1 Plasma gasification of refuse derived fuel in a single-stage
2 system using different gasifying agents

3 N. Agon^{*1,2,5}, M. Hrabovský¹, O. Chumak¹, M. Hlína¹, V. Kopecký¹, A. Mašláni¹,
4 A. Bosmans³, L. Helsen³, S. Skoblja⁴, G. Van Oost² and J. Vierendeels⁵

5 ¹Institute of Plasma Physics ASCR, Prague, Czech Republic

6 ²Department of Applied Physics, Ghent University, Ghent, Belgium

7 ³Department of Mechanical Engineering, KU Leuven, Heverlee, Belgium

8 ⁴Department of Gas, Coke and Air Protection, Institute of Chemical Technology,
9 Prague, Czech Republic

10 ⁵Department of Flow, Heat and Combustion Mechanics, Ghent University, Ghent,
11 Belgium

^{*}Nicholas.Agon@UGent.be, Sint-Pietersnieuwstraat 41, 9000 Gent, Belgium

Abstract

The renewable evolution in the energy industry and the depletion of natural resources are putting pressure on the waste industry to shift towards flexible treatment technologies with efficient materials and/or energy recovery. In this context, a thermochemical conversion method of recent interest is plasma gasification, which is capable of producing syngas from a wide variety of waste streams. The produced syngas can be valorized for both energetic (heat and/or electricity) and chemical (ammonia, hydrogen or liquid hydrocarbons) end-purposes. This paper evaluates the performance of experiments on a single-stage plasma gasification system for the treatment of refuse-derived fuel (RDF) from excavated waste. A comparative analysis of the syngas characteristics and process yields was done for seven cases with different types of gasifying agents (CO_2+O_2 , H_2O , $\text{CO}_2+\text{H}_2\text{O}$ and $\text{O}_2+\text{H}_2\text{O}$). The syngas compositions were compared to the thermodynamic equilibrium compositions and the performance of the single-stage plasma gasification of RDF was compared to that of similar experiments with biomass and to the performance of a two-stage plasma gasification process with RDF. The temperature range of the experiment was from 1400 to 1600 K and for all cases, a medium calorific value syngas was produced with lower heating values up to 10.9 MJ/Nm^3 , low levels of tar, high levels of CO and H_2 and which composition was in good agreement to the equilibrium composition. The carbon conversion efficiency ranged from 80 % to 100 % and maximum cold gas efficiency and mechanical gasification efficiency of respectively 56 % and 95 %, were registered. Overall, the treatment of RDF proved to be less performant than that of biomass in the same system. Compared to a two-stage plasma gasification system, the produced syngas from the single-stage reactor showed more favourable characteristics, while the recovery of the solid residue as a vitrified slag is an advantage of the two-stage set-up.

Keywords:

Single-stage, plasma gasification, steam gasification, refuse-derived fuel, CO_2 gasification, syngas production

1 Introduction

The emission of greenhouse gases, created by exploitation of fossil fuels, has been rising exponentially since the industrial revolution [1]. This pollution poses serious risks for ecosystems and to human health and is threatening to cause an anthropogenic climate change. This has initiated a shift towards heat and electricity generation systems based on renewable energy sources [2].

1 Concurrently, the depletion of coal, gas, oil and other natural resources makes the extraction of
2 raw materials more difficult and more energy-intensive, which results in additional environmental
3 burden [3]. The global demand for resources (energy and materials) will continue to grow, driven
4 by the fast-expanding world population and urbanization, while their future availability is lim-
5 ited. There is a broad consensus that a transition towards a resource efficient circular economy
6 is necessary in this context of increasing material demands. Sustainable waste management is an
7 important aspect in this transition as it aims at the integral valorization of waste streams and at
8 closing the material loop [4].

9 Waste is considered a very promising renewable resource, both for energy as for material purposes.
10 It will be an abundant resource for the future, since the global solid waste generation is rapidly
11 accelerating, due to the economic development and increased buying power in current developing
12 countries. Nowadays a large amount of waste is still being landfilled. One of the reasons for this is
13 the limited range of waste streams which can be processed with the currently available conversion
14 technologies. The most common method to process waste is incineration, which mainly focuses on
15 energy recovery (electricity and heat production), but it is associated with an extensive gas clean-
16 ing of large volumes of off-gases to remove hazardous emissions. The aforementioned factors have
17 led the waste industry to phase out unsustainable waste-management practices (e.g. landfills) and
18 move towards more resource-efficient and environmental-friendly technologies [5]. Plasma gasi-
19 fication is a promising alternative for conventional thermochemical conversion technologies as it
20 offers a substantially higher resource recovery potential.

21
22 Plasma gasification is an allothermal process (by means of a plasma torch) in which the organic
23 fraction of the waste is thermally decomposed into their constituent elements (syngas). Plasma
24 acts as a reforming agent for the gas phase by breaking down unwanted complex hydrocarbons in
25 the syngas. Depending on the configuration, the reforming aspect of plasma can also be applied
26 on the solid phase, by melting the inorganic fraction and converting it into a dense, inert, non-
27 leachable vitrified slag. Furthermore, the use of plasma as an energy source allows the processing
28 of a wide range of waste materials - including wastes with a high inorganics fraction - since the
29 gasification is independent of the energy content of the feedstock. Syngas as the principal product
30 can be used as feedstock for the production of chemicals such as hydrogen, ammonia, methanol
31 or other liquid hydrocarbons (via Fischer-Tropsch process). Alternatively, it can be used for elec-
32 tricity production in steam turbines, gas turbines or fuel cells [6]. The vitrified slag can be re-used

as a secondary product (e.g. interlocking blocks, tiles and bricks). The versatile plasma gasification technology can overcome several limitations of conventional autothermal gasification, such as material yield, syngas purity, dynamic response, compactness and flexibility [7] and offer the possibility of integrated resource recovery (both energy and materials). A detailed overview of possible system configurations and material types processed by plasma gasification can be found in the comprehensive reviews by Heberlein and Murphy [8] and by Gomez et al. [9].

The materials stream of interest in this work is refuse-derived fuel (RDF), which is a fuel obtained after processing of certain waste materials (e.g. municipal solid waste (MSW) and industrial waste (IW)). The research on plasma gasification of RDF is limited. In a pilot installation adapted from a system for metallurgical applications, Lemmens et al. [10] treated RDF with a transferred arc. The residual slag from the experiment was characterized to comply with the Flemish legislation for use as a secondary building material, however, no conclusive results were obtained about the performance of syngas production, because of the non-optimal design. Taylor et al. [11] treated RDF from MSW with the Gasplasma process, which comprises an oxy-steam bubbling fluidised bed gasifier and the subsequent plasma converter. The results of experiments on this two-step system show the effective generation of a clean syngas with high carbon and energy conversion efficiencies, and which composition compares well with theoretical predictions. Other research [12, 13] focused on analysing the performance of RDF plasma gasification with thermodynamic equilibrium models. Galeno et al. discussed the integration between a fluidized bed plasma torch gasification unit and a solid oxide fuel cell, which was calculated to produce a net energy output of about 4.2 MJ kg^{-1} and would have a net electric efficiency of 33 %.

Since 2005, research on the plasma gasification unit at the Institute of Plasma Physics (IPP) of the Academy of Science of the Czech Republic (ASCR) has been performed [14]. This reactor is equipped with a unique DC hybrid water/gas stabilized torch, creating a high enthalpy high velocity plasma, ideal for waste treatment [15]. In this single-stage system, the material fed to the reactor is partially gasified in-flight when it passes the high-temperature region created by the plasma. With this set-up, different types of material, i.e. biomass (sawdust and pellets) [16, 17, 18, 19], oil [20] and plastics [21] have been successfully converted to syngas in which the sum of carbon monoxide and hydrogen amounted up to 90 vol%.

In this paper, results from single-stage plasma gasification experiments with RDF, using a non-transferred arc, are presented. The specifics of the reactor configuration are explained in Section

2. The results from several cases with different mixtures of gasifying agents are analysed and their performance assessed. The measured composition of the produced syngas is compared to the theoretical composition at thermodynamic equilibrium. Additionally, process yields (e.g. carbon conversion efficiency) and energy efficiencies are calculated. Furthermore, the influence of the type of material gasified on the performance of the plasma gasification system is investigated by comparing the results of RDF experiments with previously published results from experiments with biomass. Finally, the output of these experiments is compared to that of experiments with RDF from other plasma gasification facilities.

2 Material and methods

2.1 The reactor system

The experiments were performed on the plasma gasification reactor PLASGAS at IPP. A schematic overview of the system is shown in Figure 1, reproduced from Hrabovský et al. [22]. The reactor has an inner volume of 0.22 m^3 and is coated with special refractory ceramics. Four layers of different insulation materials with a total thickness of 400 mm separate the inner surface of the reactor from the water-cooled outer walls to reduce the heat losses from the reactor. The temperature of the inner wall of the reactor is measured in six positions by thermocouples (WRe5–WRe26 and PtRh30–PtRh6) in a ceramic sheath. To prevent destruction of the ceramic coating, the reactor is pre-heated by an electric rod prior to the experiments for 24 h to temperatures of about 1200 K. Further heating is produced by the plasma torch.

The hybrid DC water/argon stabilized plasma torch is mounted on top of the volume and can operate at currents between 350 A to 550 A and arc powers of 90 kW to 160 kW. The anode of the torch is a rotating water-cooled copper disc, positioned outside of the arc chamber. This configuration generates an oxygen-hydrogen-argon plasma jet which offers a wide range of performance characteristics [23]. Both the heat losses from the reactor wall and the energy losses inside the arc chamber are determined from calorimetric measurements on the respective cooling circuits.

The material to be gasified is continuously supplied from the material container by a screw conveyor and falls into the reactor volume under gravitational force. The gas inlets for the gasifying agents (O_2 and CO_2) are located in the upper part of the reactor. The volumetric flow rates of these oxidizing gases (F_{O_2} and F_{CO_2}) are set using thermal gas mass flow controllers (Aalborg GFC–57 and Aalborg GFC–47 respectively). The inflow of liquid water as gasifying agent is posi-

Figure 1

tioned at the top of the reactor and the mass flow rate (Q_{H_2O}) is measured by weight difference. The outlet for the produced gas is positioned in the upper part of the reactor, so that the syngas passes through the high-temperature plasma jet region before exiting the volume. The gas then flows to a cylindrical quenching chamber with a length of 2 m and diameter of 0.3 m. The flow rate of the water spray is automatically controlled to keep the gas temperature at the output of the quenching chamber at 550 K. The gas temperatures are measured at the input and output of the quenching chamber by thermocouples (NiCr-NiAl with Inconel sheath and resistance thermometer Pt 100, respectively). The syngas is filtered through basalt filter bags before entering the combustion chamber where it is combusted by air flow. The produced syngas is collected for on-line composition analysis at the output of the reactor by a sampling tube which is cooled by water spray when it crosses the quenching chamber. To prevent blocking or damaging the inputs of the mass spectrometer, the gas sample circuit first passes a microfilter (Vesta MF M14). The sampled gas is then sent to the sample gas cooler (EGK 4S from Buhler Technologies) by a membrane pump (KNF) to condensate any steam from the syngas. In a final step, the sampled gas is prepared by a conditioning system (Perma Pure AmbiGASS) before being sent to the quadrupole mass spectrometer (Pfeiffer Omnistar GSD 301 T3). The mass spectrometer is calibrated to measure the relative concentrations of CO, H₂, CO₂, CH₄, O₂ and Ar. No nitrogen or air is added to the system and the reactor operates at slight overpressure, so the amount of N₂ in the syngas can be considered negligible.

2.2 Refuse derived fuel

The refuse derived fuel (RDF) is processed from waste excavated from landfill sites. It is composed of municipal solid waste (MSW, 59 %) and industrial waste (IW, 41 %). The proximate and ultimate analyses are summarized in Table 1. The compositional analysis is also shown, it provides a rough estimation of the different material types the waste is composed of. The material has a net calorific value (NCV) of 22.37 MJ/kg_{dry}. The methods followed to excavate and characterize the landfill waste are thoroughly explained in a case study [24]. It was found that the storage time of the MSW varied between 14 and 29 years; while for the IW, storage time varied between 14 and 24 years. More detailed information can be found in the study, performed by Quaghebeur et al. [24]. The compositional analysis of the mixed RDF material indicates a plastics content of 47 % (see Table 1), a relatively large fraction when compared to the RDF materials studied by other researchers [25, 26] who report plastic fractions varying from 16 % to 26 %. However, this

follows logically from the high plastics fraction present in the industrial waste (66 %), combined with the high amount of industrial waste (41 %) used to produce the mixed RDF material. The maximum particle size of the RDF is 25 mm. The main five components in the ash fraction are SiO₂, Al₂O₃, Fe₂O₃, CaO and MgO.

Table 1

2.3 Experimental parameters

Prior to the experiment, the reactor was gradually heated for 24 h to 1200 K. The total duration of the experiment, starting with the ignition of the torch after pre-heating was 4 h. Within this time period, several experimental cases can be identified, depending on the process parameters. The time to change the flow of gasifying agent(s) was less than 15 seconds and the response time in the syngas composition was approximately 30 seconds. After a stabilizing period, the output variables were averaged over a sampling period with steady-state conditions, ranging from 2 to 5 minutes. These relatively short time periods are justified by the very stable syngas composition. The screw feeder, designed for fine, homogeneous material types, was not adapted for supplying RDF to the reactor. The heterogeneous nature of the waste in particle size and material density resulted in some difficulties and fluctuations in the material feed rate. For the selected cases, the average value for the material feed rate over the test period was 29 kg h⁻¹. The torch was operated at a constant power of 120 kW and argon was added to the reactor as internal standard at a flow rate of 87 standard litres per minute (slm). From the total amount of argon entering the reactor (i.e. internal standard and argon from the torch) and the concentration of argon in the syngas, the total flow rate of syngas can be calculated. The process parameters, including the different mixtures of gasifying agents for the selected cases are summarized in Table 2.

Table 2

The equivalence ratio (ER) is defined as the ratio of the total amount of available moles of oxygen added to the process to the stoichiometric required amount of moles for the complete oxidation of material. The amount of oxygen from the moisture content of the material and from the steam fraction in the plasma were included in the total amount of oxygen added to the reactor. The oxidation reaction considered is displayed by Equation 1.

The temperature column in Table 2 shows the average value of the temperature measurements at the inner reactor wall surface. The thermocouples registered lower values than the actual temperature inside the reactor volume because of their shielded position in the water-cooled reactor wall. Nevertheless, the average of these measured temperatures will be used for the calculation of the theoretical syngas composition at thermodynamic equilibrium. Cases 4 and 5 can also be referred to as steam plasma gasification further down the paper, and Case 7 as oxy-steam plasma gasification.

3 Results and Discussion

3.1 Syngas composition

In this paragraph, the syngas composition registered by the mass spectrometer for the different cases is shown and compared with the calculated theoretical composition, assuming thermodynamic equilibrium. Based on the amount of C, H, O, N, S, Cl and Ar added to the system (waste material, argon as internal standard, gasifying agents and plasma gas), the equilibrium composition of this heterogeneous system was calculated at the given temperature using the method described by Coufal and Živný [27].

The calculated syngas composition contains a percentage of water vapour, but because the water vapour was removed from the produced syngas during the experiment to prevent blocking of the mass spectrometer, the theoretical volumetric percentages were normalized to a dry syngas comprising only the following five syngas components, i.e. CO, H₂, CO₂, CH₄ and Ar. The mass spectrometer is also calibrated for O₂, but as could be expected, there was no O₂ detected in the syngas exiting the reactor.

The argon concentration in the dry syngas content (which can amount up to 10 vol%) is specific to the set-up of the experimental system, in which it is used for estimating the syngas flow rate (through adding an internal standard of argon). The argon content should not be taken into account when assessing the syngas composition from plasma gasification of RDF for industrial applications.

The syngas compositions from the seven experimental cases are arranged according to the type of gasifying agent used. Figure 2 shows the cases in which a mixture of CO₂ and O₂ was used as gasifying agent and Figure 3 depicts the steam plasma gasification cases. The experiments with a mixture of CO₂ and H₂O and a mixture of O₂ and H₂O are grouped in Figure 4.

Specific reasons for the lower CO, higher H₂ and higher CO₂ concentrations than theoretically expected for Cases 1 to 3 can be the complete oxidation of some of the RDF (Equation 1), the further oxidation of the produced CO (Reaction 2) and the water-gas shift reaction (Equation 3).

According to the theoretical syngas compositions assuming thermodynamic equilibrium, before normalization to dry syngas, the water vapour contents for Case 1 to 3 were 12.5 vol%, 9.8 vol% and 8.5 vol% respectively. The theoretical presence of water vapour imposes the supposition that the water-gas shift reaction occurs.

Compared to Case 1, there was 25 slm less O₂ added to the process in Case 2, which results in slightly higher CO and lower CO₂ concentrations. Since less O₂ was available, more CO₂ was consumed in the gasification process and additionally, less CO₂ was produced via the CO oxidation reaction (Reaction 2). By reducing the CO₂ flow rate in Case 3 by 38 slm compared to the value in Case 2, the CO content is increased and the CO₂ concentration reduced to 11.0 vol%. The hydrogen content is also significantly higher than in the two other cases, most likely because the lower amount of CO₂ present in the system shifts the equilibrium of the water-gas shift reaction to the right. Additionally, the lower volume of added CO₂ makes a higher amount of energy available for the gasification reactions (producing CO and H₂), since less energy was consumed for heating up the gasifying agents.

Based on the evaluation of the syngas composition of these three cases, it is clear from the high concentrations of CO and H₂ and the low concentrations of CO₂ that Case 3 yields the most desirable syngas composition. Furthermore, a higher RDF to syngas conversion efficiency for Case 3 is suggested by the smaller difference between actual and theoretical argon content in the syngas. The argon concentration is only influenced by the total volume of syngas produced and is independent of the process chemistry. With the theoretical composition representing the complete RDF to syngas conversion, the smaller the difference between actual and theoretical argon concentration, the higher the gasification efficiency.

In Figure 3, the results from the composition analysis of the syngas produced from steam plasma gasification of RDF are shown. The syngas content corresponds well to the theoretically expected composition (patterned bars), except for the presence of CH_4 in the produced syngas. Hydrogen gas is the largest fraction in the composition with about 53 vol% for both cases. The difference between Case 4 and 5 is the increase in water flow rate from 300 ml min^{-1} to 385 ml min^{-1} , increasing the equivalence ratio from 0.44 to 0.55. With the extra addition of H_2O to the system, the CO concentration drops from 29.8 vol% to 27.2 vol%, the CO_2 concentration increases from 3.6 vol% to 5.9 vol% and the H_2/CO ratio increases from 1.77 to 1.95. This is possibly due to a shift in equilibrium of the water-gas shift reaction towards the right according to Le Chatelier's principle. This shift in equilibrium is slightly promoted by the marginally lower temperature in Case 5 than in Case 4.

The actual syngas composition shows a higher argon concentration than the theoretical composition, while the exact same amount of argon (i.e. the sum of argon from plasma and argon added as internal standard) is represented by the argon fraction in both compositions. This means that the total volume of produced syngas is lower than the theoretical calculated volume considering complete conversion. The gasification process thus achieves 82.3 % and 83.1 % of the theoretical maximum conversion to dry syngas for Case 4 and 5, respectively.

Figure 4

The syngas composition analysis of the plasma gasification with a mixture of CO_2 and H_2O (Case 6) and a mixture of O_2 and H_2O (Case 7) is displayed in Figure 4. For Case 6, the measured volume fractions of CO and of H_2 are lower and the volume fraction of CO_2 is higher than expected from theoretical calculation. The standard enthalpies of the heterogeneous gasification reaction with CO_2 and with H_2O are both endothermic and have similar values. As a result of these two competing reactions, the volumetric percentages of CO and H_2 are alike (H_2/CO ratio of 0.88), in contrast to previous cases where either CO or H_2 is predominantly present.

In Case 7, the calculated concentrations of CO and H_2 are almost identical. The measured CO concentration is lower and the H_2 concentration higher than their theoretical counterparts. The fact that the measured argon volume percent is lower than the calculated value suggests that the total produced volume of dry syngas is higher than theoretically expected. This could be due to small error margins on the material feed rate and gas flow rates, or due to water reacting through the water-gas shift reaction, which would augment the volume of dry syngas. Another possibility is that the oxy-steam plasma gasification converted some additional previously unreacted material

to syngas during the sampling period, thanks to the favorable process conditions.

3.2 Performance yields and energy efficiencies

Besides syngas composition, other frequently used indicators for analysing the performance of plasma gasification processes are carbon conversion efficiency (CCE), CO yield and H₂ yield. Carbon conversion efficiency is defined as the ratio of the amount of carbon in the syngas to the amount of carbon in the feed (i.e. from waste and from CO₂ as gasifying agent). CO yield is the ratio of the number of carbon atoms in the CO fraction of the syngas to the total number of carbon atoms injected. The definition of H₂ yield is the ratio of the number of hydrogen atoms in the H₂ fraction of the syngas to the total number of hydrogen atoms injected. The values of these performance indicators for all seven cases are plotted in Figure 5.

Figure 5

For Case 3, the carbon conversion efficiency is 86 %, the CO yield 67 % and the H₂ yield 76 %. The biggest increase in performance can be noticed from Case 2 to Case 3, in which the CO₂ flow rate is reduced by 38 slm. This is in line with the postulation in Paragraph 3.1 of a higher RDF to syngas conversion for Case 3, partially because a bigger part of the energy is available for the gasification reactions instead of for heating the (excess) gasifying agents.

For the steam plasma gasification, Cases 4 and 5, the additional 85 ml min⁻¹ of water resulted in a marginally higher carbon conversion efficiency of 84 %, while the CO and H₂ yields of 66 % were reduced to 61 % and 59 %, respectively.

It is interesting to notice that the performance indicators of Case 4 and Case 6 are nearly identical. Although these cases showed very different syngas compositions, the similar equivalence ratio and similar enthalpies of reaction for the overall gasification reaction with H₂O and with CO₂ resulted in almost equal process efficiencies. For Cases 1 to 6, the different (combinations of) gasifying agents and equivalence ratios do not seem to impact the carbon conversion efficiency to a great extent. The values of the CCE for these cases stay in the limited range from 80 % to 86 %.

Case 7 shows distinctively different values for the parameters in Figure 5 than the other cases. The CO and H₂ yield reach 82 % and 83 %, respectively, and the CCE exceeds 100 %. The high values for these performance criteria, especially the latter, are in line with the result of a higher volume of produced syngas than the theoretical maximum (see Paragraph 3.1). Possible explanations for the slight overestimation of carbon conversion efficiency exceeding 100 % are error margins on the material feeding rate and/or gas flow rates, or the gasification of previously unreacted material

during the sampling period. Corrections on these high performance criteria should however remain small and are most likely in the range of a few percent. Despite the small incongruity, these results demonstrate the high performance of the process of plasma gasification of RDF with a mixture of O_2 and H_2O as gasifying agents.

In terms of energy efficiency, the cold gas efficiency (CGE) and mechanical gasification efficiency (MGE) for the different cases are summarized in Table 3, together with syngas yield and lower heating value (LHV) of the syngas. The mechanical gasification efficiency is the ratio between the chemical energy content in the produced syngas compared to the chemical energy in the fuel:

$$MGE = \frac{LHV_{syngas} F_{syngas}}{LHV_{RDF} \dot{m}_{RDF}} * 100 \quad (4)$$

The cold gas efficiency is the ratio between the chemical energy content in the syngas to the sum of the chemical energy in the fuel and the electric power consumed by the plasma torch:

$$CGE = \frac{LHV_{syngas} F_{syngas}}{LHV_{RDF} \dot{m}_{RDF} + P_{plasma}} * 100 \quad (5)$$

with F_{syngas} the volumetric flow rate of syngas, $\dot{m}_{RDF}$ the mass flow rate of RDF and P_{plasma} the torch power. The lower heating value of syngas is expressed in volumetric units and that of RDF in mass units.

Table 3

In all cases, the single-stage plasma gasification of RDF produced a medium calorific value syngas with a lower heating value (or net calorific value) ranging from 9.0 MJ/Nm³ to 10.9 MJ/Nm³. For the plasma gasification of RDF with a mixture of CO_2 and O_2 (Cases 1 to 3), the calorific values of the produced syngas are the lowest, mainly because of the high levels of CO_2 in the syngas composition. Case 3 with the lowest equivalence ratio and lowest CO_2 concentration in the syngas of the first three cases, yielded the highest CGE and MGE with respective values of 48 % and 82 %.

The energy efficiencies for steam plasma gasification are significantly higher with values of 56 % and 94–95 % for CGE and MGE, respectively. Up to 1.88 Nm³/kg of syngas is produced with the highest calorific values of all cases (10.7–10.9 MJ/Nm³). The energy efficiencies and syngas properties only differ one digit between Case 6 and Case 7 and their values are similar to those from steam plasma gasification.

Although Case 3 and Case 7 have identical equivalence ratios and CO_2 and H_2O as respective gasifying agent additions to O_2 have similar reaction enthalpies for the heterogeneous partial oxidation of RDF, the performance yields, syngas characteristics and energy efficiencies differ significantly between both cases. The process performance of Case 7 is better because the flow rate of oxygen alone constitutes 106 % of the theoretical necessary amount of oxygen necessary for partial oxidation of the material, compared to 90 % in Case 3. The larger share of oxygen in the mixture of gasifying agents in Case 7 than in Case 3 means that more material can react through exothermic partial oxidation and more energy is made available for the process, which allows a better conversion.

Two important remarks should be made about the energy efficiencies. First, the sensible heat of the produced syngas is not taken into account. In this experimental set-up, the produced syngas exiting the reactor at temperatures up to 1550 K is rapidly quenched. In an industrial facility however, part of the sensible heat of the syngas can be recovered and either recirculated into the system, or applied externally (for heat or electricity production).

Secondly, the cold gas efficiency is highly dependent on the material feed rate in relation to the plasma power. The value of the latter process parameter is limited in range and relatively invariable for each test campaign. The material feed rate on the other hand can easily be doubled or tripled for different experiments up to the design capacity of 100 kg h^{-1} of the system. The cold gas efficiencies in these experiments are therefore not representative for the general performance of the system, since it was not operated at its maximum capacity.

3.3 Tar analysis

The solid phase adsorption/extraction (SPA/SPE) method is used for tar sampling. Tar vapors are adsorbed on to aminopropyl-bonded silica (Discovery DSC-NH₂, 500 mg/3 ml). The SPE tubes are preconditioned with 2.5 ml of dichloromethane (DCM). Three samples of 600-900 ml are taken from the gas flow over the course of the experiment. Analytes are desorbed by DCM and the fractions analysed by GC-FID. The total tar content of these samples was 132, 370 and 543 mg/Nm³. From Table 4, it can be seen that condensed tertiary products (such as naphthalene, acenaphthylene and phenanthrene) were most abundant in the syngas samples, while the concentration of the benzene-toluene-xylene (BTX) fraction remains very low. This is in line with the chemical components generally found with high-temperature steam gasification, as reported by Elliott [28].

The measured tar concentration in the syngas produced from RDF plasma gasification was higher than the tar content in the syngas from biomass plasma gasification ($< 10 \text{ mg/Nm}^3$) [29], most likely because of the heterogeneous nature of the RDF and the coarser particle size. On the other hand, the tar level was lower than in the syngas obtained from conventional RDF gasification, which is typically in the range of 1 to 100 g/Nm^3 , depending on the type of gasifier. Nevertheless, a cleaning step would be necessary prior to downstream application of the syngas in a gas engine, gas turbine or fuel cell, which have tar tolerance levels of about 50, 5 and 1 mg/Nm^3 , respectively.

3.4 Residue analysis

After the experiments were completed, the reactor was opened and samples of the solid residue were collected from the bottom and top of the reactor. The main part of the residual ash was in the form of particulates and only at the bottom of the reactor, some molten solids could be seen in the wake of the plasma jet. A solid/liquid extraction with DCM is performed and the extracts were analysed by means of GC-MS. Additionally, a thermogravimetric analysis was performed in order to determine the ratio of volatile organic components (VOCs), fixed carbon and mineral ash residue contained in the samples. A representative sample is heated from room temperature up to 600°C ($20^\circ\text{C min}^{-1}$) with nitrogen as carrier gas. After an isothermal period of 30 min, the sample is heated further ($20^\circ\text{C min}^{-1}$) to 900°C in air. A summary of the results from the thermogravimetric analysis is displayed in Table 5. The results indicate that during the experiments, unreacted material collects at the bottom of the reactor. Based on the high amount of VOCs in the bottom sample, it is clear that the material was not completely gasified during the free-fall trajectory across the reactor volume. The further release of organic volatiles was then limited by the lower temperatures at the bottom of the reactor and the accumulation of additional unreacted material. The proximate analysis of the sample from the top layer of the accumulated residue in the reactor shows a higher weight fraction of fixed carbon and a much lower amount of VOCs. The material collected in this sample was exposed to the high-temperature flow of plasma for a longer period of time which allowed an almost complete release of the volatiles. However, because of the limited addition of gasifying agents towards the end of the experiment, a large fraction of the produced char was not oxidized to CO or CO_2 .

3.5 Comparison with single-stage biomass plasma gasification

A number of experiments with various materials have been performed on the single-stage reactor at IPP. Besides polyethylene, pyrolysis oil from waste tyres and plastic waste, biomass (spruce) in the shape of pellets or as sawdust has been the material of choice. Adapted results from experiments previously published in Hrabovský et al. [30] are qualitatively compared to the results from the RDF experiments.

The biggest differences in the material composition between biomass and RDF are the higher moisture content (12.2 wt%), the very low ash fraction and a much higher oxygen content. No quantitative comparison can be made about the syngas composition because of the different material composition and feed rate (44 kg h^{-1}) and equivalence ratios. Three experimental cases of sawdust gasification with respectively H_2O , a mixture of CO_2 and H_2O and a mixture of O_2 and H_2O as gasifying agents are therefore qualitatively compared with Case 4, Case 6 and Case 7. The operational parameters for these experiments are summarized in Table 6.

Table 6

The syngas composition (coloured bars) and the calculated equilibrium composition (patterned bars) for these biomass cases is shown in Figure 6).

Figure 6

Overall, the CH_4 concentrations are lower in the syngas from biomass gasification than from RDF gasification. The higher levels of CH_4 produced from RDF gasification are caused by the decomposition and gasification of the plastics fraction in the waste material. Aznar et al. [31] found that the methane content in the syngas from plastics gasification is significantly higher than that in syngas from biomass or coal gasification. The measured gas content does not necessarily matches the theoretical composition to a greater degree than for the RDF experiments. The same trends in the H_2/CO ratio depending on the type of gasifying agent(s) used can be noticed (Table 7).

Table 7

For both materials, the values of the H_2/CO ratio are very similar for the gasification with a mixture of CO_2 and H_2O and with a mixture of O_2 and H_2O . For steam plasma gasification, the value for RDF was significantly higher than for biomass, caused by the even bigger difference in equivalence ratio and the much larger amount of water added to the system. Hwang et al. [32] suggested an accelerated degradation of RDF in the presence of steam due to a catalytic effect of ash. Although no prove for this assertion was found in their reported reference, other research has confirmed the promoting effect of mineral matter on the steam gasification of coal [33, 34].

The CCE, CO and H_2 yields are higher for biomass than for RDF, except for the case with O_2

and H_2O . In previous analysis, it was already assumed that the actual values of the performance parameters for the RDF case with these gasifying agents were likely lower due to small error margins on the material feed rate and/or gas flow rates. Therefore no conclusive results can be deduced from the comparison between RDF and biomass gasification for this case.

The difference in carbon conversion efficiency between the two material types is not as high as the differences in the other yields. The cold gas efficiencies and mechanical gasification efficiencies are higher with biomass than with RDF with values of 65–66 % and 105–107 %, respectively. Despite the lower ER and the higher material feed rate, the plasma gasification of the single-type material (biomass) proves more performant than the plasma gasification with RDF. The small particle size (i.e. high surface area) allows better mass and heat transfer, the high oxygen and moisture content in the material means an evenly distributed oxygen availability throughout the material and more energy is available for the gasification process because less energy is spent on heating a considerable ash fraction and a larger volume of gasifying agents.

3.6 Comparison with two-stage RDF plasma gasification

Publicly available results from plasma gasification experiments with RDF are very scarce. An interesting plasma gasification facility, which is well-documented in literature is the demonstration plant of Advanced Plasma Power (APP) in Swindon (UK). This two-stage system consists of an oxy-steam bubbling fluidised bed gasification step followed by a plasma converter, in which the syngas and the solid residue from the former step are treated.

Experiments in which RDF is converted to syngas in this system are published by Materazzi et al. [35]. The main differences in RDF composition are compared in Table 8.

Table 8

The RDF used in the two-stage plasma gasification experiments has a lower ash content, higher carbon content, higher hydrogen content and lower oxygen content. The moisture content is similar and the net calorific value is slightly higher (24.92 MJ kg^{-1} as received compared to 22.37 MJ kg^{-1} dry).

All process parameters of the two-stage plasma gasification experiments are higher than those from the single-stage oxy-steam plasma gasification experiment (Case 7) (Table 9). In the two-stage gasification, the heat necessary for the gasification reactions is produced from complete oxidation of part of the material. This results in the higher CO_2 content and lower CO/CO_2 ratio compared the single-stage case. This also affects the H_2/CO ratio, which is only slightly higher, despite the

higher hydrogen content in the material and the higher steam to oxygen ratio.

Table 9

In Taylor et al. [11], the carbon conversion efficiency and mechanical energy of an experiment with RDF, similar to the one described by Materazzi et al. [35] is reported to be 99 and 94 %. These values correspond well with the ones for the oxy-steam single-stage plasma gasification in Case 7 (101 and 91 %), although those might need to be slightly downgraded. It is clear from the negligible levels of benzene, toluene, phenol and hexane after the plasma converter, published by Materazzi et al. [35], that tar removal is effective in the two-stage system. The maximum concentration of the BTEX aromatics (benzene, toluene, ethylbenzene and xylene) in the syngas samples from in-flight single-stage plasma gasification system was very low at 1.4 mg/Nm³ and slightly higher at approximately 21.2 mg/Nm³ from the two-stage process [36]. The largest tar substance groups detected in the produced syngas were naphthalenes and other polyaromatic hydrocarbons with concentrations of two orders of magnitude higher. The concentrations of these tar components after the plasma converter step in the two-stage plasma gasification process are significantly lower, with only 18 µg/m³ of naphthalene in the syngas [36].

A clear advantage of the two-stage system is that the residual inorganic fraction leaving the plasma converter was successfully vitrified into a slag, whereas the non-gasified fraction in the single-stage system did not reach its melting point and was recovered as solid particulates. The vitrified slag is suitable for further materials processing (e.g. fabrication of ceramic glass products or road construction material) [37], while the unmelted residue has little to no value as a by-product from gasification.

4 Conclusions

In this work, the results from a plasma gasification experiment with RDF were presented. The tests were conducted on the single-stage plasma gasification unit at IPP using four different combinations of gasifying agents (CO₂+O₂, H₂O, CO₂+H₂O and O₂+H₂O). The composition of the produced syngas was compared with the theoretical composition, assuming thermodynamic equilibrium and the performance of the different cases was assessed based on process yields and energy efficiencies. The plasma gasification of RDF yielded a medium calorific value syngas for all cases with a lower heating value up to 10.9 MJ/Nm³.

The carbon conversion efficiency was relatively insensitive to the type of gasifying agent used and to the equivalence ratio, and maintained a value between 80 and 86 % (except for Case 7). The CO

yield, H_2 yield and CCE for the oxy-steam gasification were significantly higher than for the other cases. It is assumed that these much larger values (e.g. CCE exceeding 100 %) should be slightly downgraded, because of possible small error margins on the material feed rate and/or gas flow rates or because of previously unreacted material which was gasified during the sampling period. Overall, the measured syngas composition was relatively close to the theoretical composition, suggesting that the conditions inside the reactor during the plasma gasification process were close to thermodynamic equilibrium. The best agreement between measured and calculated syngas composition was found for steam plasma gasification. Additionally, the energy efficiencies of Cases 4 and 5 were the highest with values of 56 % and 94–95 % for cold gas efficiency and mechanical gasification efficiency, respectively. The H_2/CO ratio of the syngas from Case 5 was 1.95, which is close to the optimum ratio needed by the Fischer-Tropsch process.

From the comparative analysis of Case 4 and Case 6, it was shown that at a constant equivalence ratio, CO_2 and H_2O as gasifying agents can be interchanged to control the syngas composition while maintaining a constant performance of the process. The tar analysis on syngas samples showed low total tar content varying from 132 to 543 mg/Nm³, which is lower than for conventional gasification, but higher than previous tar measurements during biomass plasma gasification. Further comparative analysis between RDF and biomass plasma gasification revealed similar trends in syngas composition (H_2/CO ratio) depending on the type of gasifying agent(s) used. Despite more favourable process conditions for the RDF experiments (lower material feed rate and higher ER), the performance of the gasification of the single-type biomass material was higher than that of RDF gasification. This suggests the influence of particle size, ash and moisture content, and oxygen distribution of the material on the gasification efficiency.

Finally, it can be concluded that the syngas from single-stage oxy-steam plasma gasification has some advantageous characteristics over the syngas from two-stage oxy-steam plasma gasification. The high level of CO_2 from complete oxidation of the material in the latter process lead to a lower sum of carbon monoxide and hydrogen and a lower CO/CO_2 ratio. In both systems, the high-temperature and high level of radiation from plasma successfully broke down the tar content to low levels. In the plasma converter step of the two-stage plasma gasification system, the tar content (e.g. naphthalene) was even lower and the solid residue was melted to a vitrified slag which can be valorised. In contrast, the residual material in the single-stage gasification reactor did not reach its melting point and was recovered as particulates (with mineral ash fraction of 53 %), not suitable for further applications.

The results presented in this work showed that plasma gasification is a promising treatment technology for refuse-derived fuel. The flexibility of the system allows to control the characteristics of the produced syngas by the choice of gasifying agent(s). Future work on this system will be directed towards maximizing the gasification performance by optimal adjustment of the process parameters and through CFD modelling of this plasma gasification reactor.

Acknowledgments

The authors gratefully acknowledge the financial support of the Grant Agency of the Czech Republic under the project GA15-19444S, the financial support of N. Agon through the Strategic Basic Research programme of the Agency for Innovation by Science and Technology in Flanders (IWT) and the financial support of A. Bosmans through the IWT O&O project Closing the Circle and Enhanced Landfill mining as a part of the transition to Sustainable Materials Management.

References

- [1] G. Marland, T.A. Boden, and R.J. Andres. Global, regional, and national fossil fuel CO₂ emissions. In *Trends: A Compendium of Data on Global Change*, Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, U.S. Department of Energy, Oak Ridge, Tenn., U.S.A., 2008.
- [2] F. Creutzig, J. C. Goldschmidt, P. Lehmann, E. Schmid, F. von Blucher, C. Breyer, B. Fernandez, M. Jakob, B. Knopf, S. Lohrey, T. Susca, and K. Wiegandt. Catching two European birds with one renewable stone: mitigating climate change and Eurozone crisis by an energy transition. *Renewable & Sustainable Energy Reviews*, 38:1015–1028, 2014.
- [3] M. Hoel and S. Kverndokk. Depletion of fossil fuels and the impacts of global warming. *Resource and Energy Economics*, 18(2):115–136, 1996.
- [4] D. C. Wilson. Development drivers for waste management. *Waste Management & Research*, 25(3):198–207, 2007.
- [5] A. Bosmans, I. Vanderreydt, D. Geysen, and L. Helsen. The crucial role of waste-to-energy technologies in enhanced landfill mining: a technology review. *Journal of Cleaner Production*, 55:10–23, 2013.

- [6] L. Wang, C. L. Weller, D. D. Jones, and M. A. Hanna. Contemporary issues in thermal gasification of biomass and its application to electricity and fuel production. *Biomass & Bioenergy*, 32(7):573–581, 2008.
- [7] F. Fabry, C. Rehmet, V. Rohani, and L. Fulcheri. Waste gasification by thermal plasma: a review. *Waste and Biomass Valorization*, 4(3):421–439, 2013.
- [8] J. Heberlein and A. B. Murphy. Thermal plasma waste treatment. *Journal of Physics D-Applied Physics*, 41(5), 2008.
- [9] E. Gomez, D. A. Rani, C. R. Cheeseman, D. Deegan, M. Wise, and A. R. Boccaccini. Thermal plasma technology for the treatment of wastes: a critical review. *Journal of Hazardous Materials*, 161(2-3):614–626, 2009.
- [10] B. Lemmens, H. Elslander, I. Vanderreydt, K. Peys, L. Diels, M. Oosterlinck, and M. Joos. Assessment of plasma gasification of high caloric waste streams. *Waste Management*, 27(11):1562–1569, 2007.
- [11] R. Taylor, R. Ray, and C. Chapman. Advanced thermal treatment of auto shredder residue and refuse derived fuel. *Fuel*, 106:401–409, 2013.
- [12] G. Galeno, M. Minutillo, and A. Perna. From waste to electricity through integrated plasma gasification/fuel cell (IPGFC) system. *International Journal of Hydrogen Energy*, 36(2):1692–1701, 2011.
- [13] S. Achinas and E. Kapetanios. Efficiency evaluation of RDF plasma gasification process. *Energy and Environment Research*, 3(1):150–157, 2013.
- [14] G. Van Oost, M. Hrabovský, J. Pieters, M. Tendler, and J. Verstraeten. Novel project on total plasma based treatment of waste. *Problems of Atomic Science and Technology. Series: Plasma Physics*, 10(1):157–160, 2005.
- [15] V. Březina, Hrabovský M., M. Konrád, V. Kopecký, and V. Sember. New plasma spraying torch with combined gas-liquid stabilization of arc. In *5th International Symposium on Plasma Chemistry (ISPC 15)*, Orléans, France, 2001.
- [16] M. Hrabovský, M. Konrád, V. Kopecký, M. Hlína, T. Kavka, G. Van Oost, E. Beeckman, and B. Defoort. Gasification of biomass in water/gas-stabilized plasma for syngas production. *Czechoslovak Journal of Physics*, 56:B1199–B1206, 2006.

- [17] G. Van Oost, M. Hrabovský, V. Kopecký, M. Konrád, M. Hlína, T. Kavka, O. Chumak, E. Beeckman, and J. Verstraeten. Pyrolysis of waste using a hybrid argon-water stabilized torch. *Vacuum*, 80(11-12):1132–1137, 2006.
- [18] M. Hrabovský, M. Hlína, M. Konrád, V. Kopecký, T. Kavka, O. Chumak, and A. Mašláni. Thermal plasma gasification of biomass for fuel gas production. *High Temperature Material Processes*, 13(3-4):299–313, 2009.
- [19] G. Van Oost, M. Hrabovský, V. Kopecký, M. Konrád, M. Hlína, and T. Kavka. Pyrolysis/gasification of biomass for synthetic fuel production using a hybrid gas-water stabilized plasma torch. *Vacuum*, 83(1):209–212, 2008.
- [20] M. Hrabovský, M. Konrád, V. Kopecký, M. Hlína, T. Kavka, O. Chumak, and A. Mašláni. Steam plasma gasification of pyrolytic oil from used tires. In *20th International Symposium on Plasma Chemistry*, pages 200–203, Drexel University, Philadelphia, U.S.A., 2011.
- [21] M. Hrabovský, M. Konrád, V. Kopecký, M. Hlína, T. Kavka, O. Chumak, A. Mašláni, and G. Van Oost. Plasma aided gasification of biomass and plastics using CO₂ as oxidizer. In *International Symposium on Non-Thermal/Thermal Plasma Pollution Control Technology & Sustainable Energy (ISNTP 7)*, 2010.
- [22] M. Hrabovský, M. Konrád, V. Kopecký, M. Hlína, T. Kavka, O. Chumak, G. Van Oost, E. Beeckman, and B. Defoort. Pyrolysis of wood in arc plasma for syngas production. *High Temperature Material Processes*, 10(4):557–570, 2006.
- [23] M. Hrabovský, V. Kopecký, V. Sember, T. Kavka, O. Chumak, and M. Konrád. Properties of hybrid water/gas DC arc plasma torch. *IEEE Transactions on Plasma Science*, 34(4):1566–1575, 2006.
- [24] M. Quaghebeur, B. Laenen, D. Geysen, P. Nielsen, Y. Pontikes, T. Van Gerven, and J. Spooren. Characterization of landfilled materials: screening of the enhanced landfill mining potential. *Journal of Cleaner Production*, 55:72–83, 2013.
- [25] M. Rovatti, A. Converti, M. Bisi, and G. Ferraiolo. Pyrolysis of refuse-derived fuel - kinetic modeling from product composition. *Journal of Hazardous Materials*, 36(1):19–33, 1994.
- [26] V. Cozzani, C. Nicolella, L. Petarca, M. Rovatti, and L. Tognotti. A fundamental study on conventional pyrolysis of a refuse-derived fuel. *Industrial & Engineering Chemistry Research*, 34(6):2006–2020, 1995.

- [27] O. Coufal and O. Živný. Composition and thermodynamic properties of thermal plasma with condensed phases. *European Physical Journal D*, 61(1):131–151, 2011.
- [28] D.C. Elliot. Relation of reaction time and temperature to chemical composition of pyrolysis oils. In E.J. Soltes and T.A. Milne, editors, *ACS Symposium Series 376*, Denver, Colorado (USA), 1988.
- [29] M. Hlína, M. Hrabovský, V. Kopecký, M. Konrád, T. Kavka, and S. Skoblja. Plasma gasification of wood and production of gas with low content of tar. *Czechoslovak Journal of Physics*, 56:B1179–B1184, 2006.
- [30] M. Hrabovský, M. Hlína, M. Konrád, V. Kopecký, O. Chumak, A. Mašláni, T. Kavka, O. Živný, and G. Pellet. Steam plasma-assisted gasification of organic waste by reactions with water, CO₂ and O₂. In *21th International Symposium on Plasma Chemistry (ISPC 21)*, 2013.
- [31] M.P. Aznar, M.A. Caballero, J.A. Sancho, and E. Francés. Plastic waste elimination by co-gasification with coal and biomass in fluidized bed with air in pilot plant. *Fuel Processing Technology*, 87:409–420, 2006.
- [32] I. H. Hwang, J. Kobayashi, and K. Kawamoto. Characterization of products obtained from pyrolysis and steam gasification of wood waste, RDF, and RPF. *Waste Management*, 34(2):402–410, 2014.
- [33] J. Rizkiana, G. Q. Guan, W. B. Widayatno, X. G. Hao, X. M. Li, W. Huang, and A. Abudula. Promoting effect of various biomass ashes on the steam gasification of low-rank coal. *Applied Energy*, 133:282–288, 2014.
- [34] Y. Kong, J. Kim, D. Chun, S. Lee, Y. Rhim, J. Lim, H. Choi, S. Kim, and J. Yoo. Comparative studies on steam gasification of ash-free coals and their original raw coals. *International Journal of Hydrogen Energy*, 39(17):9212–9220, 2014.
- [35] M. Materazzi, P. Lettieri, L. Mazzei, R. Taylor, and C. Chapman. Fate and behavior of inorganic constituents of rdf in a two stage fluid bed-plasma gasification plant. *Fuel*, 150(0):473–485, 2015.
- [36] M. Materazzi, P. Lettieri, L. Mazzei, R. Taylor, and C. Chapman. Reforming of tars and organic sulphur compounds in a plasma-assisted process for waste gasification. *Fuel Processing Technology*, 137:259–268, 2015.

- [37] J. Spooren, M. Quaghebeur, P. Nielsen, L. Machiels, B. Blanpain, and Y. Pontikes. Material recovery and upcycling within the ELFM concept of the Remo case. In P.T. Jones and D. Geysen, editors, *Second International Academic Symposium on Enhanced Landfill Mining*, Houthalen-Helchteren, Belgium, 2013.

Tables

Proximate analysis		Ultimate analysis		Compositional analysis	
	wt% dry		wt% dry		wt% dry
fixed carbon	8.6	C	46.8	plastics	47
volatile matter	69.3	H	5.7	wood+paper	24
ash	22.1	O ^a	22.3	textiles	10
<i>moisture</i>	<i>4.6</i>	Cl	1.60	fines	18
		N	1.25		
		S	0.26		

^aby difference

Table 1: Proximate, ultimate and compositional analysis of RDF processed from excavated waste (59 % municipal waste, 41 % industrial waste).

Case number	T (K)	F_{H_2O} (ml min ⁻¹)	F_{CO_2} (slm)	F_{O_2} (slm)	ER
1	1554	0	216	118	0.52
2	1538	0	215	93	0.46
3	1536	0	177	93	0.43
4	1429	300	0	0	0.44
5	1395	385	0	0	0.55
6	1446	144	178	0	0.42
7	1490	113	0	114	0.43

Table 2: Process parameters of the gasification cases with RDF.

Case number	CGE (%)	MGE (%)	Syngas yield (Nm ³ /kg)	LHV (MJ/Nm ³)
1	42	72	1.69	9.0
2	42	72	1.66	9.2
3	48	82	1.75	9.9
4	56	94	1.84	10.9
5	56	95	1.88	10.7
6	54	92	1.87	10.5
7	53	91	1.86	10.4

Table 3: Energy efficiencies and syngas characteristics.

Table 4: Concentrations of the most abundant tar species

Tar species (mg/Nm ³)	Sample number		
	1	2	3
BTX	0	1.4	1.1
Naphthalene	78.6	205.8	155.5
Methylnaphthalene	1.8	8.1	2.7
Acenaphthylene	7.4	90.7	35.8
Acenaphthene	2.7	7.6	5.7
Phenanthrene	8.4	67.3	51.6
Anthracene	0.7	6.9	2.0
Pyrene	7.2	31.9	29.6
Fluorene	1.8	12.6	3.9
Fluoranthene	6.7	32.3	32.9
PAHs	9.2	32.8	22.6
Biphenyl	3.2	21.1	12.4

	Bottom	Top
	wt%	wt%
VOCs	34	5
fixed carbon	16	39
ash	53	53

Table 5: Proximate analyses of solid residue samples based on TGA

Case number	T (K)	F_{H_2O} (ml min ⁻¹)	F_{CO_2} (slm)	F_{O_2} (slm)	ER
B1	1460	70.4	0	0	0.17
B2	1418	70.4	87.8	0	0.24
B3	1443	70.4	0	44.2	0.24

Table 6: Process parameters of the gasification cases with sawdust.

Parameter	Material	Gasifying agents		
		H ₂ O	CO ₂ +H ₂ O	O ₂ +H ₂ O
H ₂ /CO	RDF	1.77	0.88	1.22
	Biomass	1.24	0.83	1.17
CCE	RDF	83	83	101
	Biomass	85	88	93
CO yield	RDF	66	65	82
	Biomass	79	83	78
H ₂ yield	RDF	66	64	83
	Biomass	89	73	84

Table 7: Comparison of performance parameters of RDF experiments Cases 4, 6 and 7 and biomass experiments Cases B1, B2 and B3.

Proximate analysis (wt%dry)			Ultimate analysis (wt%dry)		
	RDF-exp	RDF-ref		RDF-exp	RDF-ref
Moisture	4.6	6.3	C	46.8	58.65
Ash	22.1	13.7	H	5.7	8.35
			O	22.3	16.03

Table 8: Comparative analysis of RDF composition between the RDF used in the experiments (RDF-exp) and the RDF from Materazzi et al. [35] (RDF-ref)

Process parameters	EXP	REF	Syngas characteristics	EXP	REF
RDF feed rate (kg/h)	29	50–60	CO	40.6	31.5
O ₂ /fuel (w/w)	0.34	0.5–0.6	H ₂	49.5	41.2
H ₂ O/O ₂ (mol/mol)	1.64	2.4–3.6	CO ₂	6.9	16.4
			CH ₄	2.9	1.6
			Inerts ^a	–	9.3
			CO/CO ₂	5.88	1.92
			H ₂ /CO	1.22	1.31
			GHV ^b (MJ/Nm ³)	12.62	9.49

^aThe inert argon fraction in the syngas from single-stage experiments is not considered because it is not inherent to the gasification process (except the negligible amount of argon from plasma)

^bThe gross heating value (GHV) is given for a dry, inert-free syngas

Table 9: Comparative analysis of process parameters and syngas characteristics between the single-stage experiments (EXP) and the two-stage experiments from Materazzi et al. [35] (REF)

Figure Captions

Figure 1. Schematic of the reactor system with the plasma jet marked in orange and a) the material hopper; b) the reactor vessel; c) the slag collection bucket; d) the quenching chamber and e) the afterburner

Figure 2. Measured (full colour) and theoretical (patterned) syngas composition for Cases 1, 2 and 3

Figure 3. Measured (full colour) and theoretical (patterned) syngas composition for cases 4 and 5

Figure 4. Measured (full colour) and theoretical (patterned) syngas composition for cases 6 and 7

Figure 5. Carbon conversion efficiency (red bar), CO yield (blue bar) and H₂ yield (green bar)

Figure 6. Measured (full colour) and theoretical (patterned) syngas composition for the biomass cases