Gasification of low-grade SRF in air-blown fluidized bed: permanent and inorganic gases characterization

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Abstract

The influence of the gasification temperature and Equivalence Ratio (ER) on the behavior of an industrial low-grade Solid Recovered Fuel (SRF) was investigated in an air bubbling fluidized bed. The studied SRF exhibits an intermediate composition between biomass-rich SRF and plastic-rich SRF. Its Lower Heating Value (14 MJ/kg) is low since its ash content is very high (35 wt.%). But surprisingly, the Cold Gas Efficiency and the Carbon Conversion were relatively high with this type of low-grade SRF. As a result, the syngas produced is quite rich (LHV > 8 MJ/m^3 STP) and it may be valorized in gas engines. H_2S, HCl, HCN and NH_3 in the syngas were analyzed. These results confirm that inorganic gases are an important issue for the valorization of SRF as fuel in gasification processes, even if significant parts of S, N and Cl are not converted into inorganic gases.

Keywords: SRF; RDF; Gasification; Syngas; Inorganic

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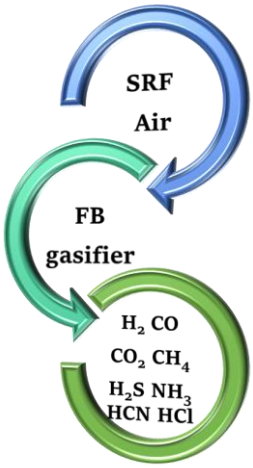
Graphical abstract



Statement of Novelty

This work is an original contribution that allows quantifying the different gas species that are obtained through SRF gasification in fluidized bed. These gas species include not only permanent gases, but also inorganic gases like H_2S, NH_3, HCN, HCl. These data are scarce in the scientific literature, whereas they are required in order to conceive a sustainable gasification process that will produce a purified syngas for CHP applications.

Declarations

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1. Introduction

The worldwide production of Municipal Solid Waste (MSW) is estimated around 2.01 billion tons per year, and around 70% of waste is disposed in landfill sites or openly dumped in natural sites [1]. This alarming situation creates catastrophic issues of air, soil, and water pollution affecting human health as well as flora and fauna life [2, 3]. It must prompt the society, starting with the scientific community, to react in order to improve and promote the collection, the recycling and the valorization of wastes [4–10]. While the most efficient solution would consist in the reduction of waste generation, this latter is unfortunately expected to increase to reach 3.4 billion tons per year by 2050 [11]. Therefore, new efficient valorization routes must be developed.

Solid recovered fuels (SRFs) can be produced by sorting different waste streams and appear as one of the promising solutions to improve waste management [12]. SRFs consist of a mixture of different non-hazardous and non-recyclable solid waste fractions, such as plastics, textiles, tires, paper and carton, biomass waste, or sludge [13]. Consequently, SRFs are very complex and heterogeneous materials, and the proportion of each fraction can vary significantly depending on the waste origin, the season, the waste sorting plant, and the SRF production technique. SRFs represent a significant fuel resource, with a potential estimated at 70 million tons per year in Europe [14]. This resource represents 25-35 Mtep of primary energy, i.e. approximately 2 % of the consumption in Europe [15]. SRFs are complex heterogeneous fuels. Therefore, a rigorous definition of SRF characteristics is difficult to provide, which hinders the development of suitable valorization processes. Currently, SRFs are mainly used as a fuel in cement kiln, but other energetic valorizations are expected to be developed.

Thermochemical processes, such as incineration and gasification, are efficient ways for the management of municipal wastes [16, 17], as they allow the decomposition of contaminants

and the concentration of some inorganic species in the ashes [18]. In the gasification process, the solid fuel is partially oxidized at high temperature (800-1000 °C) using a gasifying agent (air, steam, O_2 or CO_2). This process results in the production of syngas, composed of a mixture of H_2, CO, CO_2, CH_4, and C_nH_m having high calorific value. One of the most important advantage of gasification over combustion is the different applications existing for the syngas. Depending on its purity, syngas can be used as a fuel in different power generator systems (gas engine, gas turbine, fuel cell), or as a precursor for gaseous fuels (H_2, CH_4) or liquid fuels synthesis [19, 20]. Different gasification technologies have been developed. Among them, fluidized bed reactor is the most adapted for waste valorization at medium-scale (1 to 100 MW), due to the efficient flow mixing between reactants, the carefully controlled temperature, the high heat transfer performance, and the large operating flexibility. Indeed, fluidized bed reactor can be operated for the gasification of fuel having different properties [21, 22], such as meat waste and wastewater treatment sludge [23], tires [24, 25], poultry fuel [26], plastic wastes [27–29] etc. For this reason, fluidized bed gasifiers have been used in the past ten years for the gasification of SRFs [30, 31], these materials being very heterogeneous in terms of composition. The LHV of SRF can significantly vary depending on the waste origin and the SRF production method. The valorization of low-grade SRF by gasification process can be impeded if the syngas LHV is too low to be valorized in a gas engine. The presence of pollutants in the syngas (tar, inorganic gases, and particulate matter) also jeopardizes its valorization since it increases the syngas purification cost [32].

The pollutants content in syngas strongly depends on the gasification conditions and on the initial fuel composition [33]. For waste gasification, the tar content was proved to be slightly higher than for biomass gasification [30, 34–38]. For this reason, tar removal processes are required before valorizing syngas in gas engines. During waste gasification, the inorganic gases concentration can be significantly higher than that obtained in syngas from biomass due to the

high contents in nitrogen, chlorine, and sulphur species initially contained in the waste. Inorganic gases could lead to corrosion and clogging problems in the gasification process, to the poisoning of the catalysts used for syngas cleaning and upgrading, to acid rains [39–41], and also to combustion issue if syngas is burnt in a gas engine [42]. The main inorganic gases contained in syngas are H_2S (100-30000 ppm), HCl (1-500 ppm), NH_3 (500-14000 ppm) and HCN [32, 43–47]. Their content must be drastically reduced to reach the standards required for syngas valorization. For this reason, the measurement of the inorganic gases concentration in syngas from SRF must be accurately carried out.

In the literature, different methods have been explored to analyze inorganic gases in syngas. Most of them consists in the absorption of inorganic gases in impingers filled with different solutions which are then analyzed. The composition of the absorbing solutions as well as the analytical tools are different in the studies reported in the literature [31, 48–51]. Indeed, H_2S, NH_3, HCN and HCl after absorption and under ionic state can be analyzed by ion chromatography, potentiometry, iodometry, ion electrophoresis, or indophenols blue absorption spectrophotometry [52]. Syngas can be analyzed on-line (by IR based spectroscopy) but these methods are hardly quantitative due to important artefacts coming from H_2O and CO_2. Sulphur gases can also be directly analyzed by gas chromatography equipped with a PoraPLOT U column and Thermal Conductivity Detector (TCD), but this technique suffers from relatively high detection limit (around 1 ppm) [52, 53] which is typically too high to analyze the syngas purity after the syngas cleaning operations. Pulse Flame Photometer Detector (PFPD) are efficient detectors to analyze inorganic gases, but hydrocarbon species in syngas must be quenched prior to analysis [52]. Recently, new techniques have been developed to analyze S species in syngas of biogas, such as Optical Feedback Cavity-Enhanced Absorption Spectroscopy (OF-CEAS), or ion-molecule reactions-mass spectrometry (IMR-MS) [52].

While the decrease in tar concentration with increasing Equivalence Ratio (ER) and gasification temperature was unanimously reported [54, 55], the evolution of inorganic gases with operating conditions in bubbling fluidized bed is currently discussed in the literature.

First, concerning the effect of reactor temperature, a temperature rise was proved to increase the release of HCN, while NH_3 decreased [30, 50, 54]. The nature of the solid N-compounds strongly influences the release of nitrogenous species. In carbonaceous materials, different nitrogen groups can be present: pyrrole, pyridine, pyridinium, pyridine oxide, amine, nitro, nitroso, and cyano compounds [56]. NH_3 results from the decomposition of amino-groups, whereas HCN mainly originates from the decomposition of pyrrolic and pyridinic nitrogen [57–60]. As SRFs may be rich in plastics, the gasification performed at relatively high heating rate was proved to promote the release of HCN [61]. While part of the nitrogenous compounds can be in the form of tar [62] and char [63] after pyrolysis, secondary reactions can transform these nitrogenous compounds into HCN during gasification [64]. In addition, the drop of NH_3 release with increasing temperature can be attributed to the thermal decomposition of NH_3 into N_2 [65]. This reaction can be catalyzed by the presence of calcium, potassium and iron in the SRF ashes [66]. The HCl content drastically drops with rising temperature [30, 50]. Chlorine in SRF could originate from both organic (PVC) and inorganic (salts) sources [67] which are partially decomposed in the form of HCl during gasification. The decrease of HCl in the gas phase with rising temperature is explained by the presence of alkali metals (especially K). Indeed, at low temperature (<700 °C), alkali species are mainly in the form of alkaline carboxylates. These structures decompose at higher temperature, and alkali metals are then available to react with HCl, which decreases the HCl content in gas phase [68–70]. However, the presence of silica and sulfur in the fuel was proved to increase the HCl formation [67]. Sulfur contained in SRF originates from organic and inorganic sources, and elastomers (such as rubber) represent an important input [14]. H_2S is the main S-containing gas released during

gasification [47, 71]. A temperature rise was proved to increase the release of H_2S [38, 50, 54]. While organic sulfur is decomposed at low temperature (around 500°C) [72], inorganic sulfates in the chars have higher binding energy and are decomposed at higher temperature [73]. Thus, when the temperature increases, higher amount of H_2S is released. Besides, some inorganic species (such as Ca, K or Fe) can react with H_2S to form sulfides and immobilized sulfur in the solid phase, thus decreasing the H_2S release [73, 74]. Nevertheless, *Pinto et al.* observed no effect of temperature on the release of H_2S during the gasification of SRF [31].

Second, the influence of the ER on the release of inorganic gases in allothermal gasification reactors is a controversial topic in the literature. The release of inorganic gases could be expected to increase as ER rises, since the secondary reactions (char gasification, tar reforming) could be promoted by oxidation reactions thus favoring the release of Cl, N or S. *Pinto et al.* showed that the ratio of sulphur converted into H_2S to the amount of S in the feedstock increased with increasing ER [31]. It has been reported that the NH_3 concentration increases with rising ER [31, 49]. However, several studies showed that the concentration of inorganic gases (H_2S, HCl, HCN, NH_3) in the syngas decreases with rising ER [50, 54, 75]. This trend can be explained by the promotion of char gasification reactions which promote the contact and reactions between inorganic gases and the mineral species of the ash (Fe, Ca, K, Na) resulting in the immobilization of Cl, N or S atoms in the ashes. This decrease can also be attributed to oxidation reactions promoting the formation of SO_x and NO_x [50]. In addition, the decrease in inorganic gases concentration can result from a dilution effect due to the ER increase. Indeed, when the ER is increased in an air fluidized bed process, the syngas produced is diluted in a larger amount by nitrogen, thus decreasing the inorganic gases concentration. Rigorous measurements must be performed to better understand the distribution of S, Cl, and N.

These apparent discrepancies in literature results could be attributed both to the composition of the SRFs studied and to the nature of the bed material. Indeed, the nature of the bed material plays a significant role in the release of inorganic gases. *Pinto et al.* showed that dolomite, lime and olivine allowed to decrease the H_2S content in the syngas [31]. The more reactive materials were dolomite, lime, and finally olivine. This reactivity was attributed to the formation of sulfides by reactions between H_2S and Ca (in dolomite and lime), and to the presence of Fe in olivine. Contradictory results were reported in the literature on the effect of natural minerals on the NH_3 release. Some study highlighted the reduction of NH_3 release with natural minerals [76], while other showed that it increased as these materials catalyzed the char gasification reactions thus promoting the release of heteroatoms [31]. The type of reactor wall, as well as the sampling and analyzing methods were also proved to influence the measurement of inorganic gases [77].

Despite all these previous studies, the effect of temperature and ER on the fate of S, Cl, and N species remains unclear.

For this reason, the present study investigates the air gasification of an industrial SRF in a fluidized bed. Olivine was used as a common and cheap bed material. At industrial scale, the gasifiers are autothermal, while the reactor walls have to be heated at lab-scale to balance heat losses. Thus, it has been possible to study the respective effects of temperature and ER on the gasification efficiency by varying these two parameters independently. Gasification efficiency was evaluated based on four indicators: cold gas efficiency (CGE), carbon conversion (CC), syngas lower heating value (LHV_{syngas}), and the syngas yield (η_{syngas}). A previous article has presented the effect of gasification conditions on these 4 indicators for two SRFs (one rich in biomass and glass, and a second richer in plastics) [78]. The present article supplements this previous study with another SRF which exhibits an interesting composition between biomass-rich SRF and plastic-rich SRF. Therefore, this SRF presents a complex gasification behavior

187 of high interest for the waste management community. In order to better characterize its
188 gasification behavior, the analysis of the inorganic gases is reported in this study.

2. Materials and methods

2.1 Characterization of the Solid Recovered Fuel and Fly Ashes

The SRF studied was provided by a French company of waste management and valorization. It was selected as its composition was intermediate between biomass-rich SRF and plastic-rich SRF. The same characterization methods were used for this SRF and for the Fly ashes revovered in the cyclone after the experiments. The elemental composition was measured according to the standard NF EN 15407. The ash content was measured at 550°C according to the standard NF EN 15403. The composition of the resulting ashes was measured by X-Ray Fluorescence Spectroscopy. Inductively Coupled Plasma – Atomic Emission Spectroscopy (ICP-AES) was also used to characterize the mineral composition of the ashes after ash melting (NF-M03-042). The SRF sample was calcined at 815°C, and the remaining ashes were melted with $Li_2B_4O_7$ at 1000°C, before being dissolved in hydrochloric acid solution and detected by AES detector. Finally, ionic chromatography was used to analyze the halogen compounds (NF EN 1548 and NF EN ISO 10304-1).

The Lower Heating Value (LHV) of the SRF was measured with a calorimetric bomb (NF EN 15400). The proportion and composition of biomass, non-biomass, and inert materials were determined according to the standard NF EN 15440 that is based on manual sorting.

2.2 Gasification reactor and analysis of gas

Gasification tests were performed in a bubbling fluidized-bed constructed at CNRS Nancy and made of stainless steel 310 (Figure 1) [36, 78]. Briefly the gasifier is divided into three zones: the plenum (d=100 mm, H=300 mm), the bed zone (d=100 mm, H=800 mm), and the freeboard zone (d=140 mm, H=800 mm). The gasifying agent was air whose flow rate was controlled by a mass flow controller (Brooks 5850S). At the bottom of the gasifier, a 3mm thick inox grid was used as distributor plate to homogenize the air flow and insure an efficient fluidization. The gasifier is heated by eight electrical heater shells at a maximum temperature of 1000 °C.

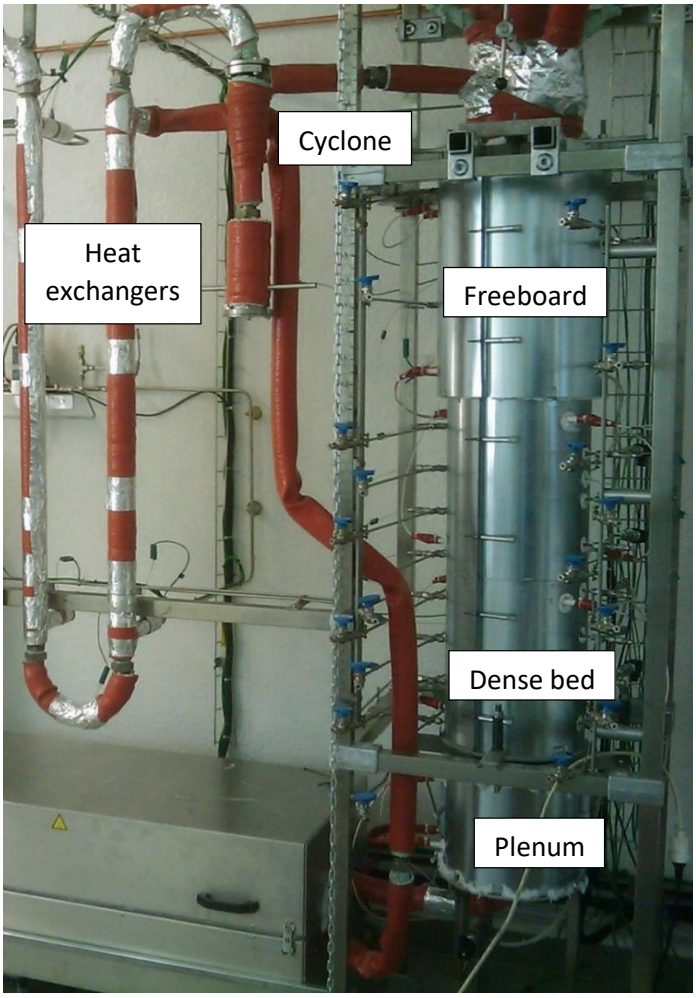


Fig. 1 Picture of the gasification unit

SRF were fed at the top of the reactor with a sloping screw. Around 3 kg of olivine was placed in the gasifier. At 800°C, the minimum fluidization velocity (U_{mf}) was 0.15 m/s as measured in this reactor by progressively increasing the air flowrate while measuring the pressure drop in the gasifier (without SRF injection). This U_{mf} is in agreement with Cluet et al. [79]. At the gasifier outlet, the syngas flowed through a cyclone to remove particles, before to be cooled with two air heat exchangers. A water Venturi scrubber was also used to remove the tars and the inorganic gases before flaring the syngas. The gasifier is equipped with 19 lateral tubes allowing to insert thermocouples which locally measure the bed and freeboard temperatures. Pressure was continuously measured below the grid and at the top of the freeboard zone.

The syngas was sampled before the Venturi scrubber and analyzed on-line by a µ-GC (Varian micro-GC 490, 4 modules) every 3 minutes. N_2, CO, CO_2, H_2, CH_4, C_2H_2, C_2H_4, C_2H_6, C_3H_4, C_3H_6, and C_6H_6 were quantified with this technique. To quantify the inorganic gases (H_2S, HCN, HCl and NH_3) present in syngas, the sampling procedure has been adapted from previous articles [51, 54]. The analysis of the solutions was performed according to French and ISO standards. 10 L of syngas was sampled in a Tedlar bag at the exit of the first heat exchanger. Then, the syngas sampled in Tedlar bag was sequentially flowed at a constant flowrate (400 mL/min) during 5 minutes in impingers filled with 200 mL of specific solutions (Table S.1 in Supplementary Material). The targeted ions S^{2-} (representing H_2S), Cl^- (representing HCl), and NH_4^+ (representing NH_3) were analyzed by spectrophotometry, while the ion CN^- (representing HCN) was quantified by ionic chromatography (Table S.1 in Supplementary Material).

2.3 Gasification experimental protocol & performance indicators

Before starting the gasification tests, the system was preheated at the desired temperature (750-900 °C) under air. When the temperature was at the target value, the air flowrate was set at the desired value. For all experiments, the air velocity was set at 4 times the minimum fluidization

velocity (thus 0.6 m/s), corresponding to an air flow rate of 4.5 m^3/h (STP). Once the temperatures were stable along the gasifier, the feeding of the SRF was started at a controlled flowrate to reach the targeted equivalence ratio (ER). When the gasification conditions were stable (gasifier temperature, and syngas composition analyzed by µ-GC), the steady-state regime was maintained at least 40 minutes (Figure S.1 in supplementary material).

The ER is defined as the operating air flow rate divided by the air flow rate required for the stoichiometric oxidation of SRF. In this study, the ER was varied between 0.18 and 0.27. The effect of the ER on the gasification efficiency was studied at 800 °C (controlled by electrical heater shells). To do so, the SRF flowrate was adjusted (between 4.67 to 6.95 kg/h) while the air flow rate and the bed temperature were kept constant. In these conditions, the gas velocity and residence time were similar for the different gasifying conditions. The SRF flow rate was found to fluctuate by +/- 10% over time. For this reason, the ER range for each experimental condition is presented in the results section. The SRF tank was continuously flushed with 10 L/min (STP) of pure N_2 to avoid the conversion of the fuel in the feeding screw. This flow rate was taken into consideration for the results analysis since N_2 is used as a tracer for the calculation of the syngas flowrate.

Four indicators of the gasification performance were used, namely: lower heating value of the dry syngas (LHV_{syngas}), syngas yield (η_{syngas}), carbon conversion (CC), Cold Gas Efficiency (CGE). Their determination based on experimental analysis was presented in a previous article [78]. In these calculations, all the light hydrocarbon species (including benzene) were considered as syngas components since their presence is not an issue for syngas valorization in gas engine.

The lower heating value of the dry syngas (LHV_{syngas}), expressed in MJ/m^3 (STP) of syngas (including N_2), is calculated according to Eq.1:

$$\mathrm{LHV_{syngas}} = \frac{\sum_i (\mathrm{x_i\ LHV_i})}{\mathrm{V_m}} \quad \text{Eq.(1)}$$

Where V_m is the molar volume of ideal gas at STP (22.4 L/mol), and x_i the molar fraction of the gas species i.

The syngas yield (η_{syngas}) is calculated as the volume of dry syngas produced (including N_2) by kg of SRF (on dry ash free basis):

$$\eta_{\mathrm{syngas}} = \frac{\mathrm{Qv_{syngas}}}{\mathrm{Qm_{SRF}}} \quad \text{Eq.(2)}$$

Where Qv_{syngas} is the volumetric syngas flowrate including N_2 (m^3/h STP) which is calculated using N_2 as a tracer, and Qm_{SRF} the mass flowrate of SRF (kg_{daf}/h).

The carbon conversion (CC) corresponds to the percentage of carbon transferred from SRF to syngas:

$$CC = \mathrm{Qm}_{syngas}\, M_C\, \frac{\sum_i \left(\frac{\omega_i}{M_i} n_i^C\right)}{Qm_{SRF}\, X_C^{SRF}} \times 100 \quad \text{Eq.(3)}$$

Where Qm_{syngas} is the mass flowrate of syngas (kg/h), M_C is the molecular weight of carbon, n_i^C is the number of carbon atoms in the molecule i, X_C^{SRF} is the mass fraction of carbon in SRF (on daf basis), and ω_i and M_i correspond to the mass fraction of the gas i in the syngas and its molecular weight, respectively

Finally, the last indicator is the Cold Gas Efficiency (CGE) which reflects the fraction of chemical energy transferred from SRF to syngas:

$$\mathrm{CGE} = \frac{\eta_{\mathrm{syngas}}\ \mathrm{LHV_{syngas}}}{\mathrm{LHV_{SRF}}} \times 100 \quad \text{Eq.(4)}$$

In addition, the distribution of H atoms and C atoms in the gaseous products was calculated, according to Eq.(5) and (6):

$$\mathrm{S}_H^i = \frac{n_H^i\, F^i}{\sum_k (n_H^k\, F^k)} \quad \text{Eq.(5)}$$

$$\mathrm{S}_C^i = \frac{n_C^i\, F^i}{\sum_k (n_C^k\, F^k)} \quad \text{Eq.(6)}$$

288 Where S_H^i and S_C^i are the molar selectivity representing the molar flow rate of H (resp. C) atoms
289 present in a given molecule divided by the total flow rate of H (resp. C) atoms present in all
290 syngas molecules. F^i is the molar flowrate of a given molecule i.

3. Results and discussion

3.1 Physico-chemical properties of the SRF

The elemental composition of SRF is presented in Table 1. The carbon content is relatively low (36.6 wt.%) while the ash content (35.1 wt.%) is significant compared to other SRFs reported in the literature. Indeed, the carbon content usually ranges from 41 to 84 wt.% while the ash content is in the range 1-27 wt.% [28, 30, 34, 48, 50, 54, 55, 80]. This composition results from the production of SRF by mechanical-biological treatment of municipal solid waste. On the contrary, the oxygen and hydrogen contents of this SRF are relatively lower than the reported values. Mainly due to its high ash content, the LHV of the SRF (14.1 MJ/kg) is lower than the values reported in the literature for SRFs (15-35 MJ/kg).

Table 1 Elemental analysis and lower heating value of the SRF

Elemental analysis (dry wt.%)	
C	36.6
H	4.6
N	1.9
S	0.8
O (by difference)	21.1
Ash	35.1
LHV (MJ/kg$_{dry}$)	14.1

The ash composition of the SRF is presented in Table 2. The main inorganic species are Si, Ca, and Al. Alkaline and alkaline earth metals (AAEM, such as Mg, Na, K) are also present in the ash composition. Some differences appear between ICP and XRF analysis. The SiO_2, Fe_2O_3, and MnO contents are higher with ICP-AES measurement, while the CaO, TiO_2, and Na_2O_3 contents were higher with XRF analysis. ICP and XRF give similar values for Al_2O_3, MgO, SO_3, P_2O_5. These results suggest that the characterization of complex wastes such as SRF must be carefully performed and slight differences can be measured despite a rigorous sampling

methodology. Regarding the potential inorganic gases release, it can be noted that the nitrogen and chlorine contents are lower than that of other SRFs studied in the literature (0.2-1.3 wt.% for N, and 0.7-1.1 wt.% for Cl) [30, 50, 54], whereas the sulphur content is slightly higher than the values reported in the literature (0-0.6 wt.%) [30, 31, 34, 48, 50, 54, 55].

Table 2 Ash composition of the SRF measured by ICP-AES and XRF

Ash composition (in wt.%)		
	ICP-AES	XRF
SiO_2	41.5	30.8
Al_2O_3	10.5	10.5
Fe_2O_3	4.1	2.6
TiO_2	1.1	1.8
CaO	24.0	34.6
MgO	4.2	4.0
Na_2O	2.6	3.3
K_2O	0.9	0.5
SO_3	9.8	10.6
P_2O_5	1.0	1.0
MnO	0.2	0.1
Total	100.0	100.0
Br	*nd*	
Cl	0.30	
F	0.04	

Figure 2 shows the proportion and composition of biomass, non-biomass, and inert fractions composing the SRF. Our previous article presented the effect of operating conditions on gasification efficiency for two SRFs (one rich in biomass and glass, and a second richer in plastics) [78]. Herein we complete our previous study with another SRF which exhibits an interesting composition between biomass-rich SRF and plastic-rich SRF. Indeed, this sample is composed of non-biomass (59.0 wt.%), biomass (38.6 wt.%), and inert (2.4 wt.%) fractions. The non-biomass fraction is rich in plastics, while the biomass fraction is mainly composed of paper/carton. Significant parts of these fractions are composed of fines for which the origin has not been identified and that may contain ash-rich materials. This would explain the high ash content of this SRF (35.1 wt.%), whereas the inert fraction is low (2.4 wt.%). This inert fraction

is only composed of rocks (not glass). It must be noted that the SRF composition strongly depends on the origin of the collected wastes and on the sorting methods used by the waste treatment plant.

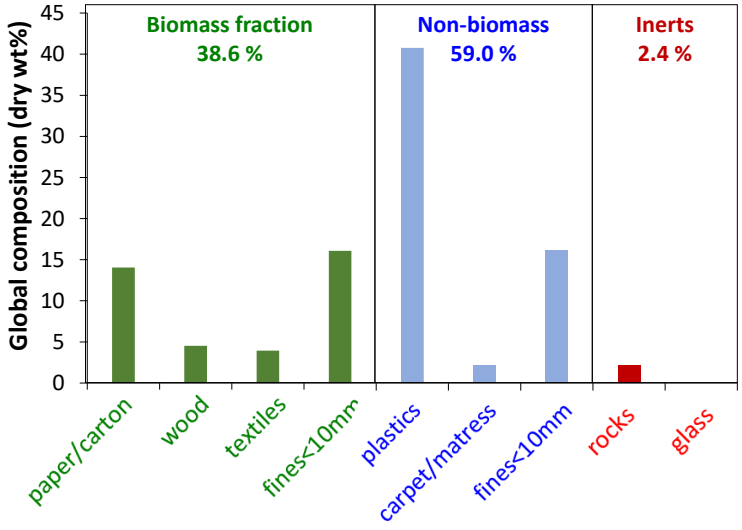


Fig. 2 Proportion and composition of biomass, non-biomass, and inert materials in the SRF

3.2 Permanent gases composition

3.2.1 Influence of the temperature

The values of the cold gas efficiency (CGE), the carbon conversion (CC), the syngas yield (η_{syngas}) and the lower heating value of the syngas (LHV_{syngas}) obtained during the gasification tests are presented in Table 3. It can be noted that the temperature increase from 750 to 800 °C does not significantly modify the gasification results. However, at 900 °C, all the gasification indicators are strongly improved. The combined increase in LHV_{syngas} (+4.5%) and η_{syngas} (+10%) result in an overall gain of 13% for the CGE (from 74.5 to 84.3 %). The temperature increase also promotes the carbon conversion (+6%). Some explanations are given thereafter.

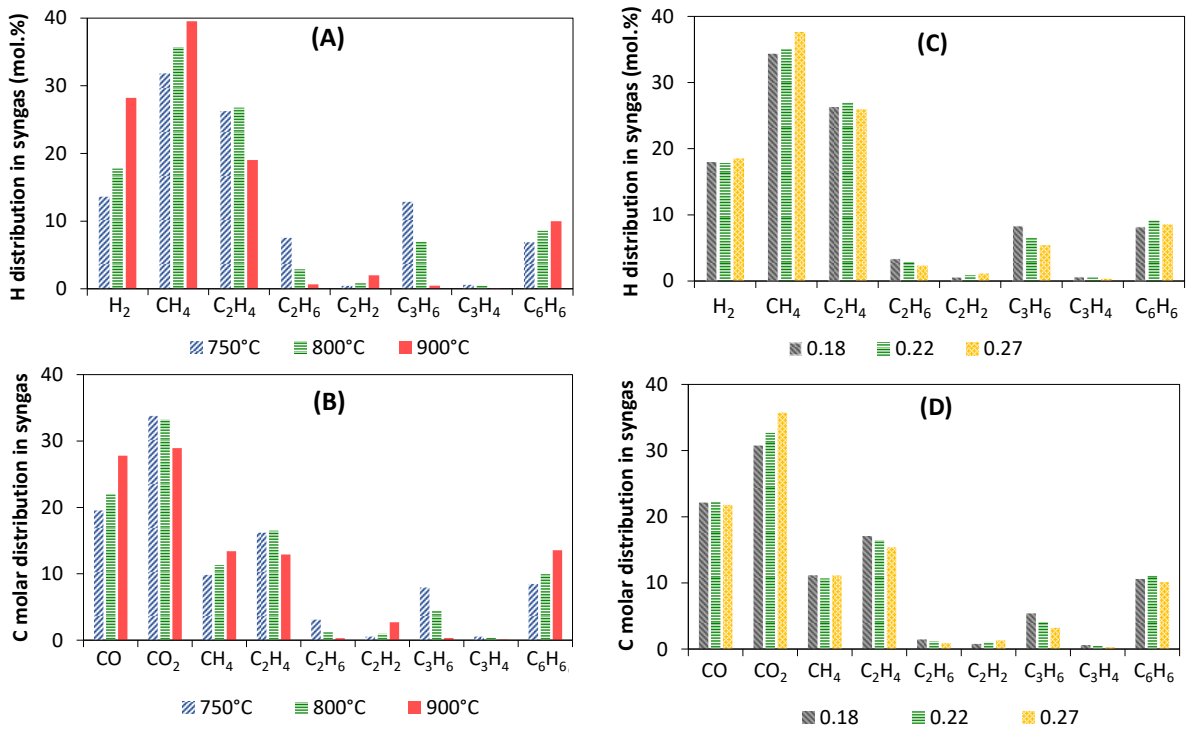
Table 3 Operating conditions and results of the gasification tests performed at different temperatures and ER=0.22 (ranging between 0.205 and 0.227), and at different Equivalent Ratio (ER) and a Temperature of 803°C

	Influence of T			**Influence of ER**		
T (°C)	750	803	902	803	803	803
Equivalence Ratio	0.22 (0.205-0.227)	0.22 (0.205-0.227)	0.22 (0.205-0.227)	0.18 (0.170-0.188)	0.22 (0.205-0.227)	0.27 (0.253-0.279)
Syngas composition (%vol.)						
N_2	59.6	57.7	54.1	53.7	57.7	63.0
H_2	4.0	5.0	8.7	5.8	5.0	4.5
CO	9.3	10.3	12.6	11.0	10.3	8.8
CO_2	16.0	15.1	13.2	15.2	15.1	14.5
CH_4	4.7	4.9	6.1	5.5	4.9	4.5
C_2H_4	3.8	3.8	2.9	4.2	3.8	3.1
C_2H_6	0.7	0.3	0.1	0.4	0.3	0.2
C_2H_2	0.1	0.3	0.6	0.2	0.3	0.3
C_3H_6	1.3	0.6	0.1	0.9	0.6	0.4
C_3H_4	0.1	0.1	0.0	0.1	0.1	0.0
C_6H_6	0.7	0.9	1.0	0.9	0.9	0.7
LHV_{syngas} (MJ/m^3 STP)	7.97	8.05	8.38	9.1	8.05	6.7
η_{syngas} (m^3 STP/$kg_{SRF\ daf}$)	2.00	2.06	2.20	1.84	2.06	2.33
Carbon conversion (%)	88.4	90.3	94.9	86.7	90.3	89.9
Cold Gas Efficiency (%)	73.0	76.2	84.3	77.0	76.2	71.7

In the literature, similar trends were reported, where rising gasification temperature at constant ER promoted the syngas yield and carbon conversion[38]. However, a significant discrepancy was reported in the literature for the evolution of CGE and LHV_{syngas}, since they were reported to decrease with increasing temperature [50, 54]. It has to be stressed out that, at industrial scale, such a temperature rise in the gasifier is obtained by increasing the ER resulting in higher syngas oxidation. In our case, ER is varied by maintaining a constant temperature thanks to the heating of the reactor walls.

The evolution of the syngas composition (Table 3) explains the increase in calorific value with rising temperature. Indeed, H_2, CO, CH_4, C_2H_2, and C_6H_6 contents significantly increase at 900 °C, while CO_2 is substantially reduced. High temperature is known to promote char gasification reaction leading to the production of H_2 and CO [78]. H_2 and CO formation at elevated temperature can also result from tar decomposition by cracking, as well as steam and dry reforming [30, 50, 54]. Dry reforming reaction can contribute to the decrease of CO_2 with increasing temperature. This set of reactions is responsible for the evolution of syngas composition and gasification efficiency with rising temperature.

It can be highlighted that, despite the high ash content, no melting phenomenon leading to bed defluidization and agglomeration were observed under these operating conditions. Compared with syngas produced by miscanthus air gasification in the same reactor under similar operating conditions [36], the syngas produced in this study has lower content of H_2 and CO, while the content in CH_4 and small hydrocarbon compounds (especially C_2H_4) is significantly higher. This high content in hydrocarbon compounds is explained by the presence of plastics which are known to produce high content in CH_4 and C_2-C_3 compounds during gasification [48, 55, 78].



366

367 **Fig. 3** Distribution of hydrogen and carbon atoms in syngas species as function of
368 gasification temperature on (A) and (B), and of ER on (C) and (D).

369 The influence of the temperature on the distribution of hydrogen and carbon atoms in the
370 gaseous products is presented in Figure 3-A and B, respectively. The main H-containing
371 species is CH_4 (Figure 3-A), resulting from the decomposition of tar compounds [81–83].
372 Rising temperature increases the selectivity in H_2, especially at temperature higher than 800
373 °C. At the same time, the selectivity in light hydrocarbons (C_2H_4, C_2H_6, C_3H_6, and C_3H_4)
374 remarkably decreases. C_2H_2 increases mainly from other C_2 conversion [84]. These results
375 confirm that light hydrocarbons are considerably reformed to H_2 and CO in the gasification
376 process when the temperature increases.

377 The carbon atoms distribution shows that the most important species are:
378 CO_2>CO>C_2H_4>CH_4>C_6H_6 (Figure 3-B). C_6H_6 is a stable tertiary product not converted in our
379 conditions [83, 85]. A decrease in CO_2 is observed at 900°C, together with an increase in CO,
380 C_6H_6, and CH_4. These evolutions suggest that dry reforming reactions are promoted at high

temperature [86]. The increase in temperature promotes the kinetics of reactions (water gas shift, hydrocarbons reforming, etc.) but also modifies the thermodynamic equilibrium of the reactive system. We have previously studied the effect of temperature on the detailed mechanisms of syngas conversion. We have especially shown that OH radicals are mainly produced by CO_2 conversion ($CO_2 + H = CO + OH$) in a syngas [84]. Therefore, under air gasification conditions, CO_2 yields are controlled by the competition between oxidation reactions (producing CO_2) and CO_2 conversion in the gas phase. In comparison with syngas produced in the same reactor under similar operating conditions with other types of SRF [78], the syngas produced by this SRF presents a CO_2 and CO contents significantly lower, while the content in CH_4 and C_2H_4, and mainly C_3H_6 are higher. The low content of CO and CO_2 results from the low O/C ratio in the plastic contained in SRF, as clearly explained by *Valin et al.* [38]. The high content in C_3H_6 with this SRF is expected to result from the fast decomposition of polymer chains of the plastics contained in this SRF, and to the low catalytic activity of olivine towards tar reforming reactions due to poisoning of active sites with inorganic gases [55].

3.2.2 Influence of the Equivalence Ratio

The evolutions of the gasification indicators with increasing ER are presented in Table 3. It can be observed that increasing ER results in a decrease of the CGE, a significant increase in syngas yield, and a drastic drop of the LHV_{syngas}. While oxidation reactions are expected to increase with higher ER, the carbon conversion is almost stable between ER=0.22 and 0.27. The large amount of inorganic species known for their catalytic activity (such as Ca, Na, K or Fe) could catalyze the gasification reactions of the carbonaceous solids and promote the carbon conversion even at low ER [87]. Nevertheless, approximatively 10 to 13 wt.% of the carbon inlet was not converted. Most of this non-converted carbon was supposed to be recovered in the form of fly ash and tar compounds. The elemental composition of the fly ash was analyzed.

Whatever the ER value, it consists mainly in ash (~87 wt.%), carbon (~12 wt.%), low amounts of hydrogen (~0.7 wt.%) and nitrogen (~0.5 wt.%). During the gasification at 800°C, the fly ash yield was 16 wt.%. Thus, the fly ash contains 5.5 wt.% of the carbon input. This result confirms that part of the carbon input is not converted during gasification and is recovered in the form of fly ash. This results exemplifies the important effect of particles elutriation on the carbon balance [88].

The increase in syngas yield with rising ER is explained by the higher ratio of air to SRF in the gasifier, leading to a higher dilution of the syngas produced into N_2 from air. To better understand the effects of increasing ER on the syngas produced, the syngas yield and the LHV_{syngas} have been calculated for N_2-free syngas (Figure S.2 in Supplementary Material). The results demonstrate that LHV_{syngas} of N_2-free syngas sharply decreases with increasing ER. Simultaneously, the syngas yield was shown to be almost invariant with rising ER. As a result, increasing ER results in the decrease of CGE.

Table 3 presents the syngas composition at the gasifier outlet (including N_2), while Figure S.3 (in supplementary material) displays the composition of the gas produced by gasification without nitrogen. Rising ER decreases the fraction of the produced gases, except for CO_2 which is generated by the oxidation reactions promoted by high ER. Indeed, syngas and char can both be oxidized with increasing ER. The syngas oxidation reactions also explain the decrease of the LHV_{syngas} with rising ER (Figure S.2). The syngas yield is not impacted by the ER variation under the actual conditions of this study. These trends are similar to that obtained during miscanthus gasification in the same reactor under similar operating conditions [36].

The distribution of hydrogen and carbon atoms in the syngas was also investigated. The results, presented in Figure 3-C and D, reveal that the distribution is poorly modified with rising ER. For H atoms distribution, the selectivity in CH_4 and C_6H_6 slightly increases with rising ER,

while that of C_3H_6 and C_2H_6 decreases. Indeed, CH_4 and C_6H_6 are known to be more stable hydrocarbons than C_3H_6 and C_2H_6 [89, 90]. Regarding the carbon atoms distribution, the main effect of rising ER consists in increasing the CO_2 selectivity. Thus, hydrocarbon molecules (notably C_2H_4 and C_3H_6, based on C atoms molar distribution) seem to be oxidized into CO_2 when the ER increases. The higher increase in CO_2 compared to H_2 (and CO) in terms of molar distribution in C or H atoms shows that higher ER promotes CO_2 (and not CO) and that steam reforming reactions are not significantly promoted by ER under our conditions.

Compared with results obtained in the same reactor under similar operating conditions with other types of SRF [78], higher carbon conversion and LHV were obtained with the present SRF. As a result, the CGE is higher than that obtained with a SRF rich in paper and another mostly composed of plastics (SRF1 and SRF2 of the previous article [78]). Thus, the mixture of soft plastics with ash-containing waste in this SRF seems to promote the gasification efficiency.

3.3 Inorganic gases composition

As explained in the introduction, conflicting results are presented in the literature about the effect of ER on the release of inorganic gases. To investigate this phenomenon, the concentrations of H_2S, HCl, NH_3 and HCN were measured at two different ER in this study: 0.22 and 0.27. In addition, fly ash and bed material after gasification were analyzed. Since the solid samples recovered were generated in different operating conditions (constant temperature but different ER), the results are only qualitative and are presented in supplementary material.

The results of inorganic gases analysis (presented in Figure 4) show that H_2S is the most important inorganic gas generated during the gasification of this SRF. Its content increases from 409 to 891 mg/Nm^3 of syngas with increasing ER. These values correspond respectively to 11% and 26% of the sulfur contained in the SRF. These values are in agreement with *Pinto et al.* [31], *while Valin et al.* reported that 45 to 65% of sulfur was transformed into H_2S during SRF air gasification [38]. To better understand the sulfur species distribution, the sulfur content of fly ash and bed materials after gasification were qualitatively analyzed in this study (Supplementary Material). Strong interactions between the olivine bed (containing iron) and H_2S are expected to immobilize the produced H_2S in the fluidized bed during SRF gasification, while a lower amount of H_2S seems to be adsorbed on the fly ash due to the presence of AAEM species and iron. Other species not analyzed in this study, such as tar molecules (thiophene, benzo- and dibenzo-thiophene, thiols, or aryl and alkyl-sulphides) could also contain part of the sulfur [31].

For nitrogenous gases, both HCN and NH_3 are generated at low ER. However, at ER=0.27, no ammonia is detected in the syngas, whereas HCN concentration increases. HCN is typically generated by the decomposition of nitrogenous polymers [61]. The significant plastic content in this SRF may explain the production of HCN. The NH_3 and HCN contents are in agreement

with previous studies dealing with SRF gasification [34, 50, 54], where HCN content was found to vary from 27 to 660 mg//Nm^3 and NH_3 from 0 to 200 mg/Nm^3. Anyway, these HCN and NH_3 content correspond to a very small part of the N present in the SRF (less than 6 %). The formation of other N-gases (such as N_2, NO_x) [39, 57], and condensable compounds (cyano-acetylene, acetonitrile, isoquinoline, indole, carbazole, quinoline, other N-heteroaromatic compounds) [49, 57, 91, 92] can explain this difference. It should be noted that the formation of N_2 is really difficult to assess since it would be highly diluted in the N_2 that comes from air. In addition, part of the syngas water could have condensed in the Tedlar bag during sampling, possibly leading to NH_3 dissolution [93]. Nevertheless, no trace of condensation was observed in the Tedlar bag during experiments. Qualitative distribution of nitrogen compounds presented in Supplementary Material highlights that the majority of N-compounds was not identified in this study. This issue was also reported by other authors [38].

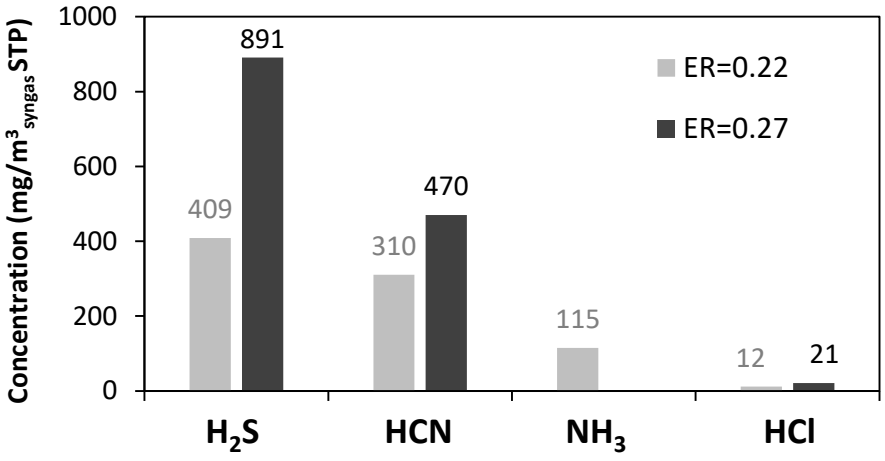


Fig. 4 Influence of the ER on the inorganic gases concentration at T=800°C

The content of HCl in the syngas is low compared both to the other inorganic gases and to the data available in the literature [30, 54]. This result can be explained by the low Cl content in this SRF (0.3 wt.%). But even at ER=0.27, HCl represents less than 2% of the chlorine present in the SRF. An explanation is that there are reactions occurring between HCl and the AAEM

485 species of SRF removing HCl from the syngas [68, 94]. The qualitative analysis of fly ash and
486 bed material presented in Supplementary Material implies that chlorine is mainly trapped in
487 the fly ash after gasification.

488 These results support the observation of several researchers suggesting that rising ER increases
489 the inorganic gases content in the syngas [31, 49, 95]. It may be due to the fact that high ER
490 promotes the char gasification reactions thus enhancing the release of heteroatoms, but in the
491 results presented in Table 3, the carbon conversion is stable when ER increases from 0.22 to
492 0.27. This stability is not logical and seems suspicious since rising ER in such a range is
493 expected to increase the carbon conversion [78]. The values for inorganic gases obtained in
494 this study are in agreement with the range of available data in the literature [30, 50, 54, 55].

495 The inorganic gases contents are significantly higher than the standard required for syngas
496 valorization in gas engine. The maximum acceptable values are around 100 mg/m^3 for H_2S, 50
497 mg/m^3 for NH_3, and 9 mg/m^3 for HCl [32, 39]. These results confirm that inorganic gases are
498 an important issue for the SRF gasification.

499 ## 4. Conclusions

500 This article studied air gasification of an industrial Solid Recovered Fuel in allothermal
501 bubbling fluidized bed. Since the valorization of low-grade SRF by gasification processes
502 could be jeopardized by the low quality of the resulting syngas, the syngas composition was
503 deeply analyzed in this study.

504 Increasing gasification temperature from 750 to 800°C had low effect on gasification, while
505 drastic improvement of gasification efficiency and syngas quality was observed at 900°C. This
506 beneficial effect was attributed to the promotion of secondary reactions (including
507 hydrocarbons conversion) and char gasification. The influence of equivalence ratio (ER) was
508 significantly less important than temperature on the gasification efficiency. The main effect

consisted in the decrease of the syngas LHV due to the promotion of oxidation reactions. As a result, the CO_2 content was found to increase while the CGE decreased.

The high content in light hydrocarbon compounds (CH_4, C_2H_4, C_3H_6) with this SRF resulted from the fast decomposition of polymer chains of the plastics contained in this SRF, and to the low catalytic activity of olivine towards tar reforming reactions due to poisoning of active sites with inorganic gases (HCl, H_2S). Compared with results obtained in the same reactor under similar operating conditions with other types of SRF, the gasification efficiency with the present SRF was higher than those obtained with a SRF rich in paper and another mostly composed of plastics. Thus, the mixture of soft plastics with ash-containing waste in this SRF seems to promote the gasification efficiency.

The concentration of H_2S, HCl, NH_3 and HCN in the syngas produced at 800°C was measured at two different ER (0.22 and 0.27). Both HCN and NH_3 were generated at low ER. However, at ER=0.27, no ammonia was recovered in the syngas, whereas HCN concentration increased. The significant plastic content in this SRF may explain the release of HCN. The nitrogen mass inventory was low, reflecting that most of nitrogen compounds were not detected in the form of NH_3 or HCN. The HCl content in syngas was low compared to the data available in the literature, due to the low Cl content in the SRF (0.3 wt.%) and to the immobilization of Cl in the fly ash containing K and Ca. H_2S was the most important inorganic gas and its content increased with increasing ER : from 409 to 891 mg/m^3 STP at ER=0.22 and 0.27, respectively. These values correspond to 11% and 26% of the sulfur present in SRF, while part of sulfur was expected to react with the olivine bed.

Even if the S, N and Cl present in the SRF are not converted completely into inorganic gases, the concentrations of H_2S, NH_3 and HCl are too high in comparison with the maximum acceptable values for syngas valorization in gas engine. Qualitative analysis of fly ash and

olivine bed after gasification tests proved that interactions between these materials and inorganic gases occur allowing to limit the inorganic gases production. More work is needed to deeply understand the exact nature of the gasification products that contained S, N and Cl, as well as to optimize waste mixture composition in SRF to promote interactions between inorganic gases and fly ash/bed material in order to limit the presence of inorganic gases in the gasifier.

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References

1. Kaza, S., Yao, L., Bhada-Tata, P., Van Woerden, F.: What a waste 2.0: A global Snapshot of Solid Waste Management to 2050. , Washington, DC (2018)
2. Kang, P., Zhang, H., Duan, H.: Characterizing the implications of waste dumping surrounding the Yangtze River economic belt in China. J. Hazard. Mater. 383, 121207 (2020). https://doi.org/10.1016/j.jhazmat.2019.121207
3. Hafeez, S., Mahmood, A., Syed, J.H., Li, J., Ali, U., Malik, R.N., Zhang, G.: Waste dumping sites as a potential source of POPs and associated health risks in perspective of current waste management practices in Lahore city, Pakistan. Sci. Total Environ. 562, 953–961 (2016). https://doi.org/10.1016/j.scitotenv.2016.01.120
4. Rego, R.F., Moraes, L.R.S., Dourado, I.: Diarrhoea and garbage disposal in Salvador, Brazil. Trans. R. Soc. Trop. Med. Hyg. 99, 48–54 (2005). https://doi.org/10.1016/j.trstmh.2004.02.008
5. Kupchik, G.J., Franz, G.J.: Solid Waste, Air Pollution and Health. J. Air Pollut. Control Assoc. 26, 116–118 (1976). https://doi.org/10.1080/00022470.1976.10470229
6. Triassi, M., Alfano, R., Illario, M., Nardone, A., Caporale, O., Montuori, P., Triassi, M., Alfano, R., Illario, M., Nardone, A., Caporale, O., Montuori, P.: Environmental Pollution from Illegal Waste Disposal and Health Effects: A Review on the "Triangle of Death." Int. J. Environ. Res. Public. Health. 12, 1216–1236 (2015). https://doi.org/10.3390/ijerph120201216
7. Plaza, P.I., Lambertucci, S.A.: How are garbage dumps impacting vertebrate demography, health, and conservation? Glob. Ecol. Conserv. 12, 9–20 (2017). https://doi.org/10.1016/j.gecco.2017.08.002
8. Schweitzer, L., Noblet, J.: Chapter 3.6 - Water Contamination and Pollution. In: Török, B. and Dransfield, T. (eds.) Green Chemistry. pp. 261–290. Elsevier (2018)
9. Lebreton, L., Slat, B., Ferrari, F., Sainte-Rose, B., Aitken, J., Marthouse, R., Hajbane, S., Cunsolo, S., Schwarz, A., Levivier, A., Noble, K., Debeljak, P., Maral, H., Schoeneich-Argent, R., Brambini, R., Reisser, J.: Evidence that the Great Pacific Garbage Patch is rapidly accumulating plastic. Sci. Rep. 8, 4666 (2018). https://doi.org/10.1038/s41598-018-22939-w
10. Haward, M.: Plastic pollution of the world's seas and oceans as a contemporary challenge in ocean governance. Nat. Commun. 9, 667 (2018). https://doi.org/10.1038/s41467-018-03104-3
11. Solid Waste Management, http://www.worldbank.org/en/topic/urbandevelopment/brief/solid-waste-management
12. Martignon, G., Edo, M.: Trends on use of solid recovered fuels. IEA Bioenergy (2020)
13. Vonk, G., Piriou, B., Wolbert, D., Cammarano, C., Vaïtilingom, G.: Analysis of pollutants in the product gas of a pilot scale downdraft gasifier fed with wood, or mixtures of wood and waste materials. Biomass Bioenergy. 125, 139–150 (2019). https://doi.org/10.1016/j.biombioe.2019.04.018

14. Combustibles solides de récupération (CSR) - Caractérisation et évaluation de leurs performances en combustion. FEDEREC et COMPTE-R (2015)
15. Consommation d'énergie primaire - Eurostat, https://ec.europa.eu/eurostat/fr/web/products-datasets/-/T2020_33
16. Brunner, P.H., Morf, L., Rechberger, H.: VI.3 - Thermal waste treatment – a necessary element for sustainable waste management. In: Twardowska, I. (ed.) Waste Management Series. pp. 783–806. Elsevier (2004)
17. Porteous, A.: Why energy from waste incineration is an essential component of environmentally responsible waste management. Waste Manag. 25, 451–459 (2005). https://doi.org/10.1016/j.wasman.2005.02.008
18. Arena, U.: Process and technological aspects of municipal solid waste gasification. A review. Waste Manag. 32, 625–639 (2012). https://doi.org/10.1016/j.wasman.2011.09.025
19. Enerkem produces renewable alternative solution to diesel fuel. Focus Catal. 2018, 6 (2018). https://doi.org/10.1016/j.focat.2018.11.097
20. Barba, A., Le Cadre, E., Forsgren, H., Gaillard, M., Gunnarsson, I., Guerrini, O., Hoff, M.V., Kara, Y., Mollema, E., Moretti, I., Ourliac, M., Overwijk, M., Peureux, G., Peltenburg, A., Tengberg, F., De Vries, T., Winjstra, S.: Europe move towards industrialization of 2G biomethane from biomass gasification and methanation. Presented at the International Gas Research Conference Proceedings (2017)
21. Ramos, A., Monteiro, E., Silva, V., Rouboa, A.: Co-gasification and recent developments on waste-to-energy conversion: A review. Renew. Sustain. Energy Rev. 81, 380–398 (2018). https://doi.org/10.1016/j.rser.2017.07.025
22. Sansaniwal, S.K., Pal, K., Rosen, M.A., Tyagi, S.K.: Recent advances in the development of biomass gasification technology: A comprehensive review. Renew. Sustain. Energy Rev. 72, 363–384 (2017). https://doi.org/10.1016/j.rser.2017.01.038
23. Campoy, M., Gómez-Barea, A., Ollero, P., Nilsson, S.: Gasification of wastes in a pilot fluidized bed gasifier. Fuel Process. Technol. 121, 63–69 (2014). https://doi.org/10.1016/j.fuproc.2013.12.019
24. Karatas, H., Olgun, H., Engin, B., Akgun, F.: Experimental results of gasification of waste tire with air in a bubbling fluidized bed gasifier. Fuel. 105, 566–571 (2013). https://doi.org/10.1016/j.fuel.2012.08.038
25. Xiao, G., Ni, M.-J., Chi, Y., Cen, K.-F.: Low-temperature gasification of waste tire in a fluidized bed. Energy Convers. Manag. 49, 2078–2082 (2008). https://doi.org/10.1016/j.enconman.2008.02.016
26. Di Gregorio, F., Santoro, D., Arena, U.: The effect of ash composition on gasification of poultry wastes in a fluidized bed reactor. Waste Manag. Res. 32, 323–330 (2014). https://doi.org/10.1177/0734242X14525821
27. Mastellone, M.L., Zaccariello, L., Arena, U.: Co-gasification of coal, plastic waste and wood in a bubbling fluidized bed reactor. Fuel. 89, 2991–3000 (2010). https://doi.org/10.1016/j.fuel.2010.05.019
28. Arena, U., Di Gregorio, F.: Energy generation by air gasification of two industrial plastic wastes in a pilot scale fluidized bed reactor. Energy. 68, 735–743 (2014). https://doi.org/10.1016/j.energy.2014.01.084
29. Wilk, V., Hofbauer, H.: Co-gasification of Plastics and Biomass in a Dual Fluidized-Bed Steam Gasifier: Possible Interactions of Fuels. Energy Fuels. 27, 3261–3273 (2013). https://doi.org/10.1021/ef400349k
30. Dunnu, G., Panopoulos, K.D., Karellas, S., Maier, J., Touliou, S., Koufodimos, G., Boukis, I., Kakaras, E.: The solid recovered fuel Stabilat®: Characteristics and fluidised bed gasification tests. Fuel. 93, 273–283 (2012). https://doi.org/10.1016/j.fuel.2011.08.061
31. Pinto, F., André, R.N., Carolino, C., Miranda, M., Abelha, P., Direito, D., Perdikaris, N., Boukis, I.: Gasification improvement of a poor quality solid recovered fuel (SRF). Effect of using natural

minerals and biomass wastes blends. Fuel. 117, 1034–1044 (2014). https://doi.org/10.1016/j.fuel.2013.10.015
32. Milne, T.A., Evans, R.J., Abatzoglou, N.: Biomass Gasifier Tars: Their Nature, Formation and Conversion. National Renewable Energy Laboratory (1998)
33. Vonk, G., Piriou, B., Felipe Dos Santos, P., Wolbert, D., Vaïtilingom, G.: Comparative analysis of wood and solid recovered fuels gasification in a downdraft fixed bed reactor. Waste Manag. 85, 106–120 (2019). https://doi.org/10.1016/j.wasman.2018.12.023
34. Arena, U., Di Gregorio, F.: Gasification of a solid recovered fuel in a pilot scale fluidized bed reactor. Fuel. 117, 528–536 (2014). https://doi.org/10.1016/j.fuel.2013.09.044
35. Recari Ansa, J.: Gasification of biomass and solid recovered fuels (SRFs) for the synthesis of liquid fuels, (2017)
36. Lardier, G., Kaknics, J., Dufour, A., Michel, R., Cluet, B., Authier, O., Poirier, J., Mauviel, G.: Gas and Bed Axial Composition in a Bubbling Fluidized Bed Gasifier: Results with Miscanthus and Olivine. Energy Fuels. 30, 8316–8326 (2016). https://doi.org/10.1021/acs.energyfuels.6b01816
37. Horvat, A., Kwapinska, M., Xue, G., Rabou, L.P.L.M., Pandey, D.S., Kwapinski, W., Leahy, J.J.: Tars from Fluidized Bed Gasification of Raw and Torrefied Miscanthus x giganteus. Energy Fuels. 30, 5693–5704 (2016). https://doi.org/10.1021/acs.energyfuels.6b00532
38. Valin, S., Ravel, S., Pons de Vincent, P., Thiery, S., Miller, H.: Fluidized bed air gasification of solid recovered fuel and woody biomass: Influence of experimental conditions on product gas and pollutant release. Fuel. 242, 664–672 (2019). https://doi.org/10.1016/j.fuel.2019.01.094
39. Woolcock, P.J., Brown, R.C.: A review of cleaning technologies for biomass-derived syngas. Biomass Bioenergy. 52, 54–84 (2013). https://doi.org/10.1016/j.biombioe.2013.02.036
40. Torres, W., Pansare, S.S., Jr, J.G.G.: Hot Gas Removal of Tars, Ammonia, and Hydrogen Sulfide from Biomass Gasification Gas. Catal. Rev. 49, 407–456 (2007). https://doi.org/10.1080/01614940701375134
41. Asadullah, M.: Biomass gasification gas cleaning for downstream applications: A comparative critical review. Renew. Sustain. Energy Rev. 40, 118–132 (2014). https://doi.org/10.1016/j.rser.2014.07.132
42. GE Jenbacher: Fuel gas quality, special gases. (2009)
43. Gupta, R.P., Turk, B.S., Portzer, J.W., Cicero, D.C.: Desulfurization of syngas in a transport reactor. Environ. Prog. 20, 187–195 (2001)
44. Lee, J., Feng, B.: A thermodynamic study of the removal of HCl and H_2S from syngas. Front. Chem. Sci. Eng. 6, 67–83 (2012). https://doi.org/10.1007/s11705-011-1162-4
45. Tijmensen, M.J.A., Faaij, A.P.C., Hamelinck, C.N., van Hardeveld, M.R.M.: Exploration of the possibilities for production of Fischer Tropsch liquids and power via biomass gasification. Biomass Bioenergy. 23, 129–152 (2002). https://doi.org/10.1016/S0961-9534(02)00037-5
46. Chiche, D., Diverchy, C., Lucquin, A.-C., Porcheron, F., Defoort, F.: Synthesis Gas Purification. Oil Gas Sci. Technol. – Rev. D'IFP Energ. Nouv. 68, 707–723 (2013). https://doi.org/10.2516/ogst/2013175
47. Kaufman Rechulski, M.D., Schildhauer, T.J., Biollaz, S.M.A., Ludwig, Ch.: Sulfur containing organic compounds in the raw producer gas of wood and grass gasification. Fuel. 128, 330–339 (2014). https://doi.org/10.1016/j.fuel.2014.02.038
48. Arena, U., Di Gregorio, F.: Fluidized bed gasification of industrial solid recovered fuels. Waste Manag. 50, 86–92 (2016). https://doi.org/10.1016/j.wasman.2016.02.011
49. Wilk, V., Hofbauer, H.: Conversion of fuel nitrogen in a dual fluidized bed steam gasifier. Fuel. 106, 793–801 (2013). https://doi.org/10.1016/j.fuel.2012.12.056
50. Berrueco, C., Recari, J., Abelló, S., Farriol, X., Montané, D.: Experimental Investigation of Solid Recovered Fuel (SRF) Gasification: Effect of Temperature and Equivalence Ratio on Process Performance and Release of Minor Contaminants. Energy Fuels. 29, 7419–7427 (2015). https://doi.org/10.1021/acs.energyfuels.5b02032

51. Berrueco, C., Recari, J., Güell, B.M., Alamo, G. del: Pressurized gasification of torrefied woody biomass in a lab scale fluidized bed. Energy. 70, 68–78 (2014). https://doi.org/10.1016/j.energy.2014.03.087
52. Gas analysis in gasification of biomass and waste - Guideline report Document 1. IEA Bioenergy Task 33 (2018)
53. Aljbour, S.H., Kawamoto, K.: Bench-scale gasification of cedar wood – Part II: Effect of Operational conditions on contaminant release. Chemosphere. 90, 1501–1507 (2013). https://doi.org/10.1016/j.chemosphere.2012.08.030
54. Recari, J., Berrueco, C., Abelló, S., Montané, D., Farriol, X.: Gasification of two solid recovered fuels (SRFs) in a lab-scale fluidized bed reactor: Influence of experimental conditions on process performance and release of HCl, H2S, HCN and NH3. Fuel Process. Technol. 142, 107–114 (2016). https://doi.org/10.1016/j.fuproc.2015.10.006
55. Arena, U., Zaccariello, L., Mastellone, M.L.: Fluidized bed gasification of waste-derived fuels. Waste Manag. 30, 1212–1219 (2010). https://doi.org/10.1016/j.wasman.2010.01.038
56. Pels, J.R., Kapteijn, F., Moulijn, J.A., Zhu, Q., Thomas, K.M.: Evolution of nitrogen functionalities in carbonaceous materials during pyrolysis. Carbon. 33, 1641–1653 (1995). https://doi.org/10.1016/0008-6223(95)00154-6
57. Leppälahti, J., Koljonen, T.: Nitrogen evolution from coal, peat and wood during gasification: Literature review. Fuel Process. Technol. 43, 1–45 (1995). https://doi.org/10.1016/0378-3820(94)00123-B
58. Leppälahti, J., Kurkela, E.: Behaviour of nitrogen compounds and tars in fluidized bed air gasification of peat. Fuel. 70, 491–497 (1991). https://doi.org/10.1016/0016-2361(91)90026-7
59. Hansson, K.-M., Samuelsson, J., Tullin, C., Åmand, L.-E.: Formation of HNCO, HCN, and NH3 from the pyrolysis of bark and nitrogen-containing model compounds. Combust. Flame. 137, 265–277 (2004). https://doi.org/10.1016/j.combustflame.2004.01.005
60. Kelemen, S.R., Afeworki, M., Gorbaty, M.L., Kwiatek, P.J., Sansone, M., Walters, C.C., Cohen, A.D.: Thermal Transformations of Nitrogen and Sulfur Forms in Peat Related to Coalification. Energy Fuels. 20, 635–652 (2006). https://doi.org/10.1021/ef050307p
61. Leichtnam, J., Schwartz, D., Gadiou, R.: The behaviour of fuel-nitrogen during fast pyrolysis of polyamide at high temperature. J. Anal. Appl. Pyrolysis. 55, 255 (2000)
62. Scott, D.S., Piskorz, J.: The continuous flash pyrolysis of biomass. Can. J. Chem. Eng. 62, 404–412 (1984). https://doi.org/10.1002/cjce.5450620319
63. Scott, D.S., Piskorz, J., Westerberg, I.B., McKeough, P.: Flash pyrolysis of peat in a fluidized bed. Fuel Process. Technol. 18, 81–95 (1988). https://doi.org/10.1016/0378-3820(88)90076-8
64. Tian, F.-J., Yu, J., McKenzie, L.J., Hayashi, J., Li, C.-Z.: Conversion of Fuel-N into HCN and NH3 During the Pyrolysis and Gasification in Steam: A Comparative Study of Coal and Biomass. Energy Fuels. 21, 517–521 (2007). https://doi.org/10.1021/ef060415r
65. Kurkela, E., Laatikainen, J., Ståhlberg, P.: Pressurized Fluidized-bed Gasification Experiments with Wood, Peat and Coal at VTT in 1991-1992: Gasification of danish wheat straw and coal. VTT (1996)
66. Glarborg, P., Jensen, A.D., Johnsson, J.E.: Fuel nitrogen conversion in solid fuel fired systems. Prog. Energy Combust. Sci. 29, 89–113 (2003). https://doi.org/10.1016/S0360-1285(02)00031-X
67. Ma, W., Hoffmann, G., Schirmer, M., Chen, G., Rotter, V.S.: Chlorine characterization and thermal behavior in MSW and RDF. J. Hazard. Mater. 178, 489–498 (2010). https://doi.org/10.1016/j.jhazmat.2010.01.108
68. Bläsing, M., Zini, M., Müller, M.: Influence of Feedstock on the Release of Potassium, Sodium, Chlorine, Sulfur, and Phosphorus Species during Gasification of Wood and Biomass Shells. Energy Fuels. 27, 1439–1445 (2013). https://doi.org/10.1021/ef302093r

731 69. Corella, J., Toledo, J.M., Molina, G.: Performance of CaO and MgO for the hot gas clean up in
732 gasification of a chlorine-containing (RDF) feedstock. Bioresour. Technol. 99, 7539–7544
733 (2008). https://doi.org/10.1016/j.biortech.2008.02.018
734 70. Lu, H., Purushothama, S., Hyatt, J., Pan, W.-P., Riley, J.T., Lloyd, W.G., Flynn, J., Gill, P.: Co-firing
735 high-sulfur coals with refuse-derived fuel. Thermochim. Acta. 284, 161–177 (1996).
736 https://doi.org/10.1016/0040-6031(96)02864-X
737 71. Jazbec, M., Sendt, K., Haynes, B.S.: Kinetic and thermodynamic analysis of the fate of sulphur
738 compounds in gasification products. Fuel. 83, 2133–2138 (2004).
739 https://doi.org/10.1016/j.fuel.2004.06.017
740 72. Tchapda, A., Pisupati, S., Tchapda, A.H., Pisupati, S.V.: A Review of Thermal Co-Conversion of
741 Coal and Biomass/Waste. Energies. 7, 1098–1148 (2014). https://doi.org/10.3390/en7031098
742 73. Knudsen, J.N., Jensen, P.A., Lin, W., Frandsen, F.J., Dam-Johansen, K.: Sulfur Transformations
743 during Thermal Conversion of Herbaceous Biomass. Energy Fuels. 18, 810–819 (2004).
744 https://doi.org/10.1021/ef034085b
745 74. Hervy, M., Pham Minh, D., Gérente, C., Weiss-Hortala, E., Nzihou, A., Villot, A., Le Coq, L.: H2S
746 removal from syngas using wastes pyrolysis chars. Chem. Eng. J. 334, 2179–2189 (2018).
747 https://doi.org/10.1016/j.cej.2017.11.162
748 75. Broer, K.M., Brown, R.C.: The role of char and tar in determining the gas-phase partitioning of
749 nitrogen during biomass gasification. Appl. Energy. 158, 474–483 (2015).
750 https://doi.org/10.1016/j.apenergy.2015.08.100
751 76. Pinto, F., Lopes, H., André, R.N., Gulyurtlu, I., Cabrita, I.: Effect of catalysts in the quality of
752 syngas and by-products obtained by co-gasification of coal and wastes. 1. Tars and nitrogen
753 compounds abatement. Fuel. 86, 2052–2063 (2007).
754 https://doi.org/10.1016/j.fuel.2007.01.019
755 77. de Almeida, V.F., Gómez-Barea, A., Arroyo-Caire, J., Pardo, I.: On the Measurement of the Main
756 Inorganic Contaminants Derived from Cl, S and N in Simulated Waste-Derived Syngas. Waste
757 Biomass Valorization. (2020). https://doi.org/10.1007/s12649-019-00879-4
758 78. Hervy, M., Remy, D., Dufour, A., Mauviel, G.: Air-blown gasification of Solid Recovered Fuels
759 (SRFs) in lab-scale bubbling fluidized-bed-Influence of the operating conditions and of the SRF
760 composition. Energy Convers. Manag. 181, 584–592
761 79. Cluet, B., Mauviel, G., Rogaume, Y., Authier, O., Delebarre, A.: Segregation of wood particles in
762 a bubbling fluidized bed. Fuel Process. Technol. 133, 80–88 (2015).
763 https://doi.org/10.1016/j.fuproc.2014.12.045
764 80. Blanco, P.H., Wu, C., Onwudili, J.A., Williams, P.T.: Characterization of Tar from the
765 Pyrolysis/Gasification of Refuse Derived Fuel: Influence of Process Parameters and Catalysis.
766 Energy Fuels. 26, 2107–2115 (2012). https://doi.org/10.1021/ef300031j
767 81. Morin, M., Nitsch, X., Hémati, M.: Interactions between char and tar during the steam
768 gasification in a fluidized bed reactor. Fuel. 224, 600–609 (2018).
769 https://doi.org/10.1016/j.fuel.2018.03.050
770 82. Dufour, A., Masson, E., Girods, P., Rogaume, Y., Zoulalian, A.: Evolution of Aromatic Tar
771 Composition in Relation to Methane and Ethylene from Biomass Pyrolysis-Gasification. Energy
772 Fuels. 25, 4182–4189 (2011). https://doi.org/10.1021/ef200846g
773 83. Dufour, A., Girods, P., Masson, E., Rogaume, Y., Zoulalian, A.: Synthesis gas production by
774 biomass pyrolysis: Effect of reactor temperature on product distribution. Int. J. Hydrog. Energy.
775 34, 1726–1734 (2009). https://doi.org/10.1016/j.ijhydene.2008.11.075
776 84. Dufour, A., Valin, S., Castelli, P., Thiery, S., Boissonnet, G., Zoulalian, A., Glaude, P.-A.:
777 Mechanisms and Kinetics of Methane Thermal Conversion in a Syngas. Ind. Eng. Chem. Res. 48,
778 6564–6572 (2009). https://doi.org/10.1021/ie900343b
779 85. Jess, A.: Mechanisms and kinetics of thermal reactions of aromatic hydrocarbons from
780 pyrolysis of solid fuels. Fuel. 75, 1441–1448 (1996). https://doi.org/10.1016/0016-
781 2361(96)00136-6

86. Phan, T.S., Sane, A.R., Rêgo de Vasconcelos, B., Nzihou, A., Sharrock, P., Grouset, D., Pham Minh, D.: Hydroxyapatite supported bimetallic cobalt and nickel catalysts for syngas production from dry reforming of methane. Appl. Catal. B Environ. 224, 310–321 (2018). https://doi.org/10.1016/j.apcatb.2017.10.063
87. Dupont, C., Jacob, S., Marrakchy, K.O., Hognon, C., Grateau, M., Labalette, F., Da Silva Perez, D.: How inorganic elements of biomass influence char steam gasification kinetics. Energy. 109, 430–435 (2016). https://doi.org/10.1016/j.energy.2016.04.094
88. Bates, R.B., Altantzis, C., Ghoniem, A.F.: Modeling of Biomass Char Gasification, Combustion, and Attrition Kinetics in Fluidized Beds. Energy Fuels. 30, 360–376 (2016). https://doi.org/10.1021/acs.energyfuels.5b02120
89. Westbrook, C.K., Dryer, F.L.: Chemical kinetic modeling of hydrocarbon combustion. Prog. Energy Combust. Sci. 10, 1–57 (1984). https://doi.org/10.1016/0360-1285(84)90118-7
90. Battin-Leclerc, F.: Detailed chemical kinetic models for the low-temperature combustion of hydrocarbons with application to gasoline and diesel fuel surrogates. Prog. Energy Combust. Sci. 34, 440–498 (2008). https://doi.org/10.1016/j.pecs.2007.10.002
91. Debono, O., Villot, A.: Nitrogen products and reaction pathway of nitrogen compounds during the pyrolysis of various organic wastes. J. Anal. Appl. Pyrolysis. 114, 222–234 (2015). https://doi.org/10.1016/j.jaap.2015.06.002
92. Chen, H., Wang, Y., Xu, G., Yoshikawa, K.: Fuel-N Evolution during the Pyrolysis of Industrial Biomass Wastes with High Nitrogen Content. Energies. 5, 5418–5438 (2012). https://doi.org/10.3390/en5125418
93. Recari, J., Berrueco, C., Abelló, S., Montané, D., Farriol, X.: Effect of Bed Material on Oxygen/Steam Gasification of Two Solid Recovered Fuels (SRFs) in a Bench-Scale Fluidized-Bed Reactor. Energy Fuels. 31, 8445–8453 (2017). https://doi.org/10.1021/acs.energyfuels.7b01507
94. Ephraim, A., Ngo, L., Pham Minh, D., Lebonnois, D., Peregrina, C., Sharrock, P., Nzihou, A.: Valorization of Waste-Derived Inorganic Sorbents for the Removal of HCl in Syngas. Waste Biomass Valorization. (2018). https://doi.org/10.1007/s12649-018-0355-1
95. Delgado, J., Aznar, M.P., Corella, J.: Biomass Gasification with Steam in Fluidized Bed: Effectiveness of CaO, MgO, and CaO−MgO for Hot Raw Gas Cleaning. Ind. Eng. Chem. Res. 36, 1535–1543 (1997). https://doi.org/10.1021/ie960273w