



Fluid bed gasification – Plasma converter process generating energy from solid waste: Experimental assessment of sulphur species



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ABSTRACT

Often perceived as a Cinderella material, there is growing appreciation for solid waste as a renewable content thermal process feed. Nonetheless, research on solid waste gasification and sulphur mechanisms in particular is lacking. This paper presents results from two related experiments on a novel two stage gasification process, at demonstration scale, using a sulphur-enriched wood pellet feed.

Notable SO₂ and relatively low COS levels (before gas cleaning) were interesting features of the trials, and not normally expected under reducing gasification conditions. Analysis suggests that localised oxygen rich regions within the fluid bed played a role in SO₂'s generation. The response of COS to sulphur in the feed was quite prompt, whereas SO₂ was more delayed. It is proposed that the bed material sequestered sulphur from the feed, later aiding SO₂ generation. The more reducing gas phase regions above the bed would have facilitated COS – hence its faster response. These results provide a useful insight, with further analysis on a suite of performed experiments underway, along with thermodynamic modelling.

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1. Introduction

Although gasification capacity to date has focused on fossil fuels (Childress, 2008), the use of solid waste feedstocks has significant potential (Knoef, 2005). Annually, some 3.4–4.0 bn tonnes of waste are produced worldwide from commercial, industrial and municipal sectors (Chalmin and Gaillochet, 2009). Huge growth in arisings can be expected as developing countries catch up (for example, ca. 10% for China in 2005) (He et al., 2009). Recent policy to tackle resource conservation and climate change has given gasification renewed impetus. Nonetheless, this remains dependent on evolving global economic and political factors, as epitomised at the United Nations (UN) Climate Conference, Copenhagen, 2009.

Research on municipal solid waste (MSW) gasification has been quite lacking (He et al., 2009). Moreover, understanding of sulphur partitioning and speciation is limited, with most research on coal and then biomass (Kuramochi et al., 2005). This represents a significant gap since the release of sulphur compounds may lead to process equipment issues, thus necessitating costly abatement measures. Nonetheless, it is reported that most feed-bound sulphur is released as H₂S under reducing gasification conditions, both for coal (Álvarez and Clemente, 2008; Jazbec et al., 2004; and Nakazato et al., 2003) and biomass (Kuramochi et al., 2005). As well as understanding the feed and its sulphur content, in order to predict partitioning and emissions, the interplay with other constituents (metals and chlorides, for instance) must be appreciated (Zevenhoven-Onderwater et al., 2001; Kuramochi et al., 2005; and Morrin et al., 2012).

Our research focuses on a novel two stage fluidbed gasification – plasma converter technology developed by Advanced Plasma Power (APP) to transform solid waste into energy at a commercial scale. The overall aim of our research is to investigate pollutant removal from the hot syngas, focusing on the partitioning and chemistry of sulphur along with other relevant components. Analysis, including thermodynamic modelling, is supported by experimental data.

Key stages to the APP Gasplasma™ process include: fuel preparation; fluid bed gasifier; plasma converter (PC); heat recovery; gas cleaning; and power generation. A summary of the commercial scale specifications are provided in Fig. 1 (detailed description provided in Morrin et al. (2012) and Materazzi et al. (2013)).

Abbreviations: UN, United Nations; MSW, municipal solid waste; APP, Advanced Plasma Power Ltd.; BFB, bubbling fluidised bed; PC, plasma converter; ID, induced draft; RDF, refuse derived fuel; SCADA, Supervisory Control and Data Acquisition; Exp., experiment; W, wood pellets; WA, sulphuric acid treated wood pellets; EPSRC, UK Engineering and Physical Sciences Research Council; EngD, Engineering Doctorate.

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As part of ongoing research and development, APP operates a demonstration plant incorporating the main process units described above (Fig. 2). Central to the process are the bubbling fluidised bed (BFB) gasifier and single carbon electrode plasma converter (PC). In this case, the enhanced syngas is cooled using a thermal fluid heat exchanger (from ca. 1000 to 200 °C), before passing through dry and wet scrubbing stages for the removal of chloride and sulphur gas species (exiting at ca. 40 °C). Slightly negative pressure (5–10 mbar) is maintained within the process using an induced draft (ID) fan located after the wet scrubber (APP, 2010a; 2010b). The syngas is then directed to either the gas engine or thermal oxidiser. Depending on feed properties, the plant may handle 20–100 kg/h of RDF, or 2–60 kg/h of wood pellets. The bed material in the BFB may be decanted and replenished during operation. Each process item is centrally controlled and monitored (for temperature, pressure, flow rates, electrical input, feed supply and gaseous species amongst others) by way of a Supervisory Control and Data Acquisition (SCADA) computer interface.

This paper focuses on two related experiments performed recently on APP's demonstration plant. Wood pellet feedstock augmented with sulphur was used with a view to understanding sulphur release during gasification. After detailing the materials and methods employed, the results are presented, analysed and discussed, followed by summary conclusions.

2. Materials

Along with the actual process, the feedstock (composition detailed in Table 1) and fluid bed material (Table 2) are integral to this research. Although the plant routinely handles RDF, the experiments reviewed in this paper focus on a wood pellet feed. The pellets were sourced locally and comply with the European standard CEN/TS 14691 (Big Barn, 2012). They are cylindrical in shape, with a diameter of 6–8 mm and varying length (≥ 3 mm). Virgin sawdust is used in their manufacture, derived from a mix of spruce (ca. 50%) and pine with Douglas fir (ca. 50%) (Rowley, 2013). Compositional analysis results are presented in Table 1. Generally pellets are manufactured by compressing dry sawdust or wood shreds under high pressure until the lignin softens and



Fig. 2. APP demonstration plant, Swindon, UK.

Table 1
Composition and calorific value of wood pellets used in experiments.^a

Composition	(wt.%)	Calorific value	(kJ/kg)
Carbon	46.55	Gross	24.075
Hydrogen	5.26	DAF	26.337
Nitrogen	0.26	Net	22.730
Sulphur	0.01		
Chlorine	0.01		
Volatile matter	78.3		
DAF volatile matter	85.6		
Total moisture	8.1		
Ash	0.5		

^a APP (2011b).

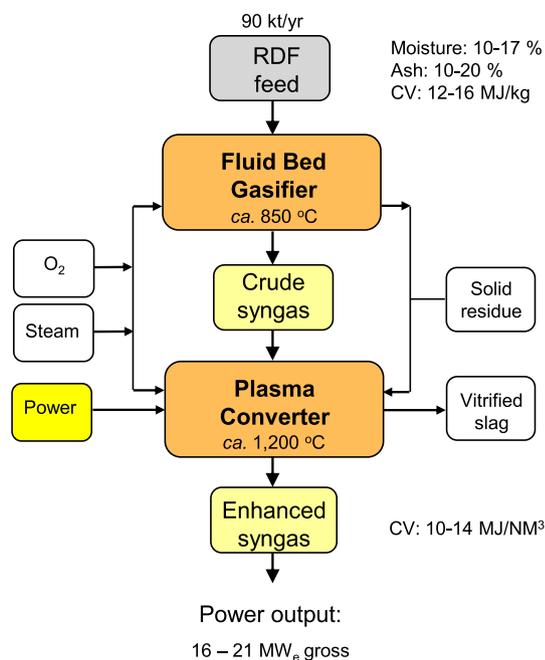


Fig. 1. APP commercial process, key parameters.

Table 2
Composition data for BFB material used in experiments.^a

Species	mg/kg	Species	mg/kg
Antimony	5.5	Thallium	<0.1
Arsenic	0.9	Tin	17.8
Cadmium	<0.1	Phosphorus	125.0
Chromium	11.1		
Cobalt	1.9	Total carbon (%) ^b	<0.01
Copper	329.3	Total sulphur (%) ^b	0.022
Lead	21.3		
Manganese	114.2	SO ₄ ²⁻ (acid sol)	390.0
Mercury	<0.1	SO ₄ ²⁻ (H ₂ O sol) (mg/l) ^b	191.0
Nickel	7.9	Chloride (2:1) (mg/l) ^b	215.0

^a APP (2012).

^b Other units.

binds the material together (Forestry Commission, 2007). This, combined with a low moisture and ash content, makes them a clean, high energy density fuel (typically two thirds that of coal). They also have a consistent composition and flow easily, making them an ideal experimental feed. By contrast, RDF has a less consistent composition and feedrate, thus introducing more variables to experiments. This can complicate analysis as well as the reproduction of and comparison between experiments.

The virgin bed material used in the BFB consists of coarse sand (Section 1). For practical reasons, the material tends to be recycled and reused from one run to the next. Sieving is performed (to a nominal 2-mm size) using a SWECO vibrating screen to remove the oversize fraction (ca. 15%) (Taylor, 2012). During a run, material may also be hand-sieved using a 5 mm screen. The reusable fraction consists of sand, along with ash and other inert materials. The composition will vary depending on the number of times the material has been recycled and the characteristics of the associated runs. A sample composition is provided in Table 2.

3. Methods

3.1. Feed preparation and conveying

Individual feed batches of 15–30 kg were made up to provide a sufficient run time through the process. This is important since it takes a certain period for the process to stabilise after the introduction of a new feed (especially if it is significantly different to the preceding feed). Depending on circumstances, it also takes time for the different sulphur reaction mechanisms to become established. Adequate time is also required to facilitate statistically valid monitoring of process parameters and species. The process was run continuously from batch to batch.

The typical range of sulphur levels in MSW is 0.10–0.35% (DePaul and Crowder, 1989). A baseline of 0.5 wt.% sulphur was set since this is the upper limit of what is normally found in MSW-based feedstocks (Yassin et al., 2009; and Borgianni et al., 2002). Concentrations of 1.0% and 1.5% were also prepared since, although extremely unlikely under normal circumstances, they would produce a more evident response from the process.

The feed generally tested in these particular set of trials was wood pellets (Section 2). In order to increase the sulphur content of the pellets, they were treated/doped with a sulphuric acid solution. Starting with the target sulphur content of the pellets, the volume and concentration of the acid solution was calculated taking account of the pellets' natural sulphur content. The acid solution was prepared by diluting concentrated H_2SO_4 (98% w/w, 1.84 specific gravity) with deionised water. In order to avoid material deterioration, 10% moisture content was also targeted. Care was taken when mixing the wood and acid being mindful of the absorptive capacity and potential friability of the pellets (an important factor when handling both manually and mechanically), as well as health and safety considerations. Once mixed, the wood/acid batches were left to stand overnight to allow the acid solution to be absorbed thoroughly and evenly.

When required, a sealed screw conveyor is used to supply RDF to the gasifier. A separate feeder is used to supply wood. In turn, the sand supply (for bed top-up) has its own dedicated feeder. Each feeder is recalibrated whenever a new feed is introduced. For RDF this includes calibration of both the transport conveyor (supplying the hopper) and metering screw (introducing feed to the gasifier), and finding a balance between the two. Calibration involves monitoring the output quantity of material over a given period. A graph of feedrate vs. motor setting is thus produced, enabling the rate to be accurately adjusted during the run.

3.2. Plant operation

Pre-heating the fluid bed is a key part to the plant's start-up routine. This is performed using a combination of propane and wood pellets in combustion mode. A propane-fuelled, under-bed preheating system is used to raise the bed temperature, in combination with heated compressed air to fluidise the bed

material. At ca. 420 °C wood pellets are introduced. Once established, the wood pellets are used to raise the bed temperature up to 850 °C. During this period operation is transitioned from an air to oxygen and steam supply. The oxygen and steam are mixed prior to injection through an upward facing nozzle beneath the bed. By altering the ratio of fuel to oxygen and steam, the system is subsequently transitioned from combustion to gasification. In turn, whilst accounting for differences in fuel properties, the process can be switched from wood to other fuels such as RDF.

The principal means of assessing system stability is by monitoring the Fourier Transform Infrared (FTIR) spectrometer data, the molar ratio of CO/CO₂ in particular (APP, 2010b). This provides an approximate guide to the quality of the syngas being produced, with ratios of 1.8–3.5 being considered to be indicative of good system control and reasonable syngas quality.

The feed/oxidant ratio is controlled to give a syngas composition in-line with that predicted for the full-scale plant and to provide stable operation. Consequently this also influences the syngas quality as well as bed temperatures. Greater fuel and steam addition will promote more gasifying conditions. The resulting endothermic reactions will reduce overall temperatures in the gasifier. The syngas quality will also potentially improve. A target bed temperature of 800–850 °C is typical under standard operating conditions (APP, 2011a).

Maintaining a stable fluid bed is essential. In this respect, oxidant rates are adjusted to sustain a fluidisation velocity of ca. 0.6–0.9 ms⁻¹. This ties-in with a target pressure differential of 50–70 mbar between the top and bottom of the bed. Agglomeration, the arising of oversize material and/or accumulation of ash may have a destabilising effect. Discharging and replenishing the bed material is therefore routinely performed during the run.

Start-up also includes preheating the PC. An electrical arc (c.a. 150–200 mm) between the graphite electrode and slag pool is established. During operation the plasma power is adjusted in order to provide sufficient energy to keep the slag in a molten state and crack the gas-bound tars and chars. This is aided by the supply of oxygen. The outlet temperature must also be kept below 1150 °C.

3.3. Monitoring and data analysis

Gas phase species are monitored continuously during the process operation using both an FTIR spectrometer (recording every thirty seconds for carbon oxides, H₂O, CH-species, N-species, COS, SO₂, HF and HCl amongst others) and Servomex analyser (for CO, CO₂, O₂). Although H₂S levels are measured intermittently using Draeger Tubes[®] and impingers, they cannot be measured continuously using the FTIR, and so are not reported here. Real-time monitoring of the process ensures optimum process operation and syngas quality for power generation. Data capture and storage also enables retrospective analysis, assessment and reporting. FTIR monitoring for this study was performed mainly post converter, at the outlet of the heat exchanger, prior to gas clean-up (Position 2). There is also provision for sampling at the gasifier outlet (Position 3) and at the inlet to the gas engine (Position 1).

The SCADA process operation system maintains a record of all operations and monitoring parameters enabling the analysis and assessment of experiments after they have been performed (Section 1). This study is interested primarily in the fluid bed and PC stages, looking at sulphur species in the gas phase along with other relevant constituents (CO and CO₂ in particular). For this reason, FTIR data from Position 2 is of primary importance.

4. Results and discussion

4.1. Introduction

This section presents the results from two related experiments from a suite performed on APP's demonstration plant as part of this research. Both experiments look at the response of the process to wood pellet feedstocks enriched to artificially high levels with sulphur. As mentioned in Section 2, in contrast to RDF, the use of wood lends consistency to experiments. The first looks at a single sulphur enriched batch. The second assesses three batches at progressively different concentrations. The analysis is based on process data recorded during each experiment, in particular data coinciding with monitoring at Position 2, prior to gas cleaning.

4.2. Experiment 1

The aim of this experiment was to monitor sulphur species emissions during gasification, using the APP process, of a feedstock artificially enriched with sulphur. The trial included a number of feed batches including wood (i.e. untreated wood pellets), sulphuric acid treated wood and a final wood batch (composition detailed in Section 2). The fluid bed material used was recycled from earlier trials. During the run, the bed was discharged and replenished intermittently. Although maintenance and cleaning is performed between experiments, for practical operational reasons, the extent of this can vary.

Key input and output data for the trial are presented in Table 3, supported by Figs. 3–5. The times presented in Table 3 refer to the actual or total duration for each batch. Those presented in Figs. 3–5 relate to the monitoring periods at FTIR Position 2, prior to gas cleaning.

The initial wood feed batch (W1) was characterised by relatively high SO₂ (147 ppmv average) in contrast to minimal COS (10 ppmv). The arising of SO₂, and to such an extent, is interesting given the reducing conditions within the gasification process (as illustrated by the CO/CO₂ trends in Fig. 4) (Section 1). The presence of SO₂ indicates the occurrence of oxidising regions and mechanisms within the process. Experience at APP points to the BFB, in particular O₂ supplied via the fluidisation nozzle beneath the bed (Chapman, 2012). In this way, sulphur species arising within the bed (either via the feed or the bed material itself) would experience highly oxidising conditions in the immediate vicinity of the nozzle. The data here suggests that SO₂ was not converted to reduced sulphur species (i.e. H₂S, COS), indicating that the reaction kinetics were such that it passed through the system sufficiently fast to remain unreacted. This is in spite of the high temperature and reducing conditions, particularly in the PC.

Wood's very low sulphur content (0.01–0.07 wt.%) might indicate the existence of some other source, for example residual sulphur retained within the fluid bed and/or other parts of the process. For instance, ash accumulated in the bed material recycled from earlier experiments, and the metals content therein (for example, Na and K), would provide both a sink for sulphur capture

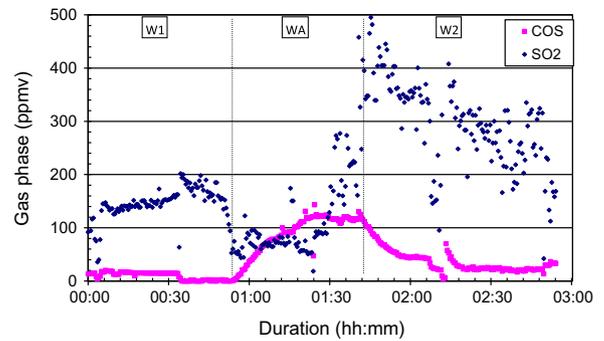


Fig. 3. Experiment 1: syngas COS and SO₂ monitored post plasma converter, prior to gas cleaning (wood pellet batches (W1 and W2) (0.01–0.07 wt.% sulphur); sulphuric acid treated wood pellet batch (WA) (0.53 wt.% sulphur)).

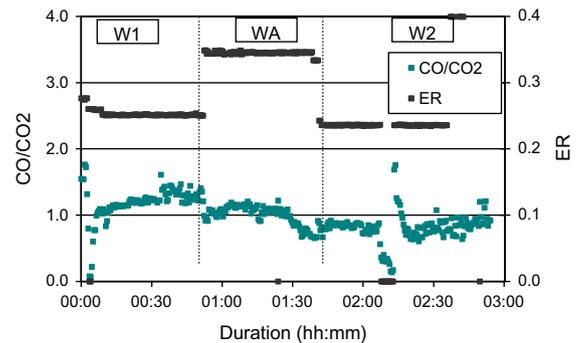


Fig. 4. Experiment 1: process CO/CO₂ and ER profile, monitored post plasma converter.

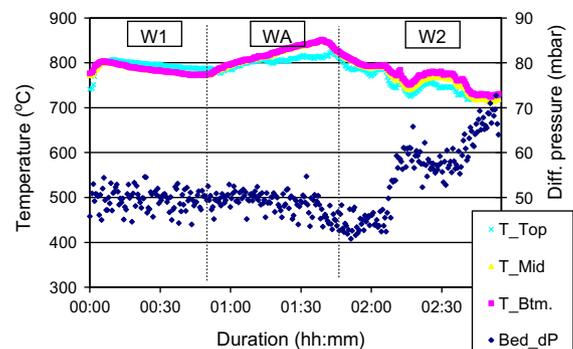


Fig. 5. Experiment 1: fluidised bed temperature and differential pressure profile.

and a source for its rerelease under favourable conditions (Kuramochi et al., 2005; Khan, 1989; and Morrin et al., 2012). The inherent physical and/or chemical properties of the wood seem to promote further release of this sulphur. For example,

Table 3

Experiment 1: key process parameters.

Inputs				Outputs ^a			
Feed label	Quantity (kg)	Duration (hh:mm)	Rate (kg/h)	Feed-S Content (wt.%)	COS Average (ppmv)	SO ₂ Average (ppmv)	CO/CO ₂ Average (–)
W1	37.0	0:52	42.7	0.01–0.07	10	147	1.19
WA	34.1	0:44	40.9	0.53	85	109	1.00
W2	52.7	1:14	42.7	0.01–0.07	39	310	0.81

^a Post plasma converter, prior to gas cleaning.

due to their relatively high density and cylindrical geometry, the wood pellets may reside and react within the bed more readily and for longer.

The introduction of the H₂SO₄ – treated wood batch (WA) resulted in quite an abrupt role reversal, with COS steadily becoming more prominent (85 ppmv) at the expense of SO₂. Over time, however, SO₂ appeared to re-establish itself (109 ppmv) – aided by a decrease in CO/CO₂. From this it may be deduced that the reaction mechanism for COS was faster than that of SO₂.

The trend for SO₂ proceeded upwards with the addition of the virgin wood (W2). An increase in the bed differential pressure coincided with this. This appears to have been due to a new (higher) set point for running the fluid bed. One way of achieving this would be to increase the mass of material residing in the bed. Consequently more bed-based reactions would be likely, including those in the more oxidising regions of the bed. However, SO₂ ebbed off as feeding progressed and residual sulphur within the system was consumed. The trend for COS also decreased; however, it appeared to reach its baseline level more rapidly. This might substantiate the aforementioned theory that SO₂ generation within this particular process tends to be bed-based, whereas COS occurs above the bed in the vapour space. Interestingly, COS did not fall to as low a level as it had been previously.

4.3. Experiment 2

A second experiment was performed to further analyse and substantiate the results discussed above. The set-up was similar, however, on this occasion three consecutive wood-sulphur loadings were trialled (namely, 0.5, 1.0 and 1.5 wt.%). Recycled bed material was again used, with replenishment taking place during the run (discharged and recharged at 9.25 and 8.95 kg/h respectively). Key parameters for the experiment are presented in Table 4 and Figs. 6–8, with output data referring to Position 2, pre gas clean-up.

Looking at the first wood batch (W1), there was essentially no COS reported. This is to be expected given the low natural sulphur content of the virgin wood pellets. Once again, relatively high SO₂ values were reported (110 ppmv). Given that there was no other feed prior to W1, this might indicate that the sulphur originated from residue within the process itself, the bed material in particular (As proposed for Experiment 1, Section 4.2).

With the introduction of the sulphur-rich feed batches (WA 1–3) SO₂ gradually lost prominence to COS. There appears to be a direct relationship, with COS trending steadily upwards as the sulphur content of the feed increased.

A number of different factors might explain COS' increased prominence during this trial. For instance, during this period CO/CO₂ trended upwards, indicating the establishment of more reducing conditions within the system (Fig. 7). This would help promote COS generation, whilst undermining SO₂. Drawing parallels with research on feed-nitrogen, the type/functionality of sulphur within the feed might also be a factor (Leppalahti and Koljonen, 1995). For

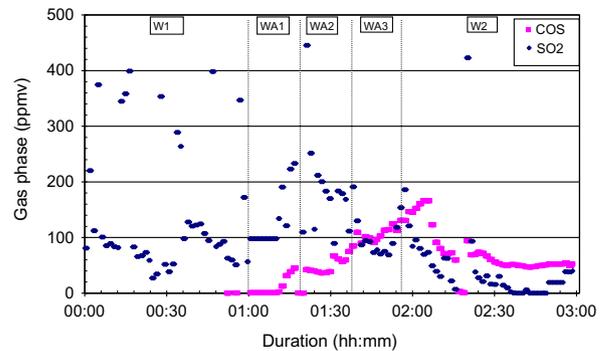


Fig. 6. Experiment 2: syngas COS and SO₂ monitored post plasma converter (W1 and W2; 0.01–0.07 wt.% sulphur); (WA1, 2, 3; 0.5, 1.0, 1.5 wt.% sulphur).

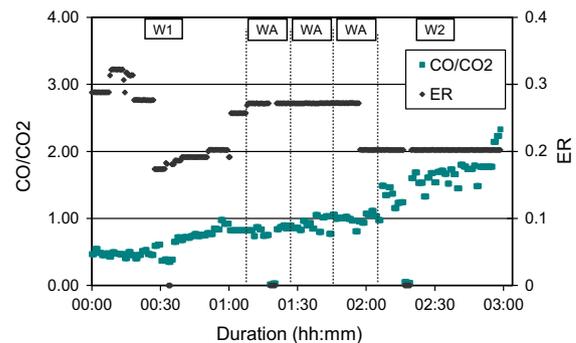


Fig. 7. Experiment 2: process CO/CO₂ and ER profile, monitored post plasma converter.

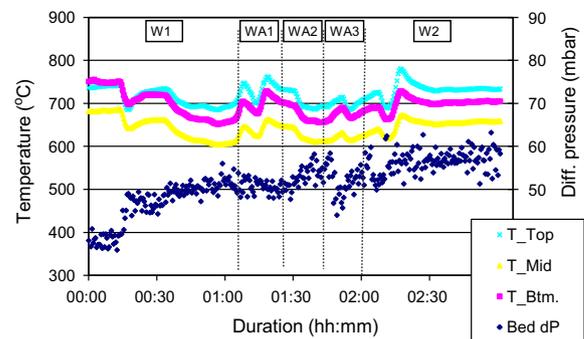


Fig. 8. Experiment 2: fluidised bed temperature and differential pressure profile.

instance, the H₂SO₄ additive is likely to be held within the wood pellets through a relatively weak sorption mechanism, rather than chemically bound. If so, it would be released more readily than sulphur bound naturally to the feed or indeed to the bed material (as inferred from Lapuerta et al. (2008) and Khan (1989)). Once in the

Table 4
Experiment 2: key process parameters.

Inputs				Outputs ^a			
Feed	Quantity (kg)	Duration (hh:mm)	Rate (kg/h)	Feed-S Content (wt.%)	COS Average (ppmv)	SO ₂ Average (ppmv)	CO/CO ₂ Average (–)
W1	51.5	1:06	46.5	0.01–0.07	–2 ^b	110	0.66
WA1	15.0	0:18	51.4	0.5	11	178	0.81
WA2	15.0	0:18	50.0	1.0	53	188	0.90
WA3	15.0	0:18	50.0	1.5	108	97	0.95
W2	62.0	0:59	63.0	0.01–0.07	73	45	1.52

^a Post plasma converter, prior to gas cleaning.

^b Negative value is a function of the very low concentrations present and subsequent interference from other monitored species.

vapour or gaseous state, it would have the opportunity to react in the more reducing environment above the bed. By spending less time within the bed, such sulphur would also have less opportunity to be sequestered by ash and/or metal species therein (for example, Na and K (Section 1)). In turn, it would be less likely to come into contact with the more oxidative regions of the bed.

Moving from the sulphur-rich wood-acid batches to the final virgin wood (W2), the trends show a swift drop in COS emissions. Levels fell from a peak of ca. 165 ppmv to a trough of ca. 50 ppmv within 30 min. Thereon in values appeared to remain quite stable, perhaps sustained by sulphur retained within the system, as proposed for Experiment 1.

The dramatic fall in SO_2 levels, in fact decreasing more than COS, was quite unlike Experiment 1. The most apparent cause would be CO's increasing prominence over the period, with the CO/CO₂ ratio migrating from ca. 0.95 to 2.00. This is in contrast to a ratio of 0.80 for Experiment 1. A review of the trends for the other process parameters does not provide an immediate explanation. There was a gradual increase in the pressure drop across the bed; however, Experiment 1 experienced a far more significant change (almost 30 mbar) at the corresponding stage. The composition of the bed material or some variation in the feed might also have played a part.

4.4. Further assessment

4.4.1. Introduction

This section compares the COS and SO_2 profiles for the two experiments in relation to CO/CO₂. Although not identical, contrasting the two experiments provides additional perspective and insight. Furthermore, reference to CO/CO₂ offers a more dynamic picture of the process and evolution of sulphur species, in contrast to the time-related assessment performed earlier.

A comparison of COS and SO_2 trends for Experiment 1 (Exp. 1) and then Experiment 2 (Exp. 2) is first presented. Subsequently, the COS trends for the two experiments are compared, followed by a similar assessment for SO_2 .

4.4.2. COS vs. SO_2

Over the course of Exp. 1, COS levels were significantly lower (45 ppmv average) than SO_2 (189 ppmv average) overall (Figs. 9 and 10). Interestingly, both COS and SO_2 arose under similar CO/CO₂ conditions, indicating that the formation mechanisms for both occurred (and were facilitated) simultaneously. As mentioned, COS was most prominent during the treated wood batch (WA) (85 ppmv), yet it was still less than SO_2 (109 ppmv). The response of SO_2 to the treated wood seemed to be delayed, becoming prominent only during the final wood batch (explanation provided earlier in Section 4.2).

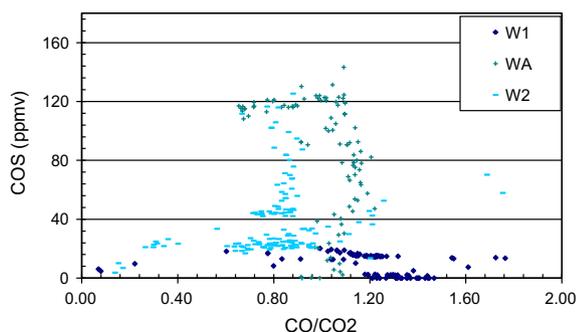


Fig. 9. Experiment 1: syngas COS vs. CO/CO₂, monitored post plasma converter (W1 and W2; 0.01–0.07 wt.% sulphur); (WA, 0.53 wt.% sulphur).

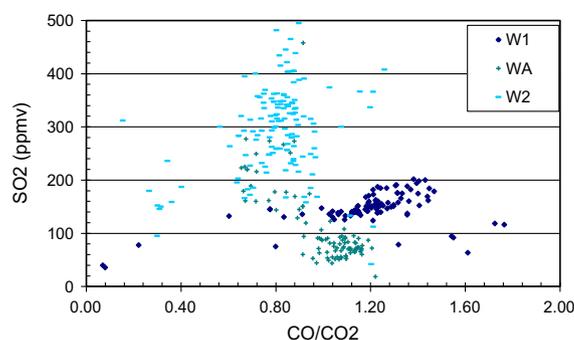


Fig. 10. Experiment 1: syngas SO_2 vs. CO/CO₂, monitored post plasma converter.

Once again, during Exp. 2 COS (61 ppmv average) was a lot less prominent than SO_2 (123 ppmv average) overall (Figs. 11 and 12). The response of COS to each treated wood batch was quite immediate and consistent. In contrast, the SO_2 response was less discrete. This might support the assumption that COS formation is more prominent in the vapour space of the fluid bed (i.e. in the gas phase), with SO_2 formation more related to the bed. Consequently, a delay in the response of the bed (entailing physical mixing and heterogeneous reaction mechanisms) to each batch might be expected (especially keeping in mind the relatively short timeframe of the treated batches).

4.4.3. COS

Considering Exp. 2 ran with higher S-content feed, the COS values for Exp. 1 were surprisingly high. The treated batch (WA) during Exp. 1 (0.53 wt.% sulphur) had an average COS of 85 ppmv. In contrast, the 0.50% batch (WA1) for Exp. 2 only achieved 11 ppmv. Trends presented earlier for Exp. 1 (Section 4.2, Fig. 3) showed COS values reaching a plateau after ca. 30 min. This suggests that the sulphur release and COS formation mechanisms had sufficient time to become established (44 min total run duration). In contrast, the acid-wood batches for Exp. 2, at only 18 min each, were unlikely to have had sufficient time. Consequently, although the COS response has been shown to be quite prompt, a longer term component also appears to have been involved.

The CO/CO₂ regime for the treated wood batches during the two experiments was quite similar (i.e. in the range of 1.00). However, the feedrate for Exp. 1 (ca. 41 kg/h) was significantly lower than for Exp. 2 (ca. 50 kg/h). The response of the system to the increased feedrate and feed-S content during Exp. 2, would have depended on process conditions and the capacity of the gasifier bed, amongst other factors. Nonetheless, an increased sulphur loading in the gasifier would be expected. Assuming the bed could contain this, the

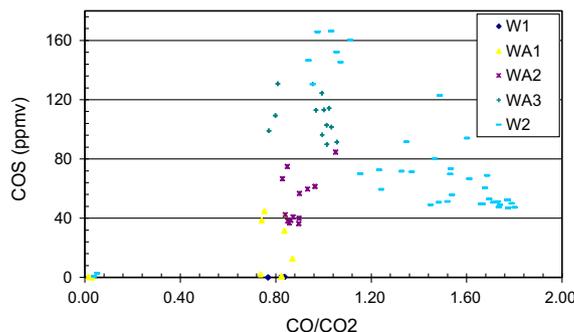


Fig. 11. Experiment 2: syngas COS vs. CO/CO₂, monitored post plasma converter (W1 and W2; 0.01–0.07 wt.% sulphur); (WA1, 2, 3; 0.5, 1.0, 1.5 wt.% sulphur).

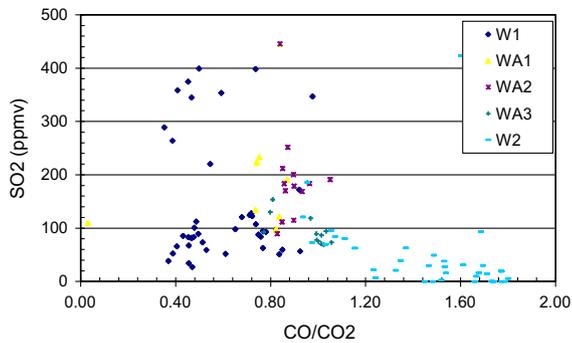


Fig. 12. Experiment 2: syngas SO₂ vs. CO/CO₂, monitored post plasma converter.

duration required to reach steady state (regarding COS and SO₂ formation) would be expected to be appreciably longer.

The CO/CO₂ trend for the final wood batches for the two experiments was quite different. Higher CO/CO₂ might be expected to result in higher COS generation. However, this was not apparent since the untreated wood could not replenish sulphur within the bed, resulting in an ever diminishing sulphur supply.

4.4.4. SO₂

With regards to SO₂, the two experiments operated within similar CO/CO₂ regimes overall. However, the picture was quite different when considering respective feed batches. For instance, the SO₂ values for Exp. 1 batch W1 (147 ppmv) were significantly higher than for Exp. 2 (110 ppmv). Having previously run on RDF (with a relatively a high ash content) over an extended period (ca. 4 h 30) may have influenced this. Interestingly, CO/CO₂ at this stage was higher than for Exp. 1. This might suggest that SO₂ generation was not so dependent on CO/CO₂.

The introduction of the treated wood during Exp. 1 coincided with a compact downward trend in SO₂. In contrast, there was an upward response during Exp. 2, albeit in a rather scattered fashion. This scatter may have been due to running smaller batches (i.e. WA1-3), with alternating sulphur concentrations and shorter durations. This would result in some overlap and interference between each batch, in terms of process response and SO₂ generation. Other differences between the experiments (in terms of SO₂ profile) may be largely attributed to the progressive divergence between their CO/CO₂ profiles.

5. Conclusions

There is growing appreciation for municipal and other solid waste streams as viable renewable content resources. Research plays an important role in advancing technologies which can harness this material, including the novel two stage gasification process examined here.

A number of observations may be drawn from the work presented. Significant SO₂ and low COS levels (before gas cleaning) were interesting features of the trials on APP's demonstration process. Such a scenario is not normally expected under reducing gasification conditions. The fact that both species evolved within the same process, under the same overall conditions, is telling – indicating that independent mechanisms at localised areas of the process were involved. Consequently, the arising of SO₂ does offer some practical benefits given the relative ease of its abatement, in contrast to COS (Sakanishi et al., 2004; and Gao et al., 2003).

The data indicates that COS levels increase quite quickly and proportionately with an increase in feed-sulphur concentration. Consequently, levels fall in a similar fashion once feed-sulphur levels are reduced. The response of SO₂ is shown to be more delayed

(i.e. rate limiting step), and indeed diffuse. Although, the actual mechanism for SO₂ generation is still being researched, analysis so far suggests that localised oxygen rich regions within the fluid bed play a role. The bed material and the feed appear to provide a source of sulphur and possibly, catalysing solid species. In fact, SO₂ has been found to be prominent even during the gasification of sulphur-lean feed. In contrast, COS is believed to originate from the more reducing regions of the gasifier, most likely above the bed in the gas phase. This would help explain the faster response of COS in comparison to SO₂. Notwithstanding, the data would also suggest that COS entails both a prompt and more delayed mechanism (albeit to a far less extent to that of SO₂). More straightforwardly, it was observed that higher COS levels coincided with high CO/CO₂.

Although insightful, limitations in the findings must be kept in mind. Due the plant's scale and practical operation, for instance, facilitating identical conditions from one run to the next can prove difficult. There are also practical constraints on the run time, thus undermining the achievement of stable system dynamics (and reaction equilibria). Monitoring at particular locations is also limited.

Nonetheless, similarities and disparities alike can provide useful insight as well as grounds for further research. Consequently, analysis on a suite of performed experiments (on RDF as well as wood) is underway. This includes a sulphur balance, to help substantiate earlier model results which indicated the prominence of sulphur in the solid phase (Morrin et al., 2012). Different sulphur additives, reflecting feed-sulphur functionalities, have also been trialled. Experimental work coincides with thermodynamic modelling.

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