Plasma-assisted gasification for Waste-to-Fuels applications

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Abstract

This paper firstly examines the experimental results from a 16 hours plasma assisted gasification trial for conversion of refuse derived fuel (RDF) into syngas suitable for biofuel production in a pilot plant. In particular the work focuses on the effect on the concurrent ash vitrification and tar reforming processes on the general composition of a syngas stream produced in a fluidised bed gasifier. The effect of plasma on tar reforming is showed by continuous monitoring of gas composition before and after the plasma converter, with reduction efficiencies typically exceeding 99%v/v for most hydrocarbons, SO_2, NH_3, NO_x and organic sulphur. The test also investigates on the effect of plasma intensity on different contaminants reforming and syngas conditioning when varying the input power value at cracking-relevant temperatures. A simplified catalytic test is undertaken under continuous flow of cleaned syngas generated by the pilot plant to identify the short-term effects of waste-derived contaminants on catalysts activity when plasma refining is not operated.

Keywords: Waste gasification; Plasma-assisted gasification; Waste-to-Fuels; Plasma reforming

1. Introduction

Biofuels have attracted considerable attention in the last decades due to the increasing demand on energy resources as well as elevated concerns about greenhouse gas emissions. First-generation biofuels are produced by biochemically processing of sugar or starch crops into ethanol fuel and oil seed crops into biodiesel [1,2]. These industries grew tremendously in the last two decades although not without controversy, including concerns about using food crops and clean water for fuel production, and debate over the environmental impact of biofuels agriculture. However, the potential of conventional biotechnologies is still limited by the availability of suitable feedstocks (e.g. lipids and high-value cellulosic biomass). New technologies that can process a wider range of materials, including waste and non-recycled plastics, are required for low carbon fuels to add a significant contribution. Advanced thermal treatments, including pyrolysis and gasification, have the advantage that they could potentially accept any organic material and decompose it to a range of reusable hydrocarbons or synthesis gas, with important savings in net CO_2 emissions [3]. Hydrocarbons are directly produced by vapours condensation and refining in pyrolysis, or synthesised from CO and H_2 gases generated in gasification. Final products can, in most cases, be upgraded to low carbon drop-in fuels, including bio-SNG (synthetic natural gas), bio-H_2, biodiesel, methanol, jet-fuels, etc. Since all of these processes make use of catalysts to synthesise or refine the products, a very clean syngas feedstock is needed to ensure stable long-term operation. When exposed to contaminants, the metal catalysts used in these processes can lose their activity through various mechanisms including sintering, carbon deposition, and irreversible chemical poisoning [4,5].

The production of fuels or chemicals from coal gasification or steam reforming of natural gas is a well-established process, being practiced for over 100 years around the world [6–8]. The same process adapted to treatment of waste or biomass, however, presents a number of unique issues. Due to the distributed nature of waste arisings and lower energy density of the feedstock, waste treating plants have to be significantly smaller than coal fuelled plants [9,10]. This has important implications on plant design, specifically for what concerns the gasification step and gas cleaning. The chemistry and form of waste, as well as scale, means that unlike coal, it cannot readily be treated using established high intensity, entrained flow gasification. For this reason, most of pilot and semi-commercial applications of waste gasification systems are based on atmospheric fluidised bed techniques [10,11]. These include bubbling [11,12], circulating flow [13,14], dual and indirect fluidised beds [15,16]. The known robustness and flexibility makes these reactors particularly suitable for treating highly heterogeneous feedstock, although they have some drawbacks, especially with relation to ash accumulation, nitrogen or sulphur release and tars contamination [17].

Tars are still considered to be the major obstacle in the application of biomass and waste gasification, especially for fixed and fluidised beds in which operating temperatures are below 900 °C [18]. In most practical cases, tar contents in the producer gas is in the order of 10 g/Nm³. In the case of waste feedstock the problem is even more serious, due the higher volatility of wastes and the high propensity to fragmentation [19]. Although not classified as tars, other volatile organic hydrocarbons can be detrimental for syngas utilization in fuel synthesis. Unsaturated hydrocarbons such as benzene, ethylene and acetylene, for example, pose serious challenges to hydrogenation catalysts leading to deactivation by carbon deposition or coke formation, especially when the synthesis catalyst is applied in adiabatic fixed bed reactors [20,21]. Unless tars and unsaturated species are not turned into permanent, saturated light hydrocarbons (e.g. methane), these would need to be removed or better converted into H_2 and CO, thus obtaining significantly higher production efficiencies.

A pool of inorganic contaminants also makes waste feedstocks particularly challenging for biorefinery applications. Sulphur and chlorine are largely present in wastes and certain biomass types, e.g. these are contained in various concentration in food residues, and manmade sources such as plastics, and 'vulcanisers' in waste electrical and electronic equipment (WEEE), and scrap from tyres [22,23]. Sulphur compounds deactivate hydrogenation catalysts by adsorbing to active metal sites. Although HCl, H_2S and SO_2 have received the most attention as major contaminants, and as such can be dealt with quite effectively at different scales, new focus is being directed to organic sulphur (thiophene, thiols, etc.), CS_2 and COS. These contaminants are detrimental sulphur-transfer reagents [24,24]. However, the problem is exacerbated by the difficulties in monitoring and removing such contaminants. Dioxins, or officially polychlorinated dibenzodioxins (PCDD), are a group of poly-halogenated compounds which can also be found in waste treatment plants [25]. These species are not necessarily a problem for the hydrogenation catalysts but are difficult to remove downstream and are highly toxic pollutants for the environment [26]. Nitrogen contaminants are in the form of HCN and NH_3, and originate mostly from the nitrogen in the feedstock. The HCN concentration in the waste derived syngas is similar to that of coal (~20-50 ppmv) [27]; NH_3 contamination in waste derived syngas, however, can be quite severe (up to thousands of ppmv compared to up to 40 ppmv for coal) due to the large presence of biomass in waste [28]. The presence of NH_3 as well as chlorine in the gas might result in the formation of NH_4Cl, a chemical that is solid at below 250°C, causing risks of fouling [25]. HCN in turn could potentially deactivate the catalysts, as reported in some studies [29].

Another problem associated to the use of conventional gasifier for processing waste feedstock is the large amount of ashes and deposits that need to be handled and eventually disposed. These solid residues often contain high levels of leachable components, residual carbon and heavy metals [30], causing decreased efficiency, unscheduled outages, and increased cleaning and maintenance costs. Furthermore, a large fraction of this residues requires dedicated hazardous landfill disposal facilities, thus adding significant cost to the overall plant economy [31,32].

The solution of all these problems, and the reduction of all problematic species down to values that are acceptable for different downstream catalysts, are of crucial importance for successful implementation of waste gasification technologies in the future, and in particular Waste-to-Fuel applications. Within this context, more recent developments see the rise of thermal plasma technologies to aid gasification of problematic and contaminated feedstocks, including municipal solid waste, automotive residues and WEEE solids, while still producing a good quality syngas [33–35]. Differently from thermal cracking, the chemical reactivity and quenching rate of plasmas is far greater [36]. This is due to temperatures which exceed those under combustion and the formation of chemically active species (CAS) – free radicals, ions and excited molecules [37]. As a result, any organic molecules exposed to the intensive radiation break down into simpler elements (e.g. H_2, CO, H_2S, etc.), with solid inorganic components (glass, metals, silicates) fusing to form a molten slag, which vitrifies on cooling [38]. This is a feature which has been exploited for many decades to inertify incineration ashes [39], or to recover valuable metals in metallurgical industries [40]. Comparing with other refining techniques, including microwave and "cold" plasmas, reforming by thermal plasma can exhibit significant advantages, such as large treatment capacity, higher flexibility and high energy conversion efficiency [41].

In previous works, the authors have investigated the effect of thermal plasma in reforming the gas produced from a pilot scale gasifier (500 kW_{th} input, 50-60 kg/h of refuse derived fuel), focusing mostly on tar species and unsaturated hydrocarbons [42]. In particular, they have concluded that tar reforming occurs under the effects of temperature and plasma-induced CAS reactions. In this work, additional species (e.g. H_2S, COS, SO_x, NO_x, HCN) relevant to catalysts operation will be monitored during changes in operating conditions, providing a new insight on contaminants evolution, in addition to hydrocarbon species. A simplified catalytic test is undertaken under continuous flow of cleaned syngas

generated by the pilot plant to identify the short-term effects of waste-derived contaminants on catalysts activity when plasma refining is not operated. The analysis could be used to inform cleaning requirements in large-scale plants for fuel synthesis.

2. DC furnace for plasma assisted gasification

Plasma refers to the 4th state of the matter, whereby at least a percentage of atoms and molecules in the gas are partially or totally ionized [36]. It forms when a sustained electrical arc is generated by the passage of electric current through a gas, which includes glow discharges, sparks, lightning, corona discharges, etc.. The identifying characteristics of an arc include high temperature (>10,000 °C, and hence strong radiation), constituents in local thermodynamic equilibrium, high ionization levels and high temperature electrode terminations [43]. Of note, the role of the plasma depends on the configuration of the reactor, including the proximity of the plasma to the input feed (gaseous or other). In this respect, interaction with the plasma may be direct or indirect (whereby energy from the plasma is transferred to a metal / slag bath, which acts to store and dissipate heat within the reactor vessel). The latter is a feature which has been used for many decades to vitrify incineration ashes or to recover metals from raw ores, and that can be further exploited in combination with conventional gasification techniques. In a two-stage plasma assisted process, plasma is used only for ash melting purposes (especially when the process requires dealing with a high amount of ashes), and as a reforming agent to promote tar and hydrocarbons conversion into hydrogen-rich syngas. The arc interacts with the gas and the entrained ash particles only, limiting significantly the electricity demand. The layout of a typical direct current (DC) furnace is shown in Figure 1. A cylindrical shell lined with refractory materials forms the furnace vessel, and contains the molten process ash. Solid materials consisting of bottom ashes, and fluxing agents can be fed into the vessel via feed ports at various locations in the roof, while the fly ash enters with the raw syngas from a side duct. Electrical power is fed to the furnace via the graphite electrode attached to the roof, and an anode connection in the hearth. Chemically active species (CAS) generated in the arc region, such as ions and metastable state molecules, are convected out from the electrode to the surrounding environment. By ionisation, both an electron and an ion are generated. Current is carried by both the electrons and the ions but, because of their much lower mass and thus higher mobility, the electrons carry the majority.
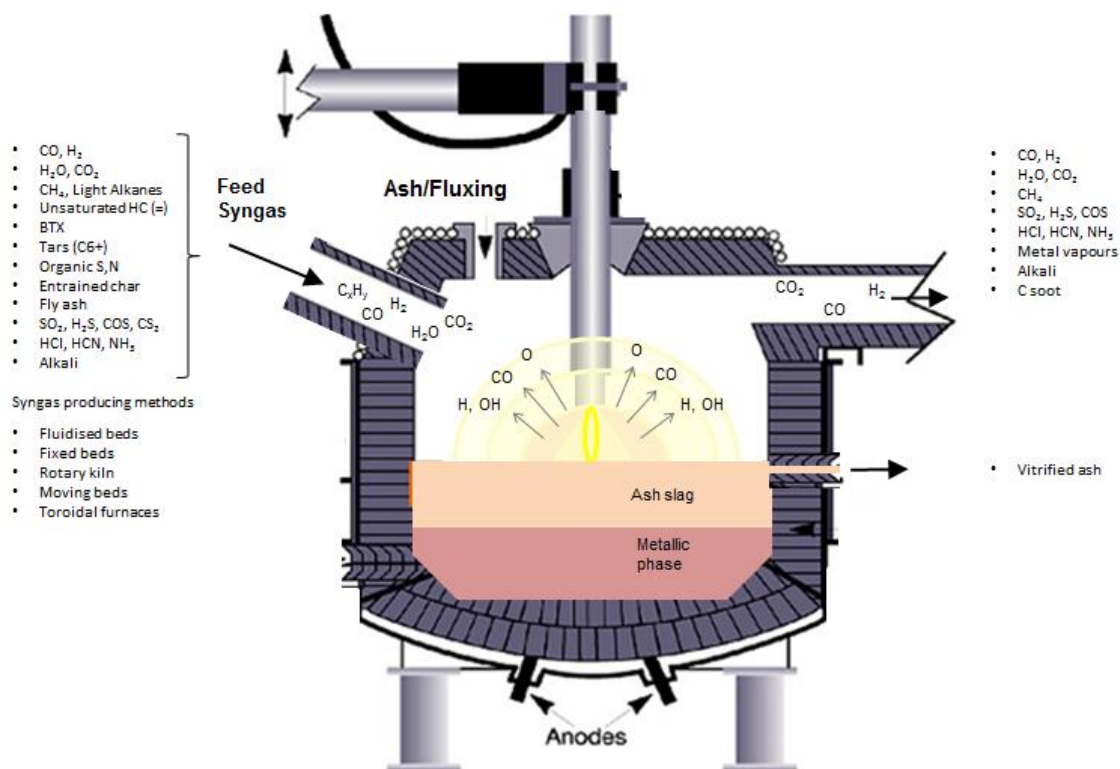
Figure 1: Generic illustration of a DC plasma furnace (or plasma converter) for the refining of raw syngas from waste pyrolysis/gasification

For a plasma converter with a slag bath, the chemical environment around the electrodes varies through the heat. After the first ash charge, the atmosphere starts off as gas contaminated with dust but it is rapidly replaced as melting progresses. Although most of the ash surface within the converter is probably only a little above melting, that is ~1500-1600 °C, the gaseous atmosphere near the electrode is much hotter (i.e. several thousands of degrees Celsius) [44]. The arc melts the ash like a very high laser cutter, splattering and evaporating some liquid ash drops around the electrode. If some organic material is present from entrained fuel-char particles, emissions of hydrogen and carbon also occur. Also all volatile components in ash (e.g. mercury, zinc, sodium, potassium, etc.) are vaporised. These are vaporised at relatively low temperatures (<1000 ˚C) and, like most metals, can augment the electrical conductivity because of their low ionisation potential. This phenomenon is normally accompanied by the unavoidable generation of fume, which are particles small enough to be carried about by the syngas, eventually being captured by the fume filter system. The role of fume inside the converter is thought to be equally important. On the one hand, fumes absorb radiation from the plasma, thus heating up the surrounding gas and preserving internal reactor walls from overheating. On the other hand, alkali vapours including K, Na and Ca enhance the catalytic cracking prompted by the high temperatures and reduce carbon soot formation [45].

In the vicinity of the arcs, where temperatures reach towards 10,000 °C, H_2, as well as CO and CO_2, dissociate into their atomic components. The products of decomposition, CO and O, for example, generated at high temperature from CO_2, are protected from reverse reactions by reacting with excess hydrogen and carbon atoms from tars decomposition, as these reaction are much faster than CO

oxidation [46]. This ensures that rapid reforming can be achieved during the residence time of the syngas inside the furnace, which is typically between 1-5 seconds [47].

3. Experimental

3.1. Gasification facility

The data generated from this study are produced in a 500 kW_{th} input pilot plant facility in Swindon (UK). A simplified schematic of the demonstration plant and integrated catalysts screening section is given in Figure 2. Its major components are the following: a waste feeder, a fluidized bed gasifier (FBG), a plasma converter (PC), a heat recovery unit, a dry filter and a wet scrubber. For this particular work, a one-stage packed bed for catalyst testing was added downstream the plant to treat a small slipstream of clean syngas and test its suitability for fuel production.

A typical UK refuse derived fuel (RDF) from Municipal Solid Waste (MSW) was initially fed to the process to transform the wastes to syngas. The composition and characteristics of the RDF, as well as the key operating conditions used in this study are reported in Table 1.

The FBG employs a heated bed of nominally 1 mm sand fluidised by a continuous flow of steam and oxygen. An equivalent ratio (ER, i.e. the ratio between the oxygen used and oxygen that would be needed for complete combustion) of 0.25 was used for this test.
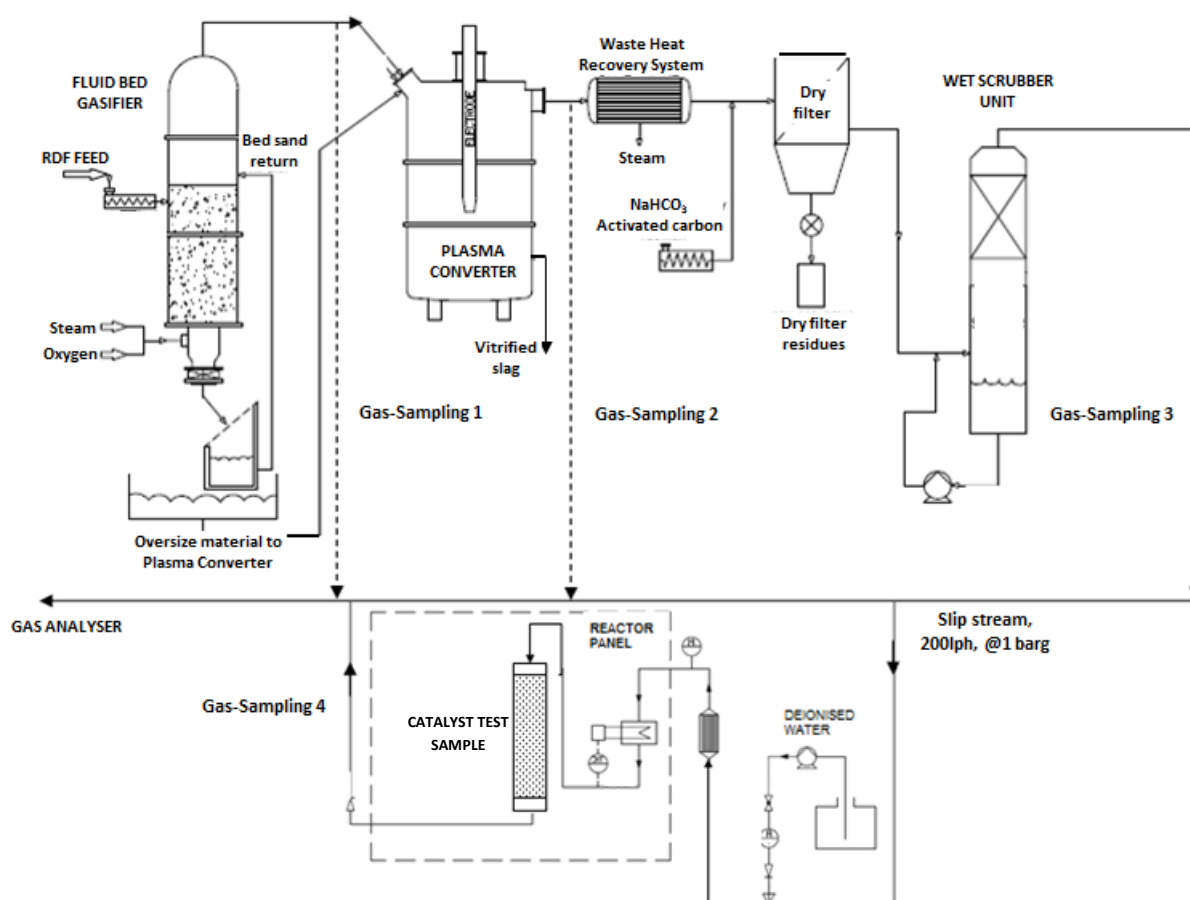
Figure 2: Schematic of the gasification pilot plant and catalyst testing panel

Table 1: FBG operating conditions, and RDF analysis

	RDF (as received)
Description:	
RDF feed rate (kg/h)	50-60
Equivalence ratio	0.25
Steam/O_2 ratio (mol/mol)	2.4-3.6
Proximate analysis, % (w/w)	
Fixed carbon	6.4
Volatile matter	59.6
Ash	19.1
Moisture	14.9
Ultimate analysis, % (w/w)	
C	41.0
H	5.7
O	17.5
N	1.2
S	0.2
Cl	0.4
Gross calorific value, MJ/kg (dry basis)	22.1

Secondary oxygen and additional steam, if required, are axially injected into the gas stream at the point of entry into the converter to augment the heat input and control the H_2:CO ratio. This would also allow controlling the reducing conditions and temperature in the converter without imposing excessive power consumption at the torch level. During operation, the power to the plasma arc is controlled to keep the slag in a molten state and maintain the temperature of gases exiting the unit to the desired temperature (normally 1050–1150 °C). The electrical power supply to the plasma furnace, therefore, depends on ash capacity and it is usually of the 100's kW order for the pilot scale. Ash particulates carried over from the gasifier drop out within the plasma converter and are assimilated within the melt. A counter electrode system is installed in the hearth of the converter to provide a return current path through the melt, which is intermittently removed from a tap hole in the bottom of the furnace. Approximately 100 kg of pig iron are added to the furnace at the beginning of each run to form a metallic melt pool as a return electrode and initial reaction zone. The velocity of the off-gas from the plasma converter is obtained using the differential pressure measurement from an s-type pitot tube device in accordance with the BS EN 13284-1 (1999) standard. The magnitude of the error associated with the measurement of the gas velocity, and hence that of residence time, was below 2%.

Downstream of the plasma arc converter, the syngas is cooled down to below 200 °C in a steam boiler prior to treatment to remove any residual particulates and acid gas contaminants (mostly, Cl− and S2− based) via conventional gas scrubbing techniques, which are commercially available at small scale. The full layout of gas cleaning and gas analysis is detailed in a recent publication [48]. Gas extractive sampling was used to analyse the syngas from different locations (see dotted lines in Figure 2). A Gasmet Fourier Transform Infrared Spectroscopy (FTIR) was used to track CO, CO_2, NO_x, SO_x, COS, NH_3 and

HCN, along with a number of light hydrocarbon species (C1-C6) to monitor their behaviour along the process. A K1550R Hydrogen Gas Analyser supplied by HiTech Instruments (with compensation from an IR600 CO_2 analyser) is also used for the direct monitoring of hydrogen. The calorific value of the gas and its Wobbe index are monitored using a CWD 2005 Calorimeter. A Biogas 5000 electro-chemical analyser is used to allow for the continuous monitoring of hydrogen sulphide (0-500 ppm).

3.2 Catalyst screening

To prove the suitability of the process for fuel synthesis, a portion of the syngas from the pilot plant was connected to a small-scale rig for catalyst testing. The flow rate of the syngas is controlled by a volume flow controller. The real-time temperatures of preheater and catalyst bed are detected by J-type thermocouples. All experiments described in this work were performed in a well insulated fix-bed reactor tube (ID 25 mm, 210 mm length). Outlet gas compositions and hydrocarbons distribution was analysed by the same FTIR device of the pilot plant (Gas sampling 4).

Catalysts considered for biofuels production are normally based on transition metals of iron, cobalt, nickel and ruthenium. The catalyst used for the test run is a typical methanation nickel based catalyst supplied in pellet form by Catal International Ltd. The choice of nickel catalyst was dictated by the high sensitivity of nickel to gas contaminants [49], which would provide a good indication of the syngas quality over the relatively short duration of the test (< 16h). Furthermore, the rapid activation of nickel for methane production, even at atmospheric pressure, is particularly suitable for the type of test performed. Other catalysts for biofuel generation such as iron and cobalt, would require days of continuous operation before reaching steady state conditions [50]. Vaporised deionised water was employed to control the reaction and limit the carbon deposition associated to low hydrogen/carbon ratio in the syngas.

4. Results

4.1 Fluidised bed operation

Following preheating of the FBG and plasma converter, the gasification system was operated for approximately 16 hours with RDF feeding.

Three temperatures are presented for the FBG in Figure 3, including the in bed (i.e. the temperature of the bulk of the bubbling sand between the gas nozzle and the RDF feeding point), the top bed (corresponding to the point of injection of RDF), and freeboard temperatures. The temperature profiles for different FBG regions were stable for the duration of the gasification test, tracking each other closely in the range 700-850 ˚C. The differences in temperature readings were mostly reflecting the volatile nature of RDF. On entering the hot FBG, the RDF floc will disintegrate and partition largely into volatiles, and to a minor extent, char constituents. The volatiles would react in the vapour space whilst being drawn upwards, along with finer constituents of char and ash. The gradual rise in temperature in the freeboard over the time, edging above that top-bed, indicates the prominence of the more oxidising gasification reactions, sustained by oxygen break-though from the bed. The temperature profile, incidentally, is also a function of the feed inlet's location above the bed. With a below-bed feed system, temperatures would be highest at the feed inlet – given the coincidence of feed and oxidant at maximum concentration. Feeding above the bed, with a rapidly volatilised RDF, as in our case, would appear to shift the maximum temperature up the vessel.

Similar behaviours have been reported in dual fluidised bed gasifiers for the treatment of wood and shredded light plastics [16].
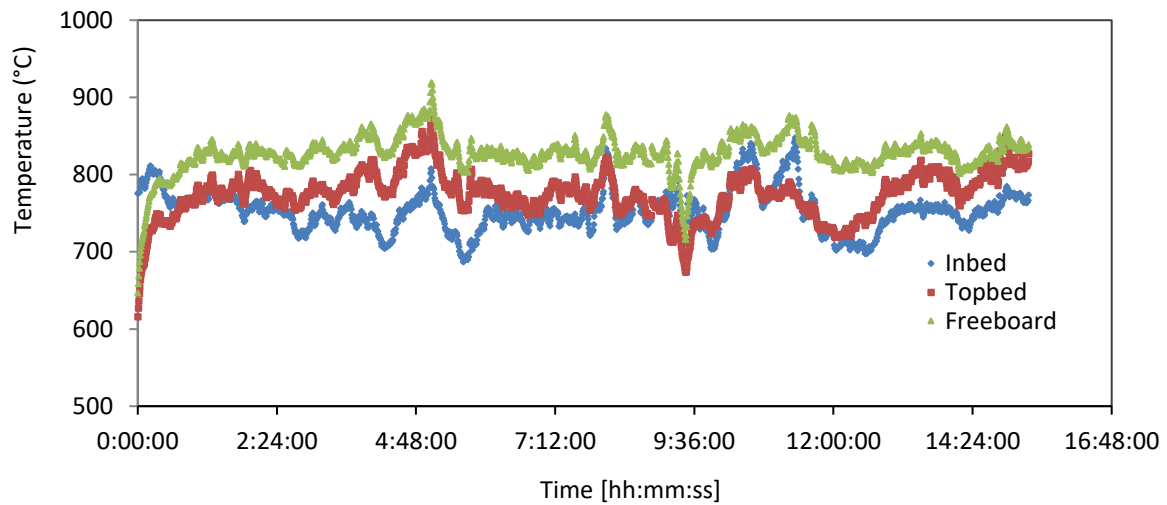

Figure 3: Temperature profile in the FBG during trial

4.2 Plasma converter

Figure 4 shows the plasma power during RDF gasification and bottom ash vitrification trial. As ash and particles drop into the melt, voltage fluctuates to establish stable arc, nevertheless current remains smooth due to the large reactor and the fast current control. Notably, plasma power increases with time as more ash is accumulating above the iron melt. Initial values are re-established when the slag is tapped out from the converter (09:15).
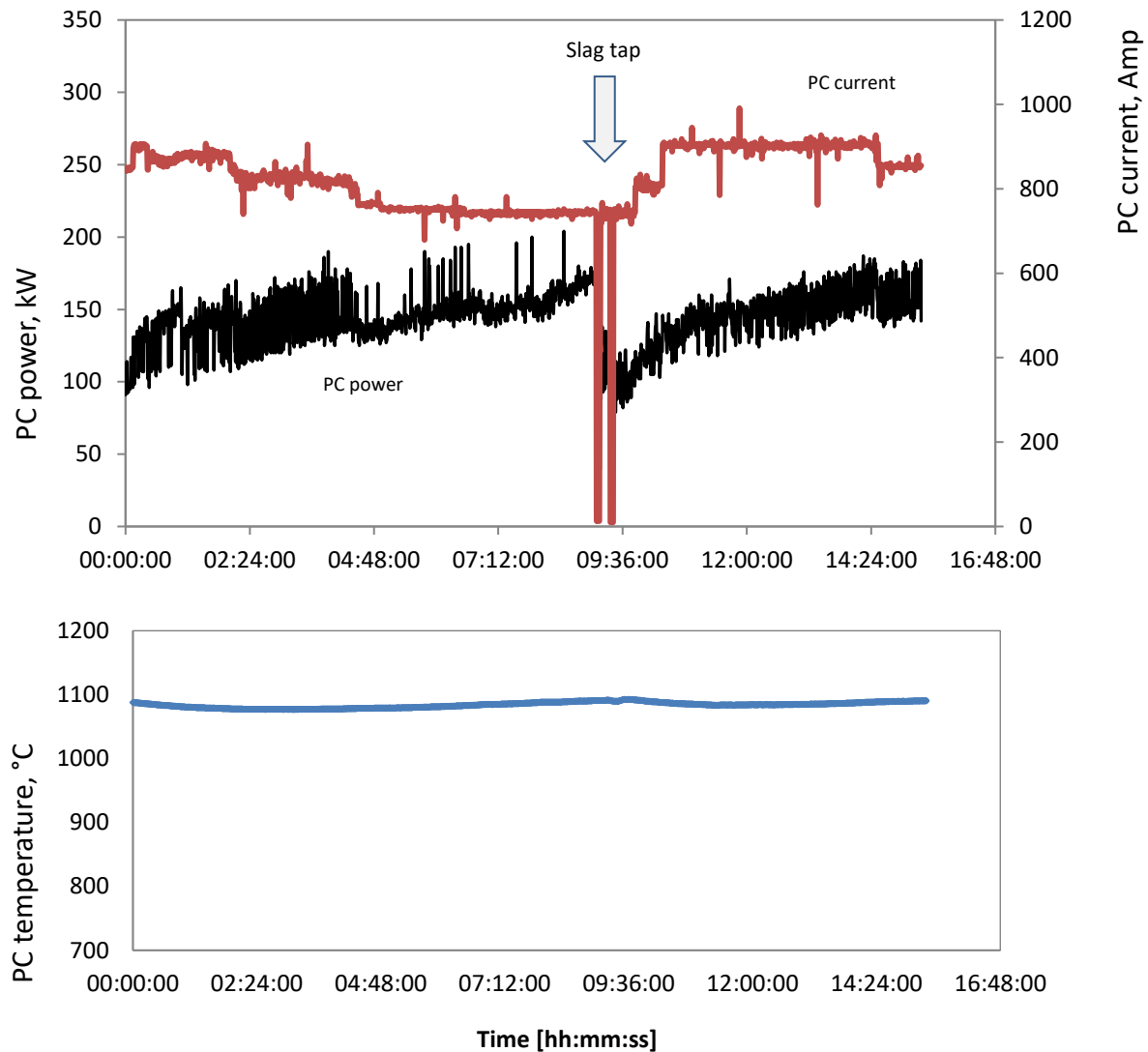
Figure 4: Operational profile of the plasma converter during trial

After preheating, the plasma furnace achieves nearly steady state conditions at 1,100 °C (i.e. temperature fluctuations below 20 °C) and the total heat loss was calculated to be ~100 kW. Thermodynamic modelling predicted a required power input of 55 kW to maintain the slag temperature at 1600 ˚C for the feed rate of ~15 kg ash/h. This is in good agreement with the recorded mean input power of 140 kW which correlates to a mean input current of 750 A and a mean voltage of 210 V. It is worthwhile to note that plasma power does not scale linearly with plant thermal capacity (or syngas throughput), but rather with ash vitrification requirement and heat loss. With waste-derived fuels, ash vitrification requirement is usually related to the feed addition rate, whereas with biomass feedstocks the ash content is generally lower and electric power is only required to overcome heat losses to maintain the slag bath in liquid state. Heat losses do not scale linearly with furnace size, being directly related to equipment surface area. As such, specific plasma power input for a larger plant (50-100 MW$_{th}$) could be sized to be around 5 to 10 % of the inlet RDF thermal input, i.e. slightly more than what is needed to compensate for heat losses in industrial high temperature reactors [51]. Nevertheless, multiple systems might still be necessary to accommodate large-scale applications to

ensure good reforming of gas, and this can be costly from a capital point of view. Hybrid solutions could also be adopted, whereby multiple injections of secondary steam and oxygen in the furnace are used to increase temperature and promote reforming reactions in the gas phase [52]. Although the fate and behavior of inorganic components in the solid phases are interesting for waste thermal treatment applications, this study focuses mostly on the gas phase evolution throughout the full operational train as this information is more relevant to assess the suitability of the syngas for synthetic fuels applications. Details on ash partition and solid residues analysis are available elsewhere [53].

4.3 Syngas evolution

The average syngas composition recorded during the 16 h FTIR monitoring periods at several locations of the plant is presented in Table 2.

Table 2: Average gas composition measured by FTIR at different location of the plant. *Measured by offline analysis [42]

Description:		Downstream FBG	Downstream PC	Downstream gas cleaning	Downstream catalyst sample
Sampling point	Units	Gas sampling 1	Gas sampling 2	Gas sampling 3	Gas sampling 4
Syngas:					
CO	vol %	8.1	22.4	28.7	22.79
H_2	vol %	20.8	32.9	42.0	35.4
CO_2	vol %	21.1	15.6	18.7	23.5
H_2O	vol %	30.6	25.1	3.4	3.9
Inerts (N_2, Argon, etc.)	vol %	2.1	2.2	5	6.9
NH_3	Ppmv	45	0.5	3	-
NO_x	Ppmv	0.1	0.03	0.02	-
SO_2	Ppmv	471	75.4	2.91	-
COS	Ppmv	56.6	52.0	13.1	-
H_2S*	Ppmv	50-60	110-180	0-1	-
Alkanes:					
Methane	vol %	9	1.8	2.1	5.8
Ethane	vol %	1.6	0.01	0.1	1.2
Propane	vol %	1.5	< 0.01	< 0.01	0.5
Butane	vol %	1.2	n.d.	n.d.	0.01
C2-C3 Olefins:					
Acetylene	ppmv	759	56.8	46.7	4000
Ethylene	ppmv	380	94	78	3488
Propylene	ppmv	345	43	16	25
C6+, Tars:					
Benzene	ppmv	8446	67.7	36	12
Toluene	ppmv	2646	27.6	25.4	8.8
Naphthalene	ppmv	2243	42	25	-
Org. sulphur* (thiophene, thiols, etc.)	ppbv	3511	43	n.d.	-
Gross Heating Value, GHV (measured, tar free)	MJ/Nm^3	7.95	7.97	8.96	9.56

Gas sampling 1 shows the composition of the gas exiting the fluidized bed gasifier; as expected, this gas is highly affected by the devolatilised RDF input, as shown by the large content of light hydrocarbons and tar species (e.g. toluene and naphthalene). Alkanes and olefins in particular are collectively more than 10% of the volume of gas species measured, which is a clear indication of the incomplete reforming reactions occurring in the gasifier. CO_2 content is also particularly high compared to that of CO, suggesting non-uniform reducing conditions within the reactor, as observed

previously. Broer et al. found a similar syngas composition for a steam-oxygen blown reactor of similar throughput [54].

As expected, the syngas from the plasma converter (gas sampling 2) appears notably different, with much lower amount of hydrocarbons and higher content in primary syngas components, H_2 and CO above all. Methane dominates the organic species, with levels of approximately 2 vol% being seen in the trial. Other major organics (benzene, acetylene, and ethane) were found to be present at negligible levels.This is a strong indication of the favourable conditions for hydrocarbons cracking and reformation routes in the plasma converter, as observed already in previous studies [19]. The same behavior is observed for substituted hydrocarbons, including heterocyclic compounds, such as thiophene. These very low levels of organic sulphur in the gas stream allow a simplified gas cleaning system downstream, as the vast majority of sulphur that has to be removed from the reformed syngas would be in its simplest and most common form, i.e. H_2S. Hydrogen sulphide was measured in the syngas immediately prior to the plasma converter and after using a portable sample extractive biogas analyser. Results of hydrogen sulphide before and after plasma refining were in the range 50 and 150 ppmv respectively, confirming that more complex sulphur species were converted into H_2S during plasma reforming. No significant hydrogen sulphide was measured in the cooled, clean syngas.

The main components in the cleaned gas product, once the steam has been condensed in the scrubber, are H_2 and CO (42.0% and 28.7% respectively), but also CO_2 (18.7%), and small amounts of methane and inerts (Gas sampling 3). The trial also shows that the combination of solid sorbents and wet scrubbers was good enough to remove more than 95.0% of sulphur species, although COS quantity was still recorded at above 10 ppm. This suggests that an additional COS hydrolyser or metal adsorption stage would be required to drop this to below the ppm range, which is needed by fuel synthesis catalysts. A further requirement that needs to be considered for fuel synthesis is the H_2:CO ratio. The H_2:CO molar ratio of the syngas produced during the test (Gas sampling 3) was between 1.2-1.5. Cobalt catalysts used for gasoline production, for example, require a gas feed having H_2:CO in the range of 1.8 to about 2.2. Nickel-based catalysts for lightweight fuels (e.g. SNG) would need an even higher H_2 content to promote early chain termination, with H_2:CO close to 3. For this reason, a commercial Waste-to-Fuel plant will likely need to have a water gas shift (WGS) reactor downstream gas cleaning for H_2:CO conditioning, as per the reaction below:

$$CO \ + \ H_2O \ \leftrightarrow \ H_2 \ + \ CO_2 \hspace{4cm} \text{Eq.1}$$

The gross heating value (GHV) of the clean syngas leaving the plant varied from 8.2 to 9.5. MJ/Nm^3, corresponding to a cold gas efficiency (waste-to-syngas) of approximately 77%.

4.4 HC content in the syngas during plasma refining

Table 2 might suggest that a stand-alone fluidised bed gasification could potentially offer advantages to final fuel synthesis due to the high content of hydrocarbons in the syngas, as well as low inherent operational costs. This is particularly true if gaseous hydrocarbons would be the desired end products from the synthesis step, as demonstrated in several bioSNG plants in Europe. In these cases, tars are removed from the original syngas using oil scrubbers or similar techniques, leaving the lightest species (e.g. methane, ethane, etc.) in the syngas stream, before methanation is undertaken [55].

For other applications where methane is not desired, the complete removal of hydrocarbons from the syngas might be the preferred solution. Current scrubbing technologies cannot remove light hydrocarbons, and incur in significant efficiency losses associated to the unused energy content of tars. Catalytic cracking/reforming of hydrocarbons within or immediately after the gasification step might solve the energy efficiency problem, although finding a catalyst that is resistant to deactivation from poisoning, carbon fouling and sintering is very challenging. The design approach here is to produce syngas inherently free of such complex hydrocarbons using plasma radiation. If on the one hand this would entail the use of energy intensive plasma, on the other hand the entire energy content of the RDF can be recovered as a tar-free syngas suitable for catalytic transformation. Whether the reduced amount of hydrocarbons in the syngas during plasma refining is due to thermal cracking or CAS induced reactions is object of the current research. In another work [47] experiments were undertaken (during start-up of the plant), to test performance of the plasma at different thermal levels, reflected by a change in the outlet gas temperature from ~ 750 °C (temperature at the outlet of the gasifier) to 1100 °C (the normal operating temperature). In this work, a symmetrical approach was attempted, by maintaining the temperature level in the 1050-1100 °C range while changing the power input to the converter. This was possible for short duration tests (< 10 mins) thanks to the large thermal inertia of the slag bath which acts like a heat sink, thus maintaining temperature within the furnace fairly constant over the time.

To illustrate the effect of additional electrical input on syngas quality, a Power Ratio (PR) coefficient was defined as the ratio between the active power transmitted from the electrode and the theoretical working power that is needed to overcome heat losses and maintain 100 kg of iron scrap (corresponding to the amount of solid material at the start of the trial) at 1600 °C.

$$Power\ ratio\ (PR) = \frac{Active\ Power\ [kW]}{Theoretical\ Working\ Power\ at\ t = 0, [kW]} \qquad \text{Eq.2}$$

In this specific case, at PR equal to 1, the furnace operates at 100 kW, which is approximately the estimated value of heat losses through the walls of the furnace. Higher values are normally required during start up to melt the initial batch, or when more ash accumulates in the slag before tapping. On the other hand, PR lower than 1 is seldom used during normal operation as this would hinder the motion of the melt, and cause arc instabilities [46]. The effect of PR variation over a short time and gas phase temperature stable at 1100 °C (+/- 10 °C), is shown in this section. It is worthwhile to mention that the PR value is not indicative of the energy required to treat a certain amount of syngas. As specified earlier, the required PR depends on heat losses and ash load only, and the resulting reforming process on the syngas quality is only a secondary effect in this case.

In Figure 5, the measured concentrations of two representative tar species, i.e. naphthalene and benzene, in the PC product gas are plotted for five different power ratio values. Residence time of the gas within the furnace is approximately 2.5 (± 0.5) seconds at all conditions explored.
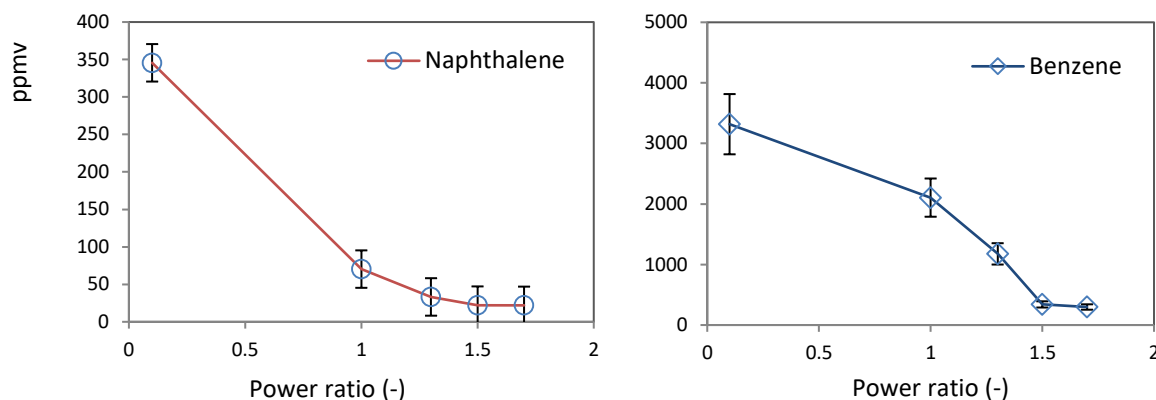
Figure 5: Effect of plasma intensity on naphthalene and benzene content in the syngas (Gas sampling 2). Recorded outlet temperature: 1089-1112 °C

The establishment of stable arc at PR higher than 1, translates into steady drop of benzene and naphthalene. In all cases explored, the quantities measured at the exit of the plasma converter (gas sampling 2) are one or two orders of magnitude lower than those at the exit of the gasifier (gas sampling 1), indicating that temperature alone plays a key factor in destabilizing the aromatic system.

The levels of naphthalene during normal operation (PR =1), are constantly below 100 ppm, and progressively reduce as PR is increased. Similarly, the benzene levels are reduced with increasing power ratio, although to a lower extent. This could be explained by the fact that at low PR values, lower presence of CAS could be expected, leaving the intermediate tar radicals produced from naphthalene cracking to recombine together into smaller aromatics (e.g. benzene). This buffering effect could be the reason of a delayed response of benzene concentration to PR variation.

The larger presence of unsaturated C2 species (Figure 6) when compared to the respective paraffine (i.e. ethane) at lower PR regime could also be explained by the predominant thermal cracking mechanism (Eq. 3, 4), which dominates over the plasma induced mechanism at low PR values.
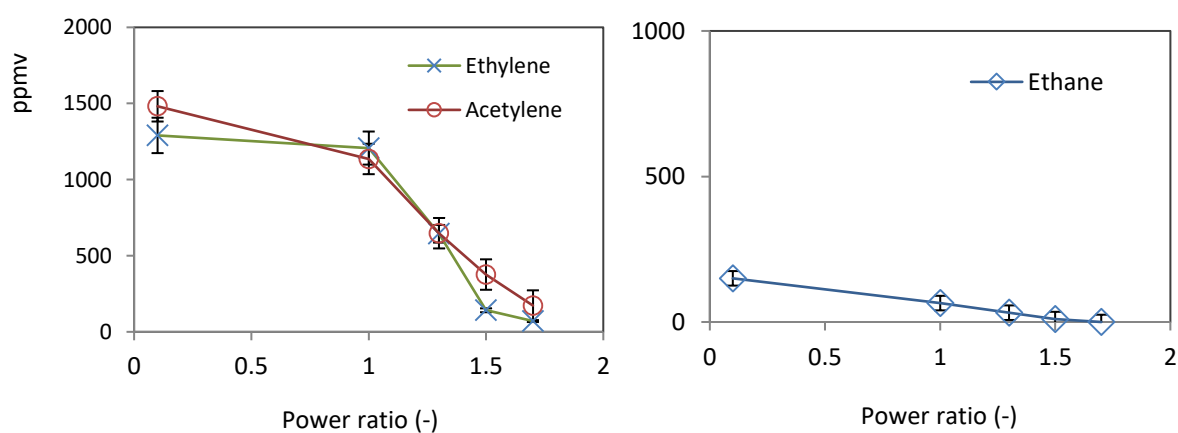
$$C_2H_6 \rightarrow 2H_2 + C_2H_2 \qquad \text{Eq. 3}$$
$$C_2H_6 \rightarrow H_2 + C_2H_4 \qquad \text{Eq. 4}$$

Figure 6: Effect of plasma intensity on C2 (saturated and unsaturated) species content in the syngas (Gas sampling 2). Recorded outlet temperature: 1089-1112 °C

More oxidative conditions, induced by either CAS activated at higher PR ratios, or by addition of secondary oxidants (steam or oxygen, as shown in other works [56,57]), would reduce unsaturated species to below 1000 ppmv. This could be particularly advantageous for fuel synthesis applications, as presence of ethylene and acetylene in the syngas has been shown to cause severe carbon deposition and catalyst pore blockage issues[58].

Mass balance calculations of the yields of components produced from plasma reforming showed that more than 95% w/w of the carbon was in the CO-CO_2 fraction and residual methane. Residual carbon could be retained in the process as process soot, which is nevertheless much lower than that produced in conventional pyrolytic processes, probably due to the presence of H_2 and steam in the syngas product which inhibit its formation.

4.5 Sulphur and nitrogen species

Most of the feedstock nitrogen and sulphur in gasification products resides in NH_3, N_2 and H_2S; however, the utilization of steam and oxygen as fluidising agents in fluidised beds could generate not insignificant quantities of NO_x, SO_2 and COS, as observed in Table 2. The strong effect of plasma intensity in reforming these to the less oxidised species is shown in Figure 7.

The fraction of SO_2 and NO_x in the reformed syngas decreases by over 60 % when PR is increased from 0.1 to 1. Over this same power range, H_2S is increased from 180 ppm to ~250 ppmv. Ammonia also is reduced drastically, to below 0.05 ppmv, under the effect of plasma. HCN was hardly detected in all cases. A slight increase in COS by increasing the PR to values greater than 1 was also observed.
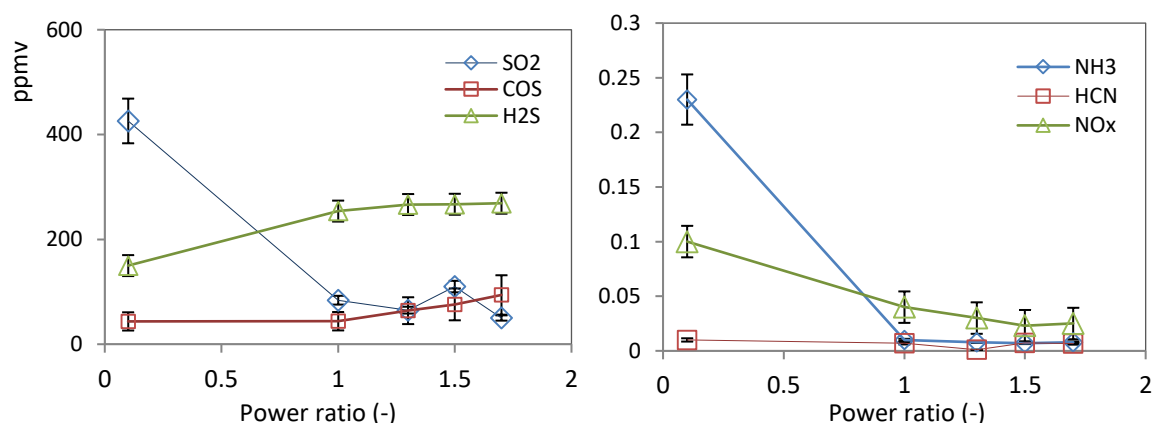

Figure 7: Effect of plasma intensity on Sulphur and nitrogen contaminants in the syngas (Gas sampling 2). Recorded outlet temperature: 1089-1112 °C

These trends would suggest that the wide pool of contaminants present in the syngas produced from RDF gasification can be potentially reduced to a narrower list when plasma reforming is applied.

4.6 CO:CO$_2$ and H$_2$:CO ratios

Figure 8 presents the CO:CO_2 and H_2:CO ratios as a function of plasma electric input. Once again yields of CO increased when the plasma voltage was increased coincident with the onset of the decomposition of the hydrocarbons as described before. A maximum was reached at PR = 1.5. In all cases, residence time and temperature are sufficiently high that thermodynamic equilibrium of the water gas shift reaction (Eq. 1) is achieved.
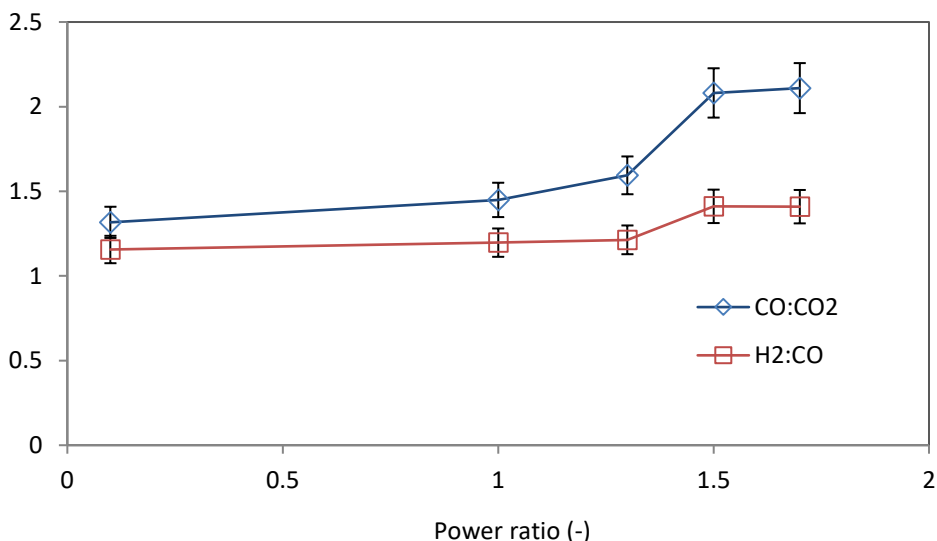
Figure 8: Effect of plasma intensity on $CO:CO_2$ and $H_2:CO$ ratio in the syngas (Gas sampling 2). Recorded outlet temperature: 1089-1112 $^\circ$C

The advantage of controlling the water gas shift equilibrium in the plasma controller can be potentially exploited further for fuel synthesis. For example, the PC reactor would be able to handle syngas with a low $H_2:CO$ ratio by producing more hydrogen as a result of adding steam to the system. Plasma-enhanced water gas shift reaction for hydrogen production or CO_2 conversion is currently object of significant research [59,60]. The costs associated with adding a shift reactor, though, are small in comparison to the total plant capital and operational costs, so a commercial plant is likely to have a WGS reactor downstream gas cleaning for $H_2:CO$ conditioning.

The CO_2 in the syngas is generally regarded as un-reactive during fuel synthesis when CO hydrogenation catalysts are employed and can therefore lower the conversion efficiency of the process by diluting the syngas. For this reason, CO_2 should be separated by the syngas stream before the catalytic process, and possibly stored for alternative utilization. An interesting and alluring opportunity would be that of recycling the CO_2 stream within the gasification process (or in the PC itself), as attempted in other studies [61].

4.7 Catalytic step

As observed in Section 4.3, the syngas produced during operation of the plant would still not be sufficiently good to take part in the next stage of the industrial process where the fuel synthesis reaction is carried out. In fact, further polishing steps would be required to reduce contaminant levels (COS in particular) at the ppb level that ensures long life of the catalysts. Furthermore, gas compression, WGS and CO_2 separation do normally take place before the synthesis step in order to increase partial pressure of the reactants to the relevant levels needed for high conversion and product yields. Nevertheless, the analysis of a catalytic step positioned right after the gas cleaning at atmospheric pressure during the short duration of the gasification run could be useful to highlight potential flaws of the system and indicate the direction of future plasma assisted Waste-to-Fuels plants development.

Figure 9 gives a clear picture of light hydrocarbons (i.e. methane and ethane) production on the nickel based catalyst with time on stream. About 40 cc of the catalyst was packed into the reactor and clean

syngas was introduced for ~9 h before plasma converter was switched off for slag tapping. CO, methane and ethane concentrations in the feed and product gases were used as indicators of catalyst activity; any decrease in methane or increase in CO concentration in sampling 4 (at stable input conditions), would mean a reduction in catalyst activity.

The catalyst exhibits a relative stability in performance, reaching a steady-state within 20-30 minutes of reaction time that is maintained until the end. It is also worthwhile noting that higher levels of hydrocarbons production are possible in an adiabatic reactor if higher hydrogen content and operating pressure are realised, in line with the stoichiometry and thermodynamics of the methanation reaction (Eq.5).

$$CO + 3H_2 \rightarrow CH_4 + H_2O \qquad\qquad \text{Eq. 5}$$

The total sulphur concentration in the clean syngas (gas sampling 3) was measured to a few ppm by combining data of the FTIR and portable biogas analyser. However, quite surprisingly, not appreciable effect could be observed on the performance of the catalyst, as the C1-C2 hydrocarbons (and CO) concentration in the outlet (gas sampling 4) remained stable over the first 9 hours. Concurrently, Table 2 showed that no sulphur could be detected in the effluent (gas sampling 4), indicating that this was being possibly adsorbed into the catalysts. We would expect that longer trials (> 100 hours) would be needed to eventually experience activity loss after sulphur adsorption reached a certain level.

At approximately 09:30, the plasma supply was interrupted for slag tapping. The peaks in methane content in both input and output readings in conjunction of this event are a clear consequence of the higher methane content in the syngas when plasma is not on operation. Although the system is rapidly restored to normal conditions after a few minutes (i.e. methane content in the input syngas goes back to the original values), a slight decline in hydrocarbons produced was observed for the remaining 5 hours of operation, with average values dropping from 7.1% to 5.8 %vol. More unstable readings after the disruption were also recorded.

Although it is not possible to make a clear connection between the two events, it is possible that some detrimental species that are normally converted/removed within the plasma refining step, slipped through the gas cleaning system when plasma was not operating, and partially contaminated the catalyst. These unexpected results may add some credence to the conjecture that, regardless the temperature during refining stage, the effect related to plasma generated CAS has an impact on the syngas quality, and therefore, on the activity and longevity of downstream catalysts. Further research will be needed to investigate this mechanism and design suitable gas cleaning techniques at the relevant scale.
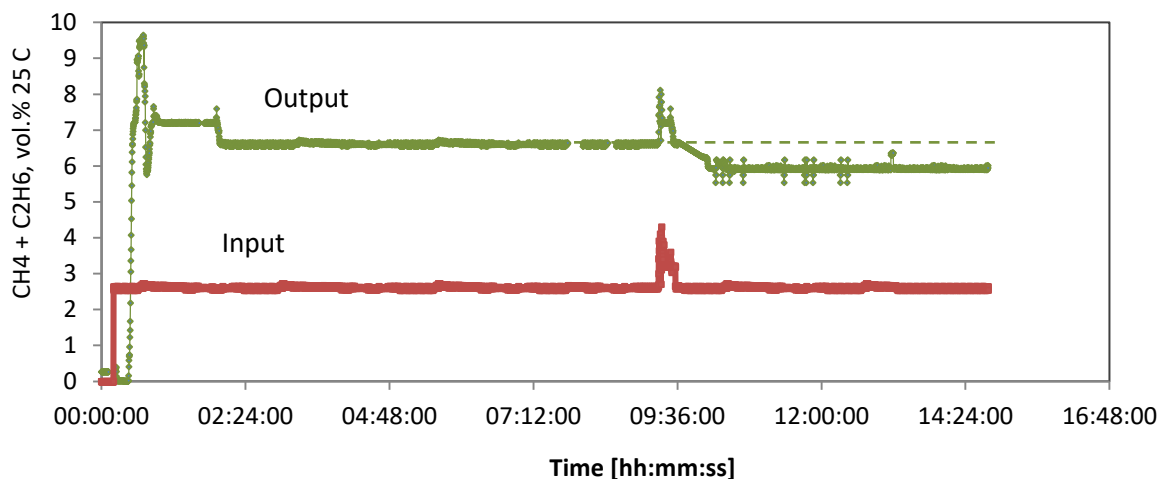
Figure 9: Production of bioSNG (e.g. methane + ethane) over the catalytic bed (Gas sampling 4) during the trial, at 380 °C, P = 1 bar, H_2/CO molar ratio = 1.6, GHSV: 19000 h^{-1}

5. Conclusions

This paper examines the experimental results from a 16 hours plasma assisted gasification trial for conversion of refuse derived fuel (RDF) into syngas suitable for biofuel production in a pilot plant. The data are generated from a 500 kW_{th} input pilot plant facility, which includes a steam-oxygen blown fluidized bed gasifier (FBG), a plasma converter (PC), a heat recovery unit, a dry filter and a wet scrubber. For this particular work, a one-stage packed bed for catalyst testing was added downstream the plant to treat a small slipstream of clean syngas and test its suitability for fuel production.

The effect of plasma on most important contaminants relevant to catalytic applications is showed by continuous monitoring of gas composition before and after the plasma converter, with reduction efficiencies typically exceeding 99%v/v for most hydrocarbons, SO_2, NH_3, NO_x and organic sulphur. Results of hydrogen sulphide before and after plasma refining were in the range 50 and 150 ppmv respectively, confirming that more complex sulphur species were converted into H_2S during plasma reforming. No significant hydrogen sulphide was measured in the cooled, clean syngas, although residual COS was present at few ppm. The test also investigates on the effect of plasma intensity on different contaminants reforming and syngas conditioning when varying the input power value at cracking-relevant temperatures. In all cases explored, the hydrocarbon quantities measured at the exit of the plasma converter are one or two orders of magnitude lower than those at the exit of the gasifier, indicating that temperature alone plays a key factor in destabilizing the aromatic system. However, the plasma activity does seemingly affect the product distribution, with lower aromatics and unsaturated hydrocarbons being produced at increasing electric power.

The content of residual sulphur in the cleaned syngas did not significantly affect the performance of the catalyst over the duration of the trial, despite this was being possibly adsorbed by the catalysts. We would expect that longer trials (> 100 hours) would be needed to eventually experience activity loss after sulphur adsorption reached a certain level. However, even a short disruption of the plasma input had seemingly a detrimental effect in catalyst activity, showing that there might be a few contaminants that could slip through conventional syngas clean-up systems in their unrefined form.

More research is needed to quantify the long term effects of the waste-derived contaminants, and to define the uncertainties related to the scaling up of the plasma reactor for commercial operation. The results of this work can guide future investigation of potential plant improvements and/or process modifications needed to ultimately implement Waste-to-Fuel solutions at global level.

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