gas/solid products [42].

The use of this novel fuel led to SO_2 emissions reduction greater than 80% in a bubbling fluidized bed [43], up to 85% in a circulating fluidized bed [42], and up to 55% in pulverized coal boiler environment [37]. This fuel and the concept behind it open a new avenue for WDF, as they could be combined with various air-emission control sorbents and tailored to react with pollutant of interest (sulfur, nitrogen, heavy metals, etc.).

6. Effect of WDF co-combustion on ash related issues

Ash-forming elements occur in solid fuels mainly as internal or external mineral grains, as simple salts (e.g., NaCl or KCl), or associated with the organic matrix of the fuel [44]. In coal, a large fraction of the inorganics is present as minerals, mainly as Si, Al, Fe, and Mn. In biomass-derived fuels, such as WDF, on the other hand, the major part of the inorganics consists of free ions and simple salts or is associated with the organic matrix, and is rich in alkali and alkali earth metals (K, Na, Ca, and Mg) [24, 44]. Therefore, while approximately 0.5–4 wt% of the

inorganics in coal vaporizes during combustion, between 30 wt% and 75 wt% of the inorganics in straw, for example, is vaporized at 1200°C [44]. Alkali metals are indeed generally released to a larger extent than the other mentioned species, vaporizing at temperature under 600°C [24]. These alkali metals, once vaporize, may react with silica to form alkali silicates, sulfates, and chlorides that melt or soften at low temperature, which make the co-combustion systems candidate to deposition issues [45].

It should be noted, though, that the release of volatile inorganics depends on a large extent in the presence of more conservative inorganic elements such as silicon and aluminum in the fuel. It has been found that higher aluminosilicate content in the fuel makes alkalis significantly less volatile during combustion [46]. Furthermore, alkali earth metals decrease the retention of alkali metals on silicates leading to the formation of less adhesive compounds [24]. Mechanisms behind ash deposition are therefore rather complex, which are quite challenging as they are of vital importance for the boiler operators. Indeed, careless cofiring of difficult alternative fuels could lead to a reduction of boiler reliability and availability, and to unscheduled plant shut downs [47].

Three major interrelated problems associated with the inorganic content of alternative fuels such as WDF have been identified: bed agglomeration, fouling/slagging, and corrosion.

6.1. Bed agglomeration

Bed agglomeration is caused by interaction between alkali species and silica sand (the bed material in fluidized bed combustors) at high temperature, which can create low melting point eutectics. These eutectics can then act as binder between bed particles, which can result in a partial or complete collapse of the bed leading to defluidization and resulting in costly shut downs [48, 49]. Bed agglomeration and defluidization are influenced by various parameters, including temperature, fluidization velocity, size of bed particles, and combustor size [48]. Detection methods for agglomeration have been developed, such as monitoring of local temperature and pressure fluctuations, which can help to forewarn the onset of defluidization [49]. Anyhow, while agglomeration can be a major problem in fluidized bed combustors fired with biomass-derived fuels only, cofiring of biofuels and coal largely decreases the risk for agglomeration [50].

6.2. Slagging and fouling

While only fluidized bed combustors are affected by agglomeration, all types of furnaces are subject to ash deposition. Heat exchanger surfaces, combustion chamber walls, and cyclones are typically sensitive areas where deposits may cause extensive operational problems [51, 52]. These deposits reduce the heat transfer intensity and cause corrosion that reduces the lifetime of the equipment [53]. In order to limit these issues, many coal-fired power plants conduct sootblowing every 8–12 h [54]. Generally, two main types of deposits can be found [55–57]:

– slagging: occurs in the high-temperature radiant sections of the furnace, directly exposed to flame irradiation, usually associated with some degree of melting of the ash, forming a highly viscous liquid layer;

– fouling: happens in the lower-temperature convective sections of the combustor, generally related to condensation on the low-temperature tube surfaces of volatile species that have been vaporized in previous sections and are loosely bonded, forming an adhesive film that can cause ash particles to adhere to the surface.

Slagging and fouling are very complex phenomena, but they generally simply start with the adhesion of the ashes in suspension on the various boiler surfaces. Ashes will adhere on a surface if it is coated with a partially melted layer. This layer can either be composed of ashes previously vaporized which condensed on the surface [58], or be due to the fusion at really high temperature of the materials composing the surface itself. These mechanisms are schematized in **Figure 6**.
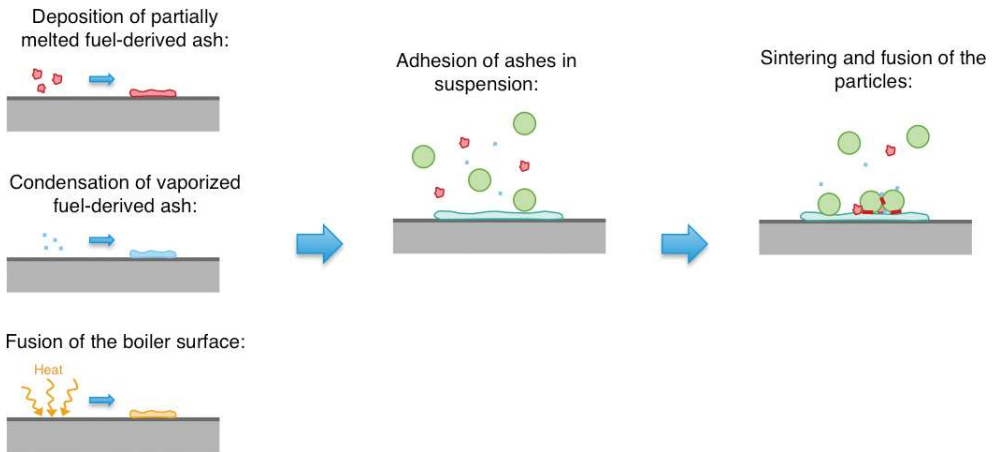

Figure 6. Schematic representation of the formation of deposits in the boilers.

Once the ashes have been deposited on the melted surface, phenomena such as sintering and fusion can produce stronger and more lasting deposits, which are therefore more problematic. These phenomena are accelerated in presence of alkali salts [59]. Therefore, the higher the ash fusion temperature, the better, so that the deposits are not melted, but are loosely bond and easy to clean with sootblowers [20]. Fusion temperature of crystals and eutectics typically present during coal and WDF co-combustion are given in **Table 2**. It can be seen that the higher the alkali content, and more precisely sodium and potassium, the lower the fusion temperature and therefore the more acute the slagging and fouling [45, 57]. At present, in purely waste-fired units, corrosive deposits and ash melting have limited their steam temperature to 420–470°C, and consequently their electric efficiency to 20–24% [28].

Component	Fusion temperature (°C)
$K_2S_2O_7$	325
$Na_2S_2O_7$	401
$Na_3K_3 Fe_2 (SO_4)_6$	552
Na_2SO_4 –NaCl	625
Na_2 S-FeS	640
$CaSO_4$ –CaS	850
Na_2SO_4	884
$K_2O.Al_2O_3 .6SiO_2$	1150
$CaSO_4$	1450
$2CaO.Al_2O_3 .2SiO_2$	1593
SiO_2	1700

Table 2. Switch the table to have the line as column and vice versa. Separation between the column is not clear for the first line. We read K2O.Al2O3CaSO4 for example [45, 60].

In order to understand and predict the ash deposition propensity of fuels, numerous research approaches have been undertaken. Among them is the development of a number of empirical indices and several laboratory methods to determine the ash fusion temperatures [47].

Four temperatures are used to characterize the ash melting behavior of laboratory prepared ash [61]: (1) the shrinking temperature (ST) defined as the temperature at which shrinking of the test piece occurs, (2) the deformation temperature (DT) defined as the temperature at which the first signs of rounding of the edges due to melting of the test piece occur; (3) the hemisphere temperature (HT) defined as the temperature at which the test piece's height becomes equal to half the base diameter; and (4) the flow temperature (FT) defined as the temperature at which the ash is spread out over the supporting tile in a layer, the height of which is equal to half the height of the test piece at the hemisphere temperature. These temperatures are represented in **Figure 7**. Over the ST ashes can be strongly adhesive, which can result in slagging [60].
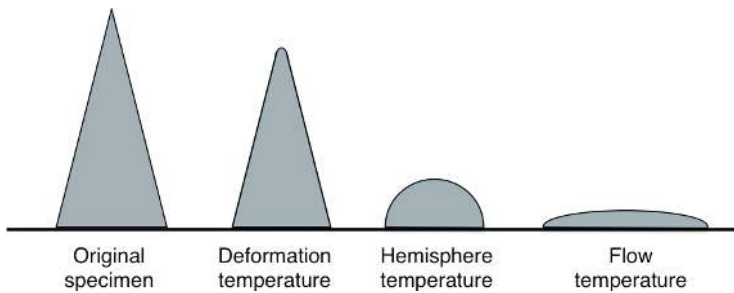

Figure 7. Ash characteristic temperatures.

From these characteristic temperatures, a slagging propensity index is evaluated as:

$$F_s = \frac{4DT + HT}{5} \tag{4}$$

with the temperatures expressed in degree Celsius. Ashes are classified as having a boiler slagging propensity medium when F_s lies between 1232 and 1342°C; high when F_s is between 1052 and 1232°C; and severe when F_s is less than 1232°C. Accordingly, MSW and paper/plastic fluff will both have a high slagging propensity [61].

Other indices are based on the finding that so-called basic compounds (or fluxing oxides) lower the deformation temperature of ashes, whereas acidic ones (also called sintering oxides) increase it [60]. This general rule of thumb, developed for coal ashes, can also be applied to WDF ashes [61]. The slagging propensity of mixes of WDF and coal ashes can therefore be correlated to the B/A ratio [60]:

$$B/A = \frac{Fe_2O_3 + CaO + MgO + Na_2O + K_2O + P_2O_5}{SiO_2 + Al_2O_3 + TiO_2} \tag{5}$$

with Fe_2O_3, CaO, MgO, Na_2O, K_2O, P_2O_5, SiO_2, Al_2O_3 and TiO_2 the weight fraction of the corresponding components in the ashes.

Intensive slagging has been observed when the index is in the 0.75–2 range. Moving away from this range in either direction has decreased the slagging intensity [47].

Finally, thermodynamic equilibrium modeling has become another tool to better understand and predict the chemical reactions of the ash-forming matter during co-combustion of coal, and WDF. Comprehensive description of thermodynamic database and model of ash-forming elements in waste combustion can be found in [62].

Such approaches can give an initial assessment of the slagging and fouling propensity of the fuels [24]. However, for a true evaluation, experimental work is greatly recommended, especially since interactions between burned coal particles and pyrolyzed WDF particles could lead to the formation of unexpected species. For example, in [47], the authors tested the co-combustion of coal and 5% RDF in a drop tube furnace and observed an unexpectedly strong effect of RDF addition, enhancing the deposition rates by a 1.5 average factor. Furthermore, they observed big molten RDF particles in the deposits. In [6], on the other hand, the authors observed in an entrained flow reactor a decrease of the ash deposition flux with the increase of the SRF share. They suggest that this decrease might be related to the relatively high calcium content of the SRF ashes, which might generate calcium components with high melting temperature. They also suggest that due to the higher char fragmentation degree of SRF particles, average ash particle size and/or density might be smaller and therefore the inertial impact efficiency decreased, resulting in reduced ash deposition rate. Another example is given in [33] where increased fouling deposits, usually composed of sulfates and chlorides, were

observed in a circulating fluidized bed boiler with the increase of the RDF cofiring share. Anyhow, even when increased slagging and fouling propensity was found, authors concluded that co-combustion of coal and WDF in power plant was feasible.

6.3. Corrosion

On top of the extent of the deposits, another important characteristic is their corrosiveness. The ratio between alkalis and chlorine in the fuels has been used to evaluate if the resulting deposit will be corrosive or not. For WDF, this ratio is likely to be <1, predicting that alkalis are likely to occur bounded to chlorine with little availability for alkali silicates formation [24]. Furthermore, the presence of melt in the salt deposit increased significantly the corrosion of the steel material, especially in presence of chlorine [63]. More details about the role of chlorine will be given in the next section, but catalytic effect between the deposit and the metal oxides covering the tube could lead to the enhanced oxidation of SO_2 to SO_3, which could lead to the formation of sodium and potassium pyrosulfates and trisulfates [20]. In temperature exceeding 550°C, these species can react with the tube protective layer of oxides, and molten deposit can exist even at temperature as low as 398°C, $Na_2S_2O_7$ existing in molten state at such low temperature [20].

The oxygen content in the flue gas is of primary importance for the corrosion process—in oxidizing conditions, the damaged oxides layer may be rebuilt, giving adequate anticorrosive protection [20, 64]. Therefore, the occurrence of reduction atmosphere in the area of super-heaters (which can take place by low-NO_x combustion in pulverized fuel boilers) strongly increases the risk of corrosion. This can also happened when the melted deposit prevent the oxygen to reach the tube metallic surface [20].

One of the major drawbacks of the utilization of WDF is the higher propensity of their ashes to deposit on the boilers surfaces. Cofiring experiments showed that even if higher slagging and fouling occur, they were of manageable magnitude. Furthermore, combining WDF to coal greatly reduces the ash-related damages, compared with the combustion of WDF alone. Cofiring is therefore doable, but caution is needed.

7. Chlorine behavior in WDF co-combustion

The origin of chlorine in the fuels can be separated as organic and inorganic chlorine. In coal, the chlorine exists mainly as semiorganic Cl that is anion Cl^- sorbed on the coal organic surface in pores, surrounded by pore moisture [65]. In WDF, inorganic chlorine (e.g., NaCl) and organic chlorine (e.g., PVC) coexist. Furthermore, their chlorine content is largely superior to that of coal, reaching up to 1.8 wt% (see **Table 1**). Therefore, during the combustion of WDF, their chlorine content reacts and is emitted in the furnaces as vapor of hydrochloric acid or as chlorides which can condense on the surfaces of the furnaces as salts and cause their corrosion [65]. Finally, HCl can also react with organic molecules and form dioxins and furans. These three potential fates are described in this section and are illustrated in **Figure 8**.
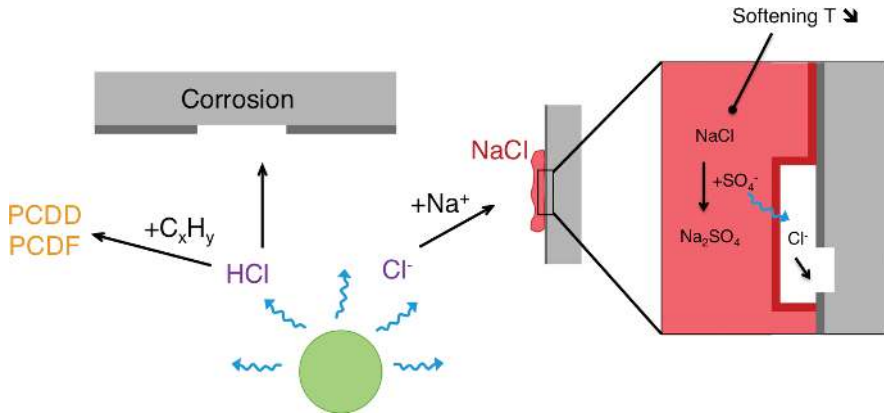
Figure 8. Illustration of the chlorine behavior in a combustion environment.

7.1. High-temperature corrosion

High-temperature corrosion in boilers is defined as the chemical attack of the metallic surfaces. In combustion units, corrosion mainly occurs when the metallic surfaces are in contact with melted salts. During combustion of coal only, the component responsible for the high-temperature corrosion is typically $(Na,K)_3Fe(SO_4)_3$, which may form a eutectic mixture at low melting temperature. Potassium, sodium, and sulfur originate from the coal, whereas the metallic surface provides the iron [59]. However, in the presence of chlorine, other corrosion mechanisms become dominant.

Chlorine in the ash deposits accelerates the corrosion by various mechanisms. First, chlorides decrease the softening temperature of the deposits, which, once melted, can damage the protective oxide layer of the metallic surfaces. Therefore, as soon as the deposits temperature exceeds the ST, the speed of corrosion increases significantly [51]. Second, the partial pressure of gaseous chlorine under the deposits containing chlorides can be significant, even at temperature lower than the ST, making chlorine available to attack the metallic surfaces through a gas phase corrosion mechanism. The presence of gaseous chlorine is mainly attributed to the sulfation of the deposited alkaline chlorides by gaseous SO_2 and to the reaction of the alkali chlorides with the metallic oxides [66]. In fact, in [63], the authors studied that when chlorine was present in the salt, corrosion could take place at temperatures clearly below any melting of the salt deposits, and only a very low amount of chlorine was needed to trigger such corrosion. These results can be explained by the presence of gaseous chlorine produced by the sulfation of the deposits.

On the other hand, other studies support that the sulfation of the alkali chlorides could reduce the deposit based corrosion [58, 67, 68]. Indeed, in [69], it was shown that a pure alkali salt, whether it contained sodium or potassium, with no chlorine did not cause any corrosion of any of the tested steels while all steel's samples showed indications of iron being volatilized

from the steel surface when the alkali salt contained chlorine. Furthermore, the corrosion by alkalis sulfates can be managed by reducing the tube surface temperature and by adequately using sootblowers [70].

It has, therefore, been established that when the S/Cl molar ratio is higher than 4, the fuel can be regarded as noncorrosive, whereas by S/Cl < 2 the corrosion occurs almost inevitably [20].

Based on the idea of a protective layer, one of the recent developments in the field of corrosion protection is the coating of the pipes by a dense ceramic layer of porosity under 1%. This layer avoids the contact between the chlorine species and the metal, thus avoiding its corrosion [71]. The thickness of these layers is generally around 75–90 μm.

7.2. Hydrogen chloride (HCl)

Even if in the high-temperature regions of the boiler chlorine can be found as alkali chloride, at lower temperature, and thus at the exit of the boiler, the majority of the chlorine is found in the flue gas as HCl [46, 72]. In [44], for example, it was observed that during the co-combustion of straw containing 0.55 wt% of chlorine, 98 wt% of it is found as HCl.

The major problem related with HCl is the active oxidation of the tubes at high temperature [20] (this kind of corrosion is however less aggressive than that of the melted alkali chlorides) and the attack of the joints and equipment downstream from the boiler, where the temperature and concentration allow the formation of liquid chloric acid [68].

However, presence of HCl could allow the oxidation of the mercury and therefore facilitates its capture and control. Indeed, it seems that the percentage of mercury leaving the furnace in its elementary form decreases drastically from 85 to 10% for coal containing more than 150–220 ppm of chlorine in dry basis, facilitating the mercury capture in the particle control devices [72].

Finally, HCl can also react with calcium, sodium oxides, and carbonates [68, 73]:

$$CaO + 2HCl \leftrightarrow CaCl_2 + H_2O \qquad (6)$$

$$Na_2CO_3 + 2HCl \leftrightarrow 2NaCl + H_2O + CO_2 \qquad (7)$$
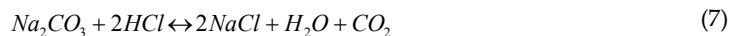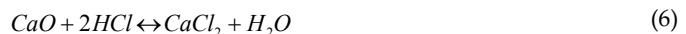
and be retained in the ashes. This phenomenon was observed, for example, in [12], where the authors measured low levels of HCl in the flue gas and higher chlorine retention in the ashes during co-combustion of coal and EF compared with coal alone in a fluidized bed. Experiments of co-combustion of RDF and coal in a vortexing fluidized bed described in [13] also concluded in a decrease of HCl in the flue gas in the presence of $CaCO_3$, as did Kim et al. [35] with their circulating fluidized bed co-combustion experiments.

7.3. Dioxins and furans formation

Another preoccupation regarding the presence of chlorine is the formation and the control of polychlorinated dioxins and furans (PCDD and PCDF). PCDD and PCDF are chemically stable components, formed at temperature around 250–400°C [35]. Present during the combustion of MSW in dedicated incinerators, they however have not been detected during the co-combustion of coal and WDF [74]. This might be explained by one of the major difference between coal power plants and waste incinerators, that is the higher sulfur level. Typical S/Cl ratio in incinerators is around 0.2, which is one order of magnitude less than what is found during coal co-combustion.

The major chlorination agent in the formation of PCDD and PCDF is Cl_2, HCl being relatively ineffective. Cl_2 may be formed via a reaction known as the Deacon reaction, which may occur during the gas cooling process [65]:

$$2HCl + 0.5O_2 \leftrightarrow H_2O + Cl_2 \tag{8}$$

Cl_2, however, is decomposed by homogeneous reaction with SO_2:

$$Cl_2 + SO_2 + H_2O \leftrightarrow 2HCl + SO_3 \tag{9}$$

Consequently, SO_2 prevents the presence of molecular chlorine and suppresses the PCDD and PCDF formation [65, 74]. Therefore, very low concentrations (<0.03 ng-TEQ/N m³) of PCDD and PCDF have been observed during WDF and coal co-combustion [33, 35, 36, 43].

8. Conclusion

The combustion of fuel derived from municipal solid waste is a promising cheap retrofitting technique for coal power plants, having the added benefit of reducing the volume of waste disposal in landfills. Furthermore, co-combustion of WDF and coal, rather than switching to WDF combustion alone in dedicated power plants, allows power plant operators to be flexible toward variations in the WDF supply.

Experiments show that substituting part of the coal feed by processed high-calorific value waste reduces the NO_x, SO_2, and CO_2 emissions of coal power plants. However, the alkaline content of WDF and its potentially harmful interaction with the coal ashes, as well as adverse effects from the presence of chlorine in the waste are important drawbacks to waste-derived fuel use in large-scale power plants. On the other hand, synergetic effects between the coal and the waste, such as suppression of the PCDD and PCDF formation by SO_2, or oxidation of mercury by HCl facilitating its capture in the particulate control device, are promising outlooks. Furthermore, in a world looking toward green energy production, re-

duction of the amount of coal used to produce energy through co-combustion of cheap part-ly renewable material that are the waste is of critical interest. Finally, waste-derived fuels can be combined with additives dedicated to the capture of targeted pollutants, improving even further the environmental performance of coal power plants.

Nomenclature

F_s	slagging propensity index (−)
DT	deformation temperature (°C)
HT	hemisphere temperature (°C)
LHV_i	lower heating value of i (kJ/kg)
W_i	mass flow of i (kg/h)
x_i^e	energetic fraction of i (−)
x_i^{wt}	mass fraction of i (−)

Subscripts

c	coal
WDF	waste-derived fuel

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