



Solid–gaseous phase transformation of elemental contaminants during the gasification of biomass



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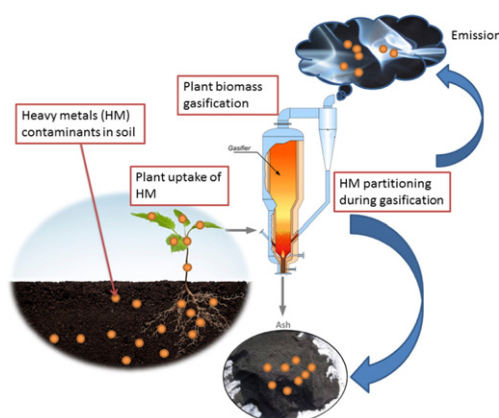
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HIGHLIGHTS

- Disposal of plants removed from metal contaminated land raises environmental concerns
- Plant samples collected from a contaminated site are shown to contain heavy metals.
- Gasification is suitable for plant disposal and its emission is modelled by MTDATA.
- As, Cd, Zn and Pb are found in gaseous emissions at a low process temperature.
- High pressure gasification can reduce heavy metal elements in process emission.

GRAPHICAL ABSTRACT



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ABSTRACT

Disposal of plant biomass removed from heavy metal contaminated land via gasification achieves significant volume reduction and can recover energy. However, these biomass often contain high concentrations of heavy metals leading to hot-corrosion of gasification facilities and toxic gaseous emissions. Therefore, it is of significant interest to gain a further understanding of the solid–gas phase transition of metal(loid)s during gasification.

Detailed elemental analyses (C, H, O, N and key metal/metalloid elements) were performed on five plant species collected from a contaminated site. Using multi-phase equilibria modelling software (MTDATA), the analytical data allows modelling of the solid/gas transformation of metal(loid)s during gasification.

Thermodynamic modelling based on chemical equilibrium calculations was carried out in this study to predict the fate of metal(loid) elements during typical gasification conditions and to show how these are influenced by metal(loid) composition in the biomass and operational conditions.

As, Cd, Zn and Pb tend to transform to their gaseous forms at relatively low temperatures (<1000 °C). Ni, Cu, Mn and Co converts to gaseous forms within the typical gasification temperature range of 1000–1200 °C. Whereas Cr, Al, Fe and Mg remain in solid phase at higher temperatures (>1200 °C). Simulation of pressurised gasification conditions shows that higher pressures increase the temperature at which solid-to-gaseous phase transformations takes place.

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1. Introduction

In the UK and globally, substantial areas of land are either unusable or have reduced utility due to contamination from heavy metals, often from previous industrial activities. In Europe, more than 34% of contaminated soils are affected by heavy metals (Panagos et al., 2013). In the UK, a recent national survey of contaminated land reports metals and metalloids are the most frequently reported contaminants that form the basis of determinations on over 80% of contaminated sites in England (Defra, 2014).

Due to the increasing demand for development and agriculture land, there is a significant drive to clean up former industrial sites contaminated with potentially high levels of heavy metal. Prior to the redevelopment of these abandoned landbanks, appropriate investigation of the contamination and removal of the existing vegetation is often required.

Plants biomass removed from these contaminated sites are likely to contain elevated heavy metals, especially when there is an active plant-metal interaction, i.e. hyperaccumulation taken place. The range of metal concentration in biomass varies significantly from different metal elements. Generally, hyperaccumulators can potentially accumulate Mn and Zn at above $10,000 \mu\text{g g}^{-1}$ on dry mass basis (Reeves and Baker, 2000); As, Co, Cu, Ni, Se, and Pb at $>1000 \mu\text{g g}^{-1}$ (Ma et al., 2001) and Cd at $>100 \mu\text{g g}^{-1}$ (Reeves and Baker, 2000). Therefore without appropriate waste management strategies, these biomass can cause adverse human health and environmental impacts (Abhilash and Yunus, 2011). Several contaminated crop disposal routes are proposed in previous studies including thermochemical treatments (incineration, gasification and pyrolysis) and direct landfill disposal (Kumar et al., 1995; Sas-Nowosielska et al., 2004). Amongst these methods, landfilling is the most direct and practical. However it is less preferable due to economic and long-term environmental concerns (Sas-Nowosielska et al., 2004).

Thermochemical routes typically achieve significant volume reductions of the waste biomass as well as producing renewable energy. Biomass gasification is a promising renewable energy technology producing syngas in an energy efficient manner (Devi et al., 2003). This process is considered to be more suitable for biomass energy conversion than direct combustion due to the high moisture content in biomass (Lievens et al., 2008). However, toxic element emissions from the gasification of biomass with high metal content presents significant technical and environmental challenges that must be addressed directly (Lievens et al., 2008; Pudasainee et al., 2014).

A number of studies investigated the fate of metal(oids) during the thermochemical treatment of biomass (Nzihou and Stanmore, 2013; Pudasainee et al., 2014; Vervaeke et al., 2006). It is clear that during gasification, there are a number of possible routes of elemental emission through the hot gas path. Heavy metal elements can react and form particles, or the vapour species condense to form particles based on the operating conditions (Kilgallon et al., 2004; Oakey et al., 2004).

Heavy metal volatilisation temperature varies significantly from one element to another. It is not difficulty to specify the solid to gas phase transition temperature of a single metal element in a system. However, in a multi-phase equilibria system with multiple elements involved such as gasification, the phase transition temperature is dependent on many other factors including pressure, gasifying agent and fuel composition. (Vervaeke et al., 2006). In addition, the behaviour of these elements depends on the presence of other elements in the fuel alongside the component materials of the hot gas paths (Kilgallon et al., 2004; Oakey et al., 2004). To study the intricate phase transition in multi-phase equilibria system, commercial simulation packages based on thermodynamic calculations are widely used. It was demonstrated in a number of studies this theoretical simulation of thermochemical process can provide valuable guidance in the design of appropriate operational parameters for large-scale trials (Cotton et al., 2014; Kilgallon et al., 2004; Ljung and Nordin, 1997).

This study analysed heavy metal concentrations at the root, stem and foliage of six wild plant species. Samples were collected from a local authority owned site in Northwest England where heavy metal concentrations are expected to be high as a result of previous industrial activities. Thermodynamic calculations were conducted using the MTDATA thermodynamic software (NPL, UK) to study the solid-to-gaseous phase transition of heavy metal contaminant under typical gasification conditions.

2. Materials & methods

2.1. Sample collection

Soil and plant samples were collected from land previously used for industrial activities. Five $1 \times 1 \text{ m}$ grids were randomly selected on the site ($\sim 300 \text{ m}^2$) for soil sampling. Within each grid, three soil samples were collected at the depth of 5–20 cm. Samples of six common wild plants grown on the site were collected including: *Corylus avellana* (common hazel), *Sonchus oleraceus* (common sow thistle), *Malva sylvestris* (common mallow), *Urtica dioica* (common nettle) and *Medicago sativa* (alfalfa). In addition to whole plant samples, foliage, stem and roots from each plant were collected separately (root samples of *C. avellana* were not collected due to its large root system, and the fine root of *M. sativa* was also not collected).

The plants and soil samples were air-dried at $35 \text{ }^\circ\text{C}$ in a drying cabinet and ground into fine powder using a centrifuge mill with a 0.5 mm mesh sieve (Retsch ZM-1, Retsch GmbH, West Yorkshire, UK) for further analysis. 15 soil samples were evenly mixed into a representative composite soil sample to be analysed in the following tests.

2.2. Sample analysis

2.2.1. Soil pH

The pH value of composite soil sample was measured in accordance with standard method (BS ISO 10390:2005). 50 ml deionised water was added into 10 g soil sample. The soil suspension was mixed thoroughly in an orbital shaker for 60 min and allowed to stand for another 60 min. The pH value of the soil slurry was measured using a pH meter (Jenway 3540, Bibby Scientific Limited, UK).

2.2.2. Metal analysis

0.5 g ($\pm 0.1 \text{ mg}$) of each plant biomass sample was weighed using an analytical balance, followed by a microwave-assisted acid digestion procedure in accordance with US EPA Method 3051. Briefly, 9 ml of concentrated nitric acid and 3 ml of concentrated hydrochloric acid were added to the sample followed by acid digestion in a microwave-assisted digestion system (MARS 6, CEM Microwave Technology Ltd., UK). The concentrations of K, Na, Ca, Al, Mg, Mn, Cr, Co, Se, Pb, Cd, Cu, Zn, Ni and As were analysed by an ICP-MS (Elan 9000, PerkinElmer Inc., UK) and the concentrations of Fe and Hg were determined by an atomic absorption spectroscopy (AAS 800, PerkinElmer Inc., UK) at the wavelength of 248.3 and 253.7 nm, respectively. Reagent blanks and calibration standards for the metals of interest were added to each batch of analysis. For quality control, all samples were prepared and analysed in triplicates. For the result of each sample, a relative standard deviation (RSD) of $<5\%$ is required for the triplicated measurements. In case of an outlier, the analysis was repeated until satisfactory accuracy was achieved.

Metal concentrations of the soil sample were analysed by a UKAS certified commercial laboratory (Marchwood Scientific Services, Southampton, UK). Representative soil samples of 1 g were aqua-regia digested by microwave following US EPA Method 3051 and analysed by an ICP-OES.

Table 1
Biomass characterisation results (on the basis of dry weight).

| | %C | %N | %H | %O | Volatile matter (%) | Ash content (%) | Experimental CV (MJ kg ⁻¹) | TCV (MJ kg ⁻¹) |
|--------------------------|-------|------|------|-------|---------------------|-----------------|--|----------------------------|
| <i>Corylus avellana</i> | 49.00 | 0.93 | 6.77 | 43.30 | 89.36 | 5.35 | 18.35 | 19.31 |
| <i>Sonchus oleraceus</i> | 44.80 | 0.85 | 6.75 | 47.59 | 78.77 | 14.08 | 16.06 | 17.17 |
| <i>Malva sylvestris</i> | 46.96 | 1.00 | 6.41 | 45.63 | 84.40 | 8.89 | 16.92 | 17.68 |
| <i>Urtica dioica</i> | 46.74 | 1.03 | 6.86 | 45.37 | 83.29 | 10.77 | 19.01 | 18.28 |
| <i>Medicago sativa</i> | 48.82 | 3.24 | 6.87 | 41.08 | 86.12 | 7.23 | 19.19 | 19.33 |
| Ave. | 47.26 | 1.41 | 6.73 | 44.59 | 84.39 | 9.26 | 17.91 | 18.35 |

2.2.3. Biomass proximate and ultimate analysis

Moisture content, ash content and volatile matter content were determined following the standard methods (BS 7755: Section 3.1:1994 and BS EN 13039:2011).

Elemental composition (C, H, N and O) of the plant samples were analysed using a Vario EL elemental analyser (Elementar Analysensysteme GmbH, Germany). The elemental analyser operates at CHN mode while the oxygen content was calculated by difference.

Plant biomass calorific values (CV) were analysed by a UKAS certified lab (Marchwood Scientific Services, Southampton, UK). Representative samples were finely ground and dried to constant weight before analysing for the higher heating values (HHV) in a bomb calorimeter.

Theoretical calorific values (TCV) of each biomass sample was calculated using the modified Dulong's formula (Demirbas, 2004; Demirbas et al., 1997) as a function of the carbon, hydrogen, oxygen, and nitrogen contents from Eq. (1):

$$\text{TCV (HHV)} = 33.5C + 142.3H - 15.4O - 14.5N \times 10^{-2} \quad (1)$$

2.3. Thermodynamic modelling (MTDATA)

Chemical equilibrium calculations, based on Gibbs free energy minimisation were carried out using MTDATA software (Version 5.10, NPL, UK) to estimate the elemental phase transition under the given gasification conditions including temperature and pressure. Modelling was undertaken for three major elements (C, O, and H) and 12 minor elements (Al, As, Cd, Co Cr Cu, Fe, Mn, Mg, Ni, Pb and Zn) based on their quantities within the biomass, volatility and environmental toxicity. The multiphase module of MTDATA was used in the modelling, combined with the Scientific Group Thermodata Europe (SGTE) database, in order to predict compound/phase formation for temperature range of 0–1800 °C. Mass quantities of each element of interest, as determined in elemental and ICP-MS analysis (average value of the five plant samples) were entered into the model.

Oxygen required for the gasification process was calculated stoichiometrically using Eq. (2), based on the carbon content in biomass.



A typical steam to oxygen ratio of 2:1 was selected for the model and the simulation was carried out for atmospheric pressure and high pressure gasification scenarios at 1 and 40 atm, respectively.

3. Results & discussions

3.1. Biomass characterisation

Proximate and ultimate analysis results of the five plant biomass are within the typical range of biomass samples, summarised in Table 1. There is a good degree of agreement between the measured and theoretical calorific values. The slightly higher calculated CV is commonly due to the mineral content in biomass which is not accounted for in elemental analysis. Oxygen content is characteristically high in biomass

fuel samples when compared to coal which contributes negatively to the HHV (García et al., 2014).

Although the wild plants collected for this study are not considered as energy crops, significant energy can be recovered providing appropriate conversion facilities are in place. Considering the global scale of contaminated land where its use is prohibited from development and agriculture, converting this resource for energy crop production has been discussed in a number of previous studies (Campbell et al., 2008; Zhuang et al., 2011). The estimated global area of abandoned land not suitable for agriculture is 385–472 million ha (Zhuang et al., 2011). The potential for producing energy is therefore in the region of 1840–2253 Mtoe (assuming annual biomass yield of 10 t per hectare and average biomass CV of 20 MJ kg⁻¹), equating ~10% of world total energy production in 2012 (International Energy Agency, 2014). Moreover, it is suggested in a previous study, if high biomass yield energy crops, e.g. *Miscanthus* sp. and *Salix* sp. are planted in these contaminated site as a commercial activity, a significantly higher energy yield and financial return can be achieved (Jiang et al., 2015). In addition to bioenergy production, cultivating plants on contaminated land is an effective and environmentally sustainable method for stabilising and cleaning up elemental contaminants, i.e. phytoextraction and phytostabilisation.

3.2. Metal uptake in plant samples

The ranges of selected metal element concentrations in the soil and plant biomass samples were shown in Table 2. There is a wide variety of heavy metals in the soil indicating a low to moderate level of site contamination of the site. All plants species studied displayed the capability for metal uptake. However, within the plant biomass there is no sign of accumulation of heavy metals, as the concentrations of heavy metals in plants are significantly lower than in soil. Therefore there are no significant concerns of toxic exposure for those in direct contact during biomass harvesting, processing and utilisation in this particular case. Due to the low ash content of plant biomass materials shown in Table 1, heavy metals are potentially concentrated by factors of 10–20 in the ash following thermochemical processing. Thus, appropriate management and disposal of the ash residue must be carefully considered.

The metal concentrations at different sections of plant tissue are shown in Table 3. In all plants tested, metal translocation from root to shoot were observed. Significantly higher concentration of Cr was

Table 2
Soil pH and selected elemental concentration (mg kg⁻¹, on dry matter basis) in soil and biomass samples.

| Metals | Soil | Plants (whole) |
|-----------|-------|----------------|
| Arsenic | 8.5 | 0.121–1.217 |
| Chromium | 36 | 1.3–11.82 |
| Cobalt | 9.2 | 0.029–1.078 |
| Iron | 17300 | 41.8–2615.4 |
| Lead | 157 | 0.71–5.39 |
| Manganese | 360 | 5.601–102.101 |
| Selenium | <0.7 | 0.055–0.5046 |
| Nickel | 28 | 0.016–4.804 |
| pH | 7.8 | – |

Table 3
Metal concentrations (mg kg⁻¹) in whole plant (W), foliage (F), stem (S) and root (R).

| | Al | As | Cd | Co | Cr | Cu | Fe | Hg | Mg | Mn | Ni | Pb | Zn | |
|--------------------------|--------|-------|--------|-------|-------|--------|-------|--------|--------|-------|-------|------------------|-------|--------|
| <i>Corylus avellana</i> | F | 133.3 | 0.18 | 0.057 | 0.14 | 2.24 | 6.54 | 639.8 | 0.013 | 2698 | 78.9 | BDL ^a | 1.20 | 32.38 |
| | S | 161.3 | 0.17 | 0.101 | 0.11 | 4.12 | 6.76 | 261.4 | 0.019 | 1250 | 40.9 | 4.20 | 1.63 | 25.78 |
| | W | 173.1 | 0.20 | 0.106 | 0.15 | 2.22 | 7.68 | 2615.4 | 0.016 | 1980 | 73.5 | 0.32 | 1.99 | 33.38 |
| <i>Sonchus oleraceus</i> | F | 100.9 | 0.27 | 1.841 | 0.12 | 3.46 | 19.54 | 186.2 | 0.017 | 2318 | 24.3 | BDL | 0.84 | 104.78 |
| | R | 460.7 | 0.59 | 1.185 | 0.62 | 55.82 | 18.94 | 164.2 | 0.021 | 670 | 19.6 | 4.38 | 5.23 | 37.58 |
| | S | 15.1 | 0.24 | 1.361 | 0.03 | 1.55 | 9.78 | 1157.0 | 0.016 | 880 | 6.1 | BDL | 0.35 | 26.98 |
| <i>Malva sylvestris</i> | W | 171.5 | 0.32 | 1.575 | 0.18 | 11.82 | 15.36 | 119.0 | 0.029 | 1446 | 16.0 | 1.90 | 1.52 | 59.78 |
| | F | 400.7 | 0.66 | 0.065 | 1.08 | 5.30 | 15.62 | 702.2 | 0.018 | 5258 | 102.1 | 4.80 | 3.89 | 68.18 |
| | R | 508.7 | 0.63 | 0.313 | 0.40 | 4.50 | 10.92 | 184.4 | 0.016 | 2598 | 26.3 | 1.92 | 5.87 | 58.78 |
| <i>Urtica dioica</i> | S | 106.3 | 0.20 | 0.039 | 0.11 | 2.84 | 8.68 | 110.6 | 0.020 | 2858 | 22.7 | 0.38 | 1.30 | 40.58 |
| | W | 636.7 | 0.73 | 0.187 | 0.69 | 5.36 | 14.22 | 218.2 | 0.019 | 3838 | 62.3 | 2.44 | 5.39 | 61.78 |
| | F | 242.7 | 0.26 | 0.035 | 0.22 | 2.30 | 17.58 | 41.8 | 0.021 | 4078 | 35.3 | 0.98 | 2.05 | 34.38 |
| <i>Medicago sativa</i> | R | 198.7 | 0.28 | 0.065 | 0.13 | 4.64 | 7.16 | 1125.2 | 0.020 | 1124 | 13.1 | 0.02 | 1.79 | 16.22 |
| | S | 22.9 | 0.15 | 0.016 | 0.04 | 1.47 | 4.58 | 297.6 | 0.015 | 768 | 5.6 | BDL | 0.59 | 13.78 |
| | W | 151.3 | 0.26 | 0.043 | 0.13 | 2.24 | 8.88 | 218.0 | 0.014 | 1624 | 17.0 | 0.06 | 1.43 | 20.98 |
| Whole plant ave. | F | 87.1 | 0.17 | 0.039 | 0.10 | 1.78 | 8.86 | 207.2 | 0.017 | 2138 | 37.3 | BDL | 0.84 | 65.38 |
| | S | 38.1 | 0.13 | 0.041 | 0.08 | 1.94 | 6.62 | 439.8 | 0.014 | 1592 | 18.7 | BDL | 0.53 | 28.78 |
| | W | 59.1 | 0.12 | 0.046 | 0.10 | 1.30 | 9.30 | 109.4 | 0.007 | 2138 | 30.5 | 0.13 | 0.71 | 53.18 |
| Whole plant ave. | 238.34 | 0.326 | 0.3914 | 0.25 | 4.588 | 11.088 | 656 | 0.017 | 2205.2 | 39.86 | 0.97 | 2.208 | 45.82 | |

^a Below the limit of detection.

found in the root of *S. oleraceus* compared to the plant shoot, suggesting a tolerance mechanism for Cr to limit the heavy metal from entering the above ground plant tissue (Shanker et al., 2005). Therefore it is a potential plant model for Cr phytoremediation and phytostabilisation as recognised in a previous study (Khan et al., 1998).

Establishing plant coverage on heavy metal contaminated land can be an effective and sustainable method to mitigate the adverse environmental impacts caused by these contaminants. The outcome potentially provides the opportunity for subsequent biomass removal and utilisation where the plant is appropriately selected. Investigations on metal uptake and tolerance are thus necessary for the selection of the most suitable plant species.

3.3. Thermodynamic calculation of gaseous–solid phase transition of metal contaminants

The MTDATA modelling was carried out to simulate phase transition of 12 elemental contaminates in typical gasification scenarios. Simulations were based on the elemental composition of a typical biomass; therefore the results provide significant insights into the future implementation of bioenergy production using energy crops produced on contaminated land.

Amongst the 12 elements; As, Cd, Pb and Zn are the most volatile, where solid–gas transition starts at temperatures below 600 °C. Under the standard atmospheric pressure and relatively low temperature,

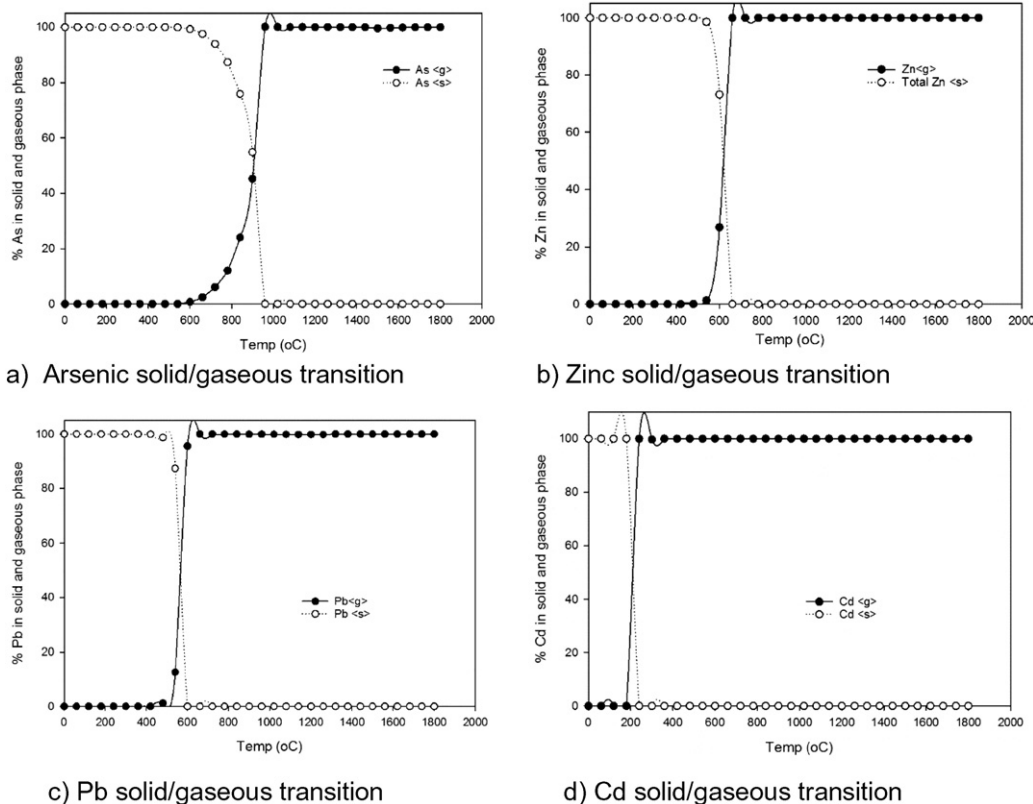


Fig. 1. Solid–gaseous phase transition curve of element with low transition temperature. Note: <s> = solid, <g> = gaseous.

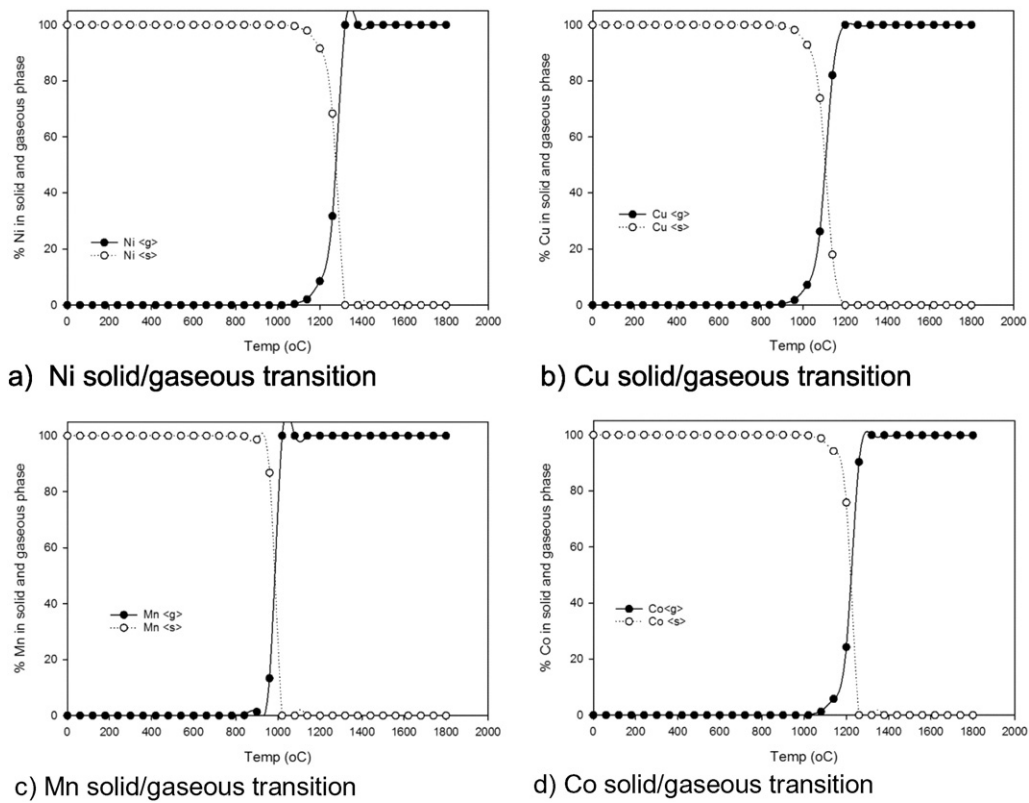


Fig. 2. Solid–gaseous phase transition curve of element with medium transition temperature.

the mass percentage of these elements in gaseous form increase rapidly in the system. Above 1000 °C, all four elements exist completely in gaseous form (Fig. 1), which indicates the majority of these elements are released from the gasification system with flue gas.

Ni, Cu, Mn and Co are key elemental soil contaminants and their uptake by plants is well documented (Keeling et al., 2003; Malik et al., 2000; Pinto et al., 2014; Poschenrieder et al., 2001). Therefore their fate during thermochemical process is of significant interest. Under

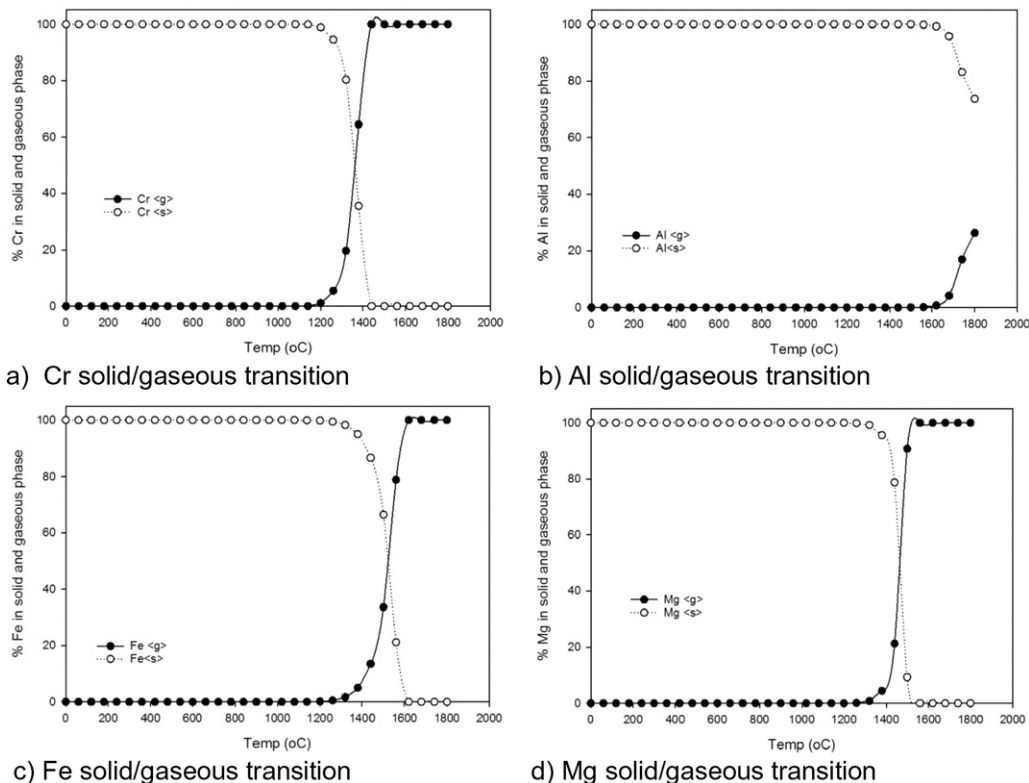


Fig. 3. Solid–gaseous phase transition curve of element with high transition temperature.

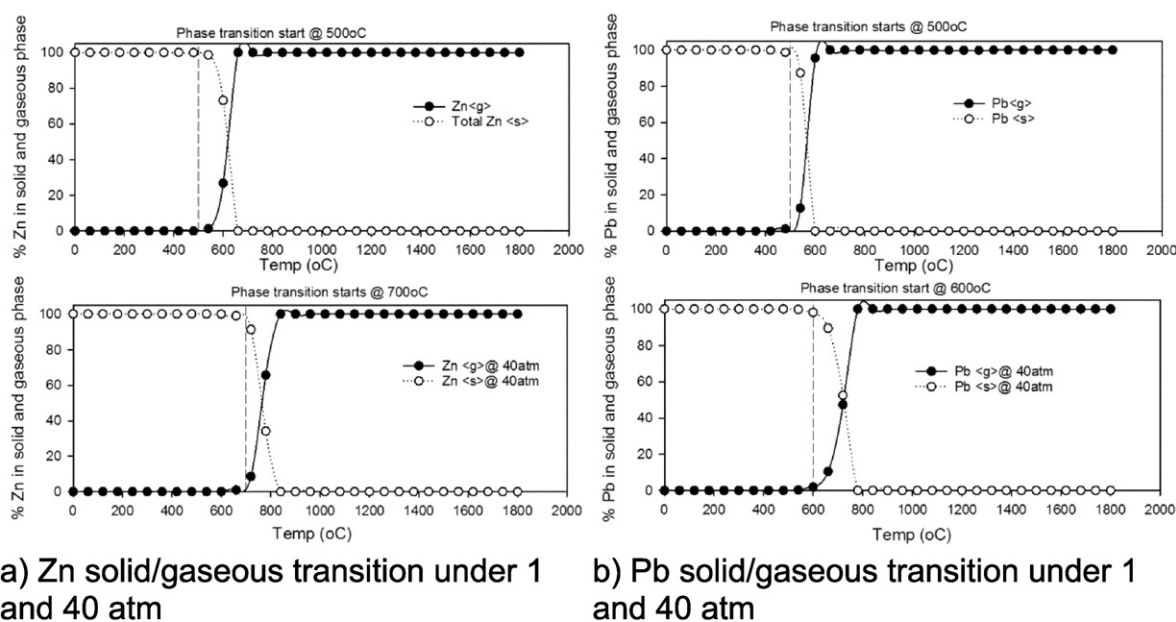


Fig. 4. Increased phase transformation temperature with high pressure.

standard atmospheric pressure, gaseous transformation starts for all four elements at the temperature range of 1000–1200 °C (Fig. 2), which is the typical temperature for biomass gasification (McKendry, 2002). To avoid gaseous emission of these metals, it is possible to maintain gasification temperatures below the phase transformation threshold. See Fig. 3

Cr, Al, Fe and Mg are generally acknowledged to be non-volatile under thermochemical conditions (Meij and te Winkel, 2007). Thermodynamic calculation results show their phase transformation temperatures are above 1200 °C, and thus unlikely to form gaseous emissions and escape the system in flue gas.

High pressure gasification can significantly increase product yield and reaction rates (McLendon et al., 2004; Sha et al., 1990). In addition, previous studies reported an increase in pressure leading to higher phase transition temperatures (Liu et al., 2006). This is confirmed in the thermodynamic simulation of gasification under 40 atm. The results show that the increased pressure from 1 to 30 atm, significantly increased the starting temperature for phase transformation by 100–200 °C (Fig. 4).

It is worth noting that compared to previous studies on coal using a similar simulation method (Liu et al., 2006), the transitional temperature for volatile elements calculated in this study are significantly higher, as a result of the difference in elemental composition and process parameters. This presents the opportunity to improve toxic elemental emissions by manipulation of the fuel biomass elemental composition through blending and optimising the process parameters, i.e. temperature and pressure.

4. Conclusion

Disposal of plant biomass removed from heavy metal contaminated land can raise significant environmental and public health concerns. In this study, determination of elemental composition (C, H, O and N), heavy metal concentrations and energy values were carried out on five plant species collected from a contaminated site. The analytical results show a low level of metal uptake in all plant species and moderate energy value from the biomass. This presents opportunities to utilise biomass removed from contaminated land for energy production via gasification, providing toxic elemental emission is properly addressed.

Thermodynamic modelling indicates that pressure, temperature and the concentration of metals present in the biomass greatly affects the interaction and behaviour of metals during gasification. As, Cd, Zn and Pb tend to transform to their gaseous forms at relatively low temperatures (<1000 °C), therefore their potential emission is of significant concern. Operating at high pressure significantly increases the starting temperature for phase transformation of heavy metals. The modelling results demonstrate the elemental emission from thermochemical biomass conversion can be manipulated by operational parameters. This provides further evidence to support that thermochemical conversion can be the key technology for disposal of contaminated land derived plant biomass.

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