

CRANFIELD UNIVERSITY

Shurooq Badri Al-Badri

**The Behaviour of Metal(loid)s Contaminants in Woody
Biomass During Advanced Thermal Conversion
Processes**

School of Water, Energy and Environment

This thesis is submitted in partial fulfilment of the requirements for
the degree of Doctor of Philosophy

Supervisor: Dr Stuart Thomas Wagland
Associate Supervisor: Dr Ying Jiang
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Abstract

A remarkable proportion (about 64%) of renewable biomass energy is produced from woody biomass (wood and its wastes). However, waste wood (WW) often exhibits a high level of chemical contaminants, likely due to the presence of metal(loid) elements in preservatives, paintings, coatings, and other related activities. By thermally treating WW, the metal(loid)s will end up in the bottom ash and/or be emitted into the atmosphere, causing severe environmental concerns and technical damages (e.g. slagging and corrosion). Thus, it is necessary to understand the behaviour of metal(loid)s during the woody biomass thermal conversion process, specifically gasification and pyrolysis. While a great deal of knowledge is available on this matter, there is still uncertainty surrounding the identification and characterisation of metal(loid) elements in relation to woody biomass utilisation, as well as the influences of reaction atmosphere composition in terms of interactions and interferences. In addition to that, knowledge is needed on partitioning profiles of the key metal(loid) elements during the gasification and pyrolysis of WW in order to evaluate the emission potential of these elements.

This thesis firstly provides a highly informative dataset that contains comprehensive details about the characterisation and elemental composition of key metal(loid) elements (As, B, Co, Cr, Cu, Fe, Ni, Pb, Mn, Hg and Ti) that are regularly present in woody biomass. Moreover, chemical equilibrium calculations were performed to predict elemental phase transformation and speciation formation under given gasification and pyrolysis operation conditions. Among the results, it was found that Ni-As interactions form the dominant species As_2Ni_5 and $\text{As}_8\text{Ni}_{11}$, which increase the solid-gaseous phase transformation of As. In addition, the Ca-Cr interaction forms C_3Cr_7 ; meanwhile, the absence of Ca creates instability in the Cr phase transformation due to the generation of the species $\text{Cr}_2\text{Na}_2\text{O}_4$.

Subsequently, a set of experiments were conducted using a TGA analyser with different heating rates to understand the thermal behaviour of woody biomass and define the operational conditions of the pyrolysis process. Tube furnace

experiments were also conducted to investigate the distributions of Al, As, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Na, Mn, Mo, Ni, Pb, Si, Ti, V, and, Zn during the operation of pyrolysis. Experimental results indicated that Cd and Hg are exceedingly volatile elements, whereas Al, Co, Cr, Cu, Fe, Mo, Ni, Si, Ti, and V are non-volatile elements. The elements As, Mn, Pb, and Zn exhibited differences in partitioning across all experiments. Importantly, this study provides unique insight into the behaviour of As in terms of As-Ni interaction. That is, the presence of Ni should be regarded in combination with its associated concentration profile.

Finally, the experimental data and the calculation results are complementary rather than competitive. Overall, the experimental results are within acceptable validation limits.

Keywords:

Wood waste; Advanced thermal conversion; Thermodynamic equilibrium modelling; Interactions; Interferences.

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List of Abbreviations

α	Degrees of conversion
β	Heating rate
Φ	Gasifier efficiency
Q	Desired output power
A	Pre-exponential factor
AS	Artificial samples
BFR	Biomass feed rate
BFR	Biomass feed rate
BS	Blending waste wood sample
daf	Dry Ash-free basis
DTG	Differential thermogravimetric analysis
E	Activation energy
ETI	Energy Technologies Institute
GP	Mass percentage in gaseous phase
H_{daf}	Hydrogen mass fractions
HHV_{daf}	Higher heating value
L.d.	Landfill
LHV_{Bio}	Biomass lower heating value
M	Mean (M)
M_{daf}	Moisture mass fractions
Metal(loid)s	Metals and metalloids
R	Gas constant
RSD	Relative standard deviation
SGTE	Scientific Group Thermodata Europe
SP	Mass percentage in solid phase
STD	Standard deviation
TCV	Theoretical calorific value
TG	Thermogravimetric
TGA	Thermogravimetric analysis
WW	Waste wood

Chapter 1 Introduction

This chapter provides essential information on the main topics of this PhD thesis, including the background, aim, objectives, scope of the study, and thesis structure.

1.1 Background

The utilization of biomass for energy production has increased exponentially (Gavrilescu, 2008; Slade et al., 2011; Sriram and Shahidehpour, 2011) due to the intensification of both energy demands and environmental concerns. From 2010 to 2040, the global energy demand is expected to increase continuously at an annual rate of 1.7% (Sieminski, 2014). Presently, biomass as a source of energy contributes 10–14% of global energy production (Ahmad et al., 2016). Compared to fossil fuels, the biofuels produced from biomass generate remarkably lower emissions of hazardous gases including SO_x and NO_x (Sharma, Pareek and Zhang, 2015). Forms of biomass that can serve as solid fuel resources include woody biomass (wood and its wastes); agricultural, herbaceous, and municipal solid waste; human and animal wastes; industrial waste; aquatic biomass; and mixtures of these materials (Alakoski et al., 2016; Vassilev et al., 2010; Demirbaş, 2005). Among these, the most commonly used is the woody biomass, which is utilised as feedstock in various thermochemical conversion processes to produce second-generation biofuels including liquid (such as methanol and ethanol) and gaseous (such as synthetic natural gas and hydrogen) (Molino, Chianese and Musmarra, 2018).

Biomass can be converted into various energy forms via three principal types of conversion processes: thermochemical, biochemical and physical/chemical (Grønli, 1996a). Among these, thermochemical conversions have been widely used because of their higher yields and production rates of hydrogen (Tripathi, Sahu and Ganesan, 2016b). Typical thermochemical techniques consist of exposing biomass feedstocks to high temperatures under oxygenated conditions to yield solid, liquid and gas products, which can be further processed to a range of usable fuels. The most promising pathways of thermochemical processing are

gasification and pyrolysis, as they can achieve considerable reductions of the waste biomass while at the same time generating renewable energy (Jiang et al., 2016). Furthermore, gasification and pyrolysis offer several advantages over conventional combustion, the most important of which is the possibility of adjusting their operational parameters to produce suitable products.

Despite the availability of diverse varieties of biomass feedstocks, woody biomass represents the majority (approx. 64%) of the total volume of biomass used for energy production (Demirbaş, 2005). This is attributed to its abundant supply, low recycling costs, and satisfactory biofuel characteristics (Edo, 2016; McKendry, 2002). However, woody biomass, especially waste wood (WW), is considered to possess a high degree of contamination (Edo, 2016), since it comprises a wide range of wood materials mostly obtained from demolition and construction operations and from industrial and commercial activities (Brack, 2017; Brown and Kearley, 2012a; Defra, 2012a; Korhaliller, 2010). Waste wood is, therefore, a very inhomogeneous fuel (Huron et al., 2017; Vassilev et al., 2010) containing physical and chemical contaminants. Physical contaminants can simply be separated out via sorting or mechanical techniques. However, the vast majority of the chemical contaminants are linked directly to the metals¹ and metalloids² contained in woods that have been treated with preservatives, paintings, coatings, and other related activities. For example, woods treated with preservative compounds and surface agents contain elevated levels of the metal(loid) elements As, Cr, Cu, Ni and Pb (Tsai and Wu, 2013). With the thermal treatment of WW, metal(loid) elements will end up in the bottom ash or be emitted to the atmosphere (Jiang et al., 2016; Kilgallon, Simms and Oakey, 2002; Lundholm, 2007; Nzihou and Stanmore, 2013; Reed, Dugwell and Kandiyoti, 2001a), causing not only severe environmental and human health concerns but also significant technical damage to facilities. In fact, even burning virgin wood

1. Metals are chemical elements that are “lustrous, hard, malleable, heavy, ductile, and tenacious and usually are good conductor of heat and electricity” (John D. Hsu, John Michael, 2008).

2. Metalloids are chemical elements “with properties intermediate between metals and non-metals” (Sherameti, Irena, 2010).

can result in emitting metal(loid)s in fly ash (Ange Nzihou and Brian Stanmore, 2013).

Although studies have been conducted to assess the behaviour and impact of metal(loid)s in woody biomass during the thermochemical processes (Froment et al., 2013; Kramb et al., 2016; Jerzak, 2017; Said et al., 2018), there is still uncertainty around many issues including the identification of the metal(loid)s of utmost concern with regard to woody biomass utilization and the detailed investigations of the fate of key metal(loid)s during gasification and pyrolysis of a single type of woody biomass as well as blended woody feedstocks. Moreover, as gasification and pyrolysis are very complex processes involving multiple inter-dependent reactions, the possible interactions and interferences between the metal(loid)s in woody biomass alongside their associated impacts are still not understood and require sustained research. Accordingly, it is essential to address these issues prior to placing any prominent scheme for impeding and/or limiting the harmful impacts consequence of the presence of metal(loid) contaminants in woody biomass, particularly through providing a more comprehensive understanding and insightful analysis of the fate of key metal(loid)s during the advanced thermochemical processes: gasification and pyrolysis.

This PhD project has studied the behaviour of metal(loid)s contaminants that are regularly present at high concentrations in both heavily and slightly treated woods as well as wood from landfills during the advanced routes of thermochemical processes. Based on published information and available standard databases, thermodynamic equilibrium modelling was carried out using multiphase module of the MTDATA software to predict the fate of the key metal(loid) elements (As, B, Co, Cr, Cu, Fe, Ni, Pb and Ti) during the gasification and pyrolysis of the waste wood (WW) samples. The modelling enabled the optimization of the processes' operational conditions and parameters by means of threshold temperatures of key metal(loid)s phase transformations, meanwhile revealing the type and amount of dominant chemical species of these elements. For the models' validation, a set of experimental trials were performed based on the optimized operational conditions and parameters of the processes. On this basis, improved

understandings of the distribution and phase transformation of key metal(loid)s during the gasification and pyrolysis of woody biomass were achieved.

During the gasification and pyrolysis of metal(loid)s contaminated woody biomass, uncertainties concerning the interactions and interferences among metal(loid) elements cannot be disregarded, since these elements may interact and/or interfere with each other. Such interactions can result in the formation of new chemical species, which may induce substantial influences on the mobilisation behaviours of metal(loid)s. Furthermore, a dataset was generated comprising detailed elemental composition of key metal(loid)s, drawn from the available literature and from experimental analysis of different types of WW samples collected from waste streams, industrial, and landfill sites. In this study, both simulations and experiments were conducted to identify the interactions and interferences occurring among key metal(loid) elements and to investigate their fates with respect to their distributions during the gasification and pyrolysis of individual, blended, and artificial woody biomass samples. Consequently, a novel understanding of the behaviour of key metal(loid)s in terms of interactions and interferences is presented, suggesting that the negative impacts of toxic metal(loid) elements can be effectively mitigated through systematically blending different types of woody materials prior to any advanced thermal conversion processes. In this way, better thermal conversion and cost saving can be achieved.

Parts of this study have already been presented (as oral presentations and papers in international conferences) and published in journals (see Appendix A).

1.2 Aim and objectives

Aim

The overall aim of this PhD was to study and understand the behaviour of key metal(loid) elements in waste wood materials during advanced thermochemical conversion processes.

Objectives

- To critically review the literature to identify the key metal(loid)s in waste wood materials and their sources; discuss the gaps in the scientific understanding to enable the development of a programme of work leading to a significant contribution to knowledge;
- To develop biomass waste wood gasification and pyrolysis models using specialised software to predict the fate of the key metal(loid)s in terms of the compositions of phase transition during these processes;
- To investigate the possible interactions and interferences between the key metal(loid)s using the developed model;
- Develop and undertake valid waste wood sample collection from a range of sources including those with high levels of contamination. Complete a comprehensive analysis of the samples using standard methods for proximate, ultimate and elemental content;
- To validate the developed pyrolysis models using experimental data, including thermal degradation behaviours, and optimise the operational parameters of the models.

1.3 Scope of study

To achieve the stated objectives, the following methodology has been applied:

- Critical review: A systematic search of the scientific literature using internet and library resources (e.g., Scopus, ISI Web of Knowledge databases) as well as available standard databases was conducted to identify the key metal(loid)s contaminants and their associated ranges of concentrations in waste wood.
- Development of the models: The modelling set up and initial elemental composition were selected based on the findings of the literature review. The most likely elemental concentration ranges were estimated from the data drawn from the literature review via the Risk Analysis and Simulation Add-In for Microsoft Excel. The actual elemental compositions were obtained using mass balances of the gasification and pyrolysis. Then,

thermodynamic equilibrium modelling was carried out using multiphase module of the MTDATA software to predict the fate of metal(loid)s during the gasification and pyrolysis of WW. The modelling allowed to explore the type and quantity of the formed chemical species, and also to reveal the relationship between the threshold temperatures of phase transitions and operational parameters.

- Interactions and interferences: The calculations were carried to study the effects of the occurred interactions and interferences on the fate of metal(loid)s as consequence of various contents of the metal(loid)s and other elements in WW samples. A total of 162 different scenarios were considered and simulated.
- Collection of WW samples: WW samples were collected from different sources, including waste streams, industrial and landfill sites. Each sample was prepared and analysed. The analysis procedures involve: full chemical characterisation and determination of elemental composition. The analysis results were considered as reference profiles for the thermodynamic equilibrium modelling and experiments.
- Models validation and optimisation: For all of the presented models, a thermogravimetric analyser (TGA) was employed to determine the thermal characteristics of woody biomass samples under pyrolysis operation conditions across a temperature range of 30-900°C with N₂ pure gas at 40.0ml/min. Then, the validation and optimisation were carried out using tube furnace. In addition, artificial fuel samples contain species with different concentrations of metal(loid) elements were prepared and analysed to provide insightful understanding of the occurred interactions and interferences.

1.4 Thesis structure

This thesis consists of seven chapters, references, and appendices. A general outline of the chapters is given below.

- **Chapter Two** reviews the available literature related to WW sources, classification of WW, contamination in WW, thermal biomass conversions, thermodynamic modelling, metal(loid)s in woody biomass, behaviour of metal(loid)s during the gasification and pyrolysis of feedstock materials, and interactions and interferences.
- **Chapter Three** details the development of thermodynamic equilibrium modelling for gasification and pyrolysis of waste wood. The modelling procedure comprises data selection and pre-processing, mass balance calculation, calculation protocol, and models applications. The predictive results are also reported and discussed in this chapter.
- **Chapter Four** presents the thermodynamic equilibrium modelling to investigate the interactions and interferences among the metal(loid)s in different scenarios. It also presents a discussion of the obtained predicted results.
- **Chapter Five** covers the preparation and analysis of the collected waste wood samples. The analysis results are reported (full chemical characterisation and determination of elemental composition) and discussed.
- **Chapter Six** presents the work conducted to experimentally optimise the operational conditions of the pyrolysis process and to determine the kinetic parameters of waste wood using TGA. Also, the fate of metal(loid)s in waste wood and artificial samples are investigated using a tube furnace, from which the distributions of metal(loid)s in these samples are determined. Finally, comparisons between the experimental data and simulation results are made to validate the models.
- **Chapter Seven** summarises the findings, highlights the significant contribution to knowledge of the thesis, and suggests ideas for future works.

Chapter 2 Literature Review

This chapter critically reviews the available knowledge on the metal(loid)s contents and their concentrations levels in various types of waste wood. It also presents detailed explanation about the biomass thermochemical conversion processes and thermodynamic modelling approaches to these processes. Further, it reports the experimental and simulation results from previous studies on the fate of contaminant metal(loid) elements in biomass during thermochemical processing.

2.1 Waste wood sources and demands

Waste wood (WW) can be collected from diverse sources such as construction, demolition, commercial, industrial, and municipal waste streams (Defra 2012; M.Brown and V.Kearley 2012; WRAP and BSI 2012; Anon 2011; Edo et al. 2016; Agency and Note 2014; DEFRA 2015; BERR 2008; POYRY 2009; Remade Scotland 2004).

The landfilling of biodegradable waste, including WW, contributes to greenhouse gas emissions (Defra, 2013). Waste wood can be economically attractive when it is not sent to landfill (Eunomia research and consulting, 2012), and there have been efforts by authorities to reduce the volume of WW sent to landfill (Defra 2012) by increasing gate fees to landfill, through the landfill tax escalator. In fact, the average gate fees for disposing a ton of WW in UK landfill has been raised steadily during the previous years from approximately £32 in 2007 to £86 in 2017/2018 (Wrap UK, 2018). This high gate fees level is likely to maintain until 2020 (Defra, 2013).

According to the UK Department for Environment, Food, and Rural Affairs (Defra, 2013) the estimated amount of WW disposal via landfilling will decrease from approximately 800,000 tons in 2009 to 300,000 tons in 2024 as shown in Figure 2-1.

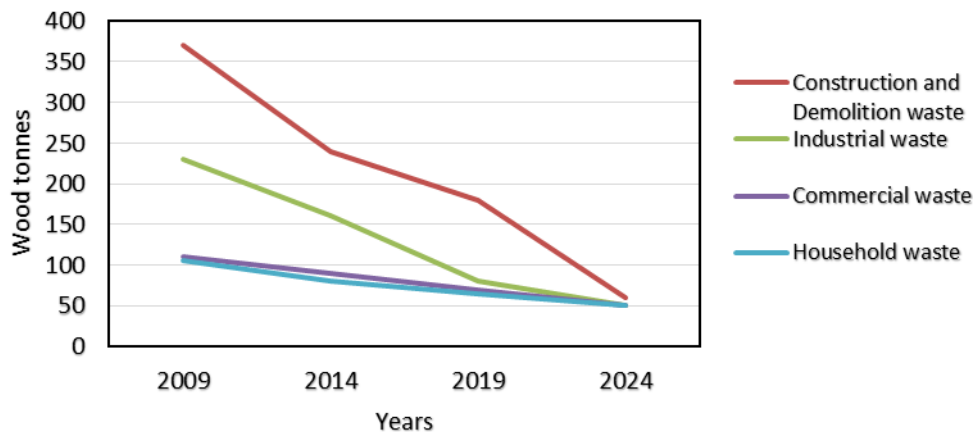


Figure 2-1. Estimation of WW sends to landfill in UK between the periods 2009 to 2024.
Source: (Defra, 2013)

Consequently, demand for WW as a source of biomass in the UK will be increased as shown in Table 2-1. Perrin, Donahue, and Long's estimate the percentage of rivalry between 2012 to 2040 to be 0.5% (Perrin, Donahue and Long, 2015).

Table 2-1. The demand for WW as a source of biomass in UK.

Years	2007	2011	2015	2020/2021
Demand	5.1Mt	1.1Mt	1.6Mt	3.2Mt
Percentage (%)	58%	31%	85%	95%

Sources: (Anon 2011; Defra 2012; Clegg 2017)

2.2 Classification of waste wood

Waste wood can be classified into four classes, namely A, B, C, and D, based on the level of hazardous materials that they contain (Waste & Resources Action Programme 2012; Alakangas et al. 2015; Defra 2012; Anon 2011; Defra 2008; Report 2011; WRAP and BSI 2012; Agency and Note 2014) as depicted in Table 2-2. Classes A, B, and C represent clean wood, industrial feedstock, and solid fuel. Whereas class D is wood treated with combination of preservatives and related activities and considered as a hazardous waste.

Table 2-2. Classification of waste wood.

Class	Substances	Non-wood contents prior to process	Usage	Recovery/disposal cost/income (per tonne)
A (Clean - Recycled wood)	Solid soft wood and hard wood, packaging waste, packing cases, scrap pallets, as well as cable drums. Procedure off-cuts from joinery manufacturing.	Nails, metal elements, Slight quantities of paint, as well as surface coatings.	Producing animal bedding and mulches	Potentially income of up to £150
B (Industrial-Feedstock)	Possibly will be contained up to 60% from class A material. As above, in addition building as well as demolition materials and domestic furniture are made from solid wood.	Nails, metal fixing, some paints, plastics, glass, grit coatings, binders and glues. Limits on treated or coated materials as defined by WID.	Making panel board	Cost of fees per tonne £5 to £30
C (solid biofuel)	All aforementioned, plus fencing products, flat pack furniture made from board products and DIY materials. In height content of panel products for instance, MDF, fibreboard, chipboard, OSB and plywood.	Nail, metal fixing, coatings and glues, paper, plastics, rubber, glass, and grit, as well as covered and treated timber (non CCA or creosote).	Biomass fuel	Equivalent landfill cost in 2015 £80 per tonne in UK
D (Hazardous-waste)	All aforementioned adding fencing, transmission poles and Cooling towers.	Copper, Chrome, and Arsenic preservation treatments creosote.		If contaminated with carbohydrates assumed the fees per tonne is £157

Sources: (Defra 2012; Anon 2011; Defra 2008; Report 2011; WRAP and BSI 2012; Waste & Resources Action Programme 2012; Agency and Note 2014; Alakangas et al. 2015)

2.3 Contaminations in waste wood

As the vast majority of waste wood resulted from demolition and construction operations and from industrial and commercial activities (Brown and Kearley 2012; Defra 2012; Clegg 2017), it may incorporate both physical and chemical contaminants (Edo, 2016; Vassilev et al., 2010). Physical contaminants, such as nails and screws, can easily be separated by sorting or using mechanical techniques. However, the major chemical contaminants usually linked to the metal(loid) elements contained in wood that treated with preservations, paintings, coatings, and other related activities, and, of course, mechanical separation is inapplicable.

The aforementioned operations and activities can provide a steady supply and massive scale of WW materials (Ange Nzihou and Brian Stanmore, 2013; Brown and Kearley, 2012b; Defra, 2012b). However, the utility of these WW materials is heavily restricted, since they contain different chemical contaminants, primarily attributed to the wood treatment compounds. Table 2-3 concludes the compiled information with respect to the key metal(loid) elements in this type of WW coupled with their origins and respective concentrations ranges.

Table 2-3. Main metal(loid)s contaminants in WW and their sources.

Metal(loid)s	Sources of contaminations		Concentrations (ppm)
	Preservatives	Pigments	
Arsenic (As)	√		1.243
Copper (Cu)	√		1.262
Chromium (Cr)	√		1.1243
Boron (B)	√		7.40
Barium (Ba)		√	2.60
Cobalt (Co)		√	1-4
Lead (Pb)		√	7.80
Zinc (Zn)		√	1.10
Iron (Fe)		√	17200
Titanium (Ti)		√	2.80
Cadmium (Cd)		√	0.5-1

Sources: (Connell, 2005; Cui et al., 2010; Edo et al., 2016; Harrison, 2014; Huron et al., 2017; Kenney et al., 2011; Kinata et al., 2012; Krook, Mårtensson and Eklund, 2006; Meier, 2013; Mercer and Frostick, 2012; Nzihou and Stanmore, 2013; Solo-Gabriele et al., 2002; Vassilev et al., 2010; WRAP and BSI, 2012)

In addition, Table 2-4 gives the composition data of demolition WW samples drawn from the standard PHYLLIS2 (ECN) database (www.ecn.nl/phyllis2) and confirms that the chemically-contained preservatives and pigments are the main sources of the key metal(loid)s contaminants. These metal(loid)s with their associated concentrations ranges are: Cu (4.8-385 mg/kg), Cr (0.8-25 mg/Kg), As (1.3-13 mg/Kg), B (5.6-10.1 mg/Kg), Co (0.8-25 mg/Kg), Ni (6-46 mg/Kg), Pb (73-444 mg/Kg), Ti (10-1408 mg/Kg), and Fe (408-1082 mg/Kg). Table 2-4 also indicates that some non-metallic elements present in WW, such as Cl (113-1146

mg/Kg) and S (0.03-0.15%), which can negatively affect the conversion of WW to energy.

Table 2-4. Types and concentrations of the chemical elements of WW samples from demolition site.

Sample Number	S1	S2	S3	S4	S5	S6	S7	S8	S9
Proximate Analysis (%)									
Moisture content	8.6	21	4.68	33	9	21.4	9.57	15.30	13.0
Ash content	1.92	4.35	2.85	6.27	2.5	0.79	70.41	6.18	13.57
Volatile matter	70.65		71.59	48.64		62.96	1.77	63.27	59.86
Fixed carbon	18.83		20.88	12.09		14.67	18.25	15.25	13.57
Ultimate Analysis (%)									
Carbon (C)	44.5		49.65	45.45	48.13	49.8	48.41	46.03	43.31
Hydrogen (H)	5.6		5.75	5.51	5.93	5.84	5.93	5.7	5.26
Nitrogen (N)	1.1	0.79	0.29	1.79	0.47	0.19	1.06	1.93	1.92
Sulphur (S)	0.09		0.05	0.03	0.11	0.06	0.06	0.18	0.15
Oxygen (O)	44.7		41.21	37.85	42.64	42.85	40.91	37.34	37.13
Elements (mg/Kg)									
Arsenic (As)	4.8	5	8.9	1.3	13	4	1.5		
Cadmium (Cd)	0.5	3	0.9	0.2	0.3	2	0.2		
Cobalt (Co)	1.5	25	1.5	0.8		2	2.3	3	3
Chromium (Cr)	23.7	30	35	21	33	30	29	37	33
Copper (Cu)	12.3		53	4.8	385	28	10	11	5
Manganese (Mn)	84.9		70	93.1		92	54	109	73
Nickel (Ni)	32.6	6	2.8	6.9		46	24	11	11
Lead (Pb)	163.8	410	410	190	275	270	78	444	73
Vanadium (V)	1.1		0.9	1.6			1.5	3	1.5
Zinc (Zn)	227	670	400	114.5	715	340	63	612	156
Barium (Ba)	244		210	99.3		220	121	559	99
Molybdenum (Mo)	0.2		0.4	1.2			2.5		
Selenium (Se)	2.1		0.3	0.3			0.2		
Mercury (Hg)		0.3			0.1	2			0.1
Aluminium (Al)	468.9		330	985		150	459	1369	696
Potassium (K)	728.1		720	808		370	909	1029	805
Sodium (Na)	649.7		360	544		210	556	1571	1613
Calcium (Ca)	3479		2700	4940		2200	2290	6537	4037
Silicon (Si)	1135.4		2700	3612			2049	11407	4193
Magnesium (Mg)	399.3		330	373		250	501	789	488
Iron (Fe)	340.3		680	1047		480	480	1082	482
Phosphorus (P)	141.3		75	115		120	485	125	67
Titanium (Ti)	985.4		160	133.5		10	228	1408	168
Tin (Sn)	0.1		2	2.5	1	3	0.1		
Boron (B)	10.1		5.6	9.6			6	7	6
Antimony (Sb)	2.9		1.8	1.5	4		2.1		
Strontium (Sr)	18.7		16	19.5		13	12	28	15
Chlorine (Cl)	1000	885	550	113	175.8	350	487	1 146.0	910
Fluorine (F)	30	21	30			20.2		43	88

Source: S1, S2, S3, S4, S5, S6, S7, S8, and S9 represent #2712, #1779, #1448, #1364, #871, #679, #3498, #2900, #2901 in Phyllis Database, respectively (www.ecn.nl/phyllis2)

It should be noted here that presence of metal(loid)s contaminants in WW may be attributed to other sources such as agricultural lands, forestry residues, landfills, etc. For example, (Peralta-Videa et al., 2009) reviewed and summarised the mechanism of uptake, transformation and bioaccumulation of metal(loid)s As, Cd, Cr, Hg, and Pb by plants. A detailed analysis of the heavy metals concentrations in agricultural topsoil of the EU was introduced by G. Toth, T.Hermann, and M.R. Da Silva 2016. Jiang et al. 2016 analysed the metal(loid) elements Al, As, Cd, Co, Cr, Cu, Fe, Hg, Mg, Mn, Ni, Pb, and Zn and their concentrations levels at the root, stem and foliage of six plant species collected from agricultural site where the heavy metal concentrations are expected to be elevated.

- **Wood preservatives**

The most commonly used preservatives in the wood preservation industry are CCA (chromate, copper, and arsenic) and CCB (chromate, copper, and boron) (Helsen and Van Den Bulck, 2000, 2008; Huron et al., 2017; Issues et al., 2001; Kartal et al., 2008; Nzihou and Stanmore, 2013; Solo-Gabriele et al., 2002). According to the active ratios of the elements Cr, Cu, and As, CCA preservative can be divided into three types A, B, and C, and the chemical formulations of both CCA and CCB preservatives are detailed in Table 2-5. These preservatives can be sources of chemical contaminant species, particularly, when the impregnated wood is thermally treated. For instance, Cr(VI) ($\text{CrO}(\text{OH})_2$), As(III,V) (As_2O_3 or As_4O_6), and Cu(II) (CuO) are the key toxic compounds that release from the direct burning of CCA-treated woods (Helsen and Van Den Bulck, 2008; Kramb et al., 2016; Lundholm, 2007; WRAP and BSI, 2012).

Table 2-5. The chemical formulations of CCA and CCB preservatives.

CCA	Cr as CrO_3 (%)	Cu as CuO (%)	As as As_2O_5 (%)
Type A	65.5	18.1	16.4
Type B	35.3	19.6	45.1
Type C	47.5	18.5	34.0
CCB	Cr as $\text{KCr}(\text{SO}_4)_2$ (%)	Cu as CuSO_4 (%)	B as H_3BO_3 (%)
CCB	37.1	34.2	28.7

Sources: (Solo-Gabriele et al. 2002; Kinata et al. 2012)

2.4 Thermal biomass conversion

Conversion of biomass into different forms of energy undergoes several processes. Similar to any energy resource, the selection of biomass conversion is limited to a certain aspects: type and quantity of the biomass feedstock, form of the required energy, environmental standards, economic conditions, and project-specific factors (McKendry, 2002). According to (Grønli, 1996b), there are three principle types of conversion processes: thermochemical, biochemical, and physical/chemical. More recently, the conversion of biomass to energy is carried out via two main processes: thermochemical and biochemical (McKendry, 2002). The biochemical platform consists primarily of enzymatic conversion of cellulose and hemi-cellulose components of the biomass into sugars and subsequent fermentation and anaerobic digestion to yield biofuels and chemicals. The thermochemical conversion involves thermal decomposition of the biomass organic compounds into liquid and gaseous biofuels. The major pathways of the thermochemical conversion include combustion, gasification, and pyrolysis. Furthermore, thermochemical conversion offers several advantages over biochemical conversion, such as less reaction time, complete utilisation of biomass, independent of climatic conditions, relatively higher productivity, and pre-treatment of biomass is not required (Shirai et al., 2015; Tripathi, Sahu and Ganesan, 2016a).

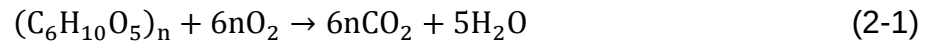
2.4.1 Thermochemical biomass conversion

The thermochemical conversion process consists of exposing biomass to high temperature under oxygen conditions to yield solid, liquid, and gas products which can be further upgraded to a range of usable fuels. The primary thermochemical biomass conversion techniques are: combustion, gasification, and pyrolysis (Shirai et al., 2015).

2.4.1.1 Combustion

Combustion is the oldest established technique for converting biomass to usable energy. It is a process by which the chemical energy is released in the form of heat by direct burning the biomass materials in the presence of oxygen.

Combustion achieves a complete oxidation of biomass, and operates at temperature range of 800-1000°C (Tripathi, Sahu and Ganesan, 2016a). Although the major constituents of biomass are cellulose, hemicellulose and lignin, the biomass combustion usually describes as cellulose combustion according to the reaction (2-1) (Klass 1996;p.191) as follows:



Combustion technique can be employed to convert any type of biomass into thermal energy, however, its feasibility is achieved only when the moisture content of the biomass less than 50% (Goyal, Seal and Saxena, 2008). Usually, natural biomass is rarely obtainable in convenient form for burning, so, in most cases, the biomass subjected to different pre-treatment mechanisms, which in turn increasing the cost and energy expenditure (Tripathi, Sahu and Ganesan, 2016a).

2.4.1.2 Gasification

Gasification is a promising technology for biomass to energy conversion. It provides a high flexibility in utilisation of feedstock materials and generation of various energy forms. More specifically, biomass gasification is a process by which the solid biomass fuels (moisture content < 50%) can be converted into usable gaseous product (syngas), consisting primarily of CH₄, CO₂, CO, H₂, and N₂ (Couto et al., 2013). From this product, different types of energy and chemicals can be derived. Gasification is exothermic partial oxidation of biomass, operates at high temperature range in presence of gasifying agents (Shirai et al., 2015; Tanger et al., 2013). The product compositions and properties vary according to the biomass materials, gasifier type, and operating conditions.

2.4.1.2.1 Chemical reactions in biomass gasification

Essentially, gasification process involves the conversion of solid carbonaceous fuels into combustible gases composed of a mixture of CO, CO₂, H₂, CH₄, H₂O, N₂ and very small quantities of low molecular weight hydrocarbons and contaminants including ash, tar, and carbon particles (Couto et al., 2013;

Kamińska-Pietrzak and Smoliński, 2013). Further, the compositions and properties of the gasification products vary according to the operational conditions (e.g., temperature, pressure), gasifier type, and biomass materials (Couto et al., 2013). In general, biomass gasification consists of four interlinked processing steps: drying, pyrolysis of dried biomass particles (de-volatilization), partial oxidation of pyrolysis gases and/or char, and char gasification (reduction) (Shirai et al., 2015), as depicted in Figure 2-2 (A.Gomez-Barea, 2010).

Technically, gasification is exothermic partial oxidation of biomass, operates at temperature range of 800-1300°C with the presence of gasifying agents including carbon dioxide, steam, and air (or a mixture of air and steam) (González-Vázquez et al., 2017; James, Yuan and Boyette, 2016; Shirai et al., 2015; Tanger et al., 2013). Whatever gasifier type being used, the principal chemical reactions in biomass gasification are given in Table 2-6.

Table 2-6. Principal chemical reactions in biomass gasification.

Reaction	Heat of Reaction ΔH° (kJ mol ⁻¹)	Name	Number
Biomass $\rightarrow$ char + tar + H ₂ O + light gases (CO + CO ₂ + H ₂ + CH ₄ + C _x H _y O _z + N ₂ + ...)	> 0	Pyrolysis and devolatilization	R1
Char combustion			
C + $\frac{1}{2}$ O ₂ $\rightarrow$ CO	-111	Partial combustion	R2
C + O ₂ $\rightarrow$ CO ₂	-394	Total combustion	R3
Char gasification			
C + CO ₂ $\rightleftharpoons$ 2CO	+173	Boudouard reaction	R4
C + H ₂ O $\rightarrow$ CO + H ₂	+133	Steam gasification	R5
C + 2H ₂ $\rightleftharpoons$ CH ₄	-75	Hydrogene gasification	R6
Homogeneous reactions			
CO + $\frac{1}{2}$ O ₂ $\rightarrow$ CO ₂	-283	CO oxidation	R7
H ₂ + $\frac{1}{2}$ O ₂ $\rightarrow$ H ₂ O	-242	H ₂ oxidation	R8
CH ₄ + 2O ₂ $\rightarrow$ CO ₂ + 2H ₂ O	-283	CH ₄ oxidation	R9
CO + H ₂ O $\rightleftharpoons$ CO ₂ + H ₂	-41	Water-gas shift (WGS)	R10
CO + 3H ₂ $\rightleftharpoons$ CH ₄ + H ₂ O	-206	Methanation	R11
Tar conversion reactions			
C _n H _m + (n/2) O ₂ $\rightarrow$ nCO + (m/2)H ₂	Highly endothermic	Partial oxidation	R12
C _n H _m + nH ₂ O $\rightarrow$ (m/2 + n)H ₂ + nCO ₂		Steam reforming	R13
C _n H _m + nCO ₂ $\rightarrow$ 2nCO ₂ + (m/2)H ₂		Dry reforming	R14
C _n H _m $\rightarrow$ (m/4)CH ₄ + (n - m/4)C		Thermal cracking	R15

Source: (Shirai et al., 2015); p.216

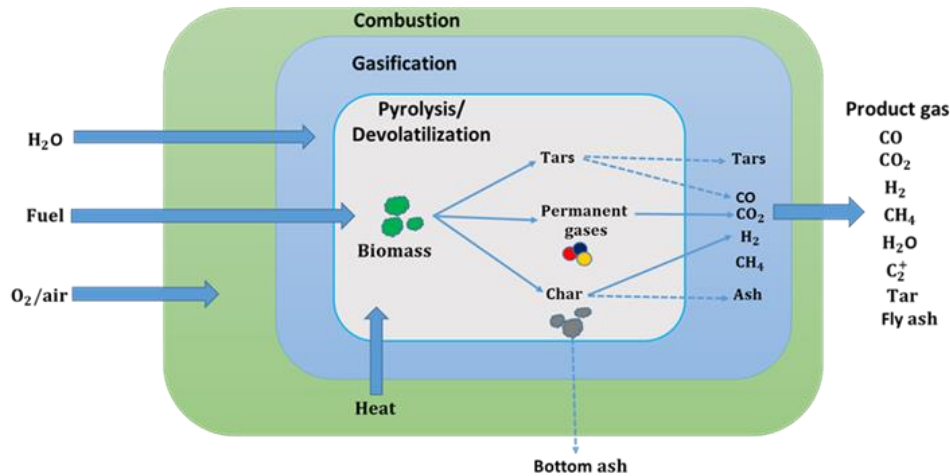


Figure 2-2. Schematic of the processes in a gasifier.

2.4.1.2.2 Biomass gasifier types

A wide range of applicable biomass gasifiers have been developed. Nevertheless, they can be categorized into two main groups: fixed bed (updraft and downdraft) and fluidized bed (bubbling and circulating) (Couto et al., 2013). This categorization is based on the way that the heat is introduced to the reactors, flow direction of both biomass and air/oxidizing agent, and supporting of the biomass in reaction vessel. The most commonly used configurations in these gasifiers are listed in Table 2-7 (Ciferno and Marano, 2002). However, fluidized bed gasifiers are widely employed because of their flexibility and efficiency, especially for large-scale projects. The main differences between the bubbling and circulating gasifiers lie in fluidizing velocity and gas path (Warnecke, 2000). The former possesses relatively low gas velocities, whereas in the latter, the velocities approach to the pneumatic flow.

Table 2-7. Configurations of biomass gasifiers.

Gasifier Type	Flow Direction		Support	Heat Source
	Fuel	Oxidant		
Fixed bed updraft	Down	Up	Grate	Combustion of char
Fixed bed downdraft	Down	Down	Grate	Partial combustion of volatiles
Bubbling fluidized bed	Up	Up	None	Partial combustion of volatiles and char
Circulating fluidized bed	Up	Up	None	Partial combustion of volatiles and char

Source: (Ciferno and Marano, 2002)

Fixed bed gasifiers are the oldest form of reactors employed for producing syngas. Due to their simplicity in both design and operation coupled with a comparatively high thermal efficiency, fixed bed gasifiers have been extensively studied and used, specifically for small-scale (<10 MW) power generation (Shirai et al., 2015). The primarily fixed bed gasifiers are updraft and downdraft as depicted in Figure 2-3 (de Lasa et al., 2011). Typical fixed bed gasifiers have lower heat and mass transfer (Shi, Si and Li, 2016), and more designs that combine properties of both updraft and downdraft gasifiers have also been developed.

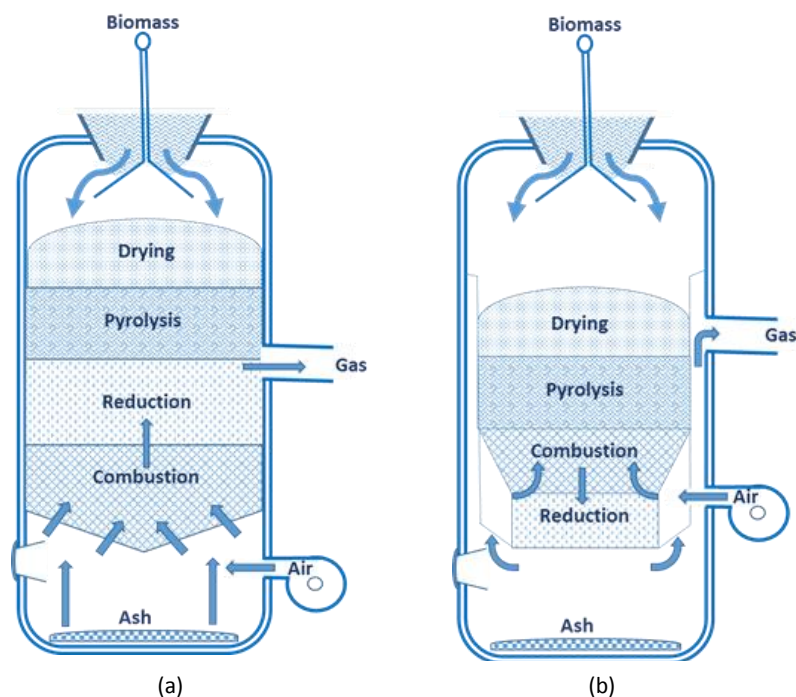


Figure 2-3. Schematic of (a) Updraft gasifier and (b) Downdraft gasifier.

Updraft gasifier is considered the simplest configuration. It consists of four zones: upper drying, upper-middle pyrolysis, lower-middle reduction, and lower combustion. The biomass feed is supplied from the top, while the gasifying agent is supplied from the bottom below the grate, and flows upward through the reactor.

In this gasifier, the biomass is first dried in drying zone. Then, the biomass is pyrolysed in pyrolysis zone, producing volatile species and a sizeable amount of tar. Thereafter, in reduction zone, volatiles are converted into permanent gases. When the residual biomass be near grate, solid char and remaining biomass combusted at 1000°C. Further, the ash falls through the grate once char combustion with air is completed. The produced hot gases from combustion flow upward and interact with the downward moving uncovered biomass in reduction zone. The tars partially condense in pyrolysis zone, and/or leave the reactor with permanent gases. The product gases from this gasifier contain considerable portion of tars and hydrocarbons. This type of gasifiers has ability to handle biomass with high both moisture and inorganic (Ciferno and Marano, 2002; de Lasa et al., 2011; Shirai et al., 2015).

The design of downdraft gasifier is basically similar to that of updraft gasifier expecting that the air is supplied at or above the reduction zone. In this configuration, dried biomass moves downward to pyrolysis zone, enabling the de-volatilization and the tar conversion reactions to take place. Subsequently, both uncovered tars and gases evolve towards oxidation zone, wherein combustion occurs at 1000-1400°C. The formed chemical species move through the lower reduction zone where the contents of both H₂ and CO₂ are increased. Downdraft gasifiers produce gas that typically has low particulates and tars (~1g/Nm³) C (de Lasa et al., 2011; Shirai et al., 2015). The performance data of the fixed bed gasifiers as well as the fluidized bed gasifiers are given in Table 2-8.

2.4.1.1 Pyrolysis

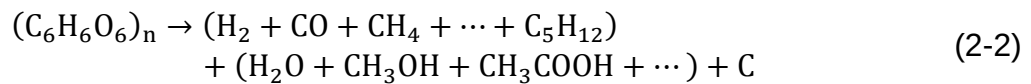
Pyrolysis forms the first step of biomass thermochemical conversion. It is an endothermic process for converting biomass (moisture content < 50%) in the absence of oxygen into highly heterogeneous intermediates gas, liquid (bio-oil), and solid (char) products (Tanger et al., 2013). The respective proportion of each product from pyrolysis process strongly depends on the choice of operation conditions (temperature and pressure) and other factors such as heating rate, residence time and particles size (Tripathi, Sahu and Ganesan, 2016a).

Table 2-8. Performance data of fixed bed and fluidized bed gasifiers.

Gasifier	Scale	Typical Temperatures		Fuel Requirements		Cold gas Efficiency (%)	Char conversion (%)	Tar content in raw producer gas/g/m ³	Efficiency	Gas characteristics	Other notes
		Operating	Outlet	Moisture content (%)	Flexibility						
Downdraft Fixed Bed	5 kW _{th} to 2 MW _{th}	1000°C	800°C	< 20%	<ul style="list-style-type: none"> •Less tolerant of fuel switching •Requires uniform particle size •Large particles 	<70	<70	10-40	Very good	<ul style="list-style-type: none"> •Very low tar •Moderate particulates 	<ul style="list-style-type: none"> •Small Scale •Easy to control •Produces biochar at low temperatures •Low throughput •Higher maintenance cos
Updraft Fixed Bed	< 10 MW _{th}	1000°C	250°C	up to 50% – 55%	<ul style="list-style-type: none"> •More tolerant of fuels switching than downdraft 	50-70	70-95	5-12	Excellent	<ul style="list-style-type: none"> •Very high tar (10% to 20%) •Low articulates •High methane 	<ul style="list-style-type: none"> •Small-and Medium-Sca •Easy to control •Can handle high moistu content •Low throughput
Bubbling Fluidized Bed	< 25 MW _{th}	850°C	800°C	< 5 to 10%	<ul style="list-style-type: none"> •Very fuel flexible •Can tolerate high ash feedstocks •Requires small particle size 	30-60	<85	0.015-0.5	Good	<ul style="list-style-type: none"> •Moderate tar •Very high in particulates 	<ul style="list-style-type: none"> •Medium Scale •Higher throughput •Reduced char •Ash does not melt •Simpler than circulating bed
Circulating Fluidized Bed	A few MW _{th} up to 100 MW _{th}	850°C	850°C	< 5 to 10%	<ul style="list-style-type: none"> •Very fuel flexible •Can tolerate high ash feedstocks •Requires small particle size 	20-60	40-85	30-150	Very Good	<ul style="list-style-type: none"> •Low tar •Very high in particulates. 	<ul style="list-style-type: none"> •Medium to Large Scale •Higher throughput •Reduced char •Ash does not melt •Excellent fuel flexibility •Smaller size than bubbli fluidized bed

Source: (Heidenreich and Foscolo, 2015; Roos, 2010)

Basically, the procedure of pyrolysis consists of two main stages: primary pyrolysis and secondary pyrolysis. In the first stage, the biomass decomposed and devolatilized into its major constituents by heating. Devolatilization process includes dehydration, decarboxylation and dehydrogenation. Second stage consists of cracking of the heavy compounds into char or gases such as CO, CO₂, CH₂ and CH₄, as well as bio-oil. Based on pyrolysis conditions, cracking can be considered as either thermal or catalytic, and it can be expressed by the following reaction (2-2) (Tripathi, Sahu and Ganesan, 2016a).



In above reaction, the first, second, and third parts of the right-hand side, respectively, representing the produced gases, liquids, and solids.

2.4.1.2 Types of pyrolysis

There are different types of pyrolysis processes: slow, fast, flash, vacuum, intermediate, and hydro (Tripathi, Sahu and Ganesan, 2016a). Each of which has a certain advantages and disadvantages. Nevertheless, the selection of an appropriate type depends the type of biomass and desired compositions of final products (Fallis, 2013). The typical operating parameters of the six pyrolysis types are highlighted in Table 2-9.

Table 2-9. Typical operational parameters of the pyrolysis processes.

Type of pyrolysis	Temperature (°C)	Pressure (MPa)	Heating rate (°C/s)	Particle size (mm)	Residence time (s)
Slow	550-950	0.10	0.1-1.0	5-50	300-550
Fast	850-1250	0.10	10-200	<1	0.5-10
Flash	900-1200	0.10	>1000	<0.5	>1
Intermediate	500-650	0.10	1.0-10	1-5	0.5-20
Vacuum	300-600	0.01-0.02	0.1-1.0	Not available	0.001-1.0
Hydro	350-600	5-20	10-300	Not available	>15

Source: (Tripathi, Sahu and Ganesan, 2016a)

2.5 Behaviour of metal(loid)s during thermochemical conversions

Numerous studies have examined the behaviour of metal(loid) elements during biomass combustion (Huron et al., 2017; Jano-Ito, Reed and Millan, 2014; Nzihou and Stanmore, 2013; Vassilev, Baxter and Vassileva, 2014), however, the fate of these elements when conducting gasification or pyrolysis has been less investigated.

(Vervaeke et al., 2006) assessed the behaviour of Cd, Cr, Cu, Ni, Pb and Zn present in willow wood harvested from a contaminated dredged sediment disposal site using a small downdraft gasifier. The concentration levels of Cd, Cr, and Pb at about 4 mgkg⁻¹, whereas Cu 6 mgkg⁻¹, Ni 2 mgkg⁻¹ and Zn 150 mgkg⁻¹. Three tests were conducted, each lasted around (3h) and the upper heating value of the gas about 5 MJNm⁻³. As resulted from the gasification, an estimated 6% of the gasified wood (270 kg) recovered as ashes such that 3.1% bottom ash, 0.7% cyclone ash, 0.2% filter ash and 1.8% bed ash. Further, the most volatile metals were Cd, Pb and Zn and they retained to a large extent in filter ash. Conversely, 50% of Cr, Cu and Ni retained in bottom ash and bed ash. A study by (Šyc et al., 2011) examined the distribution of Cd, Cu, Ni, Pb and Zn in solid and gaseous gasification products. A homogenized mixture of hardwood and flax (w/w = 60/40) grown on brownfields contaminated by heavy metals was gasified via fluidized bed steam gasifier at 850°C; the steam to biomass ratio was 1.01 kgkg⁻¹. The concentrations of these metals were analysed in bed ash and cyclone ash as well as in downstream producer gas. The analysis reported that under such conditions the order of metals volatility was Cd > Pb > Zn > Cu > Ni, and their concentrations in producer gas were in the range of 0.37 – 4.2 mgm⁻³, whereas in bed ash and cyclone ash in the ranges of < 0.51-94 mg/kg and < 0.66-190 mg/kg, respectively. The constituents of bottom and fly residues produced by pyro-gasification of pelletized wood were analysed by (Tafur-Marinos et al., 2014). It was found that ash contributed to 7% of the bottom residue and to 38% of the fly residue. Assessment of element distributions in both residues showed that the present of Ca, Mg, S, P, Cu, Si and Na were almost comparable, while Cd, Cr, Pb and Zn concentrated in fly residue. It also confirmed that 550°C is an appropriate temperature for elemental analysis.

Beside the inherent properties of metal(loid)s, their distribution in ash fractions depending on different factors such as feedstock characteristics, operational conditions and flue gas treatments. For example, (Wu, Lin and Zeng, 2014) observed that the amounts of Pb, Cr and Cd increased in fly ash with the increasing of gasification temperatures, however, their amounts were decreased as the gas velocity increased which improved the chemical reactions between bed material and heavy metals, hence, most of these metals were absorbed into bed material. In terms of particle size, they reported that the increasing of particle size leads to increase heavy metal concentrations in fly ash because a reduced interaction between bed material and heavy metals can occur. Furthermore, they also showed that heavy metals content in bed material increased as both gasification temperature and particle size decreased; in contrast, gas velocity increased. The study by (Zhou et al., 2016) examined the influence of Ni-Ca catalyst supported by $\gamma - \text{Al}_2\text{O}_3$ on heavy metals transformation during gasification. They reported that Ni-Ca catalyst can effectively absorb heavy metals and reduce their emissions. Under various temperatures and redox atmospheres, (Dong et al., 2015) investigated the evaporation of Cd, Pb, Zn, Cu, Cr and Ni. The results indicated that the heavy metals proportion in gas phase increased with the temperature, and the redox atmosphere strongly affected the evaporation of these metals such that the volatility of Pb, Cr, Cu and Ni were promoted under oxidative atmosphere, however, Cd and Zn more volatilized under reductive atmosphere. The volatilization of Hg, Se and As in three types of coal were investigated during underground coal gasification by (Liu et al., 2006a). The observed volatilities were in order of $\text{Hg} > \text{Se} > \text{As}$, which, as reported, were mainly affected by elemental properties and their occurrence modes as well as coal reactivity.

The behaviour of Cr, Cu and As during low-temperature ($< 500^\circ\text{C}$) pyrolysis of the CCA treated wood was evaluated by (Helsen and Van Den Bulck, 2008). They found that the increasing of temperature or residence time decreased As content in pyrolysis residue, and these parameters have the same influence on the released Cr and Cu, however, retrained amounts of Cr and Cu were higher than that of As. They further reported that minimal metal realization and maximal mass reduction were obtained at 350°C and residence time of 20 min. Under such conditions, 25% of the As was released using nitrogen at flow rate of $5 \text{ Nm}^3/\text{h}$, and the mass reduction was 56.7%.

However, pyrolysis of CCA treated wood at 300°C for 20 min shows indecisive releases of Cr, Cu and As (Helsen et al., 2003). Nevertheless, they showed that As releases were substantial in all the conducted experiments at 320°C. Moreover, speciation study showed the presence of trivalent As in pyrolysis residue gives indication that As presence in pentavalent state in both CCA solution and treated wood partially reduced to trivalent state. In a study by (Stals et al., 2010), flash pyrolysis was used as a technique for metal contaminated biomass (willow stems and leaves), and the targeted metals were Zn, Cd, Pb and Cu. The measured levels of metals content in pyrolysis oil at 623K was very low (Cu and Zn < 5 ppm; Cd and Pb < 1 ppm), whereas at 723K minimal amounts of Zn and Cd were found, besides, at 823K severe metals volatilization were observed. (Keller et al., 2005) reported that the volatility of Zn and Cd can be optimized, hence the subsequent recovery, when they pyrolysed under reduced conditions.

Quite obviously, the mass of distribution of metal(loid) elements during thermochemical conversion process is rather complex problem. Several studies presented in literature take advantage of thermodynamic equilibrium modelling based on Gibbs energy minimization to clarify the fate of metal(loid) elements during thermochemical processes (Bunt and Waanders, 2010; Froment et al., 2013; Konttinen et al., 2013; Kramb et al., 2016; Lundholm et al., 2007; M. Diaz-Somoano, 2003). For instance, (Froment et al., 2013) performed thermodynamic equilibrium calculations using Fact Sage software to assess the volatilization and condensation of some trace and major elements present in woody biomass during various gasification technologies. With the regard of fluidized bed reactor, the calculations were performed at temperature range from 500 to 1500°C, while the pressure range was set from 1 to 10 bar. Simulation results demonstrated that Zn, Hg, Pb, Cd, Se, F, Cl, Sb, S and N completely volatilized as either elemental or species, whereas, Ca, P, Si, Al, Ti, Fe, Cu, Mn, Cr, Ba and Mg completely remained in condensed phase as oxides, except the copper which condensed as Cu₃As. Five elements (Ag, K, As, B, and Mg) were semi-volatilized. It also confirmed that the total pressure delayed elemental volatility. Another study by (Bunt and Waanders, 2010) examined the behaviour of Ba, Co, Cr, Mn and V in a fixed bed gasifier alongside data of ash samples and FactSage equilibrium modelling. In terms of ash distribution, it showed a good agreement

between the experimental data and model predictions. In the same area, (Kramb et al., 2016) modelled the behaviour of As during the gasification of CCA-treated wood using thermodynamic equilibrium calculations conducted with Excel-interface ChemSheet. The modelling was performed for six conditions such that three of them modelled inside conditions of the gasifier at 850°C and the rest modelled conditions where the product gas cooled to 260°C and at which, as concluded, above 99.6% of As can be captured.

MTDATA (developed by NPL, UK) is a standout amongst the most widely used thermodynamic software packages to predict the behaviour of metal(loid) elements during thermochemical conversions. It was utilized to examine the fate of these elements during co-combustion of wood-bark with waste (Miller, Dugwell and Kandiyoti, 2006) and sewage sludge with Polish coal (Miller, Kandiyoti and Dugwell, 2004) as well as during combustion of MSW (Sørum, Frandsen and Hustad, 2003) and post-combustion of CO₂ captured from coal (Cotton, Patchigolla and Oakey, 2014). MTDATA was also used to predict the speciation of trace elements in oxy-fuel coal combustion (Jano-Ito, Reed and Millan, 2014).

Similarly, (Thompson and Argent, 2002) modelled Prenlfo gasifier MTDATA-based to predict the distribution of trace elements across the product streams. According to the obtained results, trace elements were grouped into “virtually immobile (Cr, Ni, Ba, V), somewhat mobile (Mo, Cu, Be), mobile (Sb, B) and almost totally mobilized (As, Cd, Pb, Sn, Zn)”. In a previous study (Kilgallon, Simms and Oakey, 2002), theoretical predictions of the potential fate of trace contaminants during gasification of coal and biomass fuels were performed. Within the considered temperature ranges, calculation results indicated which of the trace elements in gasifier products are solids or gases and whether the pressure conditions, chlorine/sulphur impacted their phase transformations. Speciation predictions of As, B, Be, Cd, Co, Cu, Pb, Sb, Sn, V and Zn in fuel gas from a gasifier were demonstrated by the work of (Reed, Dugwell and Kandiyoti, 2001a). Based on the predicted dominant phase at temperature range from 700 to 900K, trace elements were categorized into three groups such that condensed phase (Be, Co, Cu, V, Zn; at $T_{50} \gg 900K$), gas phase (As without Ni, B without Ca, Sb, Sn), and condensed phase (As with Ni, B with Ca, Cd, Pb; at $T_{50} < 900K$); where

T_{50} a temperature at which 50% of the system amount in condensed form. The speciation distribution of As, Cd, Ni, Pb, Sb and Se were predictively calculated during underground coal gasification under specific agent injection and pressures (Liu et al., 2006b). The results, under oxygen-steam injection, showed that Se was the most volatile element and present in the form of $H_2Se(g)$ in gas phase. As, Cd, Pb and Sb were also found in gas phase, but their respective volatilities were less than that of Se. These elements were evaporated from the coal at lower temperatures and completely present in gas phase in which they formed $As_2(g)$, $Cd(g)$, $PbS(g)$ and $SbCl(g)$, respectively; also, when cold-cleaning process was conducted, they predicted to large extent be condensed and enriched in fly ash. Furthermore, the distribution of As, Sb and Se was impacted by the gasification pressures such that at high pressures hydrides formation of these elements were promoted and their condensation points were increased. A study by (Bradshaw, Simms and Nicholls, 2008) examined the trace elements content in gases produced from biomass and waste-fuels gasification via series of thermodynamic assessments showed that eight elements (As, Cd, Hg, Pb, Te, Sb, Se, and Sn) and alkali metals remained in fuel gas. Additional calculations pointed that the species of Cd, Pb and Sb could pass through the path of fuel gas, thus form surface deposits relying on their dew points. The identified species were $CdSO_4$, $PbSO_4$ and SbO_2 .

In a study by (Jiang et al., 2016), chemical equilibrium calculations were carried out to predict phase transformation of the metal(loid)s present in five biomass samples during typical gasification scenarios. Only 12 elements (Al, As, Cd, Co, Cr, Cu, Fe, Mn, Mg, Ni, Pb and Zn) were selected depending on their quantities, volatilities and toxicities, and then provided as inputs to the MTDATA. Simulation results demonstrated that, under standard atmosphere pressure, the most volatile elements were Cd, Pb, Zn and As; all of them at temperatures $>1000^{\circ}C$ were totally present in gaseous form. Whilst, Mn, Cu, Co and Ni were moderately volatilized and their gaseous transformations at temperature range from 1000 to $1200^{\circ}C$. Phase transition temperatures of Cr, Fe, Mg and Al were $>1200^{\circ}C$. Another result showed that, increased pressure leads to increase the starting temperature of phase transition by 100- $200^{\circ}C$; this has been confirmed in studies by (Froment et al., 2013; Liu et al., 2006b).

Eventually, Table 2-10 provides the partitioning behaviour of some selected metal(loid)s during the combustion, gasification, and pyrolysis of woody biomass.

Table 2-10. Partitioning behaviour of metal(loid)s during thermochemical conversions of woody biomass.

Metal(loid)s found as contamination	Concentration or (%) of contamination of the substance in types of ash (A) or source (S)	Starts volatilising temperature °C	Types of thermodynamic conversion and operating conditions	Source of wood contamination	Source
As	11706 mg/Kg (S), 24% (A)	400°C	Combustion (T until 800°C & P=1 atm)	P.vittata	(Yan et al., 2008)
	0.326 mg/Kg (S), 100% in solid phase (A)	≤600°C	Gasification (standard atmospheric)	Plant	(Jiang et al., 2016)
	100% in solid phase (A)	327°C	Pyrolysis	Treatment wood	
Cu	11.088 mg/Kg (S), 100% in solid phase (A)	≤900°C	Gasification (standard atmospheric)	Plant	(Jiang et al., 2016)
	100% in solid phase (A)	≤ 900°C (when S & Cl existing) 1100°C (when S & Cl no existing)	Combustion (T =100 -1600°C & P=1 atm)	Plants (Salix)	(Ljung and Nordin, 1997)
	6.7 mg/Kg (S), 30% in solid phase (A)		Gasification (at 550°C and 1 KWh/Kg)	Willow wood	(Vervaeke et al., 2006)
	422 mg/Kg		Pyrolysis (T from 500°C, P=1 atm, and used N ₂)	Woody waste	(Hwang et al., 2007)
Cr	4.588 mg/Kg (S), 100% in solid phase (A)	≤1200°C	Gasification (standard atmospheric)	Plant	(Jiang et al., 2016)
	4.1 mg/Kg (S), 7% in solid phase (A)		Gasification (at 550°C & 1 KWh/Kg)	Willow wood	(Vervaeke et al., 2006)
	100% in solid phase	1000°C (when S existing) 350°C (when S no existing)	Combustion (T from 100 to 1600°C & P=1 atm)	Plants (Salix)	(Ljung and Nordin, 1997)
	2532 mg/Kg		Pyrolysis (T from 500°C, P=1 atm & used N ₂)	Woody waste	(Hwang et al., 2007)

Table 2-10. Partitioning behaviour of metal(loid)s during thermochemical conversions of woody biomass.

Metal(loid)s found as contamination	Concentration or (%) of contamination of the substance in types of ash (A) or source (S)	Starts volatilising temperature °C	Types of thermodynamic conversion and operating conditions	Source of wood contamination	Source
Pb	3.5 mg/Kg (S), 4% in solid phase (A)		Gasification (at 550°C & 1 KWh /Kg)	Willow wood	(Vervaeke et al., 2006)
	100% in solid phase	550°C (when S & Cl existing)	Combustion (T=100 - 1600°C & P=1 atm)	Plants (Salix)	(Ljung and Nordin, 1997)
	2.208 mg/Kg (S), 100% in solid phase (A)	≤3500°C	Gasification (standard atmospheric)	Plant	(Jiang et al., 2016)
	673 mg/Kg		Pyrolysis (T= 500°C & P=1 atm used N ₂)	Woody waste	(Hwang et al., 2007)
	53 mg/Kg		Pyrolysis (T = 905°C & P=1 atm)	Wood contamination	(Stals et al., 2010)
Ni	2.2 mg/Kg (S), 13% in solid phase (A)		Gasification (at 550°C and 1 KWh /Kg)	Willow wood	(Vervaeke et al., 2006)
	100% in solid phase	1450°C	Combustion (T =100 - 1600°C & P=1 atm)	Plants (Salix)	(Ljung and Nordin, 1997)
	0.97 mg/Kg (S), 100% in solid phase (A)	≤1000°C	Gasification (standard atmospheric)	Plant	(Jiang et al., 2016)
Zn	150 mg/Kg (S), 13% in solid phase (A)		Gasification (at 550°C & 1 KWh /Kg)	Willow wood	(Vervaeke et al., 2006)
	100% in solid phase	≤1170°C	Combustion (T =100 - 1600°C & P=1 atm)	Plants (Salix)	(Ljung and Nordin, 1997)
	2593 mg/Kg		Pyrolysis (T = 500°C & P=1 atm & N ₂)	Woody waste	(Hwang et al., 2007)
	45.82 mg/Kg (S), 100% in solid phase (A)	≤350°C	Gasification (standard atmospheric)	Plant	(Jiang et al., 2016)
	1138 mg/Kg		Pyrolysis (T = 905°C & P=1 atm)	Wood contamination	(Stals et al., 2010)

Table 2-10. Partitioning behaviour of metal(loid)s during thermochemical conversions of woody biomass.

Metal(loid)s found as contamination	Concentration or (%) of contamination of the substance in types of ash (A) or source (S)	Starts volatilising temperature °C	Types of thermodynamic conversion and operating conditions	Source of wood contamination	Source
Cd	100% in solid phase	600°C (when S & Cl existing) 700°C (when S & Cl no existing)	Combustion (T = 100 - 1600°C & P=1 atm)	Plants (Salix)	(Ljung and Nordin, 1997)
	3.8 mg/Kg (S), 6% in solid phase (A)		Gasification (T= 550°C & 1 kWh / Kg)	Willow wood	(Vervaeke et al., 2006)
	1.0 mg/Kg		Pyrolysis (T = 500°C & P=1 atm & N ₂)	Woody waste	(Hwang et al., 2007)
	0.3914 mg/Kg (S), 100% in solid phase (A)	≤200°C	Gasification (standard atmospheric)	Plant	(Jiang et al., 2016)
	7.3 mg/Kg		Pyrolysis (T = 905°C & P=1 atm)	Wood contamination	(Stals et al., 2010)
Fe	656 mg/Kg (S), 100% in solid phase (A)	≤1300°C	Gasification (standard atmospheric)	Plant	(Jiang et al., 2016)
Co	0.25 mg/Kg (S), 100% in solid phase (A)	≤1000°C	Gasification (standard atmospheric)	Plant	(Jiang et al., 2016)
V	100% in solid phase	1200°C	Combustion (T = 100 - 1600°C & P=1 atm)	Plants (Salix)	(Ljung and Nordin, 1997)

2.6 Interactions and interferences

As the thermochemical conversions are very complex processes, different competing internal reactions may occur. More specifically, during the gasification and pyrolysis of metal(loid)s contaminated woody biomass, metal(loid) elements can interact and or interfere each other's metal(loid) elements can interact and or interfere each other's, metalloid) elements can interact and or interfere each other's, primarily related to elemental concentration and reactivity, leading to generate new chemical species, which can induce substantial influences on the mobilization behaviours of these elements.

The integration of predictive results and experimental data will be useful to provide qualitative and quantitative understanding of metal(loid) elements behaviours in terms

of phase transformation and speciation formation as results of the occurred interactions and interferences. Hence, identifying mitigation strategies for controlling metal(loid)s emissions and depositions.

2.6.1 Interactions

In this context, the term interaction refers to the chemical reaction that occurs between two or more metal(loid) elements, resulting in new chemical species, which cause modification to the phase transformation temperature of these elements.

So far, only two studies evaluated the impact of interactions on element behaviour during coal combustion. The interactions between the trace elements As, Hg, Cd, and Sb, were assessed by (Contreras, Arostegui and Armesto, 2009), and they reported that some species can be dominant under certain conditions. For instance, As-Cd interaction forms $\text{Cd}_3(\text{AsO}_4)_2$ species, which may reduce gaseous oxides concentration. Also, (Yan, Gauthier and Flamant, 2000) showed the interactions between As, Hg, and Se can lead to form AsSe(g) and HgSe(g) and which considered dominant species under reducing conditions.

2.6.2 Interferences

The term interference refers the influence of one element on the other, and usually take places due to ionization effects and molecular speciation formation (Dobrowolski, Dobrzyńska and Gawrońska, 2015; Galuch et al., 2018; Koirtzmann and Pickett, 1966; Nagiev, 2015). Interferences can lead to generate new chemical species, which in turn modify the threshold temperature of elemental phase transformation. However, the consequence influences of this phenomenon on the fate of metal(loid)s during biomass thermal conversion are still unclear. In fact, only a study by K. Svoboda (Svoboda et al., 2017) investigated the simultaneous interferences of both HCl and HF on H_2S sorption.

2.7 Conclusions

It is clear from the reviewed literature that woody biomass constitutes the basis for the most thermochemical conversion processes that utilize the energy value of this biomass. Nevertheless, woody biomass in forms of WW is very often contaminated

with metal(loid)s at elevated levels causing toxic emissions and technical damages during thermal treatment. While much studies have been conducted based on modelling, experiments (or combination of both) to explore the behaviour and impact of metal(loid)s in woody feedstocks during the thermochemical processes. However, there is still uncertainty regarding many issues, mainly the identification of the key metal(loid)s of greatest concern with woody feedstocks utilization and the detailed understanding of the distribution of key metal(loid)s during gasification and pyrolysis of a single type of woody biomass and a mixture of woody feedstocks. Furthermore, interactions and interferences between metal(loid)s during the thermal treatment of woody biomass together with their relevant impacts are still not understood and requires sustained research. Therefore, it is very important to address the aforesaid issues prior to placing any effective and efficient scheme for impeding and/or limiting the negative influences consequence of the presence of metal(loid)s contaminants in woody biomass.

Most importantly, with the use of thermodynamic equilibrium models, elemental partitioning behaviour can be quantified under optimized operational conditions, which provide substantial support to the experimental works. Consequently, integrating both modelling results and experimental data can enable insightful understanding of the fate of key metal(loid) elements during advanced thermochemical conversion processes, and offering the necessary knowledge towards controlling the emissions and dispositions of these elements.

Chapter 3 Thermodynamic Equilibrium Modelling

The purpose of this chapter is to cover the development and implementation of thermodynamic equilibrium modelling for woody biomass gasification and pyrolysis. For each process, the modelling procedure consists of data selection and pre-processing, mass balance calculation, calculation protocol, and models application.

Part of this work has already presented (oral) and published in a journal (see list of publication in Appendix A).

3.1 Introduction

As mentioned in the previous chapter, the phase distribution and speciation of metal(loid)s strongly depending on the type of process, operational conditions, metal(loid)s content in feedstock, and presence of other elements and compounds. With such diverse factors, the usual approaches for predicting metal(loid)s partitioning during thermochemical conversion processes are benefited from the use of thermodynamic models (Bradshaw, Simms and Nicholls, 2008; Bunt and Waanders, 2010; Dong et al., 2015; Kilgallon, Simms and Oakey, 2002; Said et al., 2018; Šyc et al., 2011).

Thermodynamic equilibrium modelling can efficiently predict the equilibrium composition of multiple elements reacting in a process at various ranges of temperatures and pressures (Cotton, Patchigolla and Oakey, 2014; Jiang et al., 2016; Miller, Dugwell and Kandiyoti, 2006). In addition, equilibrium modelling assumes the thermochemical process as an equilibrium reactor (Froment et al., 2013; Jano-Ito, Reed and Millan, 2014; Reed, Dugwell and Kandiyoti, 2001a) and provides detailed information about elemental phase transformation and speciation formation under given process operation conditions and configurations. Most importantly, to structure the equilibrium calculations, it is essential to specify the elements of interest and their related species as well as process operational conditions and variables in a way that provides accurate

simulation results. Accordingly, for a given process, an optimized mode of operation can be realised.

In this chapter, thermodynamic equilibrium modelling of gasification and pyrolysis processes were carried out using multiphase module of MTDATA software (Ver. 5.10 NPL, UK) combined with SGTE database, as shown in Figure 3-1. In order to provide insightful understanding of the behaviour of the key metal(loid)s contaminants (As, B, Co, Cr, Cu, Fe, Ni, Pb and Ti) in WW, the gathered information from previous studies and standard databases were integrated and utilised for setting up the modelling to ensure reliable and accurate predictions. In doing so, two vital steps (data selection and pre-processing and mass balance calculation) were undertaken to obtain the actual fuel composition prior to the calculation protocol.

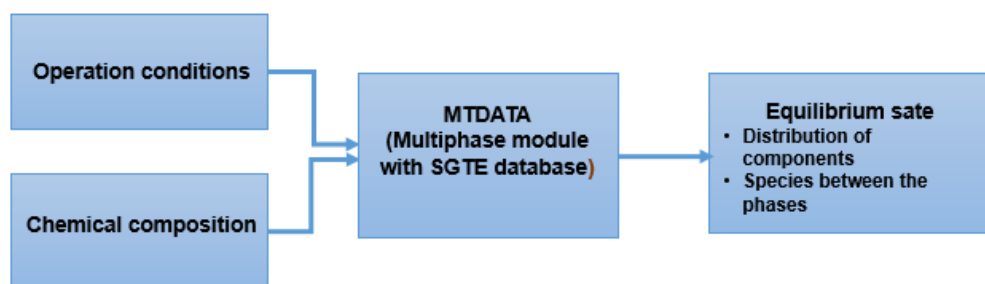


Figure 3-1. The workflow of multiphase module of MTDATA software.

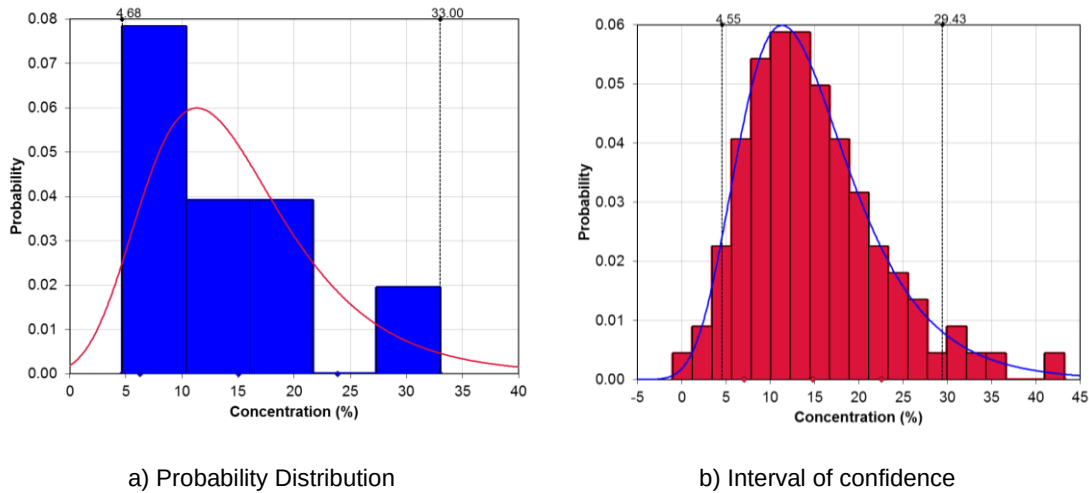
Therefore, the primary objectives of this chapter are:

- Data Selection and Pre-processing
- Mass Balance Calculation
- Calculation Protocol
- Models Application

3.2 Data selection and pre-processing

Nine contaminated demolition wood samples and 83 willow wood samples were selected from PHYLLIS2 (ECN) database (Table 2-4) and from Energy Technologies Institute (ETI) database (Appendix B1), respectively, as they presented with complete composition data. The best fit probability distribution for

composition data was obtained through @Risk analysis simulation package (Ver.6.1, Palisade Corp. Ithaca, NY, USA). Figure 3-2 exhibits the statistical analysis of the moisture for the selected samples from PHYLLIS2; the statistical results of other compositions are given in Appendices B2 (ECN) and B3 (ETI). As can see, the significance level (p-value) confirms the statistical significance of each distribution.



Mean = 13.56 and $\pm$ Std. Dev = 8.80

Figure 3-2. Statistical analysis results of the moisture content.

3.3 Mass balance calculation

In this study, two typical reaction zones in gasification were modelled: Air/steam gasification reaction (ASR) and CO₂ gasification reaction (CR). Furthermore, the modelling structure of the pyrolysis was also considered.

Prior to implementing the models, mass balance calculation was conducted to specify fuel specifications and gasifying agents. First, the dried composition was converted to actual fuel composition in terms of moles per hour (ALAH.M.KHODIER, 2011). Table 3-1 shows the resulted actual fuel composition of the selected samples from PHYLLIS2, and Appendix B4 gives examples of the conversion procedure.

Table 3-1. Conversion of fuel composition to actual fuel composition.

Fuel Composition		Weight from @Risk Analysis Simulation	Actual Fuel Composition (ar Basis)	Actual Fuel Composition (Moles/h)
Component	Basis		Weight %	
Moisture (H ₂ O)	Ar	13.56%	13.56	-
Ash	Ar	2.93%	2.93	-
C	Dry	46.5%	40.19321	33.49434
H	Dry	5.72%	4.944196	64.58383
N	Dry	1.06%	0.916232	6.544516
O	Dry	39.4%	34.05618	32.6838
S	Dry	0.08%	0.06915	0.216093
Cl	Dry	556.49 mg/kg	0.048101	0.135497
Cu	Daf	12.552 mg/Kg	0.001048	0.00165
Ni	Daf	11.17mg/Kg	0.000933	0.001589
As	Daf	2.91 mg/Kg	0.000243	0.000324
Co	Daf	1.791 mg/Kg	0.00015	0.000254
Cr	Daf	31.04 mg/kg	0.002592	0.004985
Na	Daf	527.10 mg/Kg	0.044017	0.191376
Ca	Daf	3,022.66 mg/kg	0.252413	0.631033
Fe	Daf	506.13 mg/kg	0.042265	0.07569
B	Daf	7.38 mg/kg	0.000616	0.005701
Ti	Daf	441.84 mg/kg	0.036897	0.077093
Pb	Daf	257.09 mg/Kg	0.021469	0.010361

Afterwards, the biomass feed rate (BFR) was obtained via dividing the desired output power (Q) by the product of biomass lower heating value (LHV_{Bio}) and gasifier efficiency (Φ) (Basu, 2013), as follows:

$$BFR = \frac{Q}{LHV_{Bio} \Phi} \quad (3-1)$$

where,

$$LHV_{Bio} = HHV_{daf} - 20,300 \times H_{daf} - 2260 \times M_{daf}. \quad (3-2)$$

Here, HHV_{daf} denotes the higher heating value (kJ/kg) on a dry moisture-ash-free basis, whereas H_{daf} and M_{daf} are respectively the hydrogen and moisture mass fractions in the biomass. The HHV_{daf} in equation (3-2) can be defined as $HHV_{daf} = HHV_d((1 - M)/(1 - ASH - M))$, where M denotes the moisture fraction; ASH refers to the ash fraction in fuel (on a raw-fuel basis); and HHV_d (on a dry basis) can be calculated by

$$HHV_d = 0.3491C + 1.1783H + 0.1005S - 0.0151N - 0.1034O - 0.0211ASH, \quad (3-3)$$

where ASH represents the ash in the fuel on a dry basis.

Moreover, the calculation of gasification agents depends on the type of reaction such that the Air/steam gasification reaction requires Air with steam and CO₂ gasification reaction requires CO₂; whereas the pyrolysis process uses N₂ (Zellagui et al., 2016). The required oxygen for ASR and CR were estimated using equations (3-4) and (3-5), respectively, as follows (Basu, 2013):



Note that, the Air composition (under standard dry at atmospheric pressure) consists of 75.47% N₂, 23.2% O₂, 1.28 % Ar, and 0.046% CO. The selected steam to air ratio was 2:1 (Jiang et al., 2016), and the equivalence ratio was set in the range of 0.2 to 0.38 (Basu 2013;278). Eventually, the simulation scenarios, as reported in Table 3-2, were made of three subsets: a subset for ASR (ASR_{1...5}), a subset for CR (CR_{1...5}), and the other for pyrolysis (P_{1,2}). Each scenario was assigned different process parameters in order to get more insight into the behaviour of the interested elements.

Table 3-2. Process parameters for gasification and pyrolysis models.

Parameters	Gasification										Pyrolysis	
	Air/steam gasification					CO ₂ gasification					P ₁	P ₂
	ASR ₁	ASR ₂	ASR ₃	ASR ₄	ASR ₅	CR ₁	CR ₂	CR ₃	CR ₄	CR ₅		
Equivalence ratio	0.2	0.38	0.28	0.2	0.25	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Biomass rate (Kg/h)	3.59	3.28	1.23	0.97	4.76	3.59	3.28	1.23	0.97	4.76	3.59	3.59
Air rate (nm ³ /h)	0.72	1.26	0.34	0.19	1.19	0	0	0	0	0	0	0
steam rate (m ³ /h)	1.44	2.51	0.68	0.39	2.381	0	0	0	0	0	0	0
steam/Air	2:1	2:1	2:1	2:1	2:1	0	0	0	0	0	0	0
CO ₂ (m ³ /h)	0	0	0	0	0	1.19	1.09	0.41	0.32	1.56	0	0
CO ₂ /Biomass	0	0	0	0	0	1:3	1:3	1:3	1:3	1:3	0	0
N ₂ (m ³ /h)	0	0	0	0	0	0	0	0	0	0	1.19	1.19
N ₂ /Biomass	0	0	0	0	0	0	0	0	0	0	1:3	3:1

3.4 Calculation protocol

Thermodynamic equilibrium models of the Air/steam gasification (ASR) and CO₂ gasification (CR), and pyrolysis were implemented using multiphase module of MTDATA software (Ver. 5.10 NPL, UK) coupled with Scientific Group Thermodata Europe (SGTE) database. For each model, the calculations were conducted to predict elemental phase transformation and speciation formation under the given operation conditions as outlined in Table 3-3.

Table 3-3. Models simulation conditions.

Operation conditions	Gasification		Pyrolysis
	ASR	CR	
Temperatures (°C)	0-1800°C	0-1300°C	0-900°C
Pressure (atm)	1, 20, and 40	1, 20, and 40	1, 20, and 40

In all modelling, the undertaken major elements were Ar, C, H, N, Ca, S, Na, Cl and O, meanwhile the undertaken minor elements were grouped into two sets corresponding to the types of wood treatment (i.e., CCA and CCB preservatives) shown below.

- CCA-Group: As, Co, Cr, Cu, Ni, and Fe.
- CCB-Group: B, Cr, Cu, Ni, Pb, and Ti.

For models simulations, a primary search of SGTE database was performed to reveal the related species of the elements in each group to be used in the equilibrium calculations. The species that contain one or more components were selected. A complete list of the selected species is given in Table 3-4.

Table 3-4. The adopted elemental species in equilibrium calculations.

Metal(loid)	Solid species	Liquid species	Gaseous species
As	As, As ₂ Ca ₃ O ₈ , As ₂ Co ₃ O ₈ , AsCrO ₄ , As ₂ Cr ₃ O ₈ , AsCu ₃ , AsCu ₃ O ₄ , As ₂ Cu ₃ O ₈ , As ₂ Fe ₃ O ₈ , AsFeO ₄ , AsNa ₃ , AsNa ₃ O ₄ , AsNi, As ₂ Ni ₅ , As ₈ Ni ₁₁ , As ₂ Ni ₃ O ₈ , As ₂ O ₅ , AsS, As ₂ S ₂ , As ₂ S ₃	As ₄ S ₄ , AsCL ₃	As, As ₂ , As ₃ , As ₄ , AsCl ₃ , AsH, AsH ₂ , AsH ₃ , AsN, AsO, AsO ₂ , As ₄ O ₆ , As ₄ O ₇ , As ₄ O ₈ , As ₄ O ₉ , As ₄ O ₁₀ , AsS, As ₄ S ₄
B	B, B ₄ C, B ₆ Ca, B ₂ CaO ₄ , B ₂ Ca ₂ O ₅ , B ₂ Ca ₃ O ₆ , B ₄ CaO ₇ , BCr, BCr ₂ , B ₂ Cr, B ₃ Cr ₅ , B ₄ Cr, B ₄ Cr ₃ , B ₁₀ H ₁₄ , BH ₄ Na, BHO ₂ , BH ₃ O ₃ , B ₂ H ₄ O ₄ , B ₃ H ₃ O ₃ , BN, BNaO ₂ , B ₃ NaO ₅ , B ₄ Na ₂ O ₇ , B ₆ Na ₂ O ₁₀ , B ₈ Na ₂ O ₁₃ , BNi, BNi ₂ , BNi ₃ , B ₃ Ni ₄ , B ₂ O ₃ , B ₂ O ₄ Pb, B ₄ O ₇ Pb, B ₆ O ₁₀ Pb, B ₁₀ O ₁₇ Pb ₂ , B ₂ S ₃ , BTi, B ₂ Ti	B ₅ H ₉	B, B ₂ , BC, BC ₂ , B ₂ C, BCl, BCl ₂ , BCl ₃ , B ₂ Cl ₄ , BClH, BClH ₂ , BCl ₂ H, BClHO, BClH ₂ O ₂ , BCl ₂ HO, BClO, BCl ₂ O, B ₃ Cl ₃ O ₃ , BH, B ₂ H ₂ , BH ₃ , B ₂ H ₆ , B ₅ H ₉ , B ₁₀ H ₁₄ , BH ₆ N, B ₃ H ₆ N ₃ , BHO ₂ , BH ₂ O, BH ₂ O ₂ , BH ₃ O, BH ₃ O ₂ , BH ₃ O ₃ , B ₂ H ₄ O ₄ , B ₃ H ₃ O ₃ , B ₃ H ₃ O ₆ , BHS, BN, BNaO ₂ , BO, BO ₂ , B ₂ O, B ₂ O ₂ , B ₂ O ₃ , BS, BS ₂ , B ₂ S, B ₂ S ₂ , B ₂ S ₃ , BHO, BOH, BHO, HBO
Co	As ₂ Co ₃ O ₈ , CCoO ₃ , Cl ₂ Co, Co, CoCr ₂ O ₄ , CoFe ₂ O ₄ , CoH ₂ O ₂ , Co ₃ N, CoN ₂ O ₆ , CoO, Co ₃ O ₄ , CoO ₄ S, CoS, CoS ₂ , Co ₃ S ₄ , Co ₉ S ₈		ClCo, Cl ₂ Co, Cl ₃ Co, Cl ₄ Co ₂ , Co, Co ₂ , CoH, CoHO, CoH ₂ O ₂ , CoO, CoS
Cr	AsCrO ₄ , As ₂ Cr ₃ O ₈ , C ₂ Cr ₃ , C ₃ Cr ₇ , C ₆ Cr ₂₃ , C ₆ CrO ₆ , CaCrO ₃ , CaCr ₂ O ₄ , Cl ₂ Cr, Cl ₃ Cr, CoCr ₂ O ₄ , Cr, Cr ₂ FeO ₄ , CrN, Cr ₂ N, CrNa ₂ O ₄ , Cr ₂ Na ₂ O ₄ , Cr ₂ NiO ₄ , CrO ₂ , CrO ₃ , Cr ₂ O ₃ , Cr ₅ O ₁₂ , Cr ₈ O ₂₁ , Cr ₂ O ₁₂ S ₃ , CrS		ClCr, Cl ₂ Cr, Cl ₃ Cr, Cl ₄ Cr, Cl ₅ Cr, Cl ₆ Cr, ClCrO, ClCrO ₂ , Cl ₂ CrO, Cl ₂ CrO ₂ , Cl ₃ CrO, Cl ₄ CrO, Cr, Cr ₂ , CrH, CrHO, CrHO ₂ CrHO ₃ , CrH ₂ O ₂ , CrH ₂ O ₃ , CrH ₂ O ₄ , CrH ₃ O ₃ , CrH ₃ O ₄ , CrH ₄ O ₄ , CrH ₄ O ₅ , CrN, CrO, CrO ₂ , CrO ₃ , Cr ₂ O, Cr ₂ O ₂ , Cr ₂ O ₃ , CrS, CrS ₂
Cu	CCuN, CCuO ₃ , CaCu, CaCu ₅ , Ca ₂ Cu, CaCu ₂ O ₃ , Ca ₂ CuO ₃ , ClCu, Cl ₂ Cu, Cu, CuH ₂ O ₂ , CuH ₂ O ₅ S, CuH ₆ O ₇ S, CuH ₁₀ O ₉ S, CuO, Cu ₂ O, CuO ₄ S, Cu ₂ O ₄ S, Cu ₂ O ₅ S, CuS, Cu ₂ S		ClCu, Cl ₂ Cu, Cl ₂ Cu ₂ , Cl ₃ Cu ₃ , Cl ₄ Cu ₂ , Cl ₄ Cu ₄ , Cl ₅ Cu ₅ , Cu, Cu ₂ , CuH, CuHO, CuO, CuS, Cu ₂ S
Fe	AsFeO ₄ , As ₂ Fe ₃ O ₈ , CFe ₃ , CFeO ₃ , CaFe ₂ O ₄ , Ca ₂ Fe ₂ O ₅ , Cl ₂ Fe, Cl ₃ Fe, ClFeO, Cl ₂ FeO ₄ , Cr ₂ FeO ₄ , CuFeO ₂ , CuFe ₂ O ₄ , Cu ₂ Fe ₂ O ₄ , CuFeS ₂ , Cu ₅ FeS ₄ , Fe, FeHO ₂ , FeH ₂ O ₂ , FeH ₃ O ₃ , Fe ₂ N, Fe ₂ H ₂ O ₄ , Fe ₄ N, FeNaO ₂ , Fe ₂ NiO ₄ , FeO, FeO ₄ S		C ₅ FeO ₅ , ClFe, Cl ₂ Fe, Cl ₃ Fe, Cl ₄ Fe ₂ , Cl ₆ Fe ₂ , ClFeO, Fe, Fe ₂ , FeH, FeHO, FeHO ₂ , FeH ₂ O, FeO, FeO ₂ , FeS
Ni	AsNi, As ₂ Ni ₅ , As ₈ Ni ₁₁ , As ₂ Ni ₃ O ₈ , Fe ₂ NiO ₄ , BNi, BNi ₂ , BNi ₃ , B ₃ Ni ₄ , CNi ₃ , CNiO ₃ , Cl ₂ Ni, Cr ₂ NiO ₄ , HNiO ₂ , H ₂ NiO ₂ , NiO, NiO ₄ S, NiO ₃ Ti, NiS, NiS ₂ , Ni ₃ S ₂ , Ni ₃ S ₄ , Ni ₉ S ₈ , NiTi, NiTi ₂ , Ni ₃ Ti		C ₄ NiO ₄ , ClNi, Cl ₂ Ni, Cl ₃ Ni, Cl ₄ Ni ₂ , HNi, HNiO, H ₂ NiO ₂ , Ni, Ni ₂ , NiO, NiS
Pb	B ₂ O ₄ Pb, B ₄ O ₇ Pb, B ₆ O ₁₀ Pb, B ₁₀ O ₁₇ Pb ₂ , CO ₃ Pb, CO ₄ Pb ₂ , CaPb, Ca ₂ Pb, Cl ₂ O ₂ Pb ₃ , Cl ₂ O ₃ Pb ₄ , Cl ₂ Pb, N ₂ O ₆ Pb, OPb, O ₂ Pb, O ₃ Pb ₂ , O ₄ Pb ₃ , O ₄ PbS, O ₅ Pb ₂ S, O ₆ Pb ₃ S, O ₇ Pb ₄ S, O ₈ Pb ₅ S, O ₃ PbTi, Pb, PbS		ClPb, Cl ₂ Pb, Cl ₃ Pb, Cl ₄ Pb, HPb, OPb, O ₂ Pb, Pb, Pb ₂ , PbS, PbS ₂ , Pb ₂ S ₂
Ti	BTi, B ₂ Ti, CTi, CaO ₃ Ti, Ca ₃ O ₇ Ti ₂ , Ca ₄ O ₁₀ Ti ₃ , ClOTi, Cl ₂ Ti, Cl ₃ Ti, Cl ₄ Ti<CL ₄ Ti, H ₂ Ti, NTi, Na ₂ O ₃ Ti, Na ₂ O ₅ Ti ₂ , Na ₂ O ₇ Ti ₃ , NiO ₃ Ti, NiTi, NiTi ₂ , Ni ₃ Ti, O ₃ PbTi, O ₃ Ti ₂ , O ₅ Ti ₃ , O ₇ Ti ₄ , STi, S ₂ Ti, Ti		ClOTi, Cl ₂ OTi, CITi, Cl ₂ Ti, Cl ₃ Ti, Cl ₄ Ti, Cl ₆ Ti ₂ , NTi, OTi, O ₂ Ti, STi, S ₂ Ti, Ti, Ti ₂

3.5 Models application

The gasification and pyrolysis models were applied to provide description of the metal(loid)s behaviours expressed by two factors. The first, phase transformation threshold, is the temperature at which the solid/gaseous phase transition is taking

place. The second factor, dominant chemical species, encompasses elemental speciation with relatively highest concentrations range.

3.5.1 Gasification

The ASR and CR models were applied to describe the elemental phase transition and identify the released species under specified gasifying agents (Table 3-2) and operational conditions (Table 3-3). The total moles of the elements to be introduced to MTDATA were obtained based on the actual fuel composition in Table 3-1 and process parameters of the ASR and CR in Table 3-2. That is, for each gasification reaction, 10 data sets were derived, as presented in Appendices B5.1 and B5.2 corresponding to ASR and CR, respectively. As such, the equilibrium elemental partitioning profiles were investigated across 60 simulations, thereby covering and addressing the effects of operation conditions and reaction parameters.

Additional calculations were done to illustrate the opportunities for blending different woody biomass and their subsequent influences on the elemental behaviour during ASR₁ and CR₁, at temperature ranges of 0-1800°C and 0-1300°C, respectively, under standard atmospheric pressure. A mixture of feedstock composed of demolition WW (60%) and willow wood (40%) was used. The total moles of the elements to be fed to MTDATA are given in Appendices B5.3 and B5.4. In this case, six simulations were conducted.

3.5.2 Pyrolysis

In a fashion similar to ASR and CR, the structuring of pyrolysis model was based on the actual composition data in Table 3-1, process parameters of P_{1,2} in Table 3-2, and operation conditions of pyrolysis in Table 3-3. Appendix B6 shows the total moles of the elements to be fed to MTDATA. With this model, 12 simulations were performed.

3.6 Results and discussion

3.6.1 Gasification

3.6.1.1 Air/steam gasification

Initially, the modelling of ASR was carried out at temperature range of 0-1800°C. A primary observation on the volatility of the elements As, B, Cr, Cu, Co, Fe, Ni, Pb and Ti under standard atmospheric pressure indicates that all of them remained in the solid phase below 1050°C. Further, under given operation conditions, whatever the values of biomass rates and equivalence ratios, same results were observed with respect to the phase transformation and species formation. Another observation is that increased pressure leads to increase elemental phase transition temperature by 200-500°C. In order to give a more thorough details, the obtained results for each element will present and discuss separately as follows.

3.6.1.1.1 Arsenic (CCA-Group)

Under pressure 1 atm, the gaseous transformation of As starts at 1400°C and it is completely vaporized as As compounds at temperature $\geq 1700^\circ\text{C}$ Figure 3-3a). The distribution of As species across solid and gaseous phases is shown in Figure 3-3b and Table 3-5.

Table 3-5. Arsenic species.

Temp. °C	Solid species	Temp. °C	Gaseous species
0-800	AsNa ₃	1150-1800	As, As ₂ , AsH, AsH ₂
		1150-1500	AsH ₃
850-1650	As ₂ Ni ₅	1450-1800	As ₄ , AsN, AsO, AsS

As noted, at temperatures $\leq 1400^\circ\text{C}$, As is predicated as stable solid species AsNa₃ (100%) and As₂Ni₅ (99.99-99.15%) resulting from As-Na and As-Ni interactions, respectively. As the temperature increases from 1400°C to 1800°C, the mass percentage of As decreases rapidly in solid phase, and it reforms as new gaseous species predominately by interactions. Among them, the dominant ones are As₂ (1.90-46.00%), AsH (0.24-7.13%), and As (5-46.55%).

It is well-known that As is one of the most volatile metal(loid) element (Duan et al., 2017b; Froment et al., 2013; Liu et al., 2006b, 2006a). However, in this

modelling, the phase transformation of As was significantly improved. This is mainly attributed to the dominant species AsNa_3 and As_2Ni_5 , and their contain of Na and Ni, which participates to the retention of major amount of As in solid phase below 1400°C . It also noted that under pressures 20 and 40 atm, the phase transformation temperature increased by 250 and 300°C , respectively, as shown in Figure 3-3c.

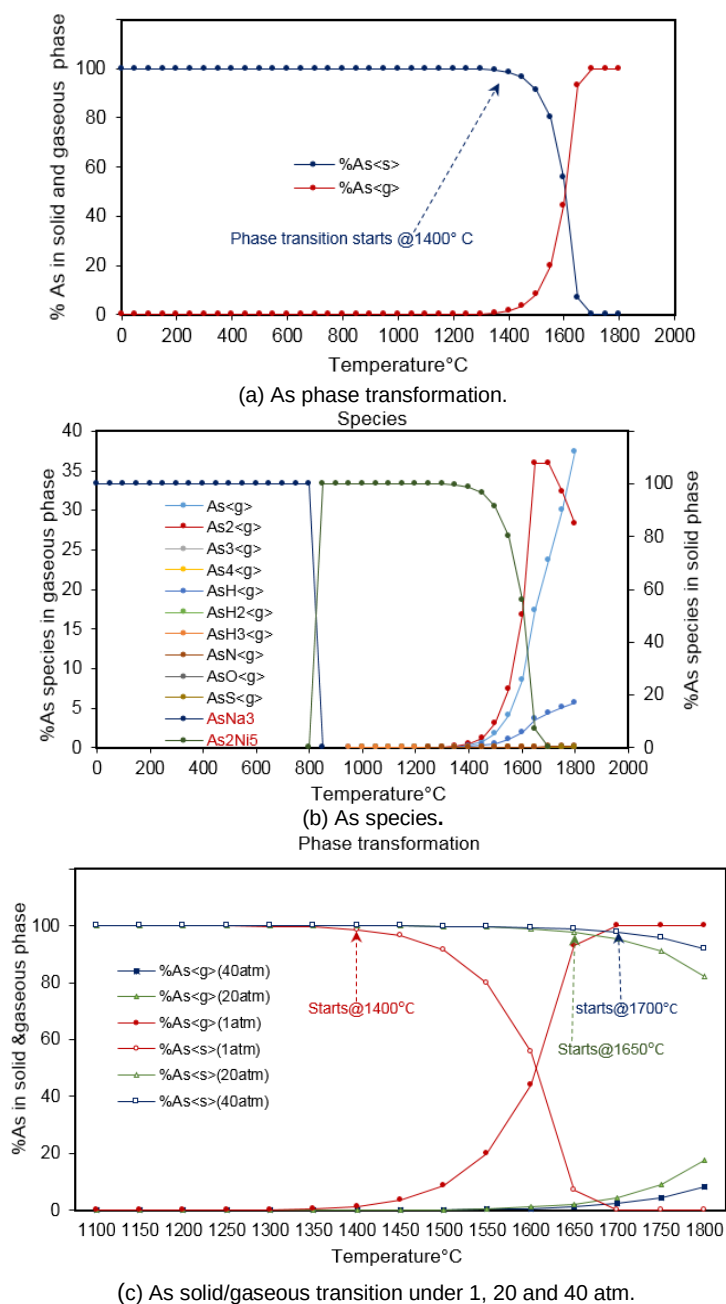


Figure 3-3. Phase transition and equilibrium speciation of As in CCA-Group.

3.6.1.1.2 Boron (CCB-Group)

Boron remains in solid phase at temperature range of 0-1800°C as shown in Figure 3-4a. This is due that the Ti and Ni-contained in the B dominant species, as depicted in Figure 3-4b and Table 3-6.

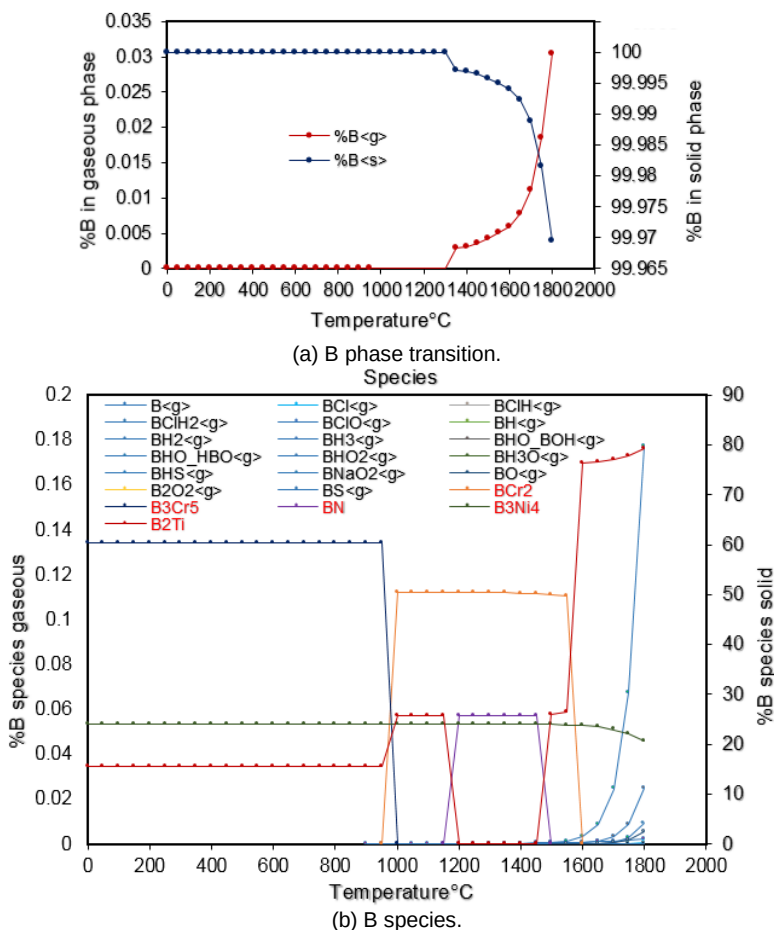


Figure 3-4. Phase transition and equilibrium speciation of B in CCB-Group.

Table 3-6. Boron species.

Temp. °C	Solid species	Temp. °C	Gaseous species
0-950	B ₃ Cr ₅	900-1800	BH ₃
		1300-1800	BHO-BHO
0-1800	B ₃ Ni ₄	1400-1800	BH ₂
		1500-1800	BCl,BClH ₂ ,BH,BNaO ₂ ,BO
0-1150-1500-1800	B ₂ Ti	1550-1800	B
		1600-1800	BHS
1000-1550	BCr ₂	1650-1800	BClH
		1700-1800	BClO
1200-1400	BN	1750-1800	BHO-BOH,BHO ₂ ,BH ₃ O,BS

Regarding pressure conditions, the results show that no gaseous species were generated under increased pressure. Also, at temperatures $\leq 900^\circ\text{C}$, B is

predicated as stable solid species B_3Cr_5 (60.45%), B_2Ti (15.58%), and B_3Ni_4 (23.97%) as result of the interactions B-Cr, B-Ti, and B-Ni, respectively. When the temperature increases from 900°C to 1450°C, the mass percentage of B in the solid specie B_3Cr_5 decreases rapidly, and it reforms as new solid species BCr_3 (50.32%-50.12%) and BN (25.63%-25.78%). Other studies (Froment et al., 2013; Reed, Dugwell and Kandiyoti, 2001a) reported that the presence of Ca in the system allows the formation of $Ca_3B_2O_6$ in the condensed phase at temperature range of 530-580°C. However, in this study, no Ca-containing B species were predicated because the high concertation of Cr, Ti, and Ni in waste wood preventing Ca to make efficient reaction with B.

3.6.1.1.3 Chromium (CCA and CCB-Group)

In both CCA and CCB groups, the phase transformation threshold of Cr is 1550°C as shown in Figure 3-5a. However, the Cr species in the solid phase are mostly different, but its gaseous phase species are identical as depicted in Figure 3-5b-c and Table 3-7.

Table 3-7. Chromium species.

CCA-Group				CCB-Group			
Temp. °C	Solid species	Temp. °C	Gaseous species	Temp. °C	Solid species	Temp. °C	Gaseous species
0-1800	C_3Cr_7	950-1300	Cr	0-950	B_3Cr_5	1000-1800	Cr
		1250-1300	CrCl			1250-1800	CrCl
		1250-1800	CrH			1300-1800	CrH
		1450-1800	Cr_2			1500-1800	Cr_2
		1500-1800	$CrCl_2$	100-1600	BCr_2	1550-1800	$CrCl_2$
		1600-1800	CrN			1600-1800	CrN
		1700-1800	CrHO,CrO			1700-1800	CrHO,CrO
		1750-1800	CrS			1750-1800	CrS
				1600-1800	C_3Cr_7		

As noted in in Figure 3-5b, at temperatures $\leq 1550^\circ\text{C}$, Cr remained in solid phase as C_3Cr_7 (100%). And, at temperatures between 1550°C and 1800°C, the mass percentage of C_3Cr_7 decreased from 100% to 67.34%, while at the same time it being released as elemental Cr (3.16-32.48%) and as a new set of gaseous species generated by Cr-Cl, Cr-H, Cr-N and Cr-O interactions; the total mass percentage of these gaseous species is less than 0.2%. In the similar manner, the equilibrium distribution of Cr in CCB group (Figure 3-5c) indicates that at temperatures $\leq 1550^\circ\text{C}$, Cr remained in solid phase as BCr_2 , B_3Cr_5 , and C_3Cr_7

(99.98%), and its gaseous phase speciation same as those released with CCA group. It also observed that a significant improvement in phase transformation temperatures of Cr comparing to those of the studies by (Froment et al., 2013) and (Jiang et al., 2016) which were 875 and 1200°C, respectively. Although these differences can be attributed to many aspects such as process parameters and type of feedstocks, the more important ones are the presence of different elements and their retention/release species; for instance, Cr₂O₃ was the unique Cr specie in solid phase in the study by (Froment et al., 2013).

Furthermore, as expected, the increased pressure leads to increase Cr phase transformation temperature by 250°C as demonstrated Figure 3-5d.

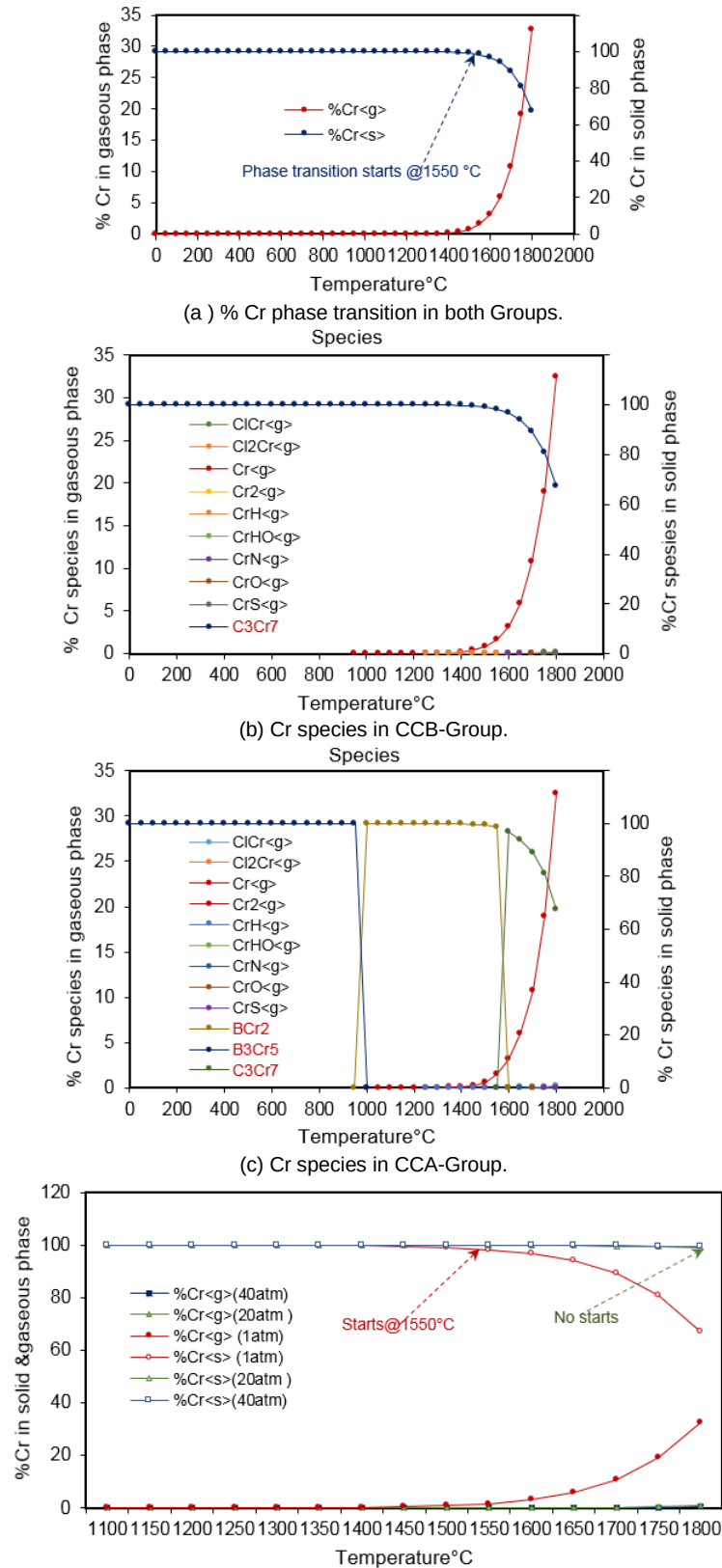
3.6.1.1.4 Copper (CCA and CCB-Group)

In both CCA and CCB groups, the phase transition temperature of Cu is 1350°C as reported in Figure 3-6a. Interestingly, the predictive calculations showed no differences in the formed species as shown in Figure 3-6b and Table 3-8.

Table 3-8. Copper species.

Temp. °C	Solid species	Temp. °C	Gaseous species
0-1400	CaCu	900-1800	CuH,Cu
1450-1600	Cu	1150-1800	Cu ₂ ,ClCu

As observed, at temperatures $\leq 1350^\circ\text{C}$, about 100% of Cu remained in solid phase as a dominant species CaCu. When the temperature increases from 1350°C to 1800°C, new gaseous species CuH (0.47-4.49%), Cu₂ (0.02-0.43%) and CuCl (5.5E-3-55.44E-2%) are released due to Cu-Cl and Cu-H interactions. At temperatures between 1450°C and 1600°C, Cu proportionally distributed as elemental between the gaseous phase (4.29-94.52%) and solid phase (88.84-33.57%). When the model operated under pressures of 20 and 40 atm, the phase transition temperatures of Cu increased by 300 and 350°C, respectively, as shown in Figure 3-6c. The obtained results showed improvement in terms of phase transition temperature comparing to other studies (Froment et al., 2013; Kilgallon, Simms and Oakey, 2002), since Ca significantly participates in the retention of Cu through the formation of Calcium-Copper species.



(d) Cr solid/gaseous transition under 1, 20 and 40 atm in both groups.

Figure 3-5. Phase transition and equilibrium composition of Cr.

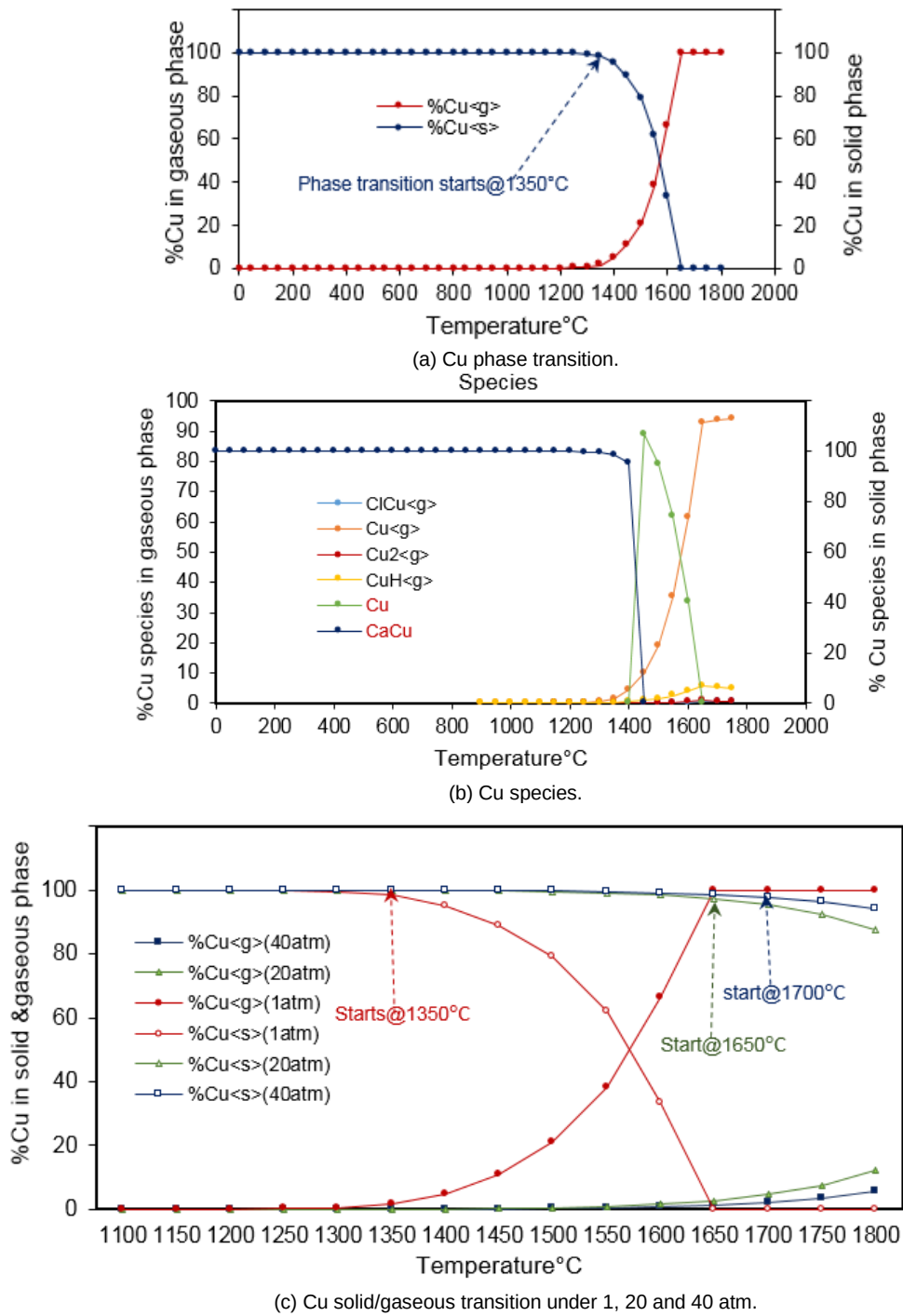


Figure 3-6. Phase transition and equilibrium composition of Cu.

3.6.1.1.5 Cobalt (CCA-Group)

The solid/gaseous phase transformation of Co starts at 1450°C as shown in Figure 3-7a. Further, the formed species are shown in Figure 3-7b and summarised in the Table 3-9.

Table 3-9. Cobalt species.

Temp. °C	Solid species	Temp. °C	Gaseous species
0-1750	Co	1000-1800	Co
		1250-1800	CoH
		1400-1800	ClCo
		1600-1800	Cl ₂ Co
		1700-1800	Co ₂

It is clear that, at temperatures $\leq 1450^{\circ}\text{C}$, Co predicated as stable solid species Co (99.98%). As the temperature increased from 1450°C to 1800°C, the mass percentage of Co decreases gradually in the solid phase, and it reforms as a set new gaseous species. Among them, the dominant ones are Co (1.90-98.80%), CoH (0.24-0.35%), CoCl (0.015-0.14%) and CoCl (0.0123-0.32%). The predictions show that the phase transformation temperature of Co increased by 350°C under increased pressure conditions as depicted in Figure 3-7c.

3.6.1.1.6 Iron (CCA-Group)

Iron shows no phase transformation within the considered temperature range, as shown in Figure 3-8a. The dominant specie in solid phase is nearly pure element (Fe), and the amount of gaseous species are very small (Figure 3-8b). Both solid and gaseous species of Fe are listed in the Table 3-10. The results also indicate that no Fe gaseous species present at pressure conditions of 20 and 40 atm.

Table 3-10. Iron species.

Temp. °C	Solid species	Temp. °C	Gaseous species
0-1800	Fe	1000-1800	Fe
		1250-1800	FeH
		1350-1800	ClFe
		1500-1800	Cl ₂ Fe
		1550-1800	Fe ₂
		1800	FeS

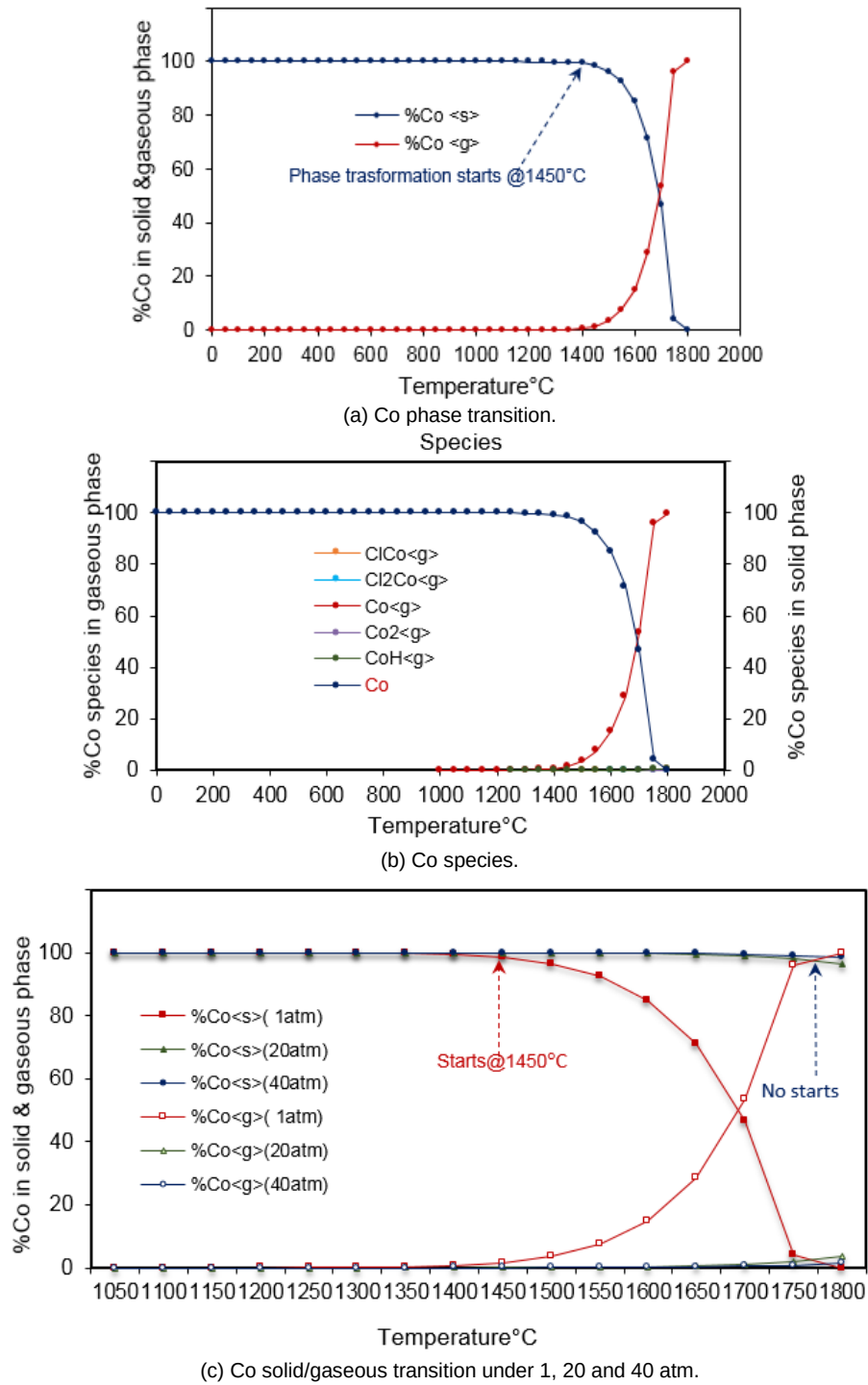
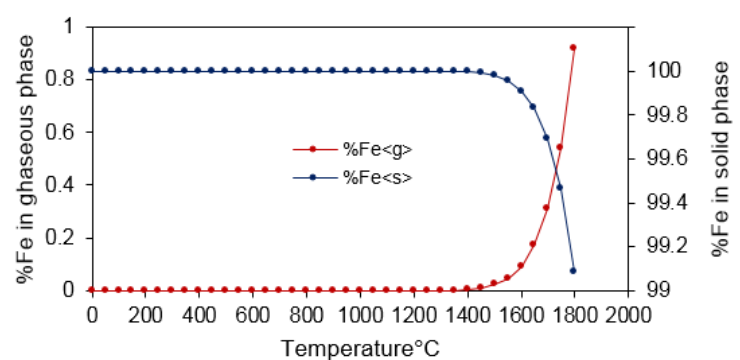
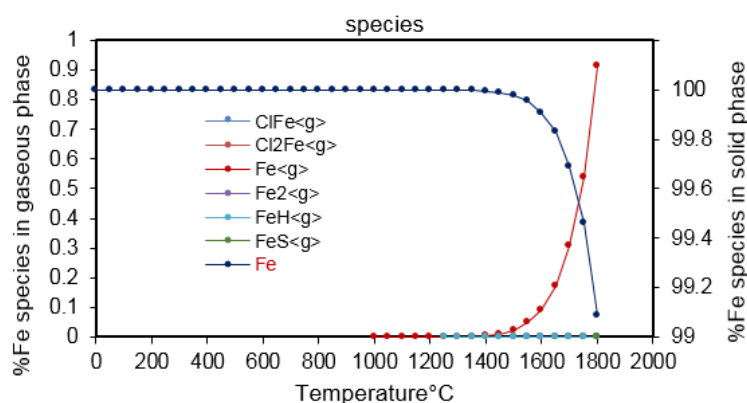


Figure 3-7. Phase transition and equilibrium composition of Co in CCA-Group.



(a) Fe phase transition.



(b) Fe species.

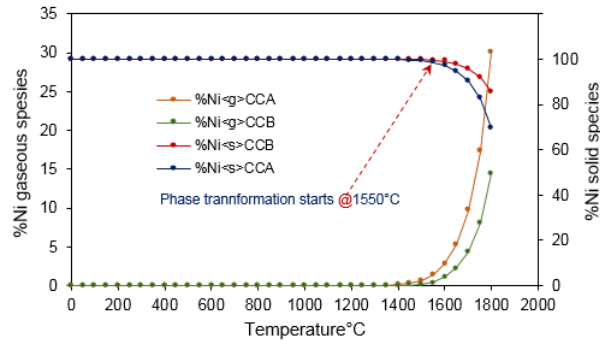
Figure 3-8. Phase transition and equilibrium composition of Fe in CCA-Group.

3.6.1.1.7 Nickel (CCA and CCB-Group)

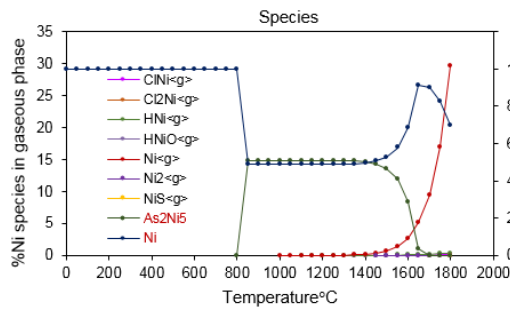
Figure 3-9a demonstrates the partitioning profile of Ni within CCA and CCB groups, where in the Ni phase transformation threshold is 1550°C. Additional results show that in both groups the Ni condensed phase species are dissimilar, but those of gaseous phase are similar as shown in Figure 3-9b-c and following Table 3-11. The results further demonstrated that under 20 and 40 atm, Ni remained in solid phase (Figure 3-9d).

Table 3-11. Nickel species.

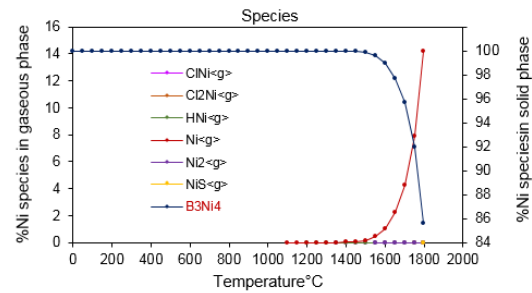
CCA-Group				CCB-Group			
Temp. °C	Solid species	Temp. °C	Gaseous species	Temp. °C	Solid species	Temp. °C	Gaseous species
0-1800	Ni	1000-1800	Ni	0-1800	B ₃ Ni	1100-1800	Ni
850-1650	As ₂ Ni ₅	1100-1800	HNi			1200-1800	HNi
		1350-1800	ClNi			1350-1800	ClNi
		1450-1800	Ni ₂			1500-1800	Ni ₂
		1700-1800	Cl ₂ Ni			1750-1800	Cl ₂ Ni
		1800	NiS			1800	NiS



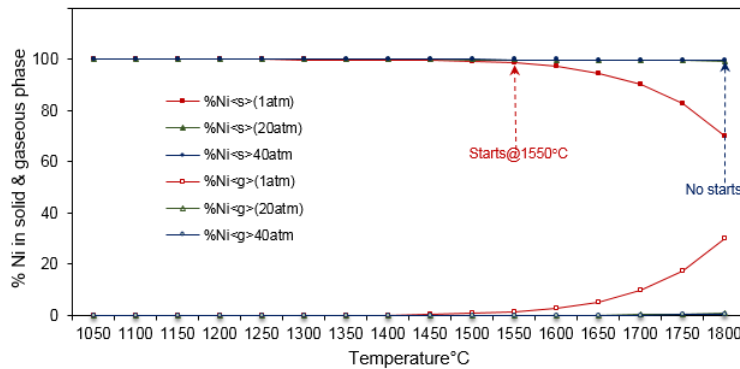
(a) Ni phase transition in CCA-Group and CCB-Group.



(b) Ni species in CCA-Group.



(c) Ni species in CCB-Group.



(d) Ni solid/gaseous transition under 1, 20 and 40 atm, in CCA-Group and CCB-Group.

Figure 3-9. Phase transition and equilibrium composition of Ni.

With CCA-group, at temperatures $\leq 1550^{\circ}\text{C}$, Ni predicated as stable solid species Ni (99.99-57.84%) and As_2Ni_5 (49.0108-40.79% between 850 - 1550°C). As the temperature increases from 1550°C to 1800°C , the mass percentage of Ni increases (ending up with 69.88%) and new gaseous species were released, including Ni (0.429-14.22%), Ni_2 (3.38-0.0014%), NiCl ($4.62\text{E}-08$ -5.29%), NiH ($1.112\text{E}-3$ -0.026%) and NiCl_2 (5-46.55%). At these same temperatures, Ni in

CCB-group, remained in solid phase as B_3Ni_4 (99.99-99.59%), and its gaseous species were identical to those predicted with CCA-group.

3.6.1.1.8 Lead (CCB-Group)

Lead predicted in solid phase as Ca_2Pb (99.99%) at temperatures less than 1300°C (Figure 3-10a). Above this temperature, Pb volatilizes as Pb-Cl, Pb-H, Pb, Pb_2 and Pb-S as shown in Figure 3-10b and Table 3-12.

Table 3-12. Lead species.

Temp. °C	Solid species	Temp. °C	Gaseous species
0-1300	Ca_2Pb	950-1800	Pb
		1150-1800	HPb
		1300-1800	ClPb
		1450-1088	Pb_2
		1700-1800	PbS

Note that, comparing to other studies (Froment et al., 2013; Jiang et al., 2016; Liu et al., 2006b) the phase transformation temperature of Pb in current study is significantly higher, mainly due to the formation of Ca-contained Pb species.

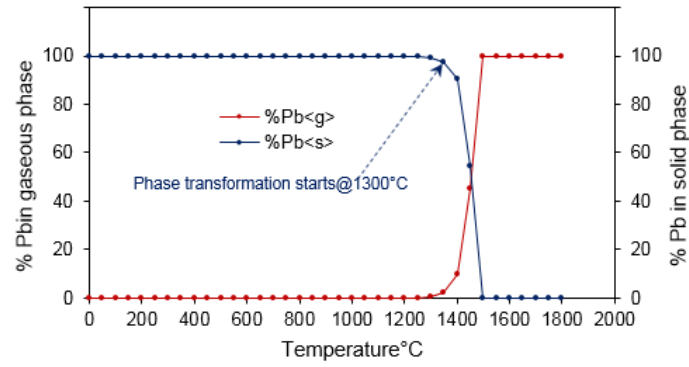
3.6.1.1.9 Titanium (CCB-Group)

At temperature range of 0-1800°C, the Ti content remained in solid phase (Figure 3-11a). The speciation distribution of Ti in the condensed and gaseous phases are illustrated in Figure 3-11b and listed in Table 3-13.

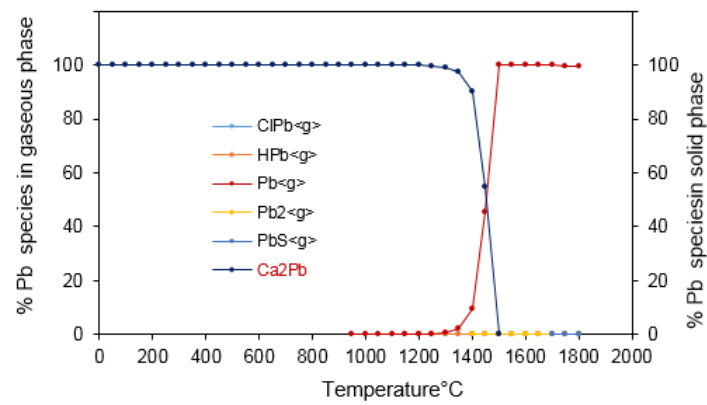
Table 3-13. Titanium species.

Temp. °C	Solid species	Temp. °C	Gaseous species
0-1150-1500-1800	B_2Ti	1500-1800	Ti
0-700-1650-1800	CTi	1600-1800	ClTi, Cl_2Ti
750-1600	NTi	1700	OTi

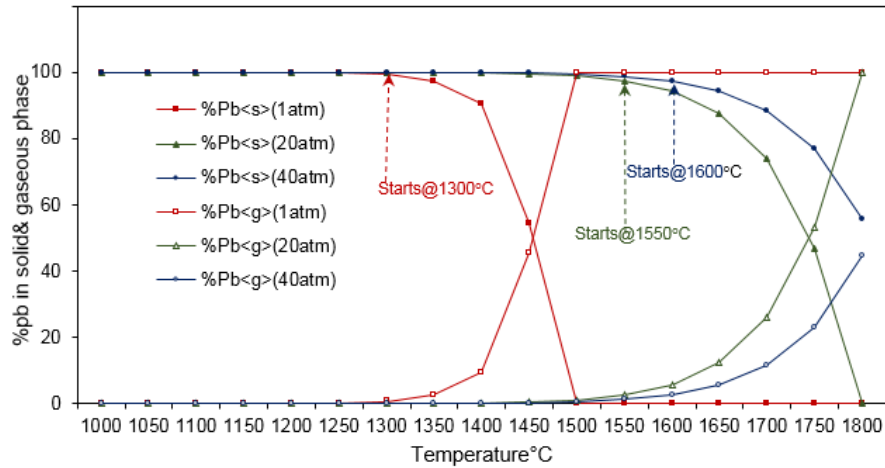
It is observed that the self-retention of Ti by B and C enriched in CCB-treated WW together with N-containing Ti specie made Ti to remain in condensed phase as B_2Ti (10-51.91%) between 0-1800°C, CTi (89.81-0%) between 0-750°C, and NTi (89.75-48.23%) between 750-1800°C. Also, the results show that at higher pressures no Ti gaseous species were released.



(a) Pb phase transition.



(b) Pb species.



(c) Pb solid/gaseous transition under 1, 20 and 40 atm.

Figure 3-10. Phase transition and equilibrium composition of Pb in CCB-Group.

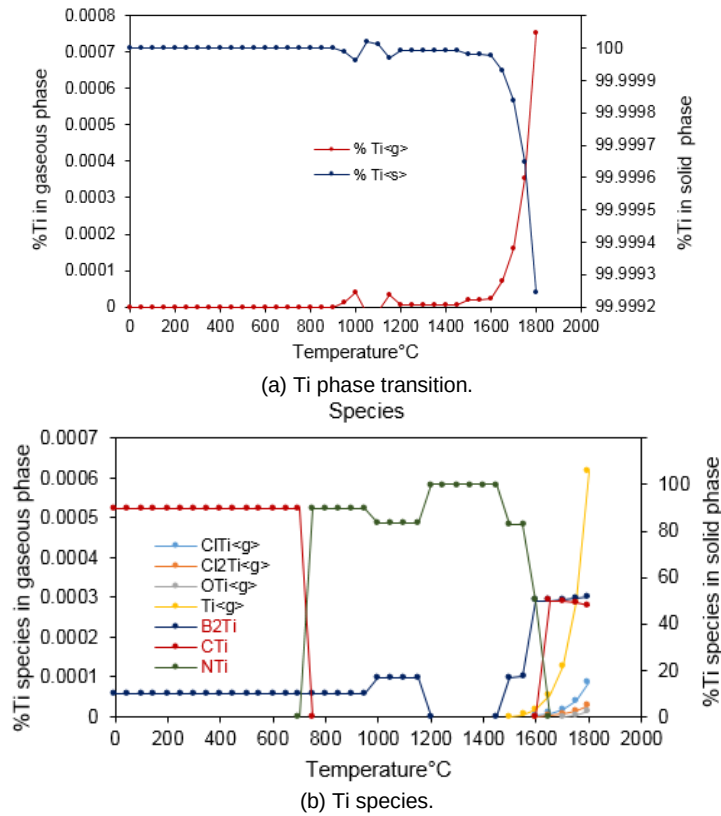


Figure 3-11. Phase transition and equilibrium composition of Ti in CCB-Group.

Lastly, Table 3-14 summarises solid/gaseous phase transformation of the CCA and CCB groups under the given operation conditions during ASR.

Table 3-14. Phase transformation temperatures under different pressure conditions during ASR.

Elements		Phase transformation temperature °C	Phase transformation temperature °C	Phase transformation temperature °C
		Solid → gaseous Under 1 atm (101325Pa)	Solid → gaseous under 20atm (2.027e+6Pa)	Solid → gaseous under 40atm (4.053e+6Pa)
CCA	Cr	1550-1800 (69.88% SP)	1800 (100% SP)	1800 (100% SP)
	Cu	1350-1650 (100% GP)	1650-1800 (87.6% SP)	1700-1800 (94.19%SP)
	As	1400-1700 (100% GP)	1650-1800 (82.2% SP)	1700-1800 (91.81%SP)
	Ni	1550-1800 (69.33% SP)	1800 (100% SP)	1800 (100% SP)
	Co	1450-1750 (100% GP)	1800 (100% SP)	1800 (100% SP)
	Fe	1800 (99.99% SP)	1800 (99.99% SP)	1800 (99.99% SP)
CCB	Cr	1550-1800 (68.12% SP)	1800 (100% SP)	1800 (100% SP)
	Cu	1350-1650 (100% GP)	1650-1800 (87.6% SP)	1700-1800 (94.19%SP)
	B	1800 (99.97% SP)	1800 (99.99% SP)	1800 (99.99% SP)
	Ni	1550-1800 (85.33% SP)	1800 (100% SP)	1800 (100% SP)
	Pb	1300-1500 (100% GP)	1500-1800 (100% GP)	1600-1800 (55.49%SP)
	Ti	1800 (99.99% SP)	1800 (99.99% SP)	1800 (99.99% SP)

SP (Mass percentage in solid phase) and GP (Mass percentage in gaseous phase)

3.6.1.2 CO₂ gasification

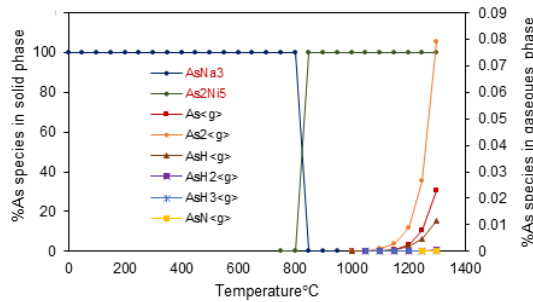
Within CR model, the simulations were carried out based upon the elemental total moles/h and operation conditions presented in Appendix B5.2 and Table 3-3, respectively. The obtained prediction results under atmospheric pressure indicate that the entire elements of CCA and CCB groups remained in solid phase below 1300°C, as depicted in Figure 3-12 (CCA-Group) and Figure 3-13 (CCB-Group). The influence of elevated pressure conditions on the elemental distribution profiles was evaluated at 20 and 40 atm, and the results show that no gaseous species were released under these pressure conditions. The predicated phase transformation and speciation formation are summarised in Table 3-15.

Table 3-15. Speciation of CCA and CCB groups during CR.

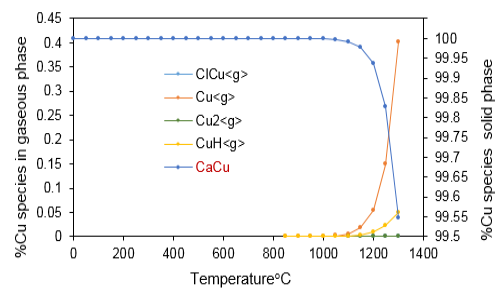
Elements		Species in solid phase and gaseous phase			
		Temperature°C	Solid species	Temperature°C	Gaseous species
CCA	Cr	0-1300	C ₃ Cr ₇	1000-1300	Cr
				1250-1300	CrCl
	Cu	0-1300	CaCu	1300	CrH
				900-1300	Cu, CuH
	As	0-800	AsNa ₃	1150-1300	Cu ₂ , ClCu
		850-1300	As ₂ Ni ₅	1150-1300	As, As ₂ , AsH, AsH ₂
	Ni	0-1300	Ni	1000-1300	AsH ₃
		850-1300	As ₂ Ni ₅	1100-1300	Ni
	Co	0-1300	Co	1000-1300	HNi
				1250-1300	Co
	Fe	0-1300	Fe	1000-1300	CoH
				1250-1300	Fe
CCB	Cr	0-850	B ₃ Cr ₅	1000-1300	Fe
		900-1300	BCr ₂	1250-1300	CrCl
	Cu	0-1300	CaCu	1300	CrH
		0-1300	B ₃ Ni ₄ , B ₂ Ti	900-1300	CuH, Cu
	B	0-850	B ₃ Cr ₅	1150-1300	Cu ₂ , ClCu
		900-1300	BCr ₂	900-1300	BH ₃
	Ni	0-1300	B ₃ Ni	1050-1300	Ni
				1200-1300	HNi
	Pb	0-1300	Ca ₂ Pb	950-1300	Pb
				1150-1300	HPb
	Ti	0-1300	B ₂ Ti, CTi		
		0-1300	NTi		

Table 3-16 shows a comparison of the solid species and their condensation temperatures of the metal(loid)s As, B, Cu, Cr, Co, Fe, Ni, and Pb predicated in this study against the results predicated by (Froment et al., 2013; Liu et al.,

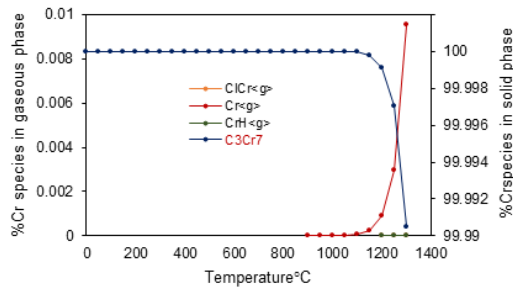
2006b; Reed, Dugwell and Kandiyoti, 2001a) at temperatures less than 1300°C. It is obvious that there are discrepancies in the results for the most elements. Possible reasons for these discrepancies may attribute to the considered feedstocks, elemental concentrations, and models parameters. Nevertheless, the As results in line to some degree with the findings of the study by (Reed, Dugwell and Kandiyoti, 2001a), in which As was speciated into As_2Ni_5 .



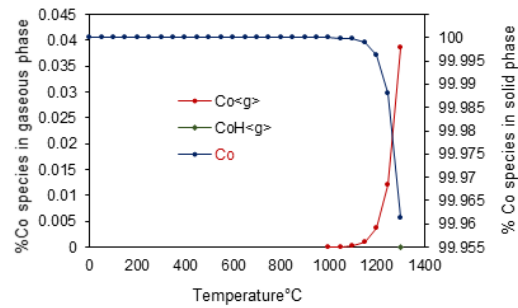
(a) As species.



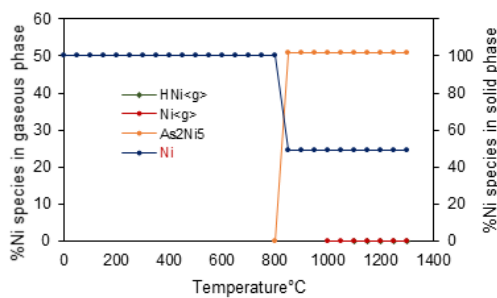
(b) Cu species.



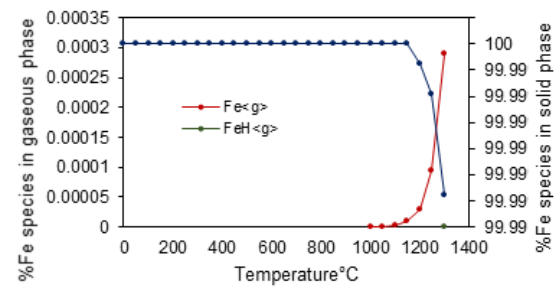
(c) Cr species.



(d) Co species.

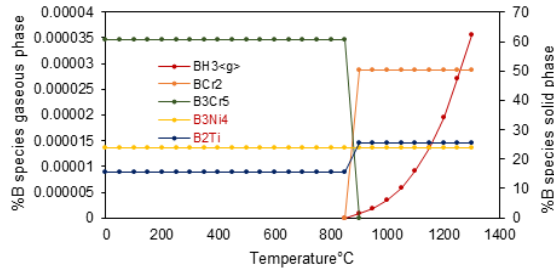


(e) Ni species.

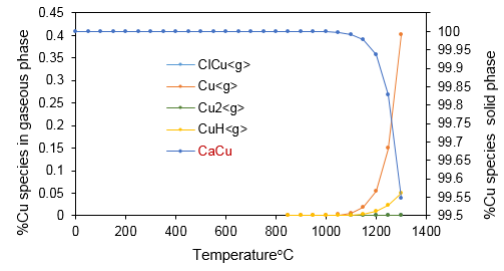


(f) Fe species.

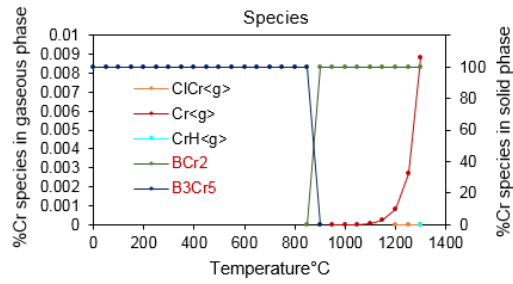
Figure 3-12. Speciation of CCA group during CO_2 gasification (CR).



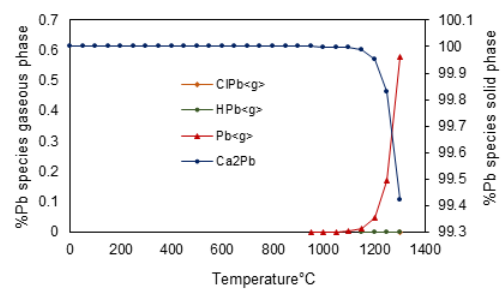
(a) B species.



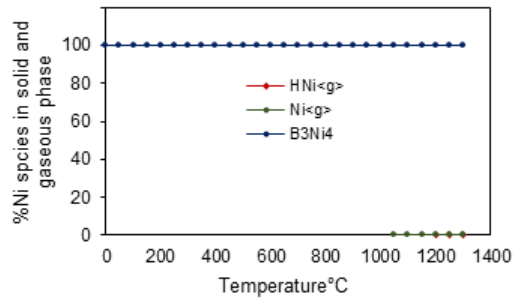
(b) Cu species.



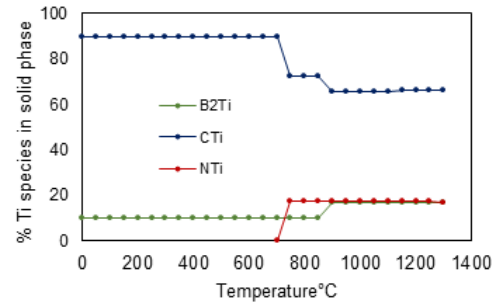
(c) Cr species.



(d) Pb species.



(e) Ni species.



(f) Ti species.

Figure 3-13. Speciation of CCB group during CO₂ gasification (CR).

Table 3-16. Comparison of the resulted solid species and their condensation temperatures with those of other studies.

Elements	Current study		Previous studies		
	Species	Temp. °C	Species	Temp. °C	Reference
As	AsNa ₃	800	Cu ₃ As	1050	(Froment et al., 2013)
			As ₂ S ₂	250	(Kontinen et al. 2013)
			As ₂ S ₂	650	(Kontinen et al. 2013)
	As ₂ Ni ₅	850-1300	K ₃ AsO ₄	≅ 530	(Liu et al., 2006b)
			As ₂ S ₂	250	(Reed, Dugwell and Kandiyoti, 2001a)
			As ₂ Ni ₅	1027	(Reed, Dugwell and Kandiyoti, 2001a)
B	B ₃ Ni ₄	1300	B ₂ Ca ₃ O ₆	530-580	(Reed, Dugwell and Kandiyoti, 2001a)
	B ₂ Ti	1300	B ₂ Ca ₃ O ₆	925	(Froment et al., 2013)
	B ₃ Cr ₅	850	KBO ₂	725	(Froment et al., 2013)
	BCr ₂	900-1300	HBO ₂	75	(Froment et al., 2013)
Cu	CaCu	1300	Cu ₂ S	827-1027	(Reed, Dugwell and Kandiyoti, 2001a)
			Cu		(Froment et al., 2013)
			Cu ₃ As	1050	(Kontinen et al. 2013)
			Cu ₂ S	650-850	(Kontinen et al. 2013)
Cr	C ₃ Cr ₇	1300	Cr ₂ O ₃	1000	(Liu et al., 2006b)
	BCr ₂	900-1300	MgO, Cr ₂ O ₃	1275	(Froment et al., 2013)
			Na ₂ O, Cr ₂ O ₃	875	(Froment et al., 2013)
			FeCr ₂ O ₄	650	(Kontinen et al. 2013)
			Na ₂ O, Cr ₂ O ₃	850	(Kontinen et al. 2013)
	B ₃ Cr ₅	850	CoO, Cr ₂ O ₃	650-850	(Kontinen et al. 2013)
Co	Co	1300	Co ₃ S ₄		(Reed, Dugwell and Kandiyoti, 2001a)
			Co ₈ S ₉	727	(Reed, Dugwell and Kandiyoti, 2001a)
			Co		(Reed, Dugwell and Kandiyoti, 2001a)
Fe	Fe	1300	Fe	1275	(Froment et al., 2013)
			Ca ₂ Fe ₂ O ₅	1150	
			FeCr ₂ O ₄	900	
			FeO	650	
			Fe ₃ O ₄	625	
Ni	Ni	1300	Ni ₃ S ₂		(Liu et al., 2006b)
	As ₂ Ni ₅	850-1300	NiS	800	
			NiS ₂		
			Ni	1100	(Kontinen et al. 2013)
	B ₃ Ni	1300	Ni ₃ S ₂	650	
			NiO, Cr ₂ O ₃	850	
Pb	Ca ₂ Pb	1300	Ni ₃ S ₂	850	(Kontinen et al. 2013)
			PbS	500-590	(Reed, Dugwell and Kandiyoti, 2001a)
			PbS	450	(Liu et al., 2006b)
			PbSe	475	(Froment et al., 2013)

3.6.1.3 Effect of blended woody biomass

Thermodynamic equilibrium calculations were also performed to assess the effect of blended woody biomass on the CCA elements behaviours and distributions during ASR₁ and CR₁ scenarios (Table 3-2), as a case study, since these elements are most likely present in relatively higher concentrations in each woody biomass. In this case, a mixture of feedstock comprises demolition WW (60%) and willow wood (40%) was considered. The models were simulated using the measured elemental data presented in Appendices B5.4 and B5.5 corresponding to ASR₁ and CR₁, respectively, and the operation conditions in Table 3-3.

3.6.1.3.1 Equilibrium calculations of CCA elements in willow wood

3.6.1.3.1.1 During ASR₁

- **Arsenic**

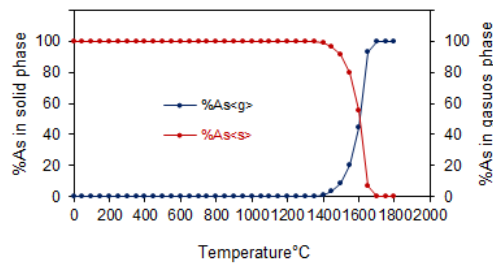
The solid-gaseous transformation of As starts at 1250°C, and completely transformed to gaseous at temperature $\geq 1400^\circ\text{C}$ (Figure 3-14a). In term of speciation, As partitioned in solid phase as dominant species AsNa₃ and As₂Ni₅, while in gaseous phase, the As species were As, As₂, As₃, AsH, AsH₂, AsH₃ and AsN as illustrated in Figure 3-14b.

- **Chromium**

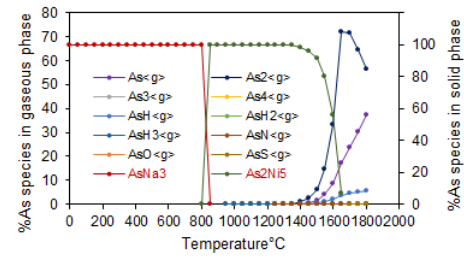
Chromium remained is solid phase as dominant specie C₃Cr₇ at temperatures less than 1350°C (Figure 3-14c). Above 1350 °C, Cr transformed to its gaseous species ClCr, Cl₂Cr, Cr, Cr₂CrH, CrHO, CrN, CrO, and CrS, as shown in Figure 3-14d.

- **Copper**

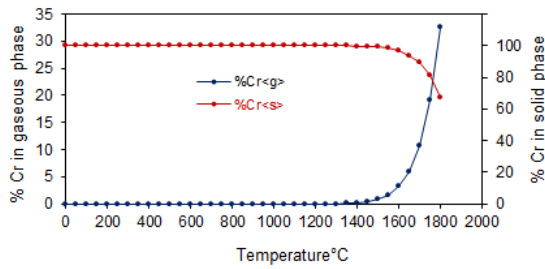
Similar to Cr, Cu remained in solid phase (Figure 3-14e) as dominant specie CaCu at temperatures less than 1350°C. At temperatures above 1350°C, Cu completely transformed into the gaseous species CuH, Cu, Cu₂, and CuCl, as shown in Figure 3-14e and f.



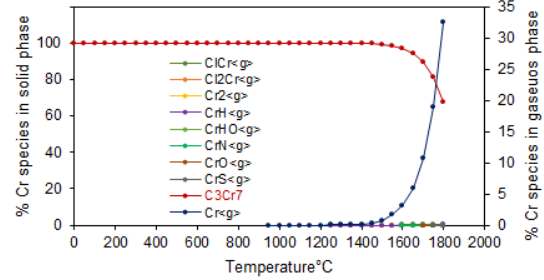
(a) % Arsenic phase transition.



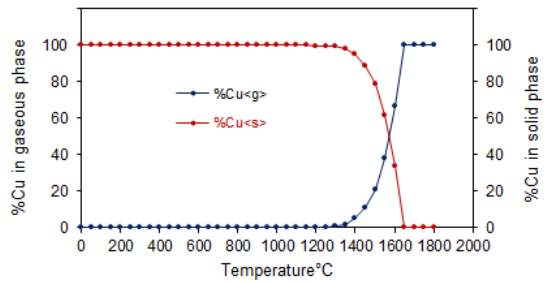
(b) % Arsenic species.



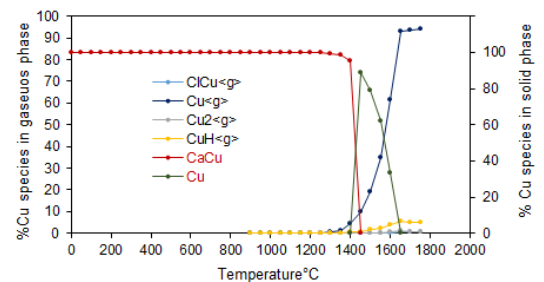
(c) % Chromium phase transition.



(d) % Chromium species.



(e) % Copper phase transition.



(f) % Copper species.

Figure 3-14. CCA elements phase transformation and equilibrium composition during ASR₁ (willow wood).

3.6.1.3.1.2 During CR₁

Under CR₁ process, the elements As, Cr, and Cu remained in solid phase at temperature less than 1100°C, as depicted in the Figure 3-15, and Table 3-17 summarized the speciation formation of these elements during CR₁. Arsenic primarily occurred in the form of AsNa₃ in solid phase at temperatures between 0 and $\sim \leq 800^\circ\text{C}$, then it reformed into dominant specie As₂Ni₅ at temperature between 800°C and 1300°C. Both Cu and Cr remained in solid phase as CaCu and C₃Cr₇, respectively, at the temperatures of the reaction.

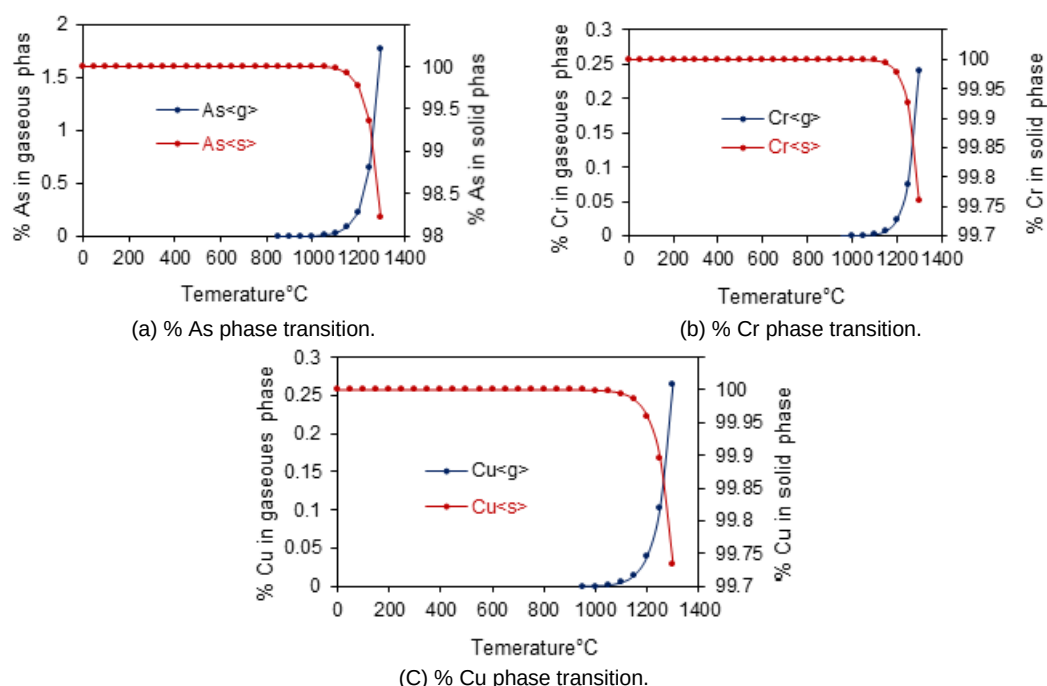


Figure 3-15. CCA elements phase transformation temperature during CR₁ (willow wood).

Table 3-17. Speciation of CCA elements during CR₁ (willow wood).

Elements	Temp. (°C)	Solid species	Temp. (°C)	Gaseous species
As	0-800	AsNa ₃	1100-1300	As, As ₂ , AsH, AsH ₂
	850-1300	As ₂ Ni ₅	1100-1300	AsH ₃
Cr	0-1300	C ₃ Cr ₇	1000-1300	Cr
			1250-1300	CrCl
			1300	CrH
Cu	0-1300	CaCu	900-1300	Cu, CuH
			1100-1300	Cu ₂ , ClCu

3.6.1.3.2 Effect of blends woody biomass on the behaviors of CCA elements

The simulation results of blended woody biomass during ASR₁ indicate that the threshold temperatures of As and Cr were improved by 150°C and 100°C, respectively, compared to those obtained when only willow wood was considered, as demonstrated in Figure 3-16a and c. This might be because of the increased concentrations of these elements can increase the stability of their solid species. However, Cu tended to behave quite similarly in both willow wood and blended woods, as shown in Figure 3-16e. This investigation reveals that blending WW with willow wood can be an effective approach towards retaining As and Cr elements.

Regarding CR₁ model, the predicated solid-gaseous phase transitions of As, Cr, and Cu are illustrated in Figure 3-16 (b, d, and f), and quite obviously each of these elements remained, about 100%, in solid phase.

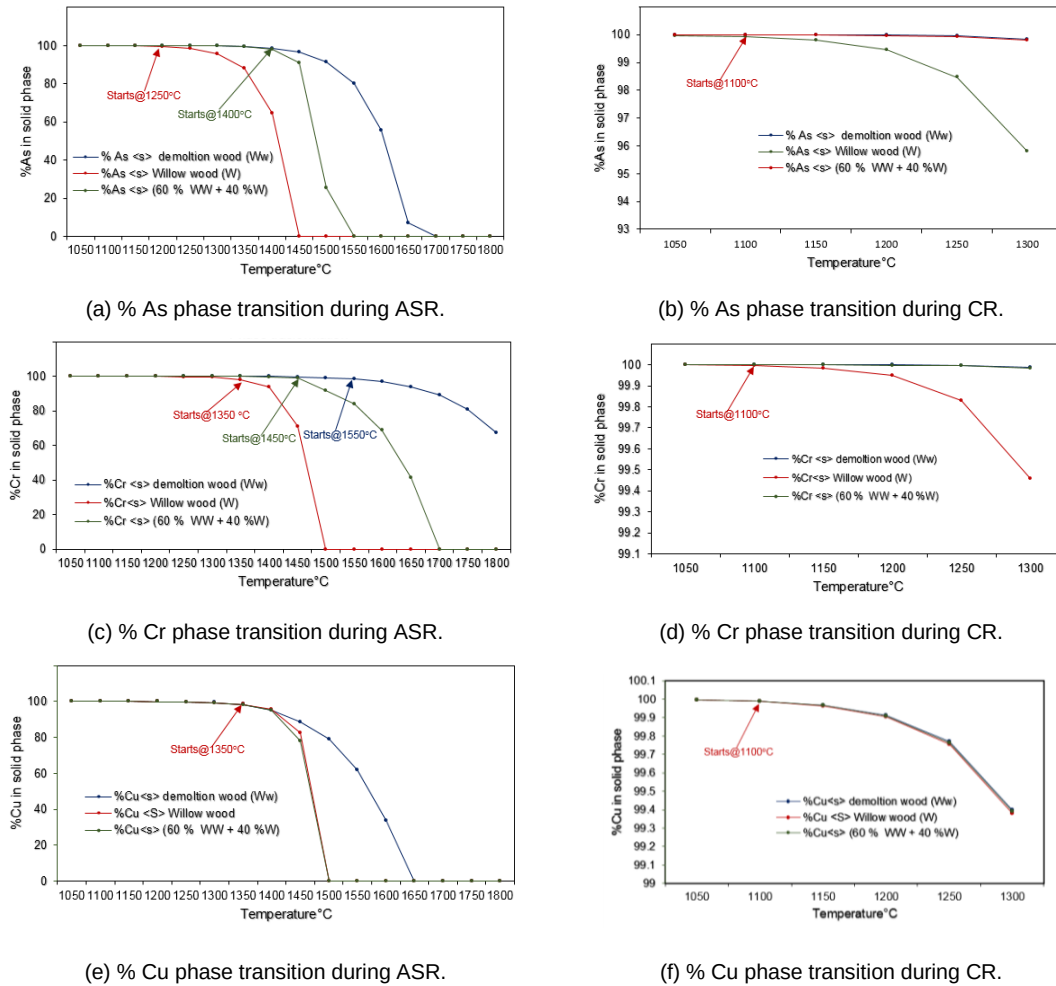


Figure 3-16. Phase transformation of CCA elements in demolition waste wood, willow wood, and blended wood (60% demolition and 40% willow).

3.6.2 Pyrolysis

With pyrolysis model, the simulations were made based on the measured elemental data in Appendix B6 and operation conditions in Table 3-3. The calculated equilibrium composition for the elements in CCA and CCB groups under atmospheric pressure reveals that all the elements in these groups remained, about 99.98%, in solid phase below 900 °C. The predicted speciation of each group is summarised in Table 3-18. Moreover, the results show that the

N₂/Biomass ratios and increased pressure conditions impose no effect on the elemental behaviour. In this sense, the predicted information exhibits that, in general, at temperature range of 0 to 900°C under atmospheric pressure, the results of pyrolysis, ASR, and CR models were similar.

Table 3-18. The main species formed of CCA group and CCB group under pyrolysis system.

Elements		Species in solid phase and gaseous phase			
		Temperature°C	Solid species	Temperature°C	Gaseous species
CCA	Cr	0-900	C ₃ Cr ₇	900	Cr
	Cu	0-900	CaCu	900	Cu, CuH
	As	0-800	AsNa ₃		
		850-900	As ₂ Ni ₅		
	Ni	0-900	Ni		
		850-900	As ₂ Ni ₅		
	Co	0-900	Co		
CCB	Fe	0-900	Fe		
	Cr	0-900	Cr	900	Cr
	Cu	0-900	CaCu	900	CuH, Cu
	B	0-900	BTi		
	Ni	0-900	NTi, NiTi ₂		
	Pb	0-900	Ca ₂ Pb	900	Pb
	Ti	0-900	BTi, CTi, NTi, NiTi ₂ , Ti		

3.7 Conclusions

In this chapter, thermodynamic modelling of gasification (ASR and CR) and pyrolysis were undertaken to assess the partitioning and speciation of the metal(loid) elements As, B, Cr, Co, Cu, Fe, Pb, Ni and Ti as classified into two groups (CCA and CCB) according the types of wood treatment. By taken into account different operations conditions and process parameters, the major conclusions of this chapter can be briefly summarised as below.

- Within CCA group, the simulation results from gasification (ASR) model show that, under 1 atm, the element Fe completely remained in solid phase. Two elements (Cr and Ni) start their solid-gaseous transition at temperature 1550°C. The gaseous transformation of Cu, As, and Co starts within temperature range from 1350 to 1450°C, and their volatilization temperatures in order of Co > As > Cu. As expected, the results also show that increased pressure conditions considerably increased the solid-gaseous transformation temperatures. That is, at pressures of 20 and 40 atm the elements Cr, Co, Fe, and Ni tended to remain in solid phase. Besides, under these pressure

conditions, the gaseous transformation of As and Cu occurs at 1650°C and 1700°C, respectively. It also observed that, in simulated gasification (CR) model, whatever the pressure conditions, all the elements in CCA group completely remained in condensed phase at temperature range of 0-1300°C.

- In the case of CCB elements, the predications of gasification (ASR) model demonstrate that, at a pressure of 1 atm, B and Ti entirely remained in solid phase. The elements Pb, Cu, Cr and Ni started to present in gaseous phase within temperature range from 1300 to 1550°C, and their volatilization temperatures varied in order of Ni,Cr > Cu > Pb. At a pressure of 20 atm, Ni and Cr remained in solid phase, while Cu and Pb, started to transform to their gaseous forms at temperatures 1650°C and 1500°C, respectively. With increasing pressure up to 40 atm, the solid/gaseous transformation of Cu and Pb occurred at temperatures 1700°C and 1600°C, respectively.
- The predicted information also clarified the behaviour of CCA elements in willow wood and blended woody biomass during gasification. The refined results of ASR model show that the solid/gaseous phase transition of As and Cr in willow wood decreased by around 11% and 16% compared to those predicted under same reaction when dealing with demolition WW. Besides that, results of blended woods revealed improvement in the phase transformation temperatures of As and Cr about 150°C and 100°C, respectively, compared to those obtained when gasifying willow wood.
- The predictive results regarding the pyrolysis of WW indicate that the transformation behaviours of the elements in CCA and CCB groups exhibited identical trend as the gasification ones at standard atmospheric pressure and temperatures between 0 and 900°C.

Taking together, the above outlined observations suggest that the predictive information can be useful for experimental works, particularly in specifying process operation conditions and parameters. The results also suggest that systematically blending WW with willow wood can play an important role in enhancing the retention of some metal(loid)s in solid phase.

Chapter 4 Interactions and Interferences

This chapter describes the modelling of gasification and pyrolysis processes in order to explore and evaluate the possible interactions and interferences among the CCA elements themselves and with Ca, Na, S, Cl, Fe, and Ni in different scenarios. A total of 162 simulations were performed covering various elemental concentrations.

Much of the work of this chapter has already presented (oral) and published in a journal (see list of publication in Appendix A).

4.1 Introduction

In the previous chapter, it was shown that the thermodynamic equilibrium modelling can be a useful tool for describing the equilibrium distributions of the targeted metal(loid)s. The knowledge gained from the modelling constitutes an important basis for clarifying the metal(loid) phase transformation and speciation formation during the gasification and pyrolysis of woody biomass. Many explanations for the fate of the key metal(loid) elements in woody biomass were then demonstrated and quantitatively estimated as a function of process conditions. However, the volatilization characteristic and occurrence mode of these elements can be influenced by possible interactions and interferences among them and other elements within the reaction courses of the thermal processing (Contreras, Arostegui and Armesto, 2009; Svoboda et al., 2017; Yan, Gauthier and Flamant, 2000). In this light, a particular attention must be given in order to explore and evaluate the mutual interactions and interferences between metal(loid)s and other elements present in woody biomass. As these two phenomena are often correlated to the elemental concentration and its inherent reactivity, their occurrences can be modelled by means of elemental contents of woody biomass.

In this chapter, thermodynamic equilibrium calculations were carried out to identify the possible interactions and interferences among the CCA-elements and Ca, Na, S, Cl, Fe, and Ni in contaminated WW during gasification and pyrolysis.

Moreover, the influences of types of wood (chip, beech, and pin) on the fate of CCA elements in terms of interactions and interferences were also investigated. Note here that, the interactions and interferences that lead to appreciable effects on elemental phase transformation temperature and species formation were ranked as significant.

The objectives of this chapter are:

- Influences of CCA elements content
- Influences of Ca, Na, S, Cl, Fe, and Ni content on CCA elements
- Assessing CCA elements reactivity
- Influence of type of wood

For setting up the models, the processes parameters of gasification (ASR₁ and CR₁) and pyrolysis (P₁) in Table 3-3 were used under atmospheric pressure and the operating temperatures are given in Table 3-4. Each modelling was undertaken for five major elements (Ar, C, N, O, and H) and ten minor elements (As, Cr, Cu, Co, Cl, Ca, Ni, S, Na, and Fe).

4.2 Calculations Methodology

To simulate the models, the species of minor elements are taken from Table 3-5. The calculations were based on the elementary composition of demolition WW in Table 3-2 and Table 4-1. Note that the mass ranges of minor elements, Table 4-1, were assumed according to the information provided by the ECN PHYLLIS2 database with respect to the contaminated woody biomass.

Table 4-1. Mass ranges of minor elements.

Element	Molar flow (mole/h)	Element	Molar flow (mole/h)	Element	Molar flow (mole/h)
As	0, 0.7, 1.4, 5	Ca	0, 100, 250, 500, 1000	Ni	0, 5, 10, 20
Cu	0, 4, 6, 8	Cl	0, 10, 50, 100	Na	0, 100, 200, 500
Cr	0, 5, 10, 21	Fe	0, 50, 100, 500	S	0, 0.05, 0.1, 0.2

Within each model, the simulations were made as function of elemental molar compositions according to the following considerations.

1. Influences of CCA elements content

In this case, the concentrations of Cu, Cr, and As were individually changed. The measured total moles of these elements are given in Appendix C.1, C.2 and C.3 corresponding to ASR_1 , CR_1 , and P_1 , respectively.

2. Influences of Ca, Na, S, Cl, Fe, and Ni content on CCA elements

Here, the levels of CCA elements were kept same as listed in Table 3-2, while the levels of Ca, Na, S, Cl, Fe and Ni were varied as demonstrated in Table 4-1. The measured total moles are given in Appendix C.4, C.5 and C.6, corresponding to ASR_1 , CR_1 , and P_1 , respectively.

3. Assessing CCA elements reactivity

In order to explore and assess the occurrences of CCA elements as results from their competing interactions, the minor elements was grouped into four clusters as follows:

- T1: As, Cu, Cr, Na, Ca, Fe, S, Cl and Ni.
- T2: As, Cu, Cr, S, and Cl.
- T3: As, Cu, and Cr.
- T4: All the minor elements are fed at molar flow of 0.25 mole/h.

In this respect, within T1 and T2 groups, it possible to examine the interactions between the CCA elements and the rest of minor elements, while group T3 is set to examine the competing interactions between the CCA elements themselves. Further, the inherent reactivity of each minor element is assessed in last group. The measured elemental molar compositions are given in Appendix C.7, C.8 and C.9 corresponding to ASR_1 , CR_1 , and P_1 , respectively.

4. Influence of type of wood

In order to determine the impact of concentrations of major elements (C, N, O, and H) on CCA elements, three types of wood (chip, beech, and pin) were selected for use in this case. The concentrations of major elements were drawn from the literature (Alauddin et al., 2010; Corte, Lacoste and Traverse, 1985; Parikh, Channiwala and Ghosal, 2005), while the concentrations of minor elements were taken from Table 3-2. The measured total moles are given in Appendix C.10, C.11 and C.12 corresponding to ASR₁, CR₁, and P₁, respectively.

4.3 Results and discussion

4.3.1 During Air/steam gasification (ASR₁)

4.3.1.1 Influences CCA elements contents

The simulation results show that the CCA elements contents exhibit almost no influence on their phase transformation temperatures, but only concentration shifts are observed as shown in Figure 4-1a, b, and c. Nevertheless, an exception is that when As concentration is relatively high (5 mole/h), its solid-gaseous transformation temperature decreased by 400°C because Ni contained becomes less than the limit to interact with As and hence capture 100% of As. Additionally, As₂Ni₅ (solid) and AsN (gaseous) are the dominant species of As.

4.3.1.2 Influences of Ca, Na, S, Cl, Fe, and Ni content on CCA element

An illustration of the occurred interactions and interferences between CCA-element and individual presence/absence of each of the elements Ca, Na, S, Cl, Fe and Ni are displayed in Figure 4-2.

4.3.1.2.1 Copper

As shown in Figure 4-2, Cu interacts with Ca and Cl; however, all Cl-Cu interactions release only a single gaseous specie ClCu. The solid and gaseous species formed by Ca-Cu interactions are listed in Table 4-2. The analysis shows that the dominant species in solid phase are CaCu, CaCu & CaCu₅, and CaCu when Ca is present, respectively, at concentrations of 250, 500, and 1000 mole/h.

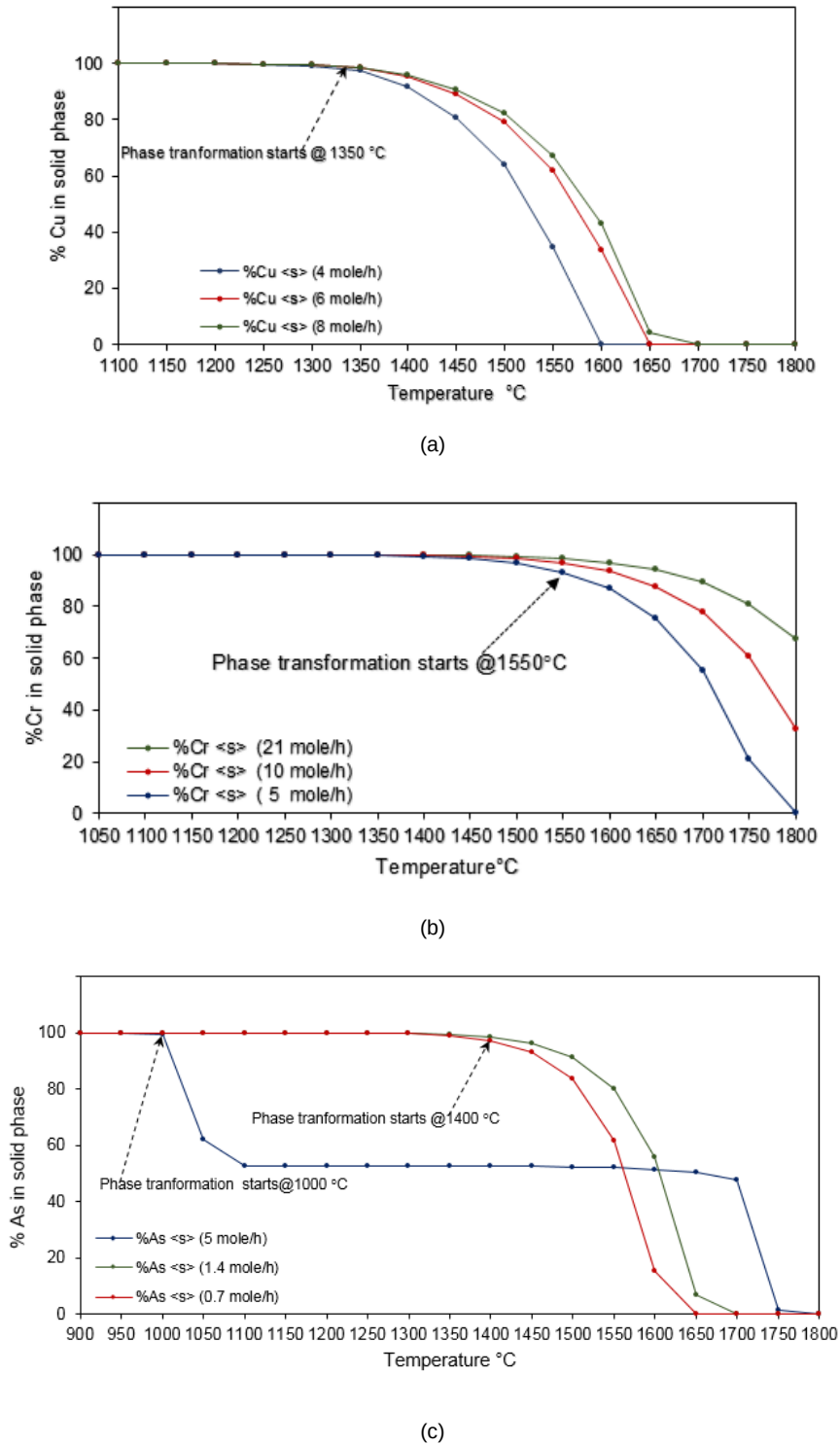


Figure 4-1. Resulting phase transformations of CCA elements by changing the concentrations of each element individually: (a) copper; (b) chromium; (c) arsenic.

On the other hand, the presence of Ca at low concentration would not be sufficient to interact with Cu; alternatively, it interacts with O and Cr, forming CaCr_2O_4 and CaO , respectively. Further, it is noted that the volatilization of Cu is

not affected by the various concentrations of Ca. Similarly, Cl-Cu interactions only form gaseous specie ClCu between 1400 and 1800°C.

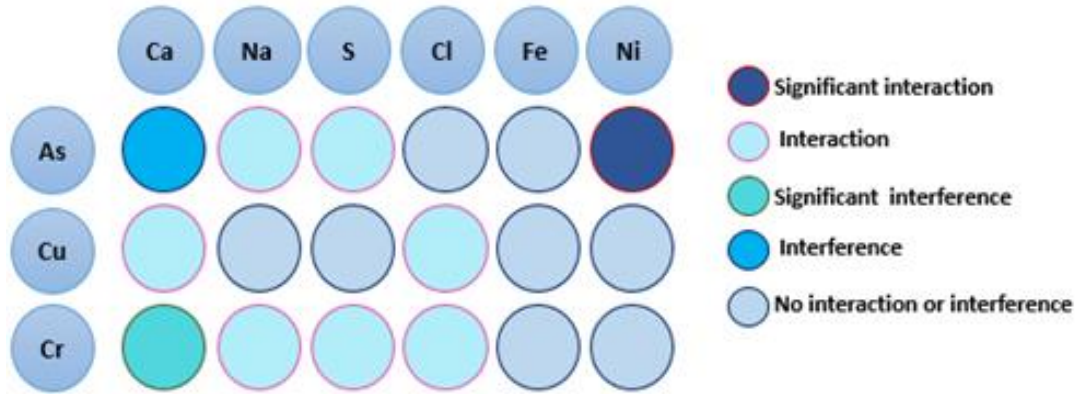


Figure 4-2. Interactions and interferences between CCA-element and each of Ca, Na, S, Cl, Fe and Ni.

Table 4-2. Calcium-copper interactions during ASR₁.

Ca (mole/h)	Species	Temperature range (°C)
100	Cu <s>	0-800
	Cu <s>, Cu <g>, CuH <g>	850- 950
	Cu <s>, ClCu <g>, Cu <g>, CuH <g>	1000-1800
250	CaCu <s>	0-800
	Cu <g>, CuH <g>, CaCu <s>	850-1150
	ClCu <g>, Cu <g>, Cu ₂ <g>, CuH <g>, CaCu <s>	1350-1800
500	CaCu <s>, CaCu ₅ <s>	0-800
	Cu , Cu <g>, CuH <g>	850- 950
	Cu <g>, CuH <g>, CaCu <s>	1000-1150
	ClCu <g>, Cu <g>, Cu ₂ <g>, CuH <g>, CaCu <s>	1250-1800
1000	CaCu <s>	0-800
	Cu <g>, CuH <g>, CaCu <s>	850- 950
	Cu <g>, CuH <g>, CaCu <s>	1000-1150
	ClCu <g>, Cu <g>, Cu ₂ <g>, CuH <g>, CaCu <s>	1250-1800

4.3.1.2.2 Chromium

The analysis reveals that Ca plays an important role on the Cr distribution across the solid and gaseous phases (Figure 4-3 and Table 4-3). That is, Na and Cr interact only when the concentration of Ca $\leq$ 100 mole/h, leading to form instable solid specie Cr₂Na₂O₄ between 1100 and 1550°C. CaCr₂O₄ (solid) is the most likely to be generated by Ca-Cr interaction when Ca is presence at 100 mole/h,

thereby about 100% of Cr remains in solid phase at temperatures $\leq 1550^{\circ}\text{C}$. As the Ca content increases (>100 mole/h), Ca-Cr interferences and C-Cr interactions take place simultaneously, forming C_2Cr_3 and C_3Cr_7 in solid phase at temperatures up to 1550°C . A most apparent observation in this case is the concentration shift in gaseous phase of Cr. Other interactions, specifically, S-Cr and Cl-Cr interactions exhibit no influences on Cr volatilization and solely yield gaseous species CrS and ClCr & Cl_2Cr , respectively.

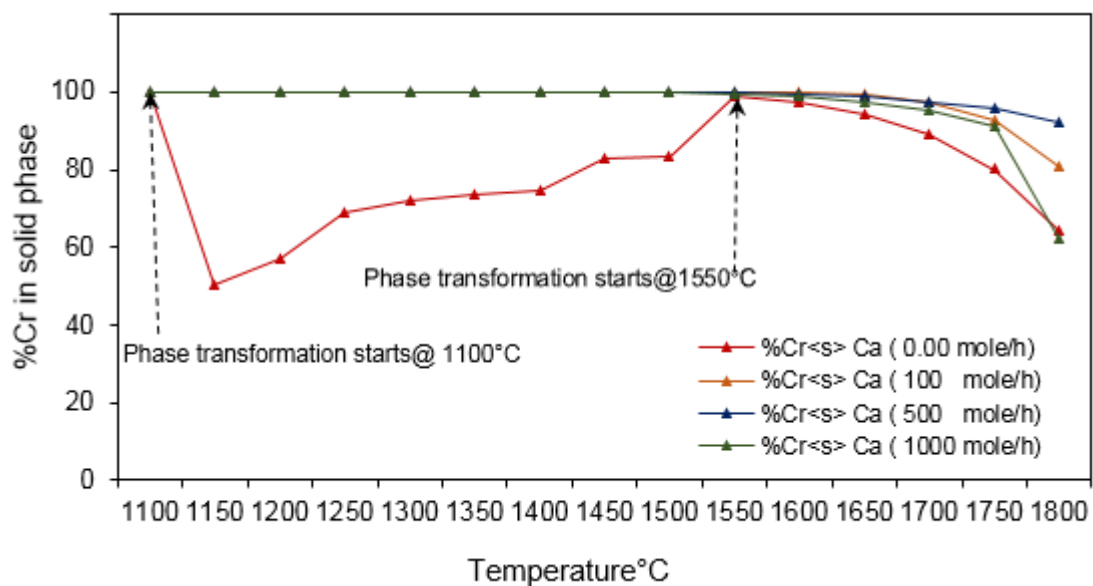


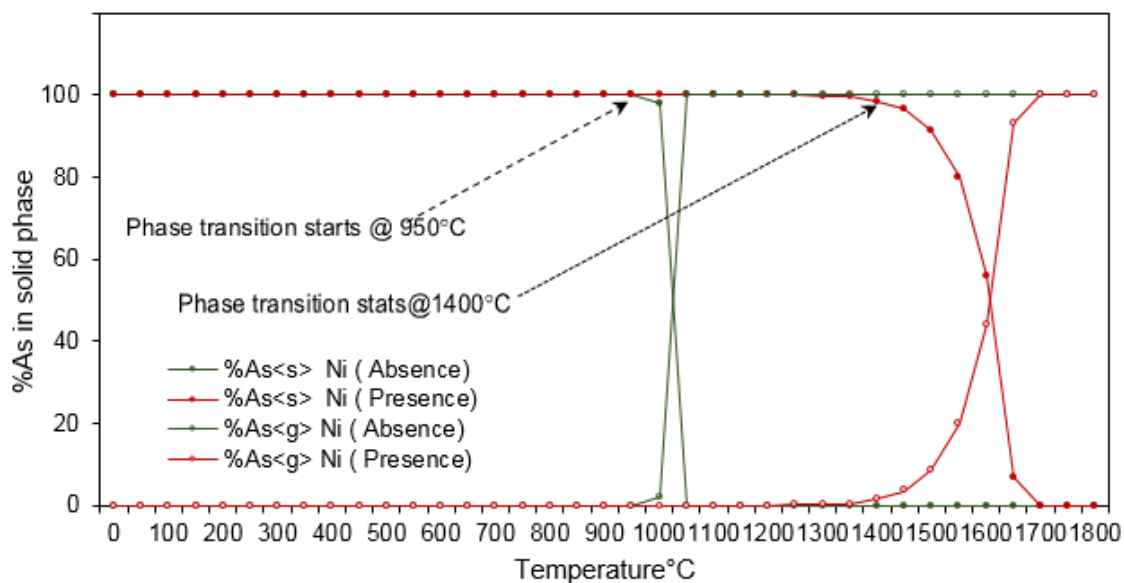
Figure 4-3. Effects of Ca on Cr phase formation.

4.3.1.2.3 Arsenic

When Ni content is present at various concentrations, all Ni-As interactions generate solid specie As_2Ni_5 , by which the phase transformation temperature of As (Figure 4-4) increases to about 450°C . In contrast, the absence of Ni leads to form As_2 (gaseous) and AsNa_3 (solid) as dominant species as shown in Figure 4-5. Similarly, Na-As interaction yields AsNa_3 . While the absence of Na shows no influence on the As phase formation, it enhances Ni to capture As, generating As_2Ni_5 (100-99.15%) up to 1400°C , as illustrated in Figure 4-6. Also, S tends to interact with As, yielding, at very low mass percentage, gaseous specie AsS between 1750°C and 1800°C .

Table 4-3. Chromium-calcium interactions.

Ca (mole/h)	Species	Temperature range (°C)
0	Cr ₂ Na ₂ O ₄ <s>	0-300
	C ₂ Cr ₃ <s>, Cr ₂ Na ₂ O ₄ <s>	350-400
	Cr ₂ Na ₂ O ₄ <s>	450-600
	Cr <g>, C ₂ Cr ₃ <s>, Cr ₂ Na ₂ O ₄ <s>	650-1200
	ClCr <g>, Cl ₂ Cr <g>, Cr <g>, CrHO <g>, CrS <g>, C ₂ Cr ₃ <s>, Cr <s>, C ₃ Cr ₇ <s>, C ₆ Cr ₂₃ <s>	1250-1800
100	C ₂ Cr ₃ <s>, CaCr ₂ O ₄ <s>, CrN <s>, Cr ₂ Na ₂ O ₄ <s>	0-300
	C ₂ Cr ₃ <s>, Cr ₂ Na ₂ O ₄ <s>	350-400
	C ₂ Cr ₃ <s>, CaCr ₂ O ₄ <s>	450-600
	ClCr <g>, Cr <g>, C ₂ Cr ₃ <s>, CaCr ₂ O ₄ <s>	650-1200
	ClCr <g>, Cl ₂ Cr <g>, Cr <g>, C ₂ Cr ₃ <s>	1250-1800
250-500	C ₂ Cr ₃ <s>	0-300
	C ₂ Cr ₃ <s>, C ₃ Cr ₇ <s>	350-600
	C ₃ Cr ₇ <s>	650-1200
	C ₂ Cr ₃ <s>, ClCr <g>, Cl ₂ Cr <g>, Cr <g>, CrH <g>, C ₃ Cr ₇ <s>, CrO <g>, CrS <g>, CrN <g>	1250-1800
10000	C ₃ Cr ₇ <s>	0-600
	Cr <g>, C ₃ Cr ₇ <s>	650-1200
	ClCr <g>, Cl ₂ Cr <g>, Cr <g>, CrH <g>, CrO <g>, CrS <g>, CrN <g>, C ₃ Cr ₇ <s>	1250-1800

**Figure 4-4.** Arsenic distribution according to the presence/absence of Ni.

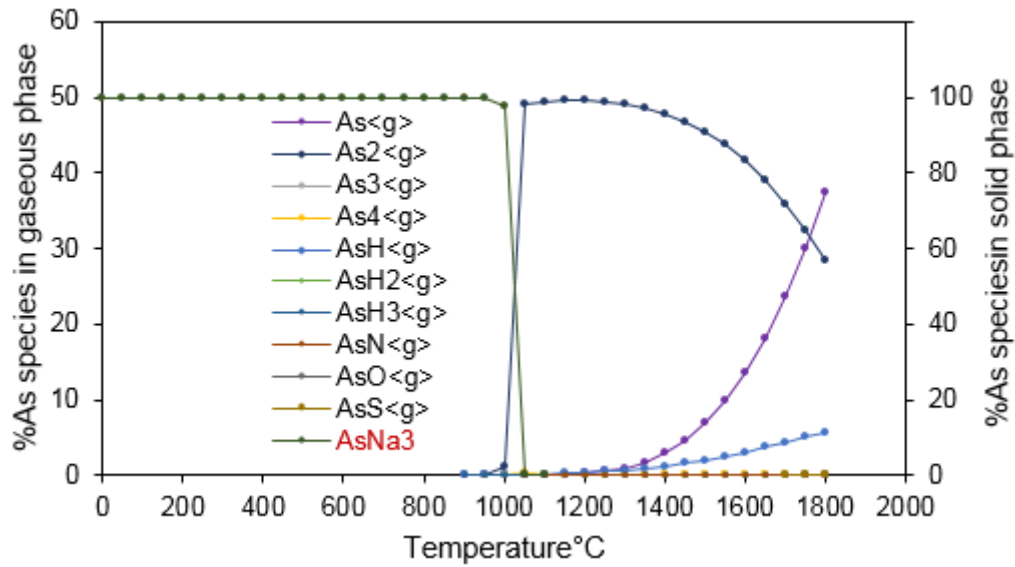


Figure 4-5. Arsenic speciation in the absence of Ni.

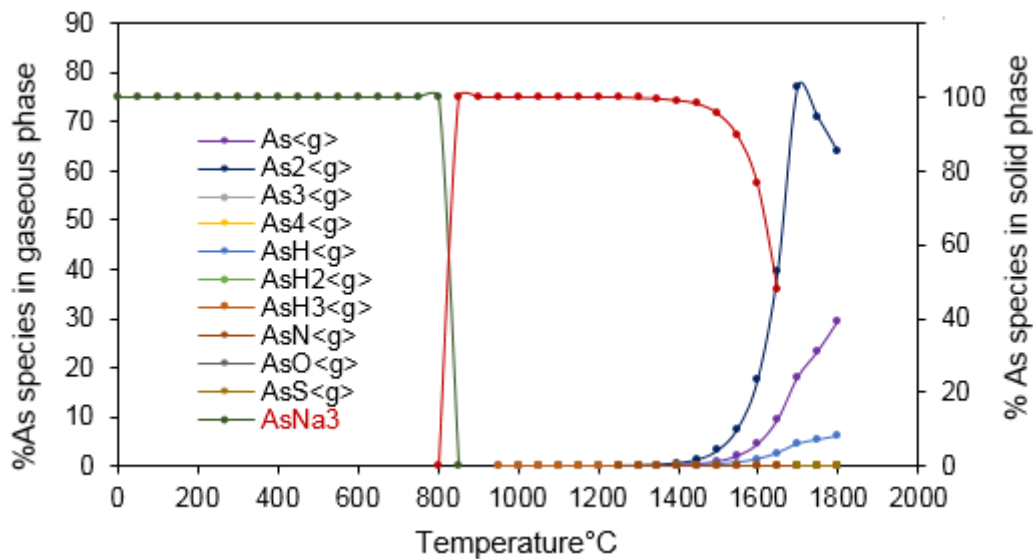


Figure 4-6. Arsenic speciation in the absence of Na.

4.3.1.3 Assessing CCA element reactivity

The results show that the presence of T1 group leads to higher phase transformation temperatures of As, Cu and Cr compared to those obtained with the presence of T2 and T3 groups. This might be because the types of equilibrium speciation, which are listed in Table 4-4. As observed, in the presence of T1, T2,

and T3, the major species of Cu in solid phase are CaCu/Cu, CuCl₂, and AsCu₃/Cu respectively. This illustrates the potential of Ca to interact with Cu, thereby increasing the latter phase transformation temperature. With respect to Cr, the presence of T1 and T2, lead to generate the dominant species (solid) C₃Cr₇ and Cl₃Cr/Cr₂O₃, respectively. Further, Cr₂O₃, CoCr₂O₄, Cr, C₂Cr₃, C₆Cr₂₃ and C₃Cr₇ are the dominant species (solid) of Cr associated with presence of T3. This indicates the possibility of C to interact with Cr, causing increases in the Cr phase transformation temperature, mainly due to the solid specie C₃Cr₇. Furthermore, with the presence of T1 and T3, the As dominant species (solid) are AsNa₃/As₂Ni₅ and AsCu₃, respectively. Whereas, the presence of T2 leads to form the specie AsS in solid phase below 50°C. Undoubtedly, the stable species of As arises from Ni-As and Na-As interactions.

Table 4-4. Main speciation and phase transformation temperatures of CCA elements during ASR₁.

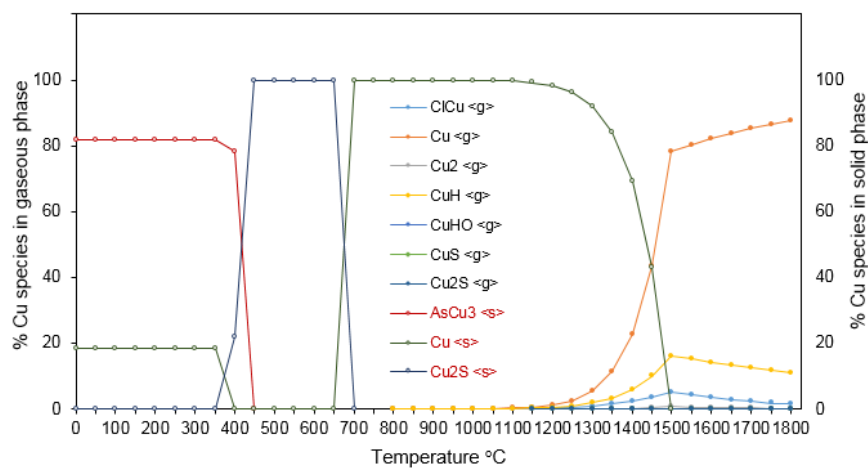
Element	Group	Phase transformation temperature 0-1800°C Solid → Gaseous Under 1atm (101325Pa)	Solid species	Gaseous species
Cu	T1	1350	CaCu, Cu	ClCu, Cu, Cu ₂ , CuH Cl ₂ Cu, ClCu, Cl ₂ Cu ₂ , Cl ₃ Cu ₃ ,
	T2	350	Cl ₂ Cu	Cl ₄ Cu ₂ , Cl ₄ Cu ₄ , Cl ₅ Cu ₅ , Cu
	T3	1300	AsCu ₃ , Cu	Cu, Cu ₂ , CuO, CuHO, CuH
Cr	T1	1550	C ₃ Cr ₇	ClCr, Cr, CrH ClCrCl ₂ , CrCl ₃ Cr, Cl ₄ Cr, ClCrO, ClCrO ₂ , Cl ₂ CrO, Cl ₃ CrO, Cr, CrH, CrHO, Cr HO ₂ , CrH ₂ O ₂ , CrO, CrO ₂ , CrS
	T2	750	Cl ₃ Cr, Cr ₂ O ₃	Cr, Cr ₂ , CrH, CrHO, CrHO ₂ , CrH ₂ O ₂ , CrN, Cr O, CrO ₂ , Cr ₂ O ₂ , Cr ₂ O ₃
	T3	600	Cr ₂ O ₃ , CoCr ₂ O ₄ , Cr, C ₂ Cr ₃ , C ₆ Cr ₂₃ , C ₃ Cr ₇	
As	T1	1400	AsNa ₃ , As ₂ Ni ₅	As, As ₂ , As ₃ , As ₄ , AsH, AsH ₃ , AsN, AsO, AsS
	T2	≅50	AsS	As, As ₂ As ₃ , As ₄ , AsCl ₃ , AsH, AsH ₃ , AsN, AsO, AsS
	T3	450	AsCu ₃	As, As ₂ , As ₃ , As ₄ , AsH, AsH ₂ , AsH ₃ , AsN, AsS, AsO

In addition, to assess the reactivity of CCA elements, all the minor elements were introduced to the model at same concentration (0.25 mole/h). In this case, the resulted speciation of CCA elements are demonstrated in Figure 4-7a, b, and c. As can see in Figure 4-7a, the behavior of Cu between 0 and 700°C indicates that Cu interacts favorably with As and S, forming the solid species AsCu_3 (81.89-78.24%) and Cu_2S (100%), respectively. At temperatures above 700°C, Cu is redistributed as elemental and a set of gaseous species, and its phase transformation temperature becomes 1200°C, which is less than about 11% of that obtained with equilibrium composition (Figure 3-5b). The predictive calculations, as shown in Figure 4-7b, originate the Cr solid species CoCr_2O_4 (100% between 0-300°C), Cr_2FeO_4 (100% between 350 and 500°C) and CaCr_2O_4 (100% between 550-1450°C) to the Co-O-Cr, Fe-O-Cr and Ca-O-Cr interactions, respectively. Figure 4-7c shows As species formation. Intuitively, AsCu_3 (27.27% between 0-400°C) and $\text{As}_8\text{Ni}_{11}$ (72.73% between 0 -800°C) are the most probably solid species from Cu-As and Ni-As interactions, respectively.

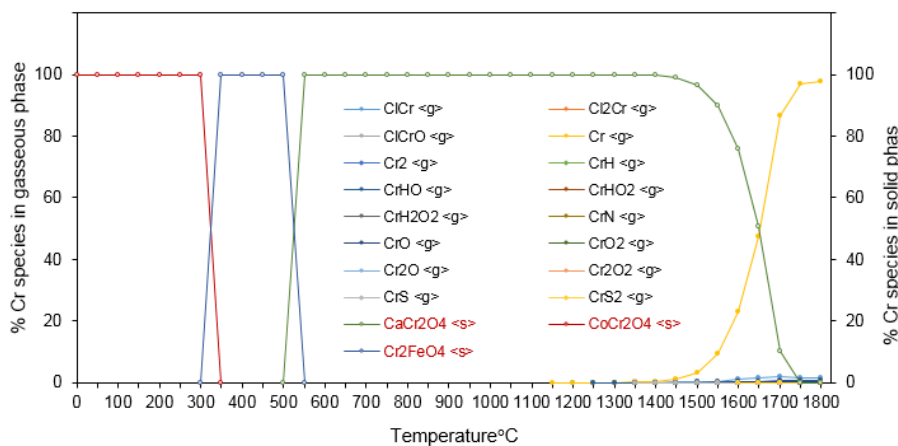
In this view, the distribution profiles of CCA elements during gasification (ASR_1) offer important trends towards their emissions control. More specifically, the presence of Ni and S enhances As and Cu capture in ash, respectively. Also, Cu and As interactions cause both of them to remain in solid phase, and the elements Ca, Co, and Fe are favored to Cr retention.

4.3.1.4 Influence of type of wood

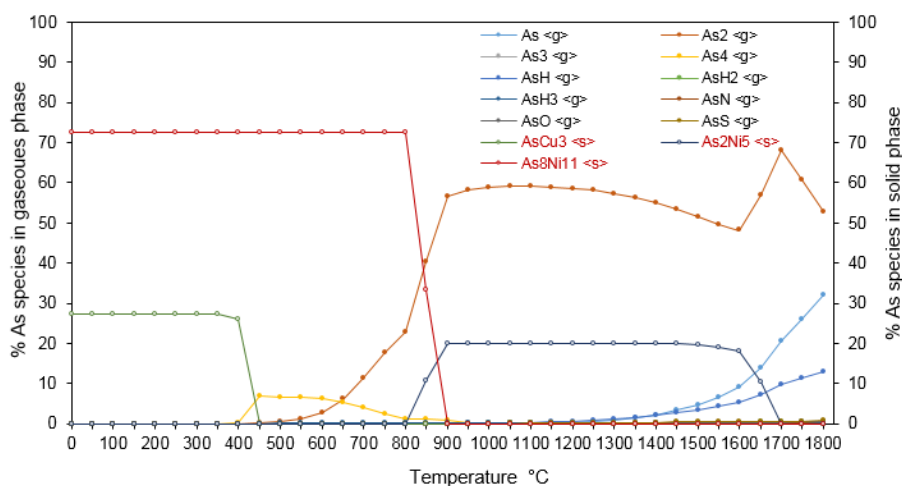
The predictive calculations for the three types of wood (chip, beech and pin) show that the major elements (C, N, O, and H) have no effects on the distribution of CCA elements during gasification (ASR_1).



(a)



(b)



(c)

Figure 4-7. Speciation of CCA elements when the all minor elements presence at same concentrations:

(a) Copper; (b) Chromium; (c) Arsenic.

4.3.2 During CO₂ gasification (CR₁)

4.3.2.1 Influences CCA elements contents

In this case, the simulation results indicate that Cu and Cr contents exhibit almost no influence on CCA elements phase transformation temperatures. But, when As level is relatively high (5 mol/h), its solid-gaseous transformation temperature decreased by 300°C as given in Figure 4-8. This is because of Ni contained becomes less than the limit to interact with As and hence capture 100% of As. Additionally, As₂Ni₅ (solid) and AsN (gaseous) are the dominant species of As.

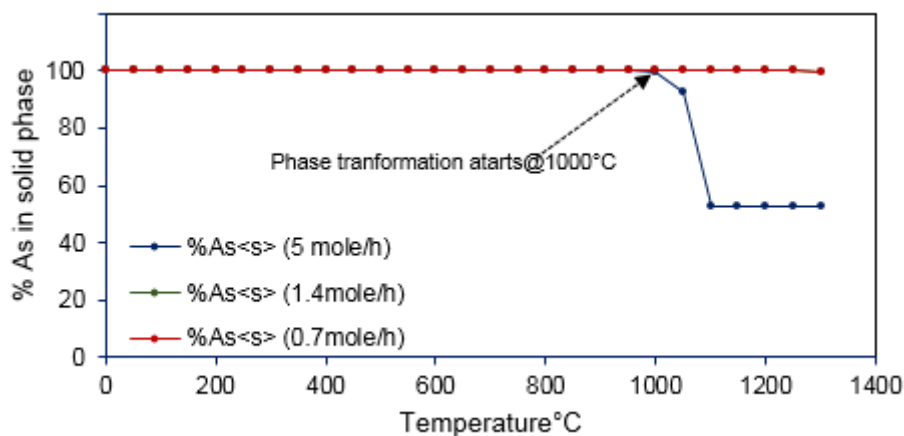


Figure 4-8. Phase transformations of As.

4.3.2.2 Influences of Ca, Na, S, Cl, Fe, and Ni content on CCA element

A summary of the reported interactions and interferences between CCA elements and the individual presence/absence of each of Ca, Na, S, Cl, Fe and Ni are demonstrated in Figure 4-9. The details of the obtained results are described in following parts.

4.3.2.2.1 Copper

The resulting species from the Ca-Cu interactions are shown Figure 4-10a-d. Obviously, the dominant species in solid phase are CaCu (Figure 4-10b), CaCu and CaCu₅ (Figure 4-10c), and CaCu (Figure 4-10c) when Ca is present at levels of 250, 500 and 1000 mol/h, respectively. On the other hand, the presence of Ca at low concentration would not be enough to interact with Cu. However, it tends

to interact with both O and Cr, generating CaCr_2O_4 and CaO . It is notable that the volatilization of Cu unaffected by the different levels of Ca. in similar manner, Cl-Cu interaction only form the gaseous specie ClCu at temperatures $> 1200^\circ\text{C}$.

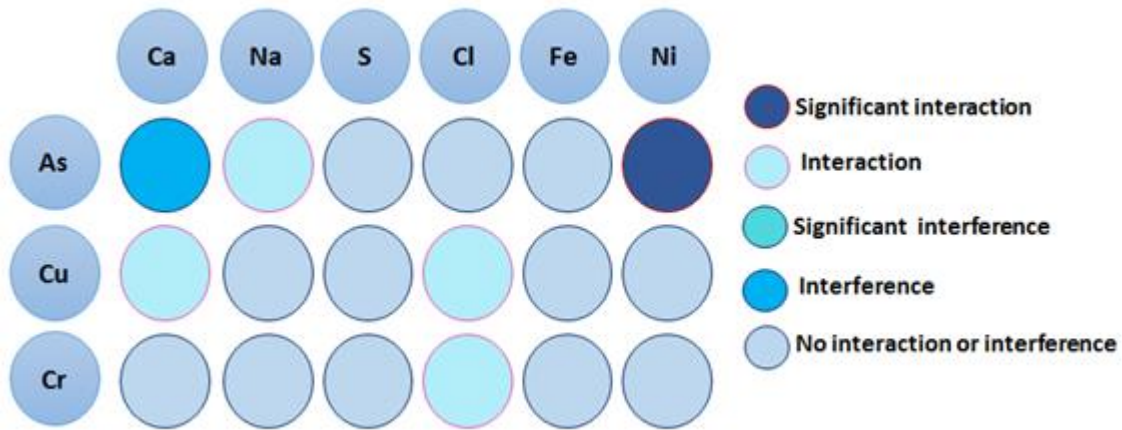
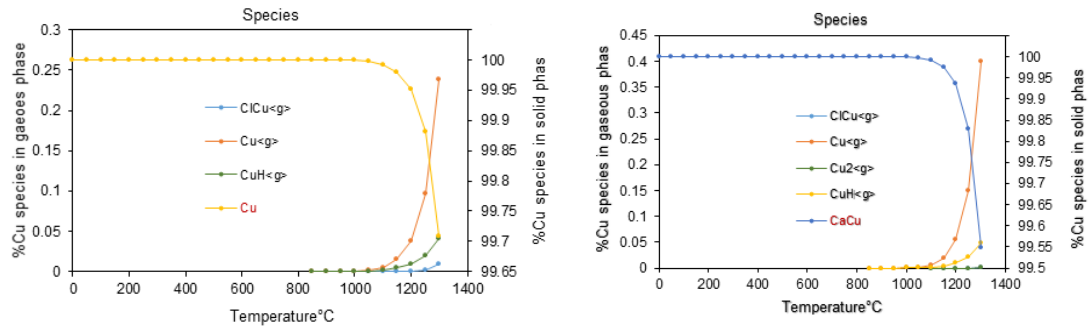


Figure 4-9. Interactions and interferences between CCA-element and each of Ca, Na, S, Cl, Fe and Ni.

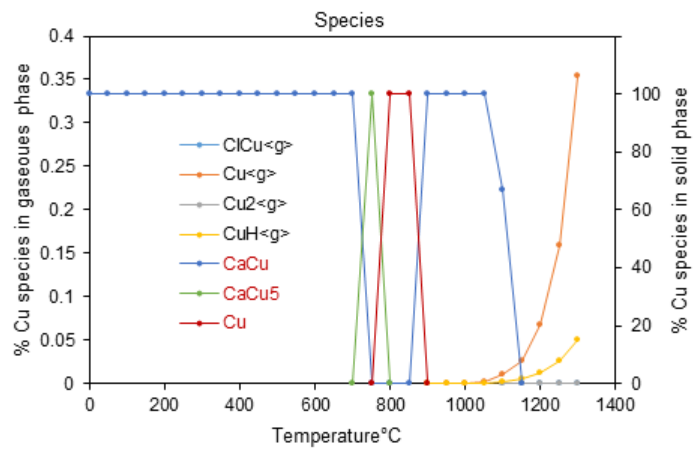
4.3.2.2.2 Chromium

Evaluation of possible interactions and interferences reveals that Ca has an important effect on Cr partitioning (Figure 4-11a-c). In this sense, Na and Cr interacts only if the level of $\text{Ca} \leq 100 \text{ mol/h}$ (Figure 4-11b), forming instable solid specie $\text{Cr}_2\text{Na}_2\text{O}_4$ between 1100 and 1300°C . Also, CaCr_2O_4 (solid) is the most likely form by Ca-Cr interaction when Ca is present at 100 mole/h , by which about 100% of Cr remained in solid phase at temperature $\leq 1300^\circ\text{C}$. As calcium content increases $>100 \text{ mol/h}$ (Figure 4-11c), Ca-Cr interferences and C-Cr interactions taken place simultaneously, generating C_2Cr_3 and C_3Cr_7 in solid phase at temperature up to 1300°C . The Cl-Cr interactions have no effect on Cr volatilization, but only form the gaseous specie ClCr as shown in Figure 4-12a-b.

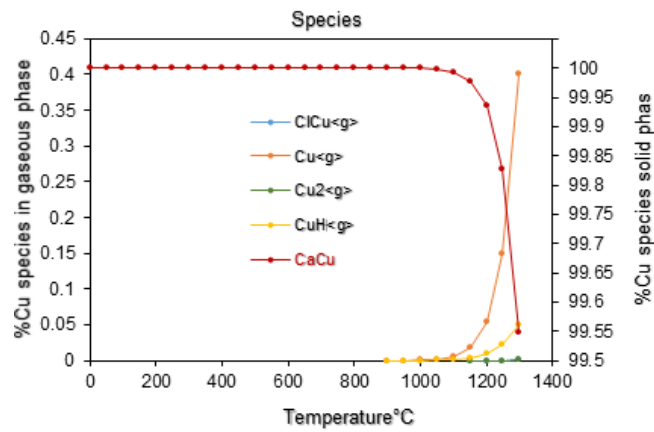


(a)% Cu species (Ca: 0-100 mole/h).

(b)% Cu species (Ca = 250 mole/h).

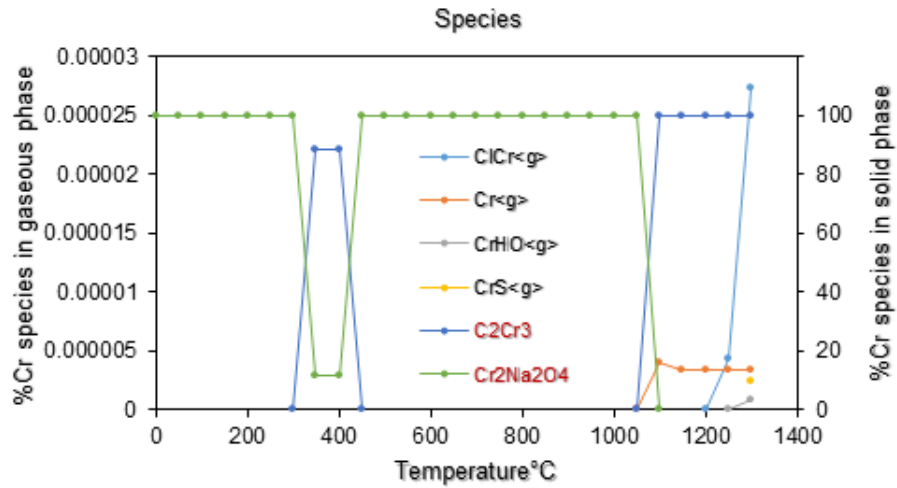


(c)% Cu species (Ca = 500 mole/h).

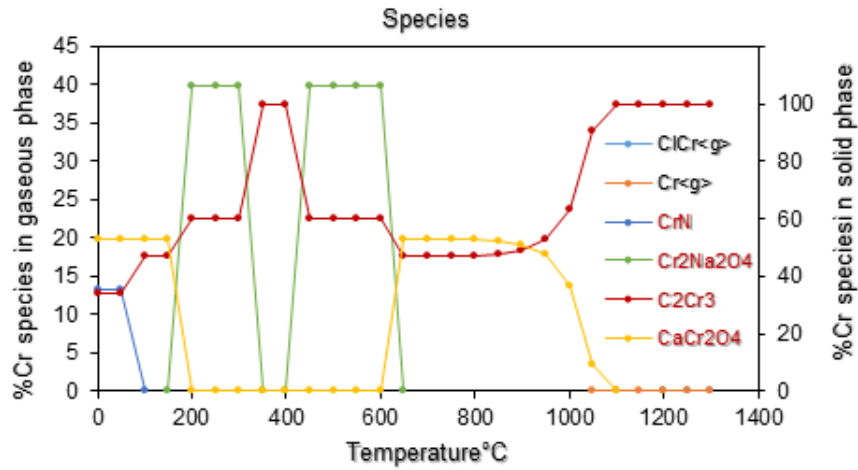


(d)% Cu species (Ca:1000-3000 mole/h).

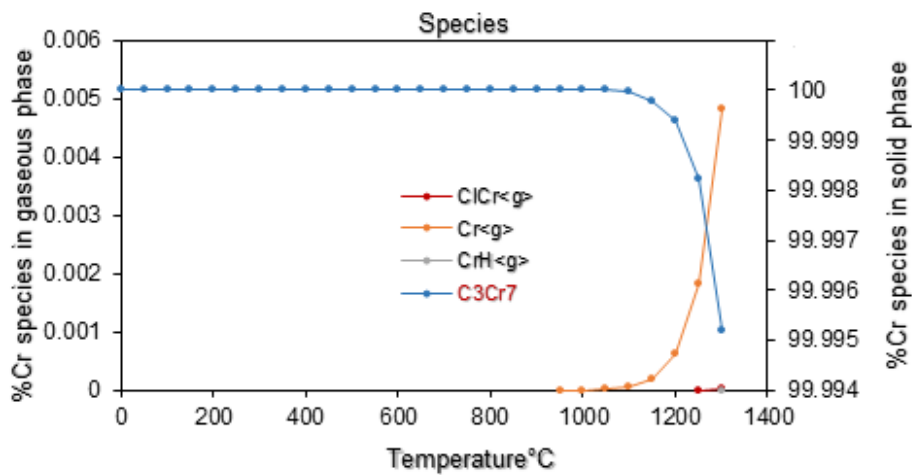
Figure 4-10. Calcium-copper interactions during CR₁.



(a) % Cr species (Ca absent).

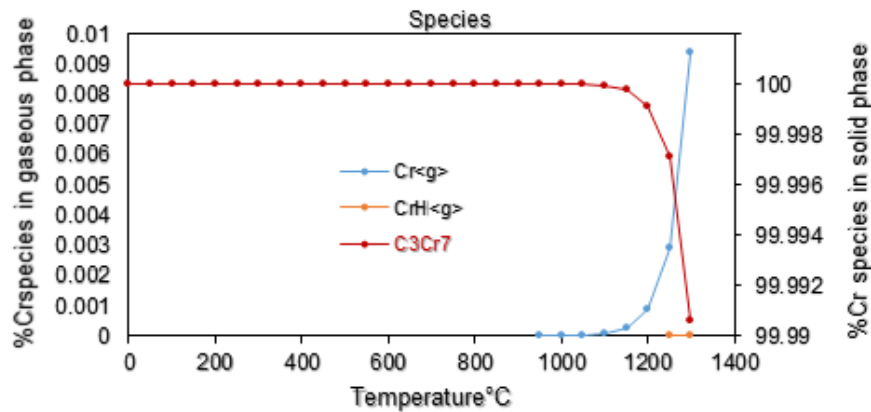


(b) % Cr species (Ca = 100 mole/h).

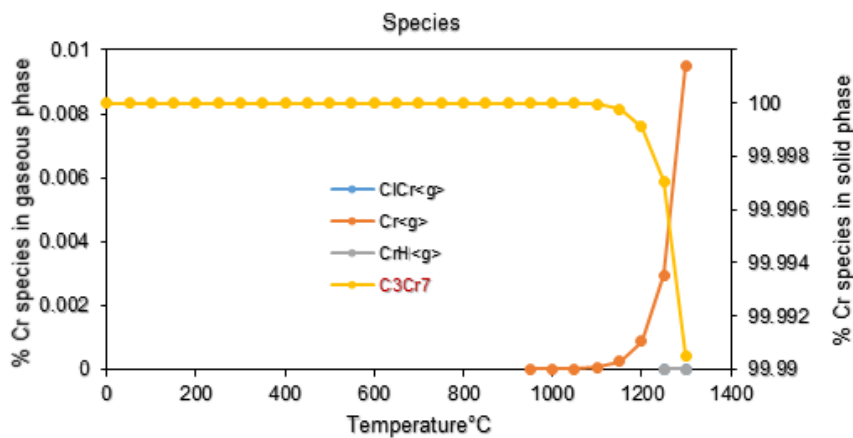


(c) % Cr species (Ca: 250-3000 mole/h).

Figure 4-11. Calcium-Chromium interactions during CR₁.



(a) % Cr species (Cl absent).



(b) % Cr species (Cl: 100-700 mole/h).

Figure 4-12. Chlorine-Chromium interactions during CR₁.

4.3.2.2.3 Arsenic

Under the CR₁ process, all the Ni-As interactions generate the solid specie As₂Ni₅, which increases the phase transformation temperature of As (Figure 4-13) about 200°C. On the other hand, the lack of Ni has led to form As₂ (gaseous) and AsNa₃ (solid) as dominant species as shown in Figure 4-14. Similarly, Na-As interaction yields AsNa₃. However, the absence of Na shows no influences on the As phase formation, but it enhances Ni to capture As, forming As₂Ni₅ (100-99.15%) up to 1300°C as demonstrated in Figure 4-15. Besides that, As-S interaction releases the gaseous species AsS when the Ca not existed in the system, as shown in Figure 4-16a-b. it also observed that no interactions nor interferences were occurred between the elements As, Fe, and Cl.

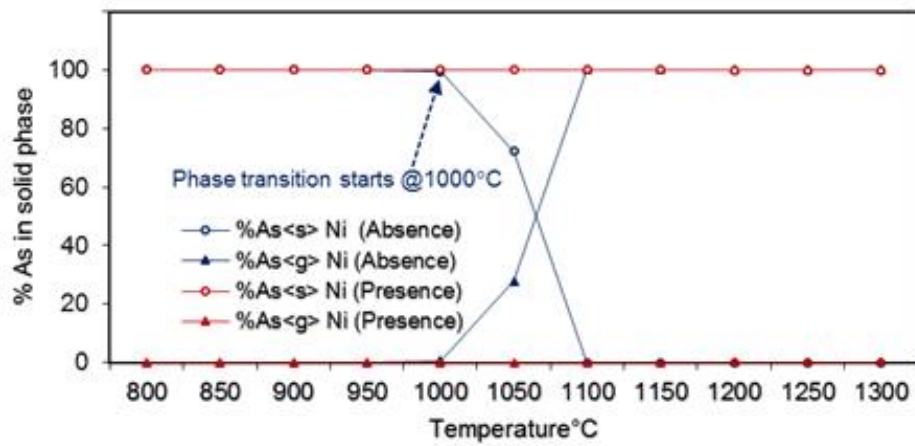


Figure 4-13. Arsenic distribution according to the presence/absence of Ni.

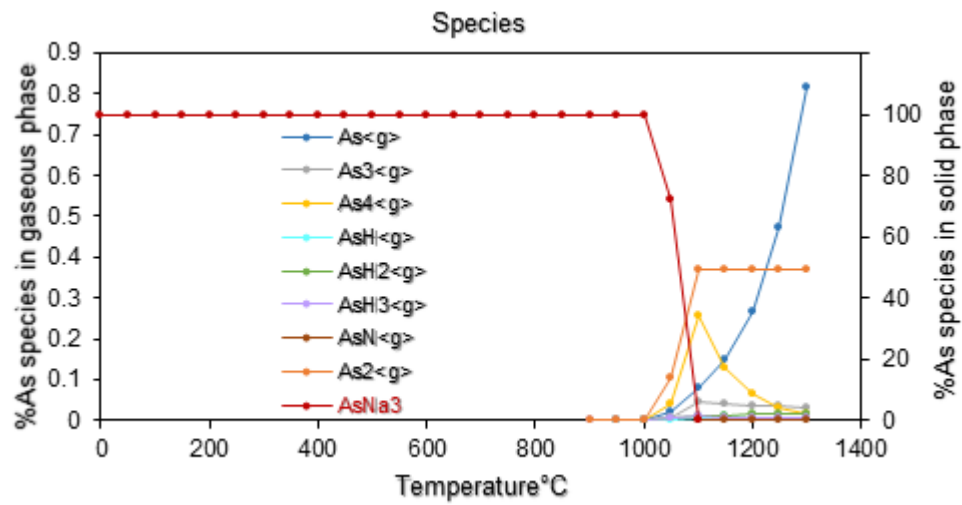


Figure 4-14. Arsenic speciation in the absence of Ni.

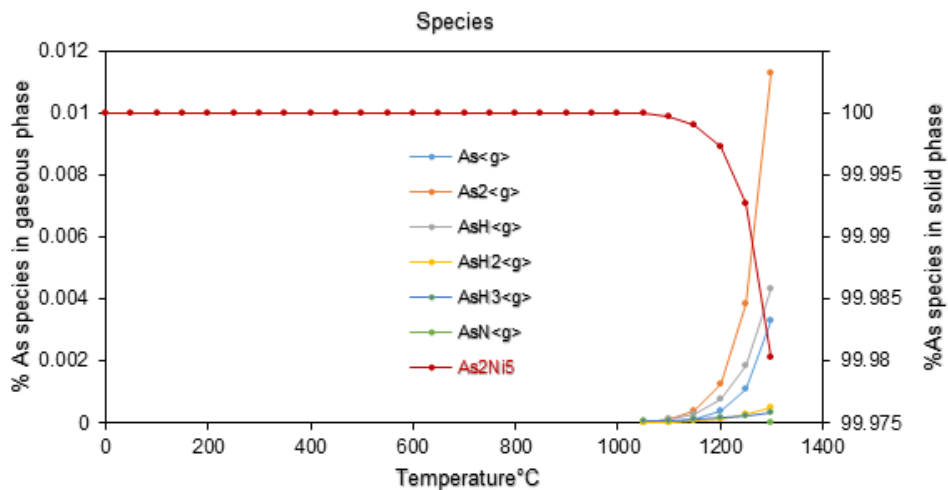
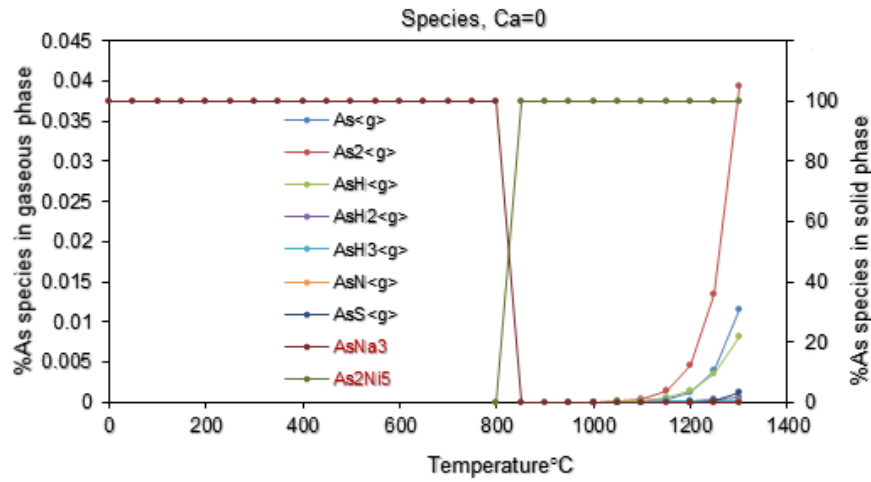
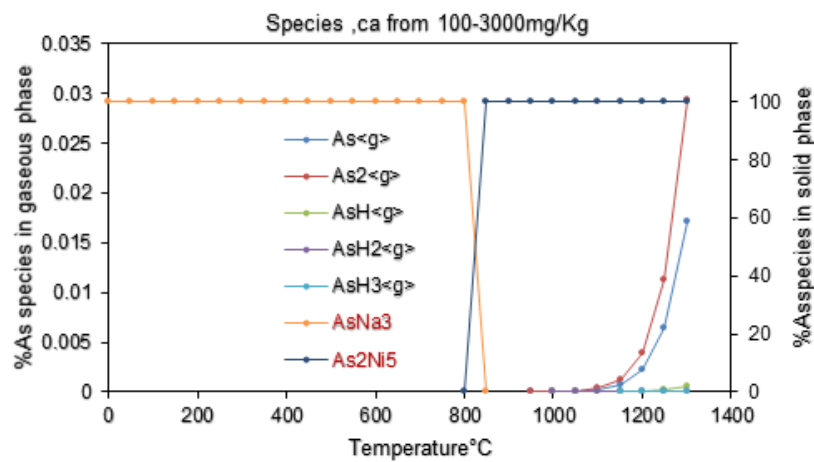


Figure 4-15. Arsenic speciation in the absence of Na.



(a) % As species (Ca absent).



(b) % As species (Ca: 100-3000 mole/h).

Figure 4-16. Calcium-Arsenic interactions during CR₁.

4.3.2.3 Assessing CCA element reactivity

With this model case, the phase transformation temperature of the CCA elements, in the presence of T1, T2, T3, and T4, are respectively shown in Figure 4-17, Figure 4-18, and Figure 4-19. And the speciation formation of these elements are exhibited in Figure 4-20, Figure 4-21, Figure 4-22, and Figure 4-23. Quite obviously, the simulation results in this case almost identical to those with ASR₁ model. The only exception is the formation of arsenic chloride AsCl_3 by the Cl-As interaction with the presence of T2 elements (Figure 4-22b).

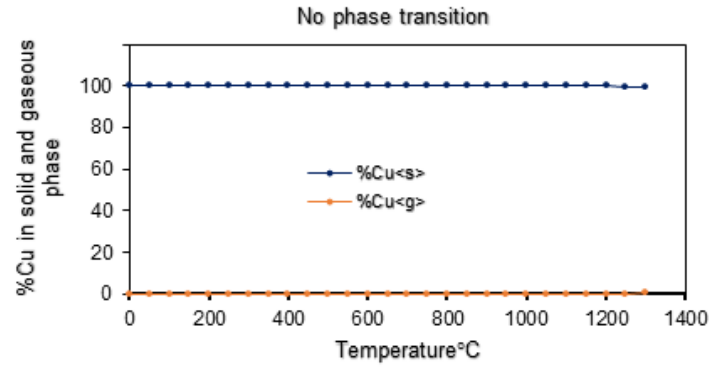
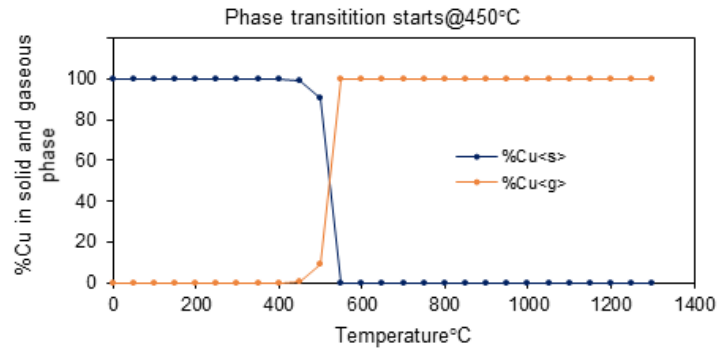
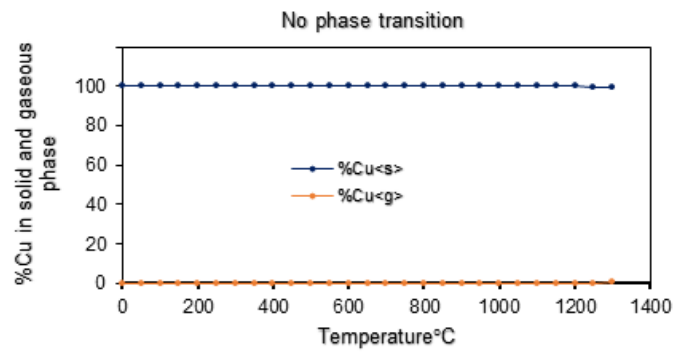
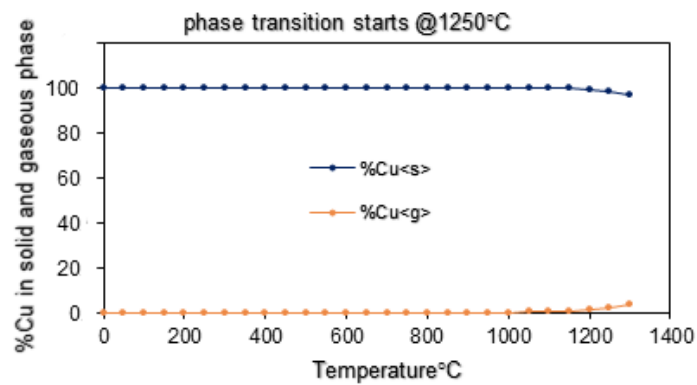
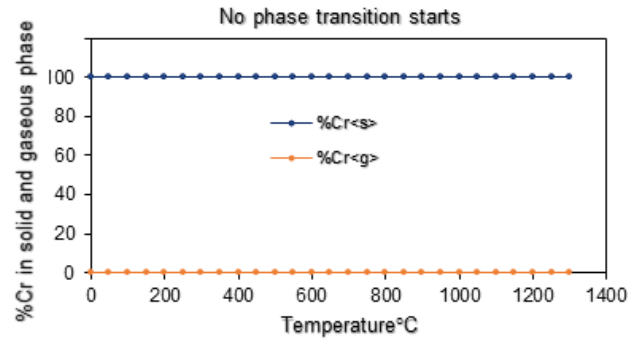
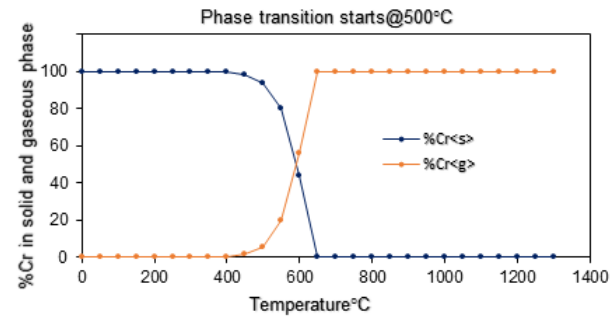


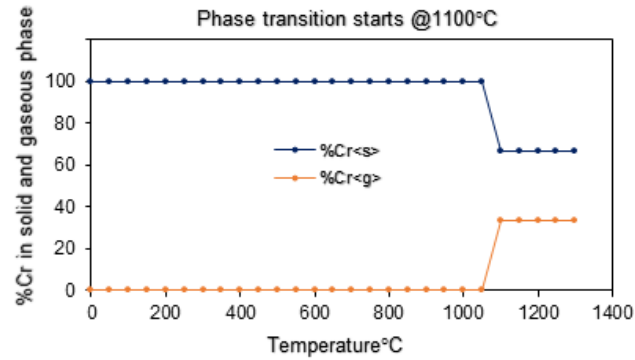
Figure 4-17. Copper phase transformation in the presence of T1, T2, T3, and T4 during CR₁.



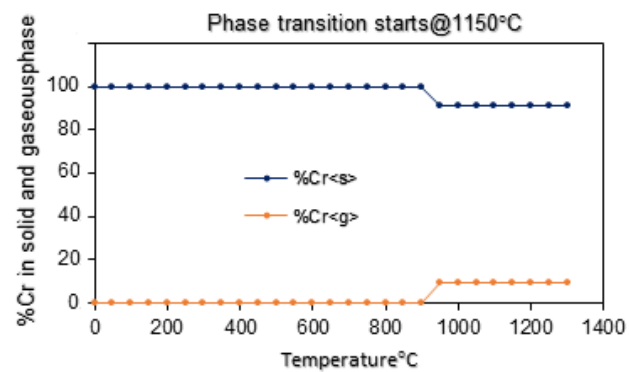
(a) T1.



(b) T2.



(c) T3.



(d) T4.

Figure 4-18. Chromium phase transformation in the presence of T1, T2, T3, and T4 during CR₁.

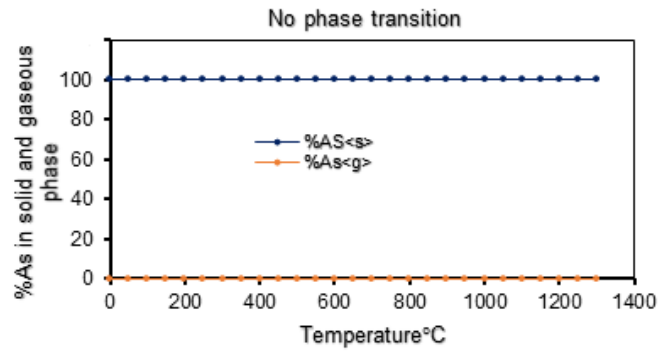
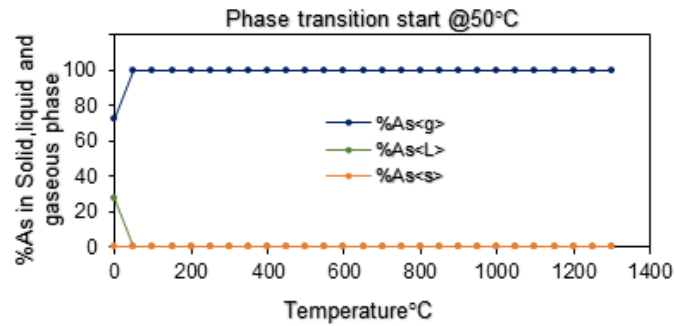
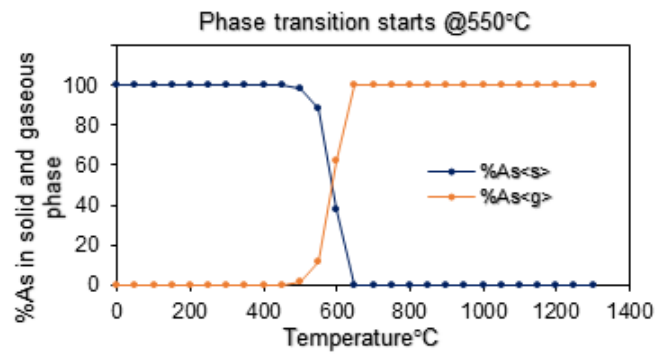
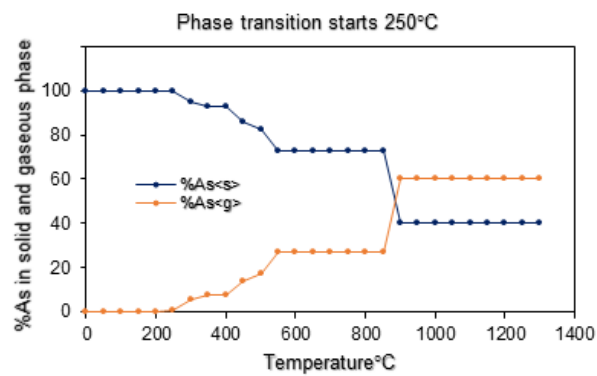
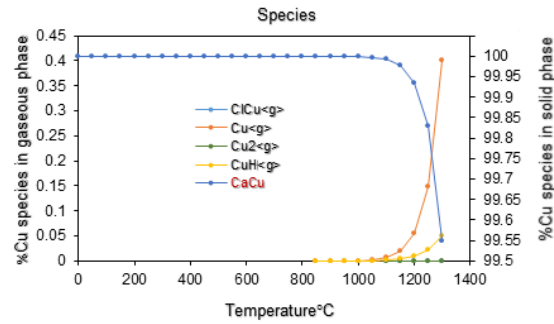
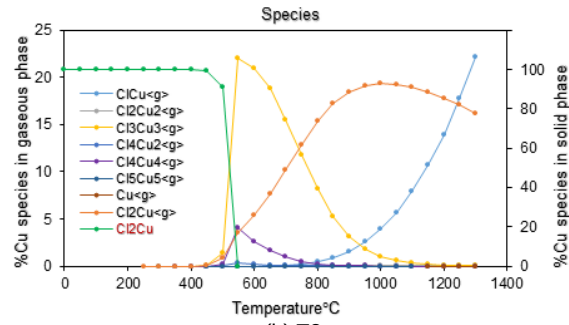


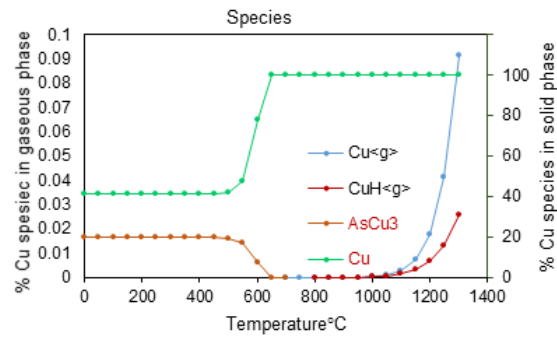
Figure 4-19. Arsenic phase transformation in the presence of T1, T2, T3, and T4 during CR₁.



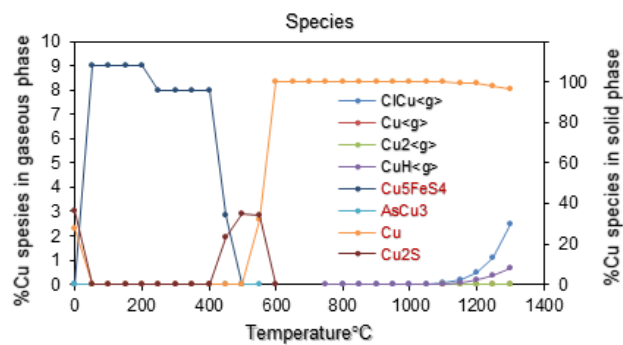
(a) T1.



(b) T2.

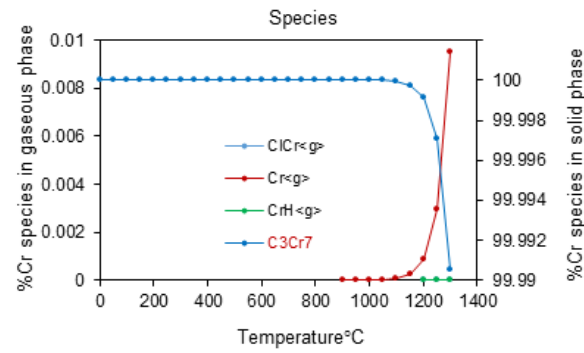


(c) T3.

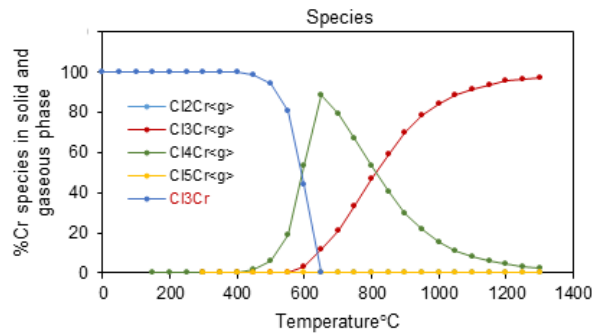


(d) T4.

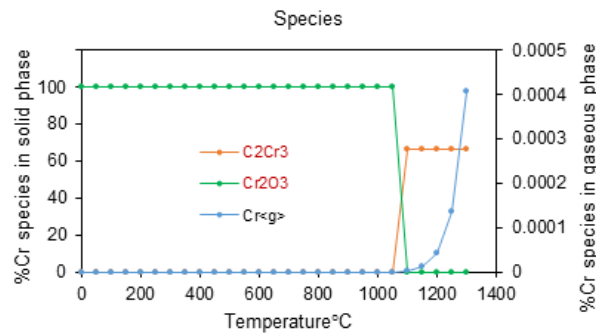
Figure 4-20. Copper species in the presence of T1, T2, T3, and T4 during CR₁.



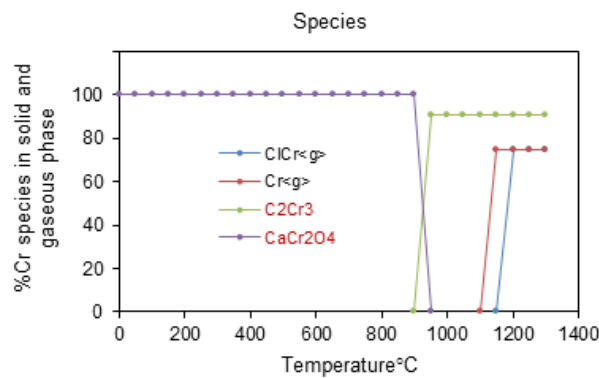
(a) T1.



(b) T2.

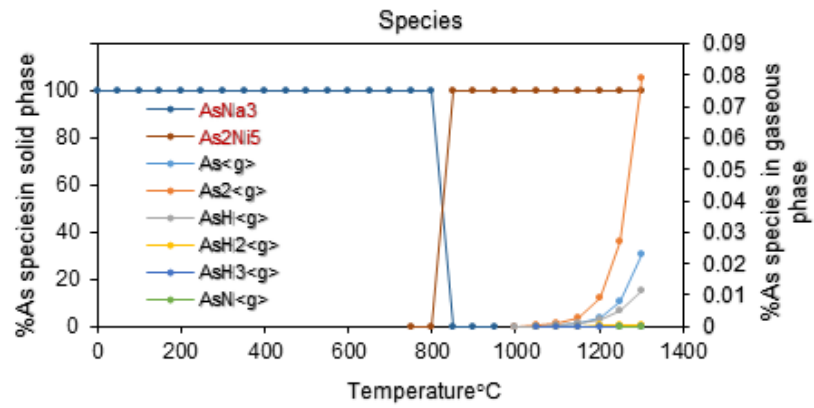


(c) T3.

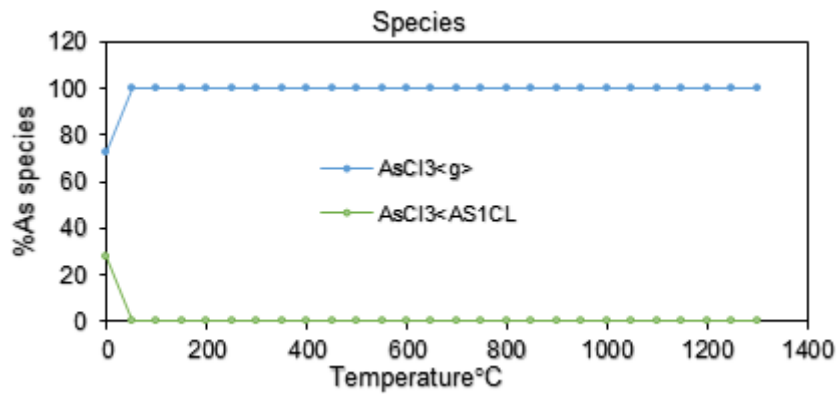


(d) T4.

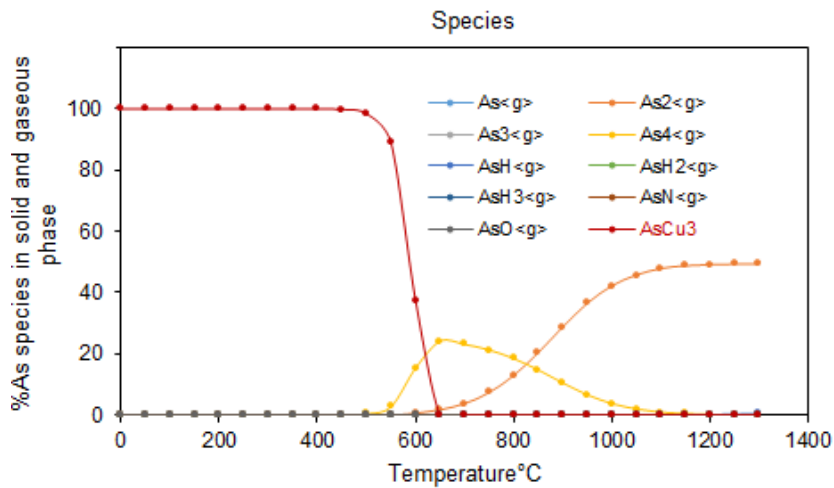
Figure 4-21. Chromium species in the presence of T1, T2, T3, and T4 during CR1.



(a) T1.



(b) T2.



(c) T3.

Figure 4-22. Arsenic species in the presence of T1, T2, and T3 during CR₁.

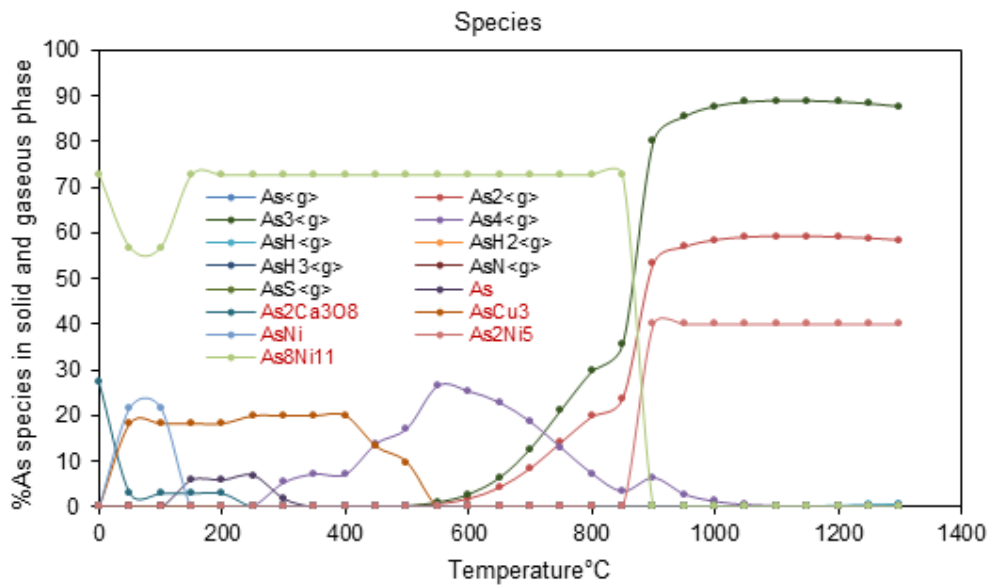


Figure 4-23. Arsenic species in the presence of T4 during CR₁.

4.3.2.4 Influence of type of wood

The simulation results for the chip, beech and pin woods indicate that the major elements (C, N, O, and H) have no impacts on the distribution profiles of CCA elements during CR₁.

4.3.3 Pyrolysis (P₁)

Under this model configuration, the investigations on the behavior of CCA elements related to the interactions and interferences do not show significant differences with the results previously observed during CR₁ under operating temperatures ranging from 0 to 900°C. This is in line with the fact that the pyrolysis is the first step of biomass thermochemical conversion. For instance, Table 4-5 shows the reactivity of CCA elements in terms of phase transformation and speciation formation in the presence of T1, T2, T3, and T4, individually.

Table 4-5. Main speciation and phase transformation temperatures of CCA elements during P₁.

Element	Group	Phase transformation 0-900°C Solid → gaseous Under 1atm (101325Pa)	Solid species	Liquid species	Gaseous species
Cu	T1	None	CaCu		ClCu, Cu, Cu ₂ , CuH Cl ₂ Cu, ClCu, Cl ₂ Cu ₂ , Cl ₃ Cu ₃ , Cl ₄ Cu ₂ , Cl ₄ Cu ₄ , Cl ₅ Cu ₅ , Cu
	T2	400	Cl ₂ Cu		
	T3	None	AsCu ₃ , Cu		Cu, CuH
	T4	None	Cu ₅ FeS ₄		CuH, Cu ₂ , Cu/ClCu
Cr	T1	None	C ₃ Cr ₇		ClCr, Cr, CrH Cl ₂ Cr, Cl ₃ Cr, Cl ₄ Cr, Cl ₅ Cr
	T2	400	Cl ₃ Cr		
	T3	None	Cr ₂ O ₃ , C ₂ Cr ₃		Cr
	T4	None	CaCr ₂ O ₄ , C ₂ Cr ₃		ClCr, Cr
As	T1	None	AsNa ₃ , As ₂ Ni ₅		As, As ₂ , As ₂ , AsH, AsH ₂ , AsH ₃
	T2	≈50		AsCl ₃	AsCl ₃
	T3	450	AsCu ₃		As, As ₂ , As ₃ , As ₄ , AsH, AsH ₂ , AsH ₃ , AsN, AsO
	T4	250	As, As ₂ Ca ₃ O ₈ , AsCu 3, AsNi, As ₂ Ni ₅ , As ₈ Ni ₁₁		As, As ₂ , As ₃ , As ₄ , AsH, AsH ₂ , AsH ₃ , AsN, AsS

4.4 Conclusions

This chapter introduces three predictive models for contaminated WW gasification (ASR₁ and CR₁) and pyrolysis (P₁) to understand the behaviour of CCA elements in terms of interactions and interferences. The refinement of the predicated results from ASR₁ modelling indicates that most of the occurred Ni-As interactions leading to about 100% of As remained in solid phase at temperatures less than 1400°C. It also shows that Ca-Cr interferences form solid specie C₃Cr₇, but the absence of Ca causes instability in Cr distribution at temperatures from

1100°C to 1550°C. Along with this, Co-O-Cr, Fe-O-Cr and Ca-O-Cr interactions reducing Cr volatilization as consequence of the generated solid species CoCr_2O_4 , Cr_2FeO_4 , and CaCr_2O_4 , respectively. Perhaps most importantly, on the basis of the models introduced, the Na and Ni content in WW played a vital role in remaining As in solid phase at temperatures $\leq 800^\circ\text{C}$. This would aid in mitigating the negative impacts of toxicity emissions associated with CCA elements through systematically mixing different types of woody biomass. For example, mixing two types of WW such that one of them is heavily contaminated with As while the other with Ni.

Chapter 5 Samples Collection, Preparation and Analysis

This chapter strives to introduce the details of collected WW samples, and their preparation and analysis. A total of 28 samples were collected from waste streams, industrial, and landfill sites. Landfilled wood waste was used to represent heavily contaminated materials, having been exposed to landfill leachate over a number of years. Samples preparation and analysis were followed standard procedures for woody biomass. For each of the 28 samples, 42 analyses were performed.

5.1 Introduction

Following a review of the available information on metal(loid) elements in WW (Chapter 2), it was found that limited attention has been devoted to exploring the concentrations of these elements in WW that could be expected to be heavily contaminated. Additionally, insufficient emphasis has been given to providing high-quality analytical characterisation and elemental composition of WW feedstocks that ensure reliable thermodynamic modelling and experimental works. As such, this chapter seeks to address these gaps and consequently create a highly informative dataset containing comprehensive details about the characterisation and elemental composition of the considered WW samples. To begin with, the physical and chemical properties include proximate, ultimate, calorific value, and elemental content were measured in accordance with standard methods and techniques. In doing so, each analysis was carried out in triplicate so that reliable values can be inferred.

Therefore, this chapter's objectives are to:

- Collect waste wood samples
- Prepare the waste wood samples
- Apply standard methods for chemical characterisation and full elemental composition of the waste wood samples.

5.2 Materials and Methods

5.2.1 Waste wood Samples

In this study, 28 waste wood samples were taken from waste streams, industrial, and a closed landfill site (previously accepted waste from households and commercial sectors, located in the East of England). The selection of these samples was made according to their interesting sources.

1. Waste streams

Five waste wood samples were obtained from Cranfield and Bletchley (UK) wastes. These samples include the following: old furniture, new furniture, mixed furniture, demolition, and unknown type.

2. Waste industrial

Two industrial fuel samples (pellets and chip) were provided by Cranfield University energy lab store.

3. Landfill site

Twenty-one waste samples were collected from a closed landfill site in UK, taken from up to 55 m depth. The core samples were extracted during gas well drilling and installation, with the core measuring around 200 mm diameter. These samples were pre-processed to remove materials such as plastics, paper/cardboard, metals, glass/ceramic, textile, soil/fine fractions between 20-6.30 mm, soil/fine fractions < 6.30 mm, batteries, and WEEE. The percentages of these materials are provided in Appendix D.1. The total percentages of wood materials are shown in Figure 5-1, which were highly variable (from 1.30% to 46.70%, with 11.81% as the mean of all samples). Note that the materials obtained from 46-48 m depth have highest percentage of wood (around 46.70%), whereas the materials from 25-27 m depth have lowest percentage of wood (around 1.30 %).

5.2.2 Preparation of the waste wood samples

The samples preparation procedure entails the following two stages (Karinkanta et al., 2018).

1. Washing and drying

Each waste wood sample from the landfill site was washed with tap water to remove dirt, sand, and other physical contaminants (Figure 5-2a), followed by air-dried (Figure 5-2b). Thereafter, the sample was further dried in an oven (Thermo Electron LED GmbH, 63505, Heratherm OMS180, Germany) at $40\text{ }^{\circ}\text{C} \pm 5\text{ }^{\circ}\text{C}$ for one hour (Figure 5-2c).

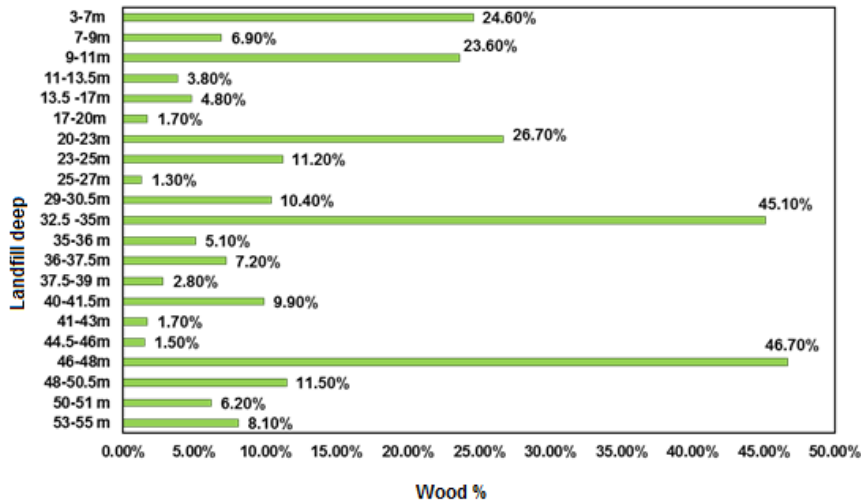


Figure 5-1. Percentage of wood material/total material (landfill 55-3 m), 2018.



Figure 5-2. Washing and drying of waste wood samples.

2. Grinding

The WW samples, including the pre-prepared landfill samples, were grinded to a fine powder. The grinding process undergoes the following four successive steps:

- Cutting the WW samples into small pieces using electric saw (Erbauer ERB567DRH) (Figure 5-3a).
- Cutting the small pieces to wedges with BLACK & DECKER, type 1 NO, 2980/MIN (Figure 5-3b).
- Chopping the wedges into < 1 cm pieces by Retsch type SM200 (Figure 5-3c).
- Finally, the chopped pieces were further grinded to wood powder < 1 mm by Retsch type ZM200 (Figure 5-3d).



Figure 5-3. Grinding of waste wood samples.

5.2.3 Characterisation and full elemental composition

Physico-chemical properties of WW samples were characterized by proximate and ultimate analysis, calorific value, and elemental analysis. Each analysis was carried out in triplicate, giving a total of 1176 analysis. The values were given as the mean (M) and standard deviation (STD). The relative standard deviation (RSD) was calculated as follows:

$$RSD = 100 (STD/M). \quad (5-1)$$

5.2.3.1 Proximate analysis

5.2.3.1.1 Moisture

Moisture content of each WW sample was determined according to the standard method E-871 for wood fuels (Basu, 2013). The method consists of the following three steps:

1. Each empty crucible was washed by detergent and tap water, and then rinsed with deionised water. After that, the crucible was placed in an oven (Thermo Electron LED GmbH, 63505, Heratherm OMS180, Germany) for drying overnight at 105°C. The dried crucible was transferred to a desiccator to cool, for at least 30 minutes, then weighed using a balance (ES 220A, Swiss).
2. Approximately 1 g (± 0.001) of wood powder was transferred into a weighed crucible. The wet wood powder was weighed using a balance with accuracy of ± 0.001 g, and then placed in an oven for drying at 105°C for 24 hours.
3. After drying the wood powder transferred to a desiccator to cool for at least one hour.

On the basis of the above steps, the moisture content (%) can be directly calculated as follows:

$$\text{Moisture (\%)} = \frac{WCS_b - WCS_a}{WCS_b - WC_E} \times 100, \quad (5-2)$$

where WC_E denotes the weight of empty crucible, and both WSC_b and WSC_a are the weights of the crucible containing wood sample before and after drying, respectively.

5.2.3.1.2 Ash

The determination of ash content was based on the standard method D-1102 (Aytenew, Nigus and Bedewi, 2018; Basu, 2013). Note here that, the procedure for drying wood powder was similar to that applied for moisture content. The dried wood powder (1 g) was placed in a muffle furnace (Scientific Laboratory supplies -CARBOLITE) and heated up to 575°C for 6 hours. Then, the ash residue was transferred to a desiccator to cool for at least 80 minutes. Following this, the ash content (%) can be determined using the following equation.

$$\text{Ash (\%)} = \frac{Ash_r}{S_i} \times 100, \quad (5-3)$$

where Ash_r and S_i stand for the weights of ash residue and dried wood powder, respectively.

5.2.3.1.3 Volatile matter

Volatile matter content was determined according to the standard method E-872 (Aytenew, Nigus and Bedewi, 2018; Basu, 2013; Calvo et al., 2004). The dried wood powder (1 g) was placed in a muffle furnace (Scientific Laboratory supplies -CARBOLITE) and heated up to 950°C for 7 minutes. The final product was weighed after cooling in a desiccator at least 80 minutes. Then, the volatile matter content (%) can be calculated as follows:

$$\text{Volatile matter (\%)} = \frac{S_i - S_f}{S_i} \times 100, \quad (5-4)$$

Where S_i and S_f , respectively, refer to the weights of dried sample and final sample.

5.2.3.1.4 Fixed carbon

Fixed carbon (FC) was determined according to the following formulae (Basu, 2013.p77).

$$FC (\%) = 1 - \text{Moisture}(\%) - \text{Volatile matter} (\%) - \text{Ash}(\%) \quad (5-5)$$

5.2.3.2 Ultimate analysis

5.2.3.2.1 Carbon, Nitrogen, and Hydrogen

Carbon (C), Nitrogen (N), Hydrogen (H), and rate of C/N were analysed using CHNS elemental analyser (elementar-vario EL III). A 0.30 mg of dried wood powder (at 105°C for 3 hour) was placed into a clip and transferred to the elemental analyser. The analyser configurations were set up according to the manufacturer's instructions included methionine, soil 5 M as standards, tungsten oxide (WO_3) as catalyst, combustion gas (Oxygen purity 99.99%), and carrier gas Helium (purity 99.99%). The operating temperature was 1150°C.

5.2.3.2.2 Oxygen

Oxygen was calculated according to the following formulae (Basu, 2013p.80),

$$\begin{aligned} \text{Nitrogen} (\%) + \text{Carbon} (\%) + \text{Hydrogen} (\%) + \text{Sulphur} (\%) \\ + \text{Oxygen} (\%) = 100\%. \end{aligned} \quad (5-6)$$

Note that the adopted percentage of Sulphur (S) content will be given later in section 5.2.3.5.

5.2.3.3 Calorific value (CV)

The calorific value (CV) was estimated using Parr 6400 Calorimeter. The ballistic bomb calorimeter was calibrated with benzoic acid (0.99841 g). Based on the manufacturer instructions, approx. 0.6 ± 0.01 g of dried wood powder was placed into a crucible, which was further placed into the combustion vessel. After closing the vessel, nitrogen and oxygen were supplied under pressures of 8 bar and 30 bar, respectively. Furthermore, the theoretical calorific value (TCV) can be determined using the following formula (Jiang et al., 2016; Onabanjo et al., 2016).

$$TCV = 33.5 \times C + 142.3 \times H - 15.4 \times O - 14.5 \times N \times 10^{-2} \quad (5-7)$$

Also, the higher heating value (HHV_d) can be calculated as follows (Basu, 2013,p.277; Onabanjo et al., 2016):

$$\begin{aligned} HHV_d = & 0.3491 \times C + 1.1783 \times H + 0.1005 \times S \\ & - 0.015 \times N - 0.1340 - 0.0211 \times \text{Ash}. \end{aligned} \quad (5-8)$$

5.2.3.4 Total halide and phosphorus

Elemental analysis of total Cl, Br, F, and P were performed according to standard method BS EN 15408 (CEN national, 2011; Zhang et al., 2013). The ion-chromatography was carried out to estimate the total halides and phosphorus in a solution of wood powder, which obtained from the ballistic bomb calorimeter. Then, the total concentration (TC) of each of the Cl, Br, F and P was measured using the following formulae.

$$TC = \frac{(CS - CS_0) \times V}{m} \times SR \times 100, \quad (5-9)$$

where, CS (mg/L) denotes the concentration of Cl, Br, F, or P, respectively, in the wood powder solution; CS₀ (mg/L) refers to the concentration of Cl, Br, F, or P, respectively, in blank solution; V(L) stands for the volume of the solution; m (mg) is the mass of the test portion (from ballistic bomb calorimeter); and SR denotes the stoichiometric ratio of the relative masses of Cl, Br, F, or P; typically, SR set to 1 and 0.3263 for halides and phosphorus, respectively.

5.2.3.5 Metal(loid)s extraction and analysis

The determination of metal(loid) concentration in woody biomass is usually made by applying digestion procedure. In this study, microwave digestion method was performed with mixture of nitric acid (HNO₃) and hydrogen peroxide (H₂O₂) (WU, FENG and WITTMEIER, 1997). Note that, the silica concentration recorded by this method will be lower than reality due to not all the silica dissolving. The procedure of the conducted digestion tests is outlined as below:

1. Approximately 0.5 g of wood powder was accurately weighed into a Teflon microwave vessel, followed by addition of 5 ml of HNO₃ (1.42 specific gravity), and the solution was kept overnight at room temperature.
2. A 5 mL of H₂O₂ (100 volumes > 30%) was added to the solution and left for two hours at room temperature. Thereafter, the solution was placed into a microwave oven (MARS Xpress X traction 230/60-Rection system 907501) and heated at 165°C for 4 hours.
3. After cooling, the dissolution of elements was filtered (using a Whatman 542 paper) and the filtrate was quantitatively transferred to volumetric flasks and completed up to 100 mL with ultrapure deionised water (18.2 MΩ).

ICP-MS (Perkin Elmer types NexION350D) was used to measure the concertation of the dissolved elements Al, As, Ca, Cd, CO, Cr, Cu, Fe, Hg, K, Mg, Mn, Mo, Na, Ni, pb, Se, Si, S, Ti, V, and Zn. The ICP-MS was calibrated with standard solutions for each element. The concentration of each element (C_E) was measured as follows:

$$C_E (\mu\text{g/kg}) = \frac{C_s - C_b}{m_d} \times 100, \quad (5-10)$$

where C_s (μg/L) and C_b (μg/L) are the concentrations of an element in the sample extract and blank extract, respectively, and m_d (g) is the mass of sample taken for digestion.

5.3 Results and discussion

The results of characterisation and elemental analysis of the waste wood samples are given in Table 5-1, which shows a list of Appendices, each of which contains the measurements of a particular attribute. Table 5-2, Table 5-3, and Table 5-4, separately, show the established datasets (characterization and compositional data) for the WW samples from streams, industrial and landfill. The data were expressed as mean of the triplicate measurements.

Table 5-1. List of Appendices.

Proximate analysis			Ultimate analysis		
Moisture	App D.2.1	Carbon	App D.3.1	C / N Ratio	App D.3.4
Ash	App D.2.2	Nitrogen	App D.3.2	Sulphur	App D.3.5
Volatile matter	App D.2.3	Hydrogen	App D.3.3	Oxygen	App D.3.6
Fixed carbon	App D.2.4				
Calorific value					
CV	App D.4.1	TCV	App D.4.2	HHV	App D.4.2
Elemental analysis					
Halides	App D.5	Major elements	App D.6	Minor elements	App D.6

Notes: App = Appendix.

5.3.1 Waste wood characterisation

The quantitative characterizations (proximate, ultimate, and calorific values) of the twenty-eight waste wood samples were within the normal ranges. It is noteworthy that the moisture content in waste wood from L (34.76%) higher than that in waste wood from streams and Industrial by 9.42% and 8.91%, respectively. This is expected since the moisture content strongly depends on the storage and environmental conditions. Furthermore, the determined C, H, O, and N contents were similar among the three types of WW.

The measured calorific values were in good agreement with the theoretical ones. It is also noted that the measured calorific value (17.83 MJ/g) of waste wood from landfill is slightly lower those of streams (18.1 MJ/g) and industrial (18.2 MJ/g) samples. This is to be expected as the wood in a landfill is likely to have partially degraded, thus the combustible content is lower. In general, these values are higher compared to other biomass. For example, the calorific values of municipal solid waste ranging from 8 to 14.84 MJ/g (Stasiek, Jewartowski and Yang, 2017; Zawadzka, Krzystek and Ledakowicz, 2010).

Table 5-2. Characterization and full elemental analysis of the WW samples collected from waste streams.

Sample type	Old Furniture	New Furniture	Mixed Furniture	Demolition	Waste Streams**
Property	Value*	Value*	Value*	Value*	Value*
Waste wood Properties					
Proximate Analysis (%wt.)					
Moisture	9.55	9.86	8.935	11.19	8.69
Ash	0.61	0.69	0.50	1.79	1.73
Volatile matter	86.32	83.85	86.59	85.22	84.99
Fixed carbon (FC)	3.53	5.6076	3.9578	1.81	4.59
Ultimate Analysis (%wt,dry)					
Carbon (C)	50.02	49.06	51.45	50.25	50.14
Hydrogen (H)	7.17	7.03	7.36	7.14	7.14
Nitrogen (N)	0.06	0.128	0.09	0.06	0.45
Sulphur(S)	0.01	0.01	0.01	0.01	0.01
Oxygen(O)	42.76	43.79	41.11	42.56	42.28
Carbon/Nitrogen (C/N)	885.99	395.79	594.36	837.56	123.37
Calorific Value					
Calorific Value (CV)	18.44	17.95	18.592	17.87	18.39
TCV	20.26	19.43	21.188	20.3048	19.51
HHVd	21.47	20.87	22.37	21.50	21.50
Chemical Analyses					
Halides					
Chlorine (Cl)	0.03	0.03	0.03	0.03	0.03
Bromine (Br)	-	-	-	-	-
Fluorine (F)	0.02	-	-	0.01	0.01
Major elements (mg/kg)					
Aluminium (Al)	103.38	41.36	35.19	218.04	263.55
Calcium (Ca)	2785.27	1011.56	1023.76	1365.78	3802.48
Potassium (K)	284.85	1125.87	611.18	252.42	1587.87
Iron (Fe)	555.49	333.01	198.35	2277.91	1375.58
Sodium (Na)	317.04	87.48	92.18	188.64	521.33
Silicon (Si)	188.42	95.94	62.25	102.77	271.87
Magnesium (Mg)	355.72	186.59	155.23	171.65	550.12
Phosphorus (P)	0.01	-	-	0.01	0.01
Titanium (Ti)	9.38	0.83	1.48	11.35	18.68
Minor elements (mg/kg)					
Arsenic (As)	0.18	0.08	0.04	0.19	5.94
Cadmium (Cd)	0.53	0.13	0.16	0.13	0.41
Cobalt (Co)	4.79	0.66	1.16	1.18	2.11
Chromium (Cr)	61.14	19.46	14.14	53.61	66.97
Copper (Cu)	9.49	3.27	10.1	6.83	20.61
Manganese (Mn)	81.6	61.25	44.99	111.14	182.21
Nickel (Ni)	11.11	21.87	11.12	28.1	46.64
Lead (Pb)	1.93	0.58	0.97	4.62	60.02
Vanadium (V)	0.48	0.14	0.12	0.37	0.66
Zinc (Zn)	271.95	12.69	64.85	28.3	111.17
Mercury (Hg)	1.72	0.11	0.38	0.22	0.43
Molybdenum (Mo)	0.86	0.66	0.38	1.21	1.3
Selenium (Se)	-	0.04	0.09	0.04	0.1

* Mean value (triplicate sample)

** Unknown

- Under limit

Table 5-3. Characterization and full elemental analysis of the WW samples collected from Industrial.

Sample type	Wood chips	Wood Pellets
Property	Value*	Value*
Waste wood Properties		
Proximate Analysis (wt. %)		
Moisture content	8.73	9.08
Ash content	2.78	0.91
Volatile matter	80.43	86.65
Fixed carbon (FC)	8.07	3.36
Ultimate Analysis wt. %(dry)		
Carbon (C)	48.29	50.69
Hydrogen (H)	6.91	7.17
Nitrogen (N)	1.97	0.09
Sulphur(S)	0.0022	0.0025
Oxygen(O)	42.83	42.06
Carbon/Nitrogen (C/N)	24.55	561.34
Calorific Value		
Calorific Value (CV)	18.21	17.9
TCV	15.26	20.51
HHVd	20.48	21.77
Chemical Analyses		
Halides		
Chlorine (Cl)	0.04	0.09
Bromine (Br)	-	-
Fluorine (F)	0.01	-
Major elements (mg/kg)		
Aluminium (Al)	247.75	83.39
Calcium (Ca)	3161.37	1512.81
Potassium (K)	580	506.49
Iron (Fe)	8074.19	200.33
Sodium (Na)	623.15	106.56
Silicon (Si)	168.38	107.82
Magnesium (Mg)	325.62	197.34
Phosphorus (P)	0.01	0.01
Titanium (Ti)	16.54	1.92
Minor elements (mg/kg)		
Arsenic (As)	16.77	0.04
Cadmium (Cd)	0.29	0.17
Cobalt (Co)	1.83	0.1
Chromium (Cr)	42.65	11.27
Copper (Cu)	23.79	7.34
Manganese (Mn)	118.39	62.43
Nickel (Ni)	5.91	2.73
Lead (Pb)	151.32	0.34
Vanadium (V)	0.73	0.19
Zinc (Zn)	66.98	14.24
Mercury (Hg)	0.71	1
Molybdenum (Mo)	0.52	0.17
Selenium (Se)	0.08	0.07

* Mean value (triplicate sample)

- Under limit

Table 5-4. Characterization and full elemental analysis of the WW samples collected from landfill.

(55-40 m depth)							
Samples depth (m)	53-55	50-51	48-50.5	46-48	44.5-46	41-43	40-41.5
Property	Value*	Value*	Value*	Value*	Value*	Value*	Value*
Waste wood Properties							
Proximate Analysis (%wt.)							
Moisture	7.73	9.89	41.48	46.29	38.35	45.56	41.32
Ash	5.43	3.77	10.60	6.18	11.59	13.28	5.79
Volatile matter	80.39	67.27	46.99	47.31	36.84	37.06	55.58
Fixed carbon (FC)	6.47	19.09	0.96	0.51	13.23	4.13	0.36
Ultimate Analysis (% wt., dry)							
Carbon (C)	47.40	45.56	43.79	46.81	38.22	42.25	49.24
Hydrogen (H)	7.02	6.98	6.56	6.77	5.97	6.18	7.42
Nitrogen (N)	0.392	0.298	0.62	0.81	0.69	0.69	0.45
Sulphur(S)	0.02	0.013	0.009	0.01	0.01	0.006	0.0043
Oxygen(O)	45.2	47.178	49.05	45.63	55.14	50.91	42.91
Carbon / Nitrogen(C/N)	115.89	153.71	73.06	61.62	54.48	63.55	113.97
Calorific Value							
Calorific Value (CV)	17.66	18.58	17.56	18.32	17.56	14.55	19.67
TCV	18.06	17.30	15.18	16.59	11.37	13.67	19.51
HHVd	20.06	19.16	17.71	19.46	14.42	16.41	21.36
HHVd	17.66	18.58	17.56	18.32	17.56	14.55	19.67
Chemical Analyses							
Halides							
Chlorine (Cl)	0.05	0.12	0.12	0.11	0.1	0.13	0.18
Bromine (Br)	-	0.04	0.04	0.04	0.04	0.04	0.04
Fluorine (F)	-	-	-	-	-	-	-
Major elements (mg/kg)							
Aluminium (Al)	260.66	269.76	2303.89	158.17	4311.36	995.89	181.69
Calcium (Ca)	6646.27	4606.52	4451.82	5538.43	11328.16	14934.45	4367.24
Potassium (K)	522.33	527.15	745.3	782.67	1156.89	861.98	608.85
Iron (Fe)	6562.35	3413.89	3634.4	1686.34	6461.27	4000.31	1821.19
Sodium (Na)	861.4	2421.33	1607.94	1571.22	2182.62	2177.49	2435.49
Silicon (Si)	296.24	259.69	302.92	246.07	361.51	519.62	161.91
Magnesium (Mg)	335.9	329.82	421.93	341.02	628.15	703.12	401.04
Phosphorus (P)	-	0.01	0.01	0.01	-	0.01	-
Titanium (Ti)	15.29	19.65	21.5	7.59	24.48	18.86	20.91
Minor elements (mg/kg)							
Arsenic (As)	2.69	10.17	6.15	1.8	7.74	81.58	1.04
Cadmium (Cd)	3.04	0.44	0.11	0.09	0.24	0.19	0.41
Cobalt (Co)	2.03	1.71	3.56	0.48	3.3	3.38	3.18
Chromium (Cr)	8.81	18.44	8.96	7.48	16.5	150.52	16.2
Copper (Cu)	7.72	19.37	38.79	3.06	61	177.23	8.26
Manganese (Mn)	37.37	30.84	33.82	33.24	92.79	44.37	19.5
Nickel (Ni)	10.77	5.9	17.38	6.88	9.68	10.55	11.66
Lead (Pb)	2130.53	407.66	94.44	6.97	98.6	70.88	603.53
Vanadium (V)	1.92	2.62	2.98	1.01	4.43	3.71	0.59
Zinc (Zn)	121.05	150	214.09	55.96	224.82	124.57	346.73
Mercury (Hg)	0.67	0.32	0.12	0.12	0.66	0.77	0.13
Molybdenum (Mo)	0.51	0.85	0.62	0.28	0.78	0.84	0.24
Selenium (Se)	0.71	0.33	0.4	0.08	0.53	0.65	0.17

* Mean value (triplicate sample)

- Under limit

Table 5-4. Characterization and full elemental analysis of the WW samples collected from landfill.

(39-23 m depth)							
Samples depth (m)	37.5-39	36-37.5	35-36	32.5-35	29-30.5	25-27	23-25
Property	Value*	Value*	Value*	Value*	Value*	Value*	Value*
Waste wood Properties							
Proximate Analysis (%wt.)							
Moisture	32.05	38.76	39.21	52.26	22.28	26.45	37.26
Ash	8.47	8.23	9.35	7.65	11.11	13.47	10.93
Volatile matter	46.42	52.62	30.05	35.42	56.77	46.82	49.35
Fixed carbon (FC)	13.0791	0.41	21.31	4.69	9.85	13.26	2.46
Ultimate Analysis (%wt,dry)							
Carbon (C)	46.04	47.18	45.22	45.46	44.16	39.09	39.76
Hydrogen (H)	6.47	7.15	6.44	6.93	6.73	6.18	6.12
Nitrogen (N)	0.48	0.85	0.89	0.70	0.51	0.54	0.98
Sulphur(S)	0.02	0.002	0.007	0.006	0.01	0.015	0.016
Oxygen(O)	48.72	44.41	47.47	46.68	46.58	51.25	50.41
Carbon / Nitrogen(C/N)	104.27	56.15	54.61	65.43	70.83	81.340	46.35
Calorific Value							
Calorific Value (CV)	17.92	18.95	17.89	18.16	17.52	18.13	17.65
TCV	15.55	17.50	15.15	16.52	16.80	13.86	13.13
HHVd	17.88	20.27	18.23	19.12	18.99	16.37	16.58
Chemical Analyses							
Halides							
Chlorine (Cl)	0.11	0.25	0.17	0.17	0.17	0.12	0.09
Bromine (Br)	0.04	0.04	0.05	0.06	0.05	0.04	0.04
Fluorine (F)	-	-	-	-	-	-	-
Major elements (mg/kg)							
Aluminium (Al)	3223.04	658.33	5189.45	479.15	1004.1	2210.29	1153.62
Calcium (Ca)	16645.77	4214.93	9682.93	4619.09	8061.14	16625.13	11684.07
Potassium (K)	1196.28	1315.58	1240.53	709.49	973	879.19	744.27
Iron (Fe)	6488.38	3278.72	4776.33	3949.18	6818.21	5700.97	3016.39
Sodium (Na)	1937.82	3418.32	2208.53	1611.46	1868.11	1607.9	1145.96
Silicon (Si)	598.51	279.41	205.87	247.56	546.38	537.87	535.57
Magnesium (Mg)	1118.15	431.44	681.41	340.48	551.52	968.25	595.08
Phosphorus (P)	-	-	-	0.01	0.01	-	0.01
Titanium (Ti)	69.36	17.63	27.02	11.01	21.04	36.86	38.69
Minor elements (mg/kg)							
Arsenic (As)	17.87	0.82	1.97	1.83	3.84	5.53	9.53
Cadmium (Cd)	0.28	0.24	0.15	0.19	0.28	0.33	0.12
Cobalt (Co)	3.2	1.88	1.79	3.38	2.6	3.48	2.35
Chromium (Cr)	28.03	7.63	12.86	5.75	25.42	13.19	26.41
Copper (Cu)	67.93	17.32	25.66	39.03	38.45	31.19	54.82
Manganese (Mn)	65.75	48.13	33.45	25.05	51.17	56.22	40.16
Nickel (Ni)	12.09	4.12	20.39	12.73	23.91	10.07	10.07
Lead (Pb)	147.92	49.49	41.24	25.09	908.13	3404.86	31.61
Vanadium (V)	9.42	3.4	6.76	1.56	4.74	4.99	4.59
Zinc (Zn)	124.84	636.73	175.46	388.26	302.92	262.19	71.4
Mercury (Hg)	0.8	0.15	0.31	0.73	0.34	0.79	0.12
Molybdenum (Mo)	1.04	1.32	0.66	0.41	2.05	0.74	1.35
Selenium (Se)	0.93	0.35	0.42	0.41	0.5	0.83	0.48

* Mean value (triplicate sample)

- Under limit

Table 5-4. Characterization and full elemental analysis of the WW samples collected from landfill.

(20-3 m depth)							
Samples depth (m)	20-23	17-20	13.5-17	11-13.5	9-11	9-7	7-3
Property	Value*	Value*	Value*	Value*	Value*	Value*	Value*
Waste wood Properties							
Proximate Analysis (%wt.)							
Moisture	27.65	38.46	45.89	39.05	38.37	27.93	33.72
Ash	6.37	12.94	17.82	11.07	5.106	2.58	1.39
Volatile matter	42.10	48.40	25.94	35.20	54.22	63.26	63.30
Fixed carbon (FC)	23.87	0.195	10.32	14.66	2.30	6.21	1.57
Ultimate Analysis (%wt,dry)							
Carbon (C)	47.26	44.68	42.61	40.61	44.39	47.99	49.36
Hydrogen (H)	7.07	6.53	6.22	6.83	6.71	7.45	7.48
Nitrogen (N)	0.67	1.3	0.75	1.43	0.91	0.216	0.19
Sulphur(S)	0.01	0.01	0.01	0.01	0.01	0.001	0.01
Oxygen(O)	42.87	47.46	50.41	51.10	47.96	44.26	42.95
Carbon / Nitrogen(C/N)	74.30	34.63	55.38	27.75	53.93	156.16	276.21
Calorific Value							
Calorific Value (CV)	18.28	17.38	16.79	16.90	17.94	18.41	18.64
TCV	18.60	14.21	13.77	12.44	15.11	19.25	20.16
HHVd	20.99	18.11	16.60	16.69	18.29	20.90	21.53
Chemical Analyses							
Halides							
Chlorine (Cl)	0.1	0.09	0.24	0.15	0.23	0.12	0.06
Bromine (Br)	0.05	0.05	0.05	0.06	0.06	0.04	0
Fluorine (F)	-	-	-	-	-	-	-
Major elements (mg/kg)							
Aluminium (Al)	539.05	947.72	2118.23	654.35	299.79	252.14	112.22
Calcium (Ca)	5511.82	8508.85	12262.1	5915.46	4283.88	3589.4	3274.69
Potassium (K)	704.06	608.35	883.79	600.36	790.06	712.59	801.01
Iron (Fe)	3982.73	4195.1	7679.29	6068.94	2349.75	1074.16	577.03
Sodium (Na)	1176.15	1008.33	2296.98	1172.84	2223.24	1459.69	761.24
Silicon (Si)	241.14	464.1	478.21	537.33	202.96	246.81	144.16
Magnesium (Mg)	366.99	411.66	624.11	523.7	317.77	307.86	279.81
Phosphorus (P)	-	-	-	0.01	-	-	0.01
Titanium (Ti)	21.72	22.38	37.68	23.01	10.45	5.29	2
Minor elements (mg/kg)							
Arsenic (As)	31.39	5.55	3.77	3.66	2.08	3.47	160.97
Cadmium (Cd)	0.2	0.15	0.46	0.19	0.1	0.04	0.07
Cobalt (Co)	4.54	1.02	6.92	3.62	2.26	1.41	1.01
Chromium (Cr)	141.56	16.1	52.14	14.31	15.15	8.54	238.88
Copper (Cu)	45.08	9.57	52.03	16.43	12.72	5.84	136.2
Manganese (Mn)	37.96	53.82	67.74	56.66	31.77	21.16	34.53
Nickel (Ni)	4.92	3.8	12.68	21.11	7.55	3.4	3.37
Lead (Pb)	106	45.23	84.77	166.29	17.69	8.77	3.3
Vanadium (V)	2.76	3.7	6.21	3.02	1.86	0.76	0.38
Zinc (Zn)	99.87	89.54	182.05	50.21	34.05	23.15	19.56
Mercury (Hg)	0.64	0.62	0.34	0.7	0.65	0.28	0.27
Molybdenum (Mo)	0.66	0.68	1.8	0.74	0.7	0.23	0.34
Selenium (Se)	0.47	0.64	0.85	0.31	0.47	0.13	0.12

* Mean value (triplicate sample)

- Under limit

5.3.2 Metal(loid)s in waste wood samples

The measured concentrations of metal(loid) elements in WW samples varied widely according to the samples sources, types, and originations. For clarification purposes, the results were divided into two parts: the first part was related to the minor elements As, Cd, Co, Cu, Hg, Mn, Mo, Ni, Pb, Se, V, and Zn, whereas the other one was related to the major elements Al, Ca, Fe, Mg, K, Si, Na, and Ti.

5.3.2.1 Stream waste wood

Figure 5-5a and b show, respectively, the concentrations of the minor and major elements in the five WW samples from streams. It is clear that the concentration of each individual element in each sample was dissimilar. For instance, the concentration ranges and their respective means of the minor elements (Zn, Mn, Cr, Ni, Cu, and Pb) and the means of the major elements (Ca, Fe, K, Mg, and Na) are shown below:

- Zn: 12.69-271.95 mg/Kg (138.15 mg/Kg)
- Mn: 44.99-182.21 mg/Kg (103.72 mg/Kg)
- Cr: 5.32-66.97 mg/Kg (48.75 mg/Kg)
- Ni: 8.3-46.64 mg/Kg (24.97 mg/Kg)
- Cu: 3.27-20.61 mg/Kg (10.59 mg/Kg)
- Pb: 0.58-60.02 mg/Kg (18.21 mg/Kg)
- Ca: 35.19-3802.48 mg/Kg (3802.48 mg/Kg)
- Fe: 198.35-2277.91 mg/Kg (1375.58 mg/Kg)
- K: 252.42-1587.87 mg/Kg (1587.87 mg/Kg)
- Mg: 55.23-550.12 mg/Kg (550.11 mg/Kg)
- Na: 87.48-521.33 mg/Kg (521.32 mg/Kg)

5.3.2.2 Industrial waste wood

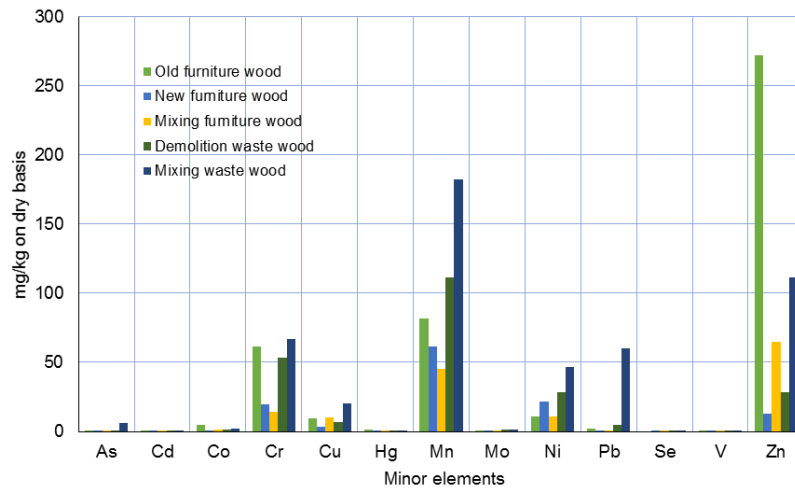
The concentrations of the minor and major elements are presented in Figure 5-6a and b, respectively. The results show that the concentrations of all metal(loid)s in chip wood are higher than those in pellets wood. This is expected because the latter has been previously pre-processed and prepared as a fuel.

5.3.2.3 Landfill waste wood

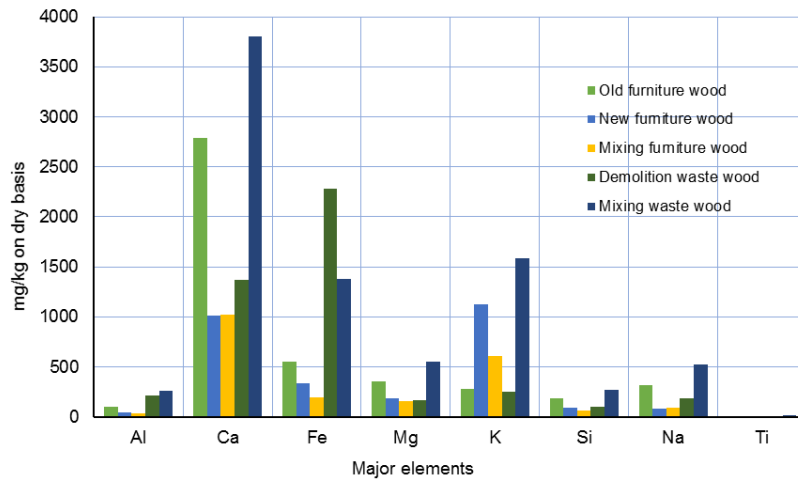
Figure 5-7a and b, separately, show the concentrations of the minor and major elements in the 21 WW samples from landfill. As observed, the concentrations of

the minor elements Cd, Co, V, Hg, Mo, and Se in all the samples show modest variation for. The maximum concentrations of these elements were 0.39, 3.56, 9.4, 1.02, 1.03, and 0.93 mg/Kg, respectively. On contrary, the concentrations of the major elements exhibit relatively large variation. For example, Ti, Mg, Na, and Fe concentrations ranged and their respective means are shown below:

- Ti: 8.16-69.36 mg/Kg (39.46 mg/Kg)
- Mg: 333.32-1118.16 mg/Kg (708.50 mg/Kg)
- Na: 276.26-1937.82 mg/Kg (1435.84 mg/Kg)
- Fe: 624.35-6488.37 mg/Kg (4176.11 mg/Kg)

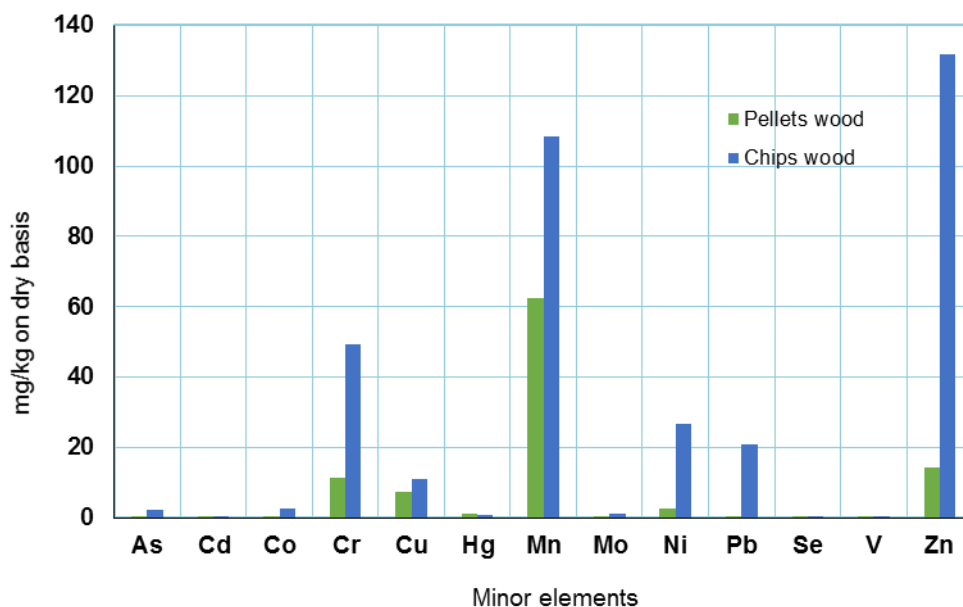


(a) Minor elements.

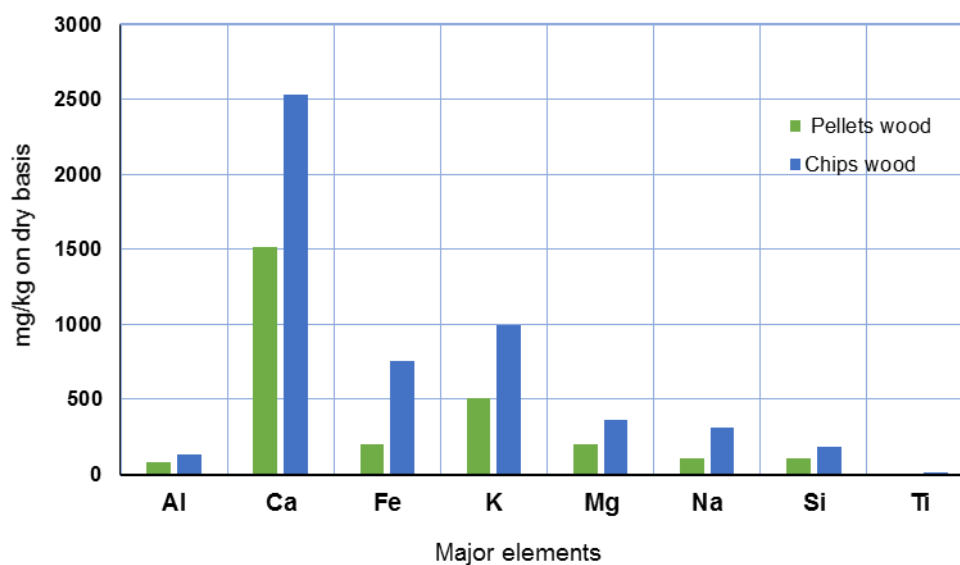


(b) Major elements.

Figure 5-4. The concentrations of metal(loid) elements in WW samples from waste streams.

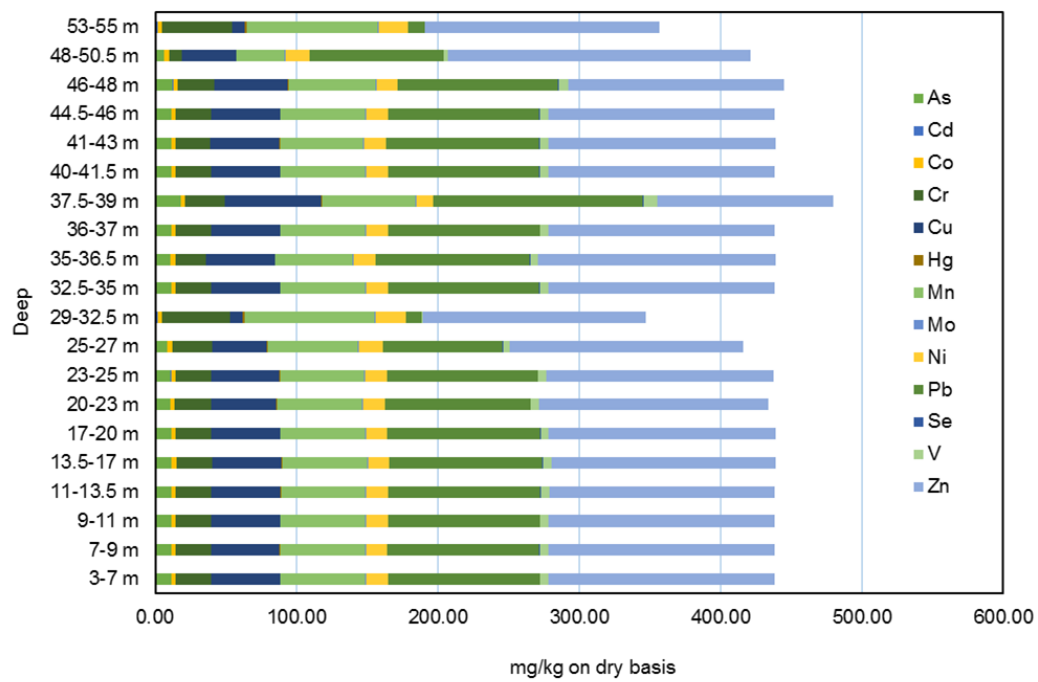


(a) Minor elements.

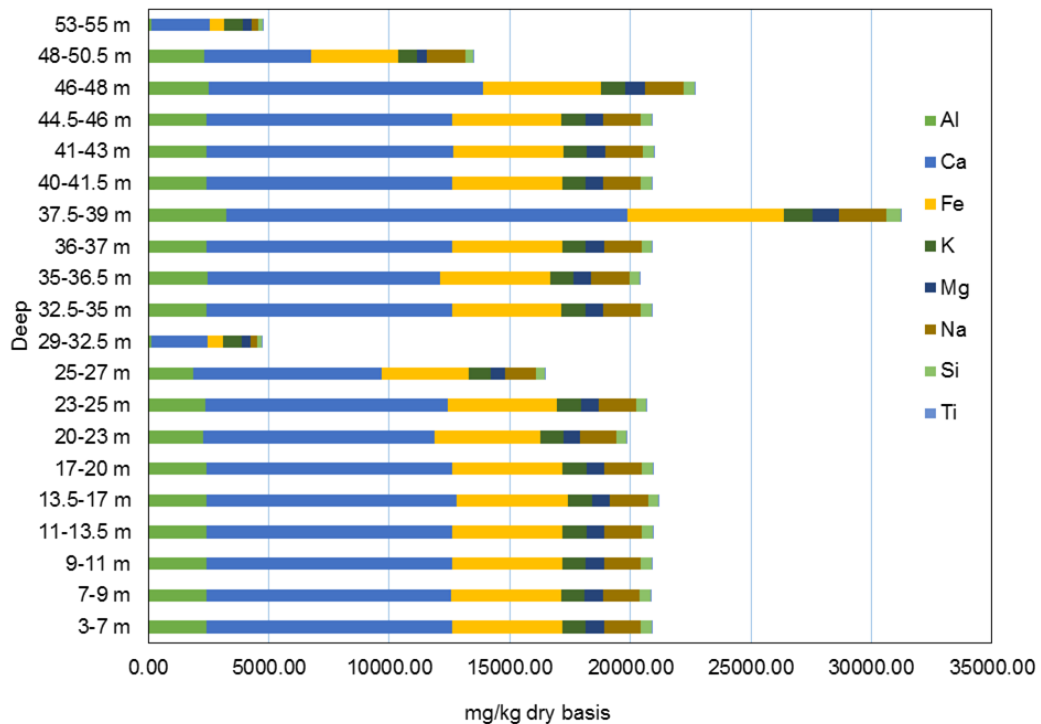


(b) Major elements.

Figure 5-5. The concentrations of metal(loid) elements in WW samples from waste industrial.



(a) Minor elements.



(b) Major elements.

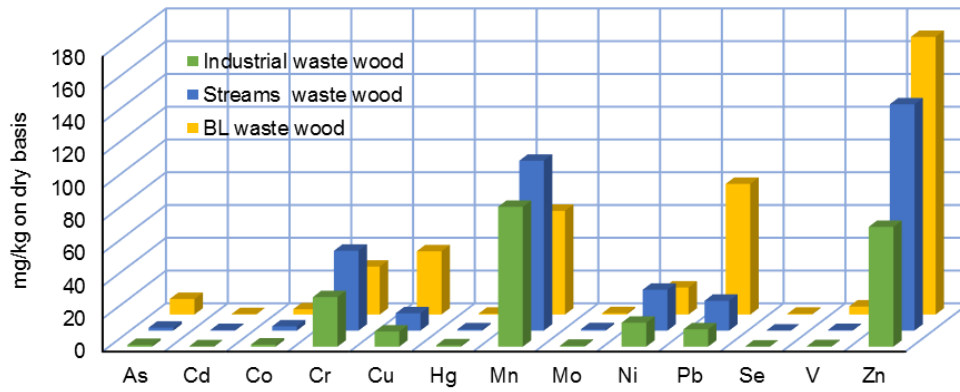
Figure 5-6. The concentrations of metal(loid) elements in WW samples from landfill site.

5.3.3 Comparison of metal(loid)s concentrations in waste wood samples

The concentrations (expressed as mean values (mg/Kg) of dry weight of the samples taken from the same site) of minor and major elements are shown in Figure 5-8a and b, respectively. It appears that there are considerable differences in elements concentrations between the three types of waste wood. As expected, compared to stream and industrial woods, the concentrations of metal(loid)s in landfill-excavated woods are generally higher except in the cases of Cd, Mo, Se and Ti, which display comparable concentrations in all WW samples. However, among the minor elements, the concentrations of Mn, Cr, and Ni in landfill woods slightly lower compared to stream woods. In addition, for most of the elements in stream woods, the concentrations are higher than in industrial woods. The following is the order of elemental concentration in each WW type.

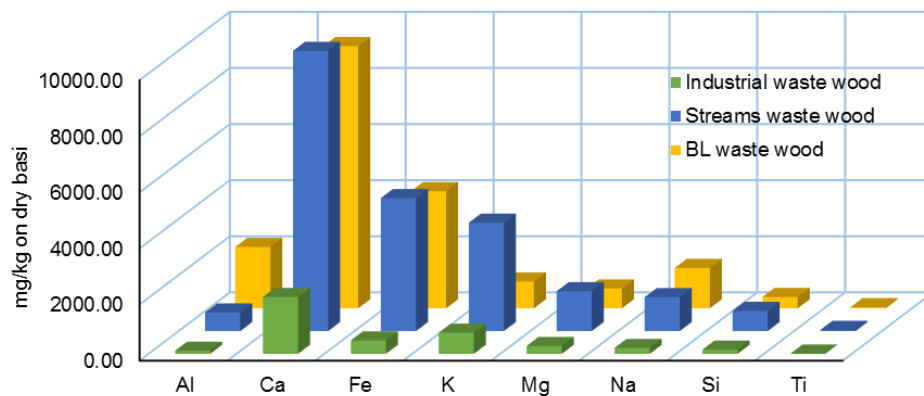
- Landfill woods: Ca> Fe> Al> Na> K> Mg> Si> Zn> Pb> Mn>Ti> Cu> Cr> Ni> As> V> Co> Mo> Hg> Se> Cd.
- Industrial woods: Ca> K> Fe> Mg> Na> Si> Al> Mn> Zn> Cr> Ni> Pb> Cu> Ti> Co> As> Hg> Mo> V> Cd > Se.
- Stream woods: Ca> Fe> K> Mg> Na> Si> Al> Zn> Mn> Cr> Ti> Ni> Pb> Cu> Co> As> Mo> Hg> V> Cd> Se.

As it is known that the considered major elements (Al, Ca, Fe, Mg, K, Si, Na, and Ti) in this study are not easily volatilized (Edo, 2016; Konttinen et al., 2013; Meier, 2013) Therefore, the most interesting elements are the minor ones, since such elements are likely to be volatilized during the thermal treatment of WW (Haynes, Boström and Nordin, 2008; Konttinen et al., 2013; Lundholm, 2007; Meier, 2013; Nzihou and Stanmore, 2013). Figure 5-9 shows the maximum concentration of each minor element in all the WW samples. It can be noted that the levels of the minor elements exhibited decreasing order such that Zn (214.09) > Pb (147.92) > Mn (92.36) > Cu (67.93) > Cr (48.29)> Ni (20.5) > As (17.87) > V (4.9) > Co (3.56). The levels of Mo, Hg, Se, and Cd were found at around ≤ 1.03 .



Minor elements

(a) Minor elements.



Major elements

(b) Major elements.

Figure 5-7. The concentrations of metal(loid) elements in the streams, industrial, and L.d. woods.

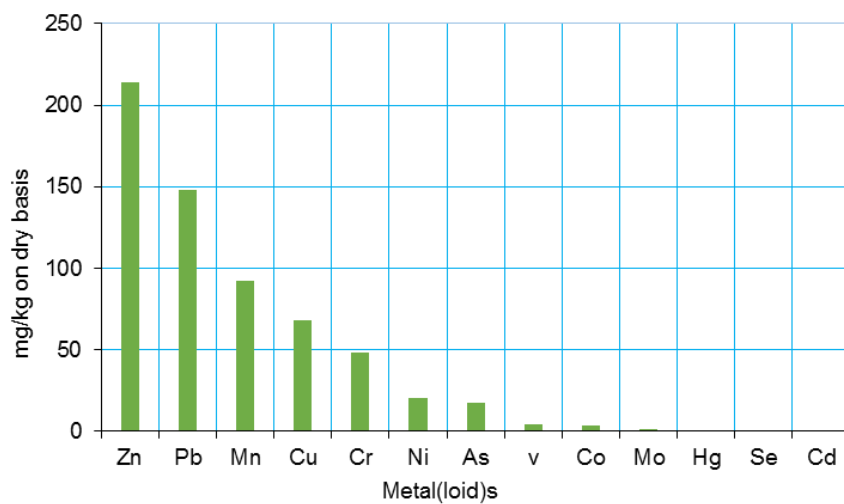


Figure 5-8. Key metal(loid)s contaminants in WW samples.

Comparing to findings from literature (Chapter 2), in this study it was observed that the elements Zn, Pb, As, Cu, Cr, Fe and Ti present at levels far higher, as shown in Table 5-8. However, in the case of Co and Cd, it was not observed any significant differences in their concentrations.

Table 5-5. Comparison between the concentrations of main metal(loid)s in WW.

Metal(loid)s	Concentrations* (mg/kg)	Concentrations** (mg/kg)
Arsenic (As)	17.87	1.243
Cadmium (Cd)	0.45	0.5
Chromium (Cr)	48.29	1.1243
Cobalt (Co)	3.56	4
Copper (Cu)	67.93	1.262
Iron (Fe)	4176.11	1720
Lead (Pb)	147.92	7.8
Manganese (Mn)	92.36	73
Titanium (Ti)	39.46	2.8
Zinc (Zn)	214.09	1.1

* Resulted in current study.

**Sources: (Ange Nzihou and Brian Stanmore, 2013; Connell, 2005; Cui et al., 2010; Edo et al., 2016; Harrison, 2014; Huron et al., 2017; Kenney et al., 2011; Kinata et al., 2012; Krook, Mårtensson and Eklund, 2006; Meier, 2013; Mercer and Frostick, 2012; Nzihou and Stanmore, 2013; Solo-Gabriele et al., 2002; Vassilev et al., 2010; WRAP and BSI, 2012).

5.4 Conclusions

The physico-chemical characterization and elemental analysis carried out on the set of WW samples enabled to obtain adequate and proper datasets on which the experimental works and thermodynamic modelling can be based.

The refinement of the obtained results shows that landfill samples have the highest moisture contents among the studied WW samples. On the contrary the calorific values of landfill samples were lower those of stream and industrial samples. In general, the C, H, O, and N contents were similar among the WW samples.

Furthermore, the concentrations of minor elements were found to be varied significantly within the twenty-eight samples except the elements Cd, Mo and Se, which maintained very close levels at around 0.39, 0.9 and 0.4 mg/kg, respectively. More specifically,

- Zn and Pb were the most abundant elements in landfill samples and their highest concentrations approx. 169.45 and 79.74 mg/kg, respectively.
- Cu and As were the next most abundant elements in landfill samples and their highest concentration at nearly 9.5 and 38.64 mg/kg, respectively.
- The concentration levels of V, Co, and Hg were respectively at around 4.9, 3.2, and 0.5 mg/kg in landfill samples.
- The concentration levels of Mn, Ni, and Cr in stream samples were found to be at about 03.7, 24.97, and 48.75 mg/kg, respectively. Also, these levels were higher by factor of 1.6 than in landfill and industrial samples.

The characteristics and elemental composition data of the WW samples obtained in this chapter will be relevant for the experimental works (TGA analysis and tube furnace) and thermodynamic modelling in the subsequent chapter.

Chapter 6 Experimental Testing and Validation of the Thermodynamic Equilibrium Models

This chapter details the experimental testing used to validate the equilibrium calculations on the fate of metal(loid)s in woody biomass (original, artificial and blends) samples under typical pyrolysis conditions. Major topics include the optimisation of process operational conditions through TGA, the experimental investigation of the distributions of metal(loid)s in tube furnace pyrolysis experiments, and the validation of modelling predictions using the experimental data.

The main contribution of this chapter is to show that systematic blending of different types of waste woods can return potential advantages over the pyrolysis of a single type. It follows that the contaminated waste wood can be utilised for clean energy production or simply disposed.

This chapter is currently being prepared for submission as papers with titles:

- Experimental and Kinetic Study of Thermal Decomposition Behaviour of Woody Biomass Pyrolysis.
- Partitioning of Metal(loid)s during Woody Biomass Pyrolysis: Experimental and Thermodynamic Equilibrium Modelling.

6.1 Introduction

Having investigated the fate of the targeted metal(loid)s in WW with the aid of thermodynamic equilibrium modelling, it is of interest to expand this study to a wider range of element and other types of woody biomass. In this respect, the current chapter studies the fate of Al, As, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Na, Mn, Mo, Ni, Pb, Si, Ti, V, and, Zn present in nine unique woody samples during the pyrolysis process. In addition, the effects of Ni on As phase transformation behaviours in blended and three artificial samples are also investigated. For all the models, a thermogravimetric analyser (TGA) was used to obtain the thermal characteristics of woody biomass samples under pyrolysis operation conditions at temperature range of 30-900°C with N₂ pure gas at 40.0ml/min. The validation

and optimisation were carried out using tube furnace. In addition, artificial fuel samples contain species with different concentrations of metal(loid) elements were prepared and analysed to provide insightful understanding of the occurred interactions and interferences.

Therefore, this chapter presents the processes and results as follows:

- Artificial waste wood samples preparation.
- Optimisation of the operational conditions and determining the kinetic parameters of pyrolysis process through analysing the thermal behaviour of the unique waste wood samples.
- Investigation into the fate of metal(loid)s in the unique waste wood samples during tube furnace pyrolysis.
- Validation of the profiles distributions of the metal(loid)s by thermodynamic equilibrium modelling.

6.2 Materials and methods

6.2.1 Samples

6.2.1.1 Preparation of samples

The considered waste wood (original) samples in this chapter are those prepared as described in chapter 5. The artificial samples were synthesised at Cranfield University. The chemical materials were purchased from Fischer Scientific UK, and the deionised water (18.2 MΩ.cm at 25°C) that was used in all experiments was obtained from Cranfield University. The artificial waste wood samples were subjected to the same analysis procedure as detailed in chapter 5.

6.2.1.2 Original waste wood samples

In order to cover different types and levels of contaminations, 10 woody biomass samples were selected from various locations, as follows:

- Four stream samples: old furniture, new furniture, mixed furniture, and demolition
- Two industrial fuel samples: pellets and chips.

- Four landfill samples: L.d. (3-7 m), L.d. (37.5-39 m), L.d. (41-43 m), and L.d. (50-51 m).

6.2.1.3 Artificial WW and blend samples

Artificial samples were synthesized to investigate the influence of the presence of Ni on the behaviour of As, as these two elements were likely to interact during the thermal treatment of biomass. Note that the analysis results of pellets in chapter 5 were considered as the baseline values when preparing the artificial samples, and the solutions of Ni and As were taken as pure elements to avoid any effects from other elements (Said et al., 2017). Furthermore, a mixture of WW (60%) and pellets wood (40%) was created to study the behaviour of As during pyrolysis.

6.2.1.3.1 Artificial samples

Three artificial samples (AS₁, AS₂, and AS₃) were prepared, each of which consisted of 5 g of original pellets wood powder. Each sample was impregnated with a specific solution (100 mL vol) as follows:

1. AS₁: As (10 mg/kg) mixed with Ni (50 mg/kg)
2. AS₂: As (30 mg/kg) mixed with Ni (80 mg/kg)
3. AS₃: As (40 mg/kg) mixed with Ni (100 mg/kg)

Note that, all the chemical solutions (Arsenic and Nickel) were purchased from Fischer Scientific UK, and the deionised water (18.2 MΩ.cm at 25°C) obtained from Cranfield University.

The resulting solutions were shaken by a shaker (Orbishake /M262) at a constant agitation speed of 200 rpm for 24 hours (Stals et al., 2010). Each sample was then filtered using a Buchner flask with a Whatman 542 paper, and was placed in an oven to dry at 40°C for 24 hours (Basu, 2013;P445). The sample then analysed in order to measure the concentrations of elements and the results are given in Table 6-5.

6.2.1.3.2 Blends of WW (60%) and pellet wood (40%)

In this case, a sample of waste wood (60%) and pellet wood (40%) (Šyc et al., 2011) was prepared by blending 6 g of landfill wood powder with 4 g of pellet

wood powder. The chemical characterisation and full elemental composition of the prepared sample were obtained in same manner as described in chapter 5.

6.2.1.4 Preparation of sampling train

The collection of the elements retained in the fly ash was based on the Ontario Hydro Method (OHM) sampling train. In this work, three types of solutions were prepared daily, including 100mL of KCl (1mol/dm^3), a mixture 150 mL of 5% V/V HNO_3 with 10% V/V H_2O_2 , and a 100 mL mixture of 4%W/V KMnO_4 with 10% V/V H_2SO_4 (Cui et al., 2018; Linak et al., 2011; Liu et al., 2016; Moreda-pin, Alonso-rodri and Guez, 2003).

6.2.1.5 Product analysis

There were two types of products: char (bottom ash) and fly ash (elements in train solution). In order to determine the concentrations of the elements in char, an aqua regain digestion procedure was applied (Rao, Bailey and Wingwafi, 2011; Siaka, Owens and Birch, 1998), as outlined below:

1. 0.1 g of char was accurately weighed in a Teflon microwave vessel, 6 mL of HCl (1.18 specific gravity) and 2 mL of HNO_3 (1.42 specific gravity) were added to the solution, and it was left overnight at room temperature.
2. The obtained solution was placed into a pressure vessel (Microwave Reaction System-Multivalve 300, Anton Paar, UK), which was then operated according to the NR-SASSOP17 method.
3. Thereafter, the dissolution of elements was cooled and filtered using a Whatman 542 paper. The filtrate was quantitatively transferred to volumetric flasks and completed up to 100 mL with ultrapure deionised water ($18.2\text{ M}\Omega\text{ cm}$ at 25°C).

The concentrations of the dissolved elements (Al, As, Ca, Cd, CO, Cr, Cu, Fe, Hg, K, Mg, Mn, Mo, Na, Ni, Pb, Se, Si, S, Ti, V, and Zn) were measured using the ICP-MS, as explained in section 5.2.3.5.

Moreover, the concentrations of the elements in train solution were measured according to the metal(loid) extraction and analysis procedure in section 5.2.3.5.

6.2.1.6 Scanning electron microscope analyses

The scanning electron microscope (SEM) combined with Energy Dispersive X-ray spectrometer (EDX) is an important tool to visualize the surface of the materials with high resolution pictures. In this work, the SEM-EDX (Oxford-Instruments) was utilised to provide information regarding the distribution of the contaminated metal(loid) elements on the surface of the waste wood samples.

6.3 Experimental set-up

6.3.1 Thermogravimetric analyser (TGA)

Measurements were performed using a thermogravimetric analyser TGA 8000 (Perkin-Elmer) under atmospheric pressure to assess the thermal behaviour of woody biomass samples, and, in turn, optimise the pyrolysis operational parameters through the kinetics of the process (Bouraoui et al., 2016; Francisco-fernández et al., 2012; Helsen et al., 2004). The pyrolysis tests were conducted using nitrogen (N₂) as the carrier gas with a flow rate of 40 mL min⁻¹. Under pyrolysis conditions, the temperature was varied from 30°C to 900°C at four different heating rates ($\beta = dT/dt$), specifically 20 °C /min, 30°C /min, 50°C /min and 80°C /min (Duan et al., 2017a). Each TGA test was performed in duplicate for the purpose of quality assurance.

6.3.1.1 Methods

6.3.1.1.1 TG and DTG curves

Isothermal thermogravimetric methods were used to investigate the thermal decomposition of woody biomass samples by means of the thermogravimetric analysis (TG) and differential thermogravimetric analysis (DTG), which are respectively the weight loss and the derivative of weight loss of the samples under heating (Barraza-burgos et al., 2015; Dtg, El-sayed and Mostafa, 2014; Fidalgo et al., 2019; Gašparovič, Koreňová and Jelemenský, 2010).

6.3.1.1.2 Kinetic study

The kinetic triplet parameters of the woody biomass samples were determined based on model-free isoconversional methods as they are sufficiently flexible to

allow for changes in the mechanisms during the reaction course (Barraza-burgos et al., 2015; Cao et al., 2014; Fidalgo et al., 2019; Mora, 2009; Vyazovkin and Wight, 1999). However, since the thermal decomposition (solid-gas) reactions of wood are very complex, several studies (Fidalgo et al., 2019; Poletto et al., 2012; Poletto, Zattera and Santana, 2012) have addressed the thermal decomposition of woody biomass as a single reaction in pyrolysis as follows:



In free-model approaches, the rate of thermal decomposition can be expressed as (Fidalgo et al., 2019; Mora, 2009):

$$d\alpha/dt = k(T)f(\alpha) \quad (6-2)$$

$$\alpha = \frac{m_0 - m_t}{m_0 - m_f} \quad (6-3)$$

where α is the degree of conversion and given by equation (6-3); m_0 , m_t , and m_f , respectively, denote the initial weight of sample, the weight of sample at time t , and the final weight of sample, $f(\alpha)$ is the reaction model function; and $k(T)$ represents the temperature-dependent constant, which can be obtained from the Arrhenius equation as follows:

$$k(T) = Ae^{-E/RT} \quad (6-4)$$

where A , E , R , and T , are the pre-exponential factor (min^{-1}), activation energy (kJ mol^{-1}), gas constant at $8.314 \text{ (JK}^{-1}\text{mol}^{-1})$, and absolute temperature, respectively (Gey et al., 1998; Poletto, Zattera and Santana, 2012). The three parameters A , E , and R are referred to as the kinetic triplet (Duan et al., 2017a).

To describe the rate of solid-state reaction, the temperature-dependent constant $k(T)$ inserted in equation (6-2) results in the following expression:

$$d\alpha/dt = Ae^{-E/RT} f(\alpha) \quad (6-5)$$

Under non-isothermal conditions with a constant heating rate ($\beta = dT/dt$), the rate expression (6-5) can be written as follows:

$$d\alpha/dt = \left(\frac{A}{\beta}\right) e^{-E/RT} f(\alpha) \quad (6-6)$$

Equation (6-6) characterises the pyrolysis reaction rate as a function of temperature and β (Barraza-burgos et al., 2015; Fidalgo et al., 2019; Mora, 2009).

The activation energy and pre-exponential values can be calculated from TGA analysis and model-free methods (Fidalgo et al., 2019; Poletto et al., 2010; Poletto, Zattera and Santana, 2012; Sánchez-jiménez et al., 2010). Accordingly, after obtaining the weight loss data from the TGA analysis, the activation energy and pre-exponential values were computed using the Kissinger (KAS) (equation (6-7)) and Flynn–Wall–Ozawa (FWO) (equation(6-8)) methods (Duan et al., 2017a; Fidalgo et al., 2019; Merad, 2012; Poletto et al., 2010).

$$\ln \frac{\beta}{T^2} = \ln \left(\frac{AR}{E} \right) - \frac{E}{RT} \quad (6-7)$$

$$\ln \beta = \ln \frac{0.0048AE}{g(\alpha)R} - 1.0516 \frac{E}{RT} \quad (6-8)$$

where $g(\alpha)$ is a function of the conversion.

The linear least-squares fit was applied to plot $\ln \beta T^{-2}$ versus $1/T$ and $\ln \beta$ versus $1/T$, thereby obtaining the values of activation energy and the pre-exponential (Duan et al., 2017a; Fidalgo et al., 2019; Poletto, Zattera and Santana, 2012; Sánchez-jiménez et al., 2010). Further, the degrees of conversion (α) ranged from 0.1 to 0.9 (Liu, Cao and Yang, 2017).

6.3.1.2 Thermogravimetric analysis

The thermal behaviour of woody biomass during pyrolysis was examined through a set of experiments using TGA. The experiments assessed the influence of thermal treatment on the decomposition of woody biomass, as well as the influence of heating rate during the thermal treatment. More specifically, the following two effects were determined:

- The Influence of thermal treatment on the decomposition of the original, artificial and blend samples
- The Influence of heating rate during the thermal treatment of the pellet and landfill depth (37.5-39 m) samples.

Furthermore, a kinetic analysis was performed to identify key information on the pyrolysis reaction and the kinetics of woody biomass conversion.

6.3.2 Tube furnace pyrolysis experiments

An electrically heated horizontal tube furnace (150 cm × 10 cm, Carbolite, England) was employed for the pyrolysis experiments. The experimental system consisted of a gas cylinder (N₂ 99.99%), a mass flow controller with a meter, seven ceramic crucibles with a ceramic holder, a heated filter, and a train solution submerged in an ice-water bath, as depicted in Figure 6-1.

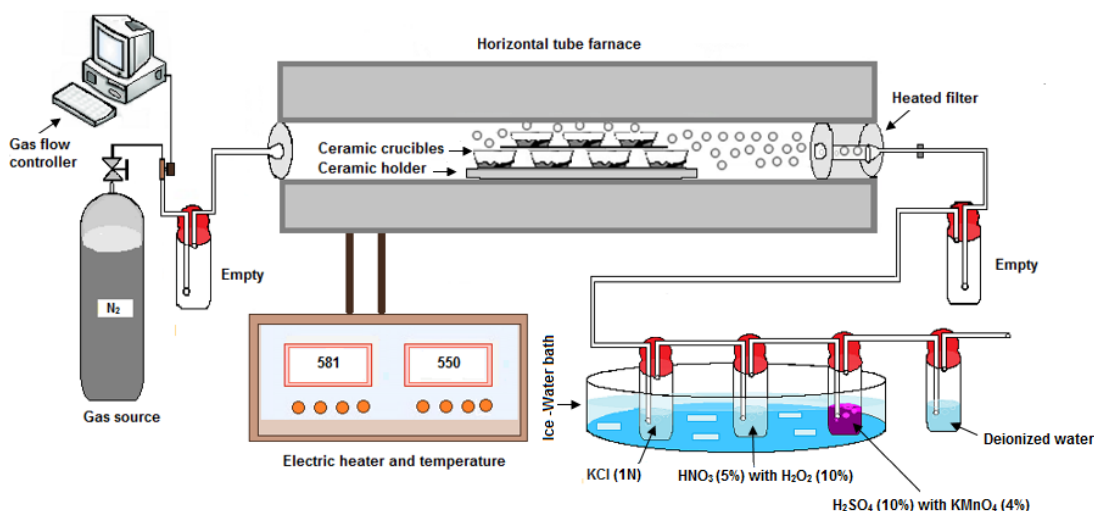


Figure 6-1. Schematic diagram of the tube furnace pyrolysis experiments.

A set of 30 experiments was designed based on the optimal operating conditions obtained from the thermogravimetric analysis. The experiments were performed to further understand the transformation behaviour of the metal(loid)s during pyrolysis of WW samples. Three temperature ranges (30-500°C, 30-700°C, and 30-900°C) were used during the experiments. Each experimental test was conducted using nitrogen (N₂) as a carrier gas with the flow rate set to 40 mL/min

under atmospheric pressure. In these experiments, one sample per day was taken as powder and tested. The details of the test conditions are given in Table 6-1.

Table 6-1. Test conditions for woody biomass samples.

Type of wood	Test	Total weight (g)	Temperature range (°C)
Original	Pellets	1,2,3	30-500, 30-700, 30-900
	Chips	4,5	30-500, 30-900
	Mixed Furniture	6,7	30-500, 30-900
	New Furniture	8,9	30-500, 30-900
	Demolition	10,11	30-500, 30-900
	L.d. 50-51 m	12,13	30-500, 30-900
	L.d. 37.5-39 m	14, (15,16,17)	500, (30-900)
	L.d. 41-43 m	18,19	30-500, 30-900
	L.d. 3-7 m	20,21	30-500, 30-900
Artificial	As ₁	22,23	30-500, 30-700
	As ₂	24,25	30-500, 30-700
	As ₃	26, (27,28)	30-500, 30-700
Blends	BS	29,30	30-500, 30-700

6.4 Thermodynamic modelling

Thermodynamic equilibrium modelling of woody biomass pyrolysis was undertaken to validate the experimental results. The calculation protocol was similar to that described in Chapter 3, but with the exception that a further 15 elements were included.

6.4.1 Mass balance calculation

The pyrolysis processes were modelled based on the obtained experimental data. The mass balance calculation consisted of two main parts:

- First, the composition data of each sample was converted to actual fuel data in terms of moles per hour according to the sample weight (fuel feed) in the experimental works.
- Second, the amount of pyrolysis agent (pure nitrogen N₂) was determined depending upon the flow rate under atmospheric pressure.

Table 6-2 shows the mass balance calculations, together with the results for the pellet fuel sample. The calculations and results for other samples are given in Table 6-3.

Table 6-2. Calculations of the total moles of the elements to be fed to MTDATA for pellets fuel.

Atomic Mass	unit	Elements	Actual fuel composition	Actual fuel composition Kg/hr (10000)	g/hr (0.001)	Fuel feed (wt.3.0492g)	Total input (MTDATA) Fuel +agent Mols/hr
12	Weight (%)	Carbon (C)	50.69	506900	506.9	1545.639	128.8033
1		Hydrogen (H)	7.17	163215.5*	163.2155	497.6767	497.6767
14		Nitrogen (N)	0.09	900	0.9	2.74428	100.0182&
32		Sulphur (S)	0.0025	25	0.025	0.07623	0.002382
16		Oxygen (O)	42.06	466357.8**	466.3578	1422.018	88.87613
35.5		Chlorine (Cl)	0.09	900	0.9	2.74428	0.077304
26.98	Weight mg/kg	Aluminium (Al)	83.39	83.39	0.08339	0.254273	0.009424
40		Calcium (Ca)	1512.81	1512.81	1.51281	4.61286	0.115322
39.0983		Potassium (K)	506.49	506.49	0.50649	1.544389	0.0395
55.84		Iron (Fe)	200.33	200.33	0.20033	0.610846	0.010939
23		Sodium (Na)	106.56	106.56	0.10656	0.324923	0.014127
28.0855		Silicon (Si)	107.82	107.82	0.10782	0.328765	0.011706
47.86		Titanium (Ti)	1.92	1.92	0.00192	0.005854	0.000122
74.92		Arsenic (As)	0.04	0.04	0.00004	0.000122	1.63E-06
112.41		Cadmium (Cd)	0.17	0.17	0.00017	0.000518	4.61E-06
58.93		Cobalt (Co)	0.1	0.1	0.0001	0.000305	5.17E-06
51.996		Chromium (Cr)	11.27	11.27	0.01127	0.034364	0.000661
63.54		Copper (Cu)	7.34	7.34	0.00734	0.022381	0.000352
54.938		Manganese (Mn)	62.43	62.43	0.06243	0.190362	0.003465
58.69		Nickel (Ni)	2.73	2.73	0.00273	0.008324	0.000142
207.2		Lead (Pb)	0.34	0.34	0.00034	0.001037	5E-06
50.94		Vanadium (V)	0.19	0.19	0.00019	0.000579	1.14E-05
65.38		Zinc (Zn)	14.24	14.24	0.01424	0.043421	0.000664
200.59		Mercury (Hg)	1	1	0.001	0.003049	1.52E-05
95.94		Molybdenum (Mo)	0.17	0.17	0.00017	0.000518	5.4E-06
78.96		Selenium (Se)	0.07	0.07	0.00007	0.000213	2.7E-06

*Total Hydrogen (from fuel + from moisture)

** Total Oxygen (from fuel + from moisture)

& Total Nitrogen (from fuel + from agent)

Moisture content -wt. %(ar) = 9.08

O from Moisture = 0.50394 4.575775

H from Moisture = 1.00788 9.15155

N₂ feeding input

Nitrogen (N₂) 40 L/min 2400 L/hr 99.822 Mols/hr

6.4.2 Calculation protocol

Equilibrium calculations were performed using the MTDATA software coupled with the SGTE database to predict the phase transformation and speciation formation of the elements (Al, As, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Na, Mn, Mo, Ni, Pb, Si, Ti, V, and Zn) during pyrolysis. Additionally, the elemental species included in the equilibrium calculations are listed in Table 6-4. Within this modelling, the elements fed to the MTDATA were grouped into major elements (Ar, C, Ca, Cl, H, K, N, Na, O, S, and Se) and minor elements (Al, As, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Na, Mn, Mo, Ni, Pb, Si, Ti, V, and, Zn).

6.4.3 Model application

The simulations were conducted at temperature range of 30-900°C under standard atmospheric pressure and agent (pure nitrogen N₂) with a flow rate of 40 mL min⁻¹. The actual fuel data used for the simulations are given in Table 6-2 and Table 6-3.

Table 6-3. List of Appendices for mass balance calculations.

Waste wood samples		Appendices
Original	Streams: new furniture, mixed furniture, and demolition	E.1.1
	Industrial: chips	E.1.2
	L.d.: 3-7 m, 37.5-39 m, 41-43 m, and 50-51 m	E.1.3
Artificial	Ni-As (As ₁ , As ₂ , and As ₃)	E.1.4
	Blends (60/40: W/W):BS	E.1.5

Experimental Testing and Validation of the Thermodynamic Equilibrium Models

Table 6-4. The used elemental species in equilibrium calculations.

Metal(loid)	Solid species	Liquid species	Gaseous species
Al	AlAs, AlAsO ₄ , Al ₄ C ₃ , Al ₂ CO, Al ₄ CO ₄ , Al ₂ Ca, Al ₄ Ca, Al ₂ CaO ₄ , Al ₂ Ca ₃ O ₆ , Al ₄ CaO ₇ , Al ₁₂ CaO ₁₉ , Al ₁₄ Ca ₁₂ O ₃₃ , Al ₂ Ca ₃ O ₁₂ Si, Al ₂ CdO ₄ , AlCl ₃ , AlCl ₃ H ₁₂ O ₆ , AlCl ₄ K, AlCl ₆ K ₃ , Al ₂ Cl ₉ K ₃ , AlCl ₄ Na, AlCl ₆ Na ₃ , AlClO, AlCo, Al ₃ Co, Al ₅ Co ₂ , Al ₉ Co ₂ , Al ₂ CoO ₄ , Al ₂ CuO ₄ , Al ₂ FeO ₄ , AlH ₃ AlH ₆ KO ₁₁ S ₂ , AlH ₂₄ KO ₂ O ₅ S ₂ , Al ₃ H ₂ KO ₁₂ Si, AlH ₂ NaO ₇ SiAlH ₃ O ₃ , AlKO ₂ , AlKO ₈ S ₂ , AlKO ₄ Si, AlKO ₆ Si ₂ , Al ₂ K ₂ O ₁₂ Si ₄ , Al ₂ K ₂ O ₁₆ Si ₆ , Al ₂ K ₂ O ₁₆ Si ₆ , Al ₂ K ₂ O ₁₆ Si ₆ , Al ₂ MnO ₄ , AlN, AlNaO ₂ , AlNaO ₄ Si, Al ₂ Na ₂ O ₁₂ Si, Al ₂ Na ₂ O ₁₆ Si, Al ₂ Na ₂ O ₁₆ Si, AlNi, AlNi ₃ , Al ₃ Ni, Al ₃ Ni ₂ Al ₂ NiO ₄ , Al ₂ O ₃ , Al ₂ O ₁₂ S ₃ , Al ₂ O ₇ Si ₂ , Al ₂ O ₅ Ti, Al ₂ O ₄ Zn, Al ₂ S ₃ , Al ₂ Se ₃ , AlTi, Al ₃ Ti.		Al, Al ₂ , AlAs, AlC, AlC ₂ , Al ₂ C ₂ , AlCl, AlCl ₂ , AlCl ₃ , Al ₂ Cl ₆ , AlClH, AlClH ₂ , AlCl ₂ H, AlClHO, AlClH ₂ O ₂ , AlCl ₂ HO, Al ₂ Cl ₈ Ni, AlClO, AlCl ₂ O, AlCu, AlCuS, AlCuS ₂ , AlH, AlH ₂ , AlH ₃ , AlHO, AlOH, AlHO, HALO, AlHO ₂ , AlH ₂ O ₂ , AlH ₃ O ₃ , AlN, AlO, AlO ₂ , Al ₂ O, Al ₂ O ₂ , Al ₂ O ₃ , AlS, AlS ₂ , Al ₂ S, Al ₂ S ₂ , AlSe, Al ₂ Se, Al ₂ Se ₂ .
As	AlAs, AlAsO ₄ , As, As ₂ Ca ₃ O ₈ , As ₂ Cd ₃ O ₈ , As ₂ Co ₃ O ₈ , AsCrO ₄ , As ₂ Cr ₃ O ₈ , AsCu ₃ , AsCu ₃ O ₄ , As ₂ Cu ₃ O ₈ , AsFeO ₄ , As ₂ Fe ₃ O ₈ , As ₂ Hg ₃ O ₈ , AsK ₃ O ₄ , AsMn, As ₂ Mn ₃ O ₈ , AsMoO ₄ , AsNa ₃ , AsNa ₃ O ₄ , AsNi, As ₂ Ni ₅ , As ₈ Ni ₁₁ , As ₂ Ni ₃ O ₈ , As ₂ O ₅ , As ₂ O ₈ Pb ₃ , As ₂ O ₈ Ti ₃ , As ₂ O ₈ Zn, AsS, As ₂ S ₂ , As ₂ S ₃ , As ₄ S ₄ , As ₂ Se ₃ , As ₂ SiZn, As ₂ Zn, As ₂ Zn ₃ .	AsCl ₃	AlAs, As, As ₂ , As ₃ , As ₄ , AsCl ₃ , AsH, AsH ₂ , AsH ₃ , AsN, AsO, AsO ₂ , As ₄ O ₆ , As ₄ O ₇ , As ₄ O ₈ , As ₄ O ₉ , As ₄ O ₁₀ , AsS, As ₄ S ₄ , AsSe,
Cd	As ₂ Cd ₃ , As ₂ Cd ₃ O ₈ , CCdO ₃ , Cd, CdCl ₂ , CdFe ₂ O ₄ , CdH ₂ O ₂ , CdN ₂ O ₆ , Cd ₂ Na, CdO, CdO ₄ S, CdO ₃ Se, CdO ₄ Se, CdO ₃ Si, CdO ₃ Ti, CdS, CdSe,		Cd, CdCl, CdCl ₂ , Cd ₂ Cl ₄ , CdH, CdHO, CdH ₂ O ₂ , CdO, CdS, CdSe
Co	AlCo, Al ₃ Co, Al ₅ Co ₂ , Al ₉ Co ₂ , Al ₂ CoO ₄ , As ₂ Co ₃ O ₈ , CCoO ₃ , Cl ₂ Co, Co, CoCr ₂ O ₄ , CoFe ₂ O ₄ , CoH ₂ O ₂ , Co ₃ N, CoN ₂ O ₆ , CoO, Co ₃ O ₄ , CoO ₄ S, CoO ₃ SeCo ₂ O ₄ Si, CoO ₃ Ti, CoO ₅ Ti ₂ , Co ₂ O ₄ Ti, CoS, CoS ₂ , Co ₃ S ₄ , Co ₉ S ₈ , CoSi, CoSi ₂ .		ClCo, Cl ₂ Co, Cl ₃ Co, Cl ₄ Co ₂ , Co, Co ₂ , CoH, CoHO, CoH ₂ O ₂ , CoO, CoS, CoSe.
Cr	AsCrO ₄ , As ₂ Cr ₃ O ₈ , C ₂ Cr ₃ , C ₃ Cr ₇ , C ₆ Cr ₂₃ , C ₆ CrO ₆ , CaCrO ₃ , CaCr ₂ O ₄ , Cl ₂ Cr, Cl ₃ Cr, CoCr ₂ O ₄ Cr, Cr ₂ FeO ₄ , CrKO ₂ , CrK ₂ O ₄ , CrK ₃ O ₄ , CrK ₄ O ₄ , CrN, Cr ₂ N, CrNa ₂ O ₄ , Cr ₂ Na ₂ O ₄ , Cr ₂ NiO ₄ , CrO ₂ , CrO ₃ , Cr ₂ O ₃ , Cr ₅ O ₁₂ , Cr ₈ O ₂₁ , Cr ₂ O ₁₂ S ₃ , CrS, CrSi, CrSi ₂ , Cr ₃ Si, Cr ₅ Si ₃ .		ClCr, Cl ₂ Cr, Cl ₃ Cr, Cl ₄ Cr, Cl ₅ Cr, Cl ₆ Cr, ClCrO, ClCrO ₂ , Cl ₂ CrO, Cl ₂ CrO ₂ , Cl ₃ CrO, Cl ₄ CrO, Cr, Cr ₂ , CrH, CrHO, CrHO ₂ , CrHO ₃ , CrH ₂ O ₂ , CrH ₂ O ₃ , CrH ₂ O ₄ , CrH ₃ O ₃ , CrH ₃ O ₄ , CrH ₄ O ₄ , CrH ₄ O ₅ , CrN, CrO, CrO ₂ , CrO ₃ , Cr ₂ O, Cr ₂ O ₂ , Cr ₂ O ₃ , CrS, CrS ₂ .
Cu	Al ₂ CuO ₄ , AsCu ₃ , AsCu ₃ O ₄ , As ₂ Cu ₃ O ₈ , CCuN, CCuO ₃ , CaCu, CaCu ₅ , Ca ₂ Cu, CaCu ₂ O ₃ , Ca ₂ CuO ₃ , ClCu, Cl ₂ Cu, Cu, CuFeO ₂ , CuFe ₂ O ₄ , Cu ₂ Fe ₂ O ₄ CuFeS ₂ , Cu ₅ FeS ₄ , CuH ₂ O ₂ , CuH ₂ O ₅ S, CuH ₆ O ₇ S, CuH ₁₀ O ₉ S, CuMoO ₄ , CuO, Cu ₂ O, CuO ₄ S, Cu ₂ O ₄ S, Cu ₂ O ₅ S, CuO ₃ Se, CuS, Cu ₂ S, CuSe, CuSe ₂ , Cu ₂ Se.		AlCu, AlCuS, AlCuS ₂ , ClCu, Cl ₂ Cu, Cl ₂ Cu ₂ , Cl ₃ Cu ₃ , Cl ₄ Cu ₂ , Cl ₄ Cu ₄ , Cl ₅ Cu ₅ , Cu, Cu ₂ , CuH, CuHO, CuO, CuS, Cu ₂ S, CuSe, Cu ₂ Se,
Fe	Al ₂ FeO ₄ , AsFeO ₄ , As ₂ Fe ₃ O ₈ , CFe ₃ , CFeO ₃ , C ₅ FeO ₅ , CaFe ₂ O ₄ , Ca ₂ Fe ₂ O ₅ , CdFe ₂ O ₄ , Cl ₂ Fe, Cl ₃ Fe, ClFeO, CoFe ₂ O ₄ , Cr ₂ FeO ₄ , CuFeO ₂ , CuFe ₂ O ₄ , Cu ₂ Fe ₂ O ₄ , CuFeS ₂ , Cu ₅ FeS ₄ Fe, FeHO ₂ , FeH ₂ O ₂ , FeH ₃ O ₃ , Fe ₂ H ₂ O ₄ , FeKO ₂ , FeK ₂ O ₂ , FeK ₄ O ₃ , Fe ₂ MnO ₄ , Fe ₃ Mo ₂ , FeMoO ₄ , Fe ₂ N, Fe ₄ N, FeNaO ₂ , Fe ₂ NiO ₄ , Fe _{0.947} O, FeOFe ₂ O ₃ , Fe ₃ O ₄ , FeO ₄ S, Fe ₂ O ₁₂ S ₃ , FeO ₃ Si, Fe ₂ O ₄ Si, FeO ₃ Ti, Fe ₂ O ₄ Ti, FeO ₄ V ₂ , FeO ₆ V ₂ , Fe ₂ O ₄ Zn, Fe _{0.875} S, FeS, FeS ₂ , FeS ₂ , FeSe ₂ , Fe _{1.04} Se, FeSi, FeSi ₂ , Fe ₂ Ti.		C ₅ FeO ₅ , ClFe, Cl ₂ Fe, Cl ₃ Fe, Cl ₄ Fe ₂ , Cl ₆ Fe ₂ , ClFeO, Fe, Fe ₂ , FeH, FeHO, FeHO ₂ , FeH ₂ O ₂ , FeO, FeO ₂ , FeS, FeSe.
Hg	As ₂ Hg ₃ O ₈ , ClHg, Cl ₂ Hg, Cl ₂ Hg ₂ , Hg, HgO, HgO ₄ S, Hg ₂ O ₄ S, HgO ₃ Se, HgS, HgSe.		ClHg, Cl ₂ Hg, HHg, Hg, HgO, HgS, HgSe.

Table 6-4. The used elemental species in equilibrium calculations.

Metal(loid)	Solid species	Liquid species	Gaseous species
Mn	Al ₂ MnO ₄ , AsMn, As ₂ Mn ₃ O ₈ , CMn ₃ , C ₂ Mn ₅ , C ₃ Mn ₇ , C ₆ Mn ₂₃ , CMnO ₃ , Cl ₂ Mn, Fe ₂ MnO ₄ , HMnO ₂ , H ₂ MnO ₂ , Mn, MnMoO ₄ , Mn ₄ N, Mn ₅ N ₂ , MnO, MnO ₂ , Mn ₂ O ₃ , Mn ₂ O ₇ , Mn ₃ O ₄ , MnO ₄ S, MnO ₃ Si, Mn ₂ O ₄ Si, MnO ₃ Ti, Mn ₂ O ₄ Ti, MnS, MnS ₂ , MnSe, MnSi, Mn ₃ Si, Mn ₄ Si ₇ , Mn ₅ Si ₃ , Mn ₁₁ Si ₁₉ .		ClMn, Cl ₂ Mn, Cl ₃ Mn, Cl ₄ Mn, Cl ₄ Mn ₂ , ClMnO ₃ , HMn, HMnO, Mn, MnO, MnO ₂ , MnS, MnSe.
Mo	AsMoO ₄ , C ₂ Mo, C ₃ Mo, C ₄ Mo, C ₅ Mo, C ₆ Mo, C ₇ Mo, CaMoO ₄ , Cl ₂ Mo, Cl ₃ Mo, Cl ₄ Mo, Cl ₅ Mo, Cl ₆ Mo, Cl ₂ MoO, Cl ₂ MoO ₂ , Cl ₃ MoO, Cl ₄ MoO, CuMoO ₄ , Fe ₃ Mo ₂ , FeMoO ₄ , MnMoO ₄ , Mo, Mo ₂ N, MoNa ₂ O ₄ , Mo ₂ Na ₂ O ₇ , MoO ₂ , MoO _{2.75} , MoO _{2.875} , MoO _{2.889} , MoO ₃ , MoO ₄ Pb, MoS ₂ , MoS ₃ , Mo ₂ S ₃ , MoSe ₂ , Mo ₃ Se ₄ , MoSi ₂ , Mo ₃ Si, Mo ₅ Si ₃ .		C ₆ MoO ₆ , ClMo, Cl ₂ Mo, Cl ₃ Mo, Cl ₄ Mo, Cl ₅ Mo, Cl ₆ Mo, ClMoO, ClMoO ₂ , Cl ₂ MoO, Cl ₂ MoO ₂ , Cl ₃ MoO, Cl ₄ MoO, HMo ₃ , HMoO, HMoO ₂ , H ₂ MoO ₂ , H ₂ MoO ₃ , H ₂ MoO ₄ , Mo, Mo ₂ , MoN, MoO, MoO ₂ , MoO ₃ , Mo ₂ O ₆ , Mo ₃ O ₉ , Mo ₄ O ₁₂ , Mo ₅ O ₁₅ , MoS, MoS ₂ .
Ni	AlNi, AlNi ₃ , Al ₃ Ni, Al ₃ Ni ₂ , Al ₂ NiO ₄ , AsNi, As ₂ Ni ₅ , As ₈ Ni ₁₁ , As ₂ Ni ₃ O ₈ , CNi ₃ , CNiO ₃ , C ₄ NiO ₄ , Cl ₂ NiCr ₂ NiO ₄ , Fe ₂ NiO ₄ , HNiO ₂ , H ₂ NiO ₂ , NNi ₃ , Ni, NiO, NiO ₄ S, NiO ₃ Se, Ni ₂ O ₄ Si, NiO ₃ Ti, NiS, NiS ₂ , Ni ₃ S ₂ , Ni ₃ S ₄ , Ni ₉ S ₈ , NiSe, NiSiNiSi ₂ , Ni ₇ Si ₁₃ , NiTi, NiTi ₂ , Ni ₃ Ti.		Al ₂ Cl ₈ Ni, C ₄ NiO ₄ , ClNi, Cl ₂ Ni, Cl ₃ Ni, Cl ₄ Ni ₂ , HNi, HNiO, H ₂ NiO ₂ , Ni, Ni ₂ , NiO, NiS.
Pb	As ₂ O ₈ Pb ₃ , CO ₃ Pb, CO ₄ Pb ₂ , CaPb, Ca ₂ Pb, Cl ₂ O ₂ Pb ₃ , Cl ₂ O ₃ Pb ₄ , Cl ₂ Pb, MoO ₄ Pb, N ₂ O ₆ Pb, OPb, O ₂ Pb, O ₃ Pb ₂ , O ₄ Pb ₃ , O ₄ PbS, O ₅ Pb ₂ S, O ₆ Pb ₃ S, O ₇ Pb ₄ S, O ₈ Pb ₅ S, O ₃ PbSe, O ₄ PbSe, O ₃ PbSi, O ₄ Pb ₂ Si, O ₆ Pb ₄ Si, O ₃ PbTi, Pb, PbS, PbSe.		ClPb, Cl ₂ Pb, Cl ₃ Pb, Cl ₄ Pb, HPb, OPb, O ₂ Pb, Pb, Pb ₂ , PbS, PbS ₂ , Pb ₂ S ₂ , PbSe.
Si	Al ₂ CaH ₄ O ₁₀ S, Al ₂ CaO ₆ Si, Al ₂ CaO ₈ Si ₂ , Al ₂ Ca ₂ O ₇ Si, Al ₂ Ca ₃ O ₁₂ Si, Al ₃ H ₂ KO ₁₂ Si, AlH ₂ NaO ₇ Si ₂ , Al ₂ H ₄ O ₉ Si ₂ , Al ₂ H ₄ O ₉ Si ₂ , Al ₂ H ₄ O ₉ Si ₂ , AlKO ₄ Si, AlKO ₆ Si ₂ , Al ₂ K ₂ O ₈ Si ₂ , Al ₂ K ₂ O ₁₂ Si ₄ , Al ₂ K ₂ O ₁₆ Si ₆ , Al ₂ K ₂ O ₁₆ Si ₆ , Al ₂ K ₂ O ₁₆ Si ₆ , AlNaO ₄ SiAl ₂ Na ₂ O ₁₂ Si, Al ₂ Na ₂ O ₁₆ Si ₄ , Al ₂ Na ₂ O ₁₆ Si ₄ , As ₂ SiZn, Ca ₂ O ₄ Si, Ca ₃ O ₅ Si, CaSi, CaSi ₂ , Ca ₂ Si, CdO ₃ Si, Co ₂ O ₄ Si, CoSi, CoSi ₂ , CrSi, CrSi ₂ , Cr ₃ Si, Cr ₅ Si ₃ , FeO ₃ Si, FeSi, FeSi ₂ , FeSi ₂ , K ₂ O ₃ Si, K ₂ O ₅ Si ₂ , K ₂ O ₉ Si ₄ , MnSi, Mn ₃ Si, Mn ₄ Si ₇ , Mn ₅ Si ₃ , Mn ₁₁ Si ₁₉ , MoSi ₂ , Mo ₃ Si, Mo ₅ Si ₃ , N ₂ O ₅ Si ₂ , N ₄ Si ₃ , Na ₂ O ₃ Si, Na ₂ O ₅ Si ₂ , Na ₄ O ₄ Si, Ni ₂ O ₄ Si, NiSi, NiSi ₂ , Ni ₇ Si ₁₃ , O ₃ PbSi, O ₄ Pb ₂ Si, O ₆ Pb ₄ Si, O ₃ SiZn, O ₄ SiZn ₂ , SSi, S ₂ Si, Si, SiTi, Si ₂ Ti, Si ₃ Ti ₅ , SiV ₃ , Si ₂ V, Si ₃ V ₅ .		CCl ₂ H ₄ Si, CCl ₃ H ₃ Si, C ₂ ClH ₇ Si, C ₂ Cl ₂ H ₆ Si, C ₃ ClH ₅ Si, C ₆ Cl ₂ H ₆ Si, C ₆ Cl ₃ H ₅ Si, C ₁₂ Cl ₂ H ₁₀ Si, C ₂ H ₆ OSi, C ₂ H ₈ Si, C ₄ H ₁₂ Si, CSi, CSi ₂ , CSi ₃ , CSi ₄ , C ₂ Si, C ₂ Si ₂ , C ₂ Si ₃ , ClHSi, ClH ₃ Si, Cl ₂ H ₂ Si, Cl ₃ HSi, ClSi, Cl ₂ Si, Cl ₃ Si, Cl ₄ Si, His, H ₂ Si, H ₃ Si, H ₄ Si, H ₆ Si ₂ , NSi, NSi ₂ , OSi, O ₂ Si, O ₂ Si ₂ , SSi, S ₂ Si, SeSi, Si, Si ₂ , Si ₃ .
Ti	Al ₂ O ₅ Ti, AlTi, Al ₃ Ti, As ₂ O ₈ Ti ₃ , CTi, CaO ₅ SiTi, CaO ₃ Ti, Ca ₃ O ₇ Ti ₂ , Ca ₄ O ₁₀ Ti ₃ , CdO ₃ Ti, ClOTi, Cl ₂ Ti, Cl ₃ Ti, Cl ₄ Ti, CoO ₃ Ti, CoO ₅ Ti ₂ , Co ₂ O ₄ Ti, FeO ₃ Ti, Fe ₂ O ₄ Ti, FeTi, Fe ₂ Ti, H ₂ Ti, MnO ₃ Ti, Mn ₂ O ₄ Ti, NTi, Na ₂ O ₃ Ti, Na ₂ O ₅ Ti ₂ , Na ₂ O ₇ Ti ₃ , NiO ₃ Ti, NiTi, NiTi ₂ , Ni ₃ Ti, O ₃ PbTi, OTi, O ₃ Ti ₂ , O ₅ Ti ₃ , O ₇ Ti ₄ , O ₄ TiZn ₂ , STi, S ₂ Ti, SiTi, Si ₂ Ti, Si ₃ Ti ₅ , Ti.		ClOTi, Cl ₂ OTi, CITi, Cl ₂ Ti, Cl ₃ Ti, Cl ₄ Ti, Cl ₆ Ti ₂ , NTi, OTi, O ₂ Ti, STi, S ₂ Ti, SeTi, Ti, Ti ₂ .
V	CV ₂ , CaO ₆ V ₂ , Ca ₂ O ₇ V ₂ , Ca ₃ O ₈ V ₂ , Cl ₂ V, Cl ₃ V, FeO ₄ V ₂ , FeO ₆ V ₂ Na ₂ O ₆ V ₂ , Na ₄ O ₇ V ₂ , Na ₆ O ₈ V ₂ , OV, O ₃ V ₂ , O ₄ V ₂ , O ₅ V ₂ , SiV ₃ , Si ₂ V, Si ₃ V ₅ , V.		Cl ₃ OV, Cl ₂ V, Cl ₃ V, Cl ₄ V, Cl ₅ V, NV, O ₂ V, O ₂ V ₂ , O ₁₀ V ₄ , SV, SeV, V.
Zn	Al ₂ O ₄ Zn, As ₂ O ₈ Zn ₃ , As ₂ SiZn, As ₂ Zn, As ₂ Zn ₃ , CO ₃ Zn, CaZn, CaZn ₂ , Cl ₂ Zn, Fe ₂ O ₄ Zn, H ₂ O ₅ SZn, H ₁₄ O ₁₁ SZn, H ₂ O ₂ Zn, N ₂ Zn ₃ , O ₄ SZn, O ₉ S ₂ Zn ₃ , O ₃ SeZn, O ₃ SiZn, O ₄ SiZn ₂ , O ₄ TiZn ₂ , OZn, SZn, SeZn, Zn.		ClZn, Cl ₂ Zn, Cl ₄ Zn ₂ , HOZn, H ₂ O ₂ Zn, HZn, OZn, SZn, SeZn, Zn.

6.5 Results and discussion

6.5.1 Samples characterisation

The quantitative characterisations (proximate, ultimate, and calorific values) of the artificial and blends samples are presented in Table 6-5. Note here that the quantitative characterisations of the original woody biomass samples were already reported in section 5.3.1.

6.5.2 Thermogravimetric analysis

The TG and DTG curves provided useful information for understanding the thermal behaviour of woody biomass and well-defined the operational conditions of pyrolysis process. These curves can also clarify the relationship between the thermal behavior of woody biomass and its inorganic compound content. This is particularly important for the metal(loid) contaminants, since the presence of such compounds in wood can significantly affect its thermochemical degradation process (Helsen et al., 1999; Kercher and Nagle, 2001; Kinata et al., 2012, 2013; Mayer, Apfelbacher and Hornung, 2012).

6.5.2.1 Influence of thermal treatment on the woody biomass samples

6.5.2.1.1 Original waste wood

The TG and DTG curves of the original waste wood samples are presented in Figure 6-2 to Figure 6-6. TG curves in all figures clearly showed that the weight loss of each sample started to decrease as soon as the temperature increased. Notwithstanding the fact that the thermal decompositions of all samples were completed at a lower temperature of approx. 500°C, there were, in general, significant differences in the final weights of the samples, as shown in Figure 6-7a and Table 6-6. However, the final weights of landfill samples were comparable. This phenomenon can be attributed firstly to the differences in the moisture content, and secondly to the differences in chemical bonds between the inorganic compounds (Helsen et al., 1999; Kercher and Nagle, 2001; Kinata et al., 2012, 2013; Mayer, Apfelbacher and Hornung, 2012).

Table 6-5. Characterization and full elemental analysis of the artificial and blends samples.

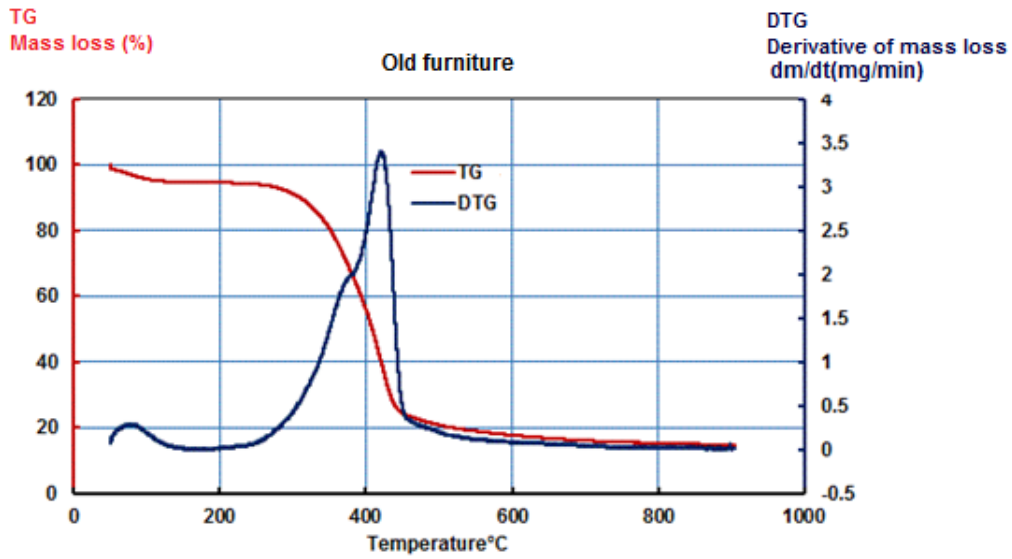
Artificial samples	AS₁	AS₂	AS₃	BS
Property	Value*	Value*	Value*	Value*
Waste wood Properties				
Proximate Analysis (%wt.)				
Moisture	9.08	9.08	9.08	8.69
Ash	0.91	0.91	0.91	1.7228
Volatile matter	86.65	86.65	86.65	84.9909
Fixed carbon (FC)	3.36	3.36	3.36	4.5963
Ultimate Analysis (% wt., dry)				
Carbon (C)	50.69	50.69	50.69	50.1398
Hydrogen (H)	7.17	7.17	7.17	7.1386
Nitrogen (N)	0.09	0.09	0.09	0.4454
Sulphur(S)	0.0025	0.0025	0.0025	0.0007
Oxygen(O)	42.06	42.06	42.06	42.2754
Carbon/Nitrogen (C/N)	561.34	561.34	561.34	123.3693
Calorific Values				
Calorific Value (CV)				
TCV	17.9	17.9	17.9	18.3849
HHVd	20.51	20.51	20.51	19.5082
HHVd	21.77	21.77	21.77	21.501
Chemical Analyses				
Halides				
Chlorine (Cl)	0.09	0.09	0.09	0.03
Bromine (Br)	-	-	-	-
Fluorine (F)	-	-	-	0.01
Major elements (mg/kg)				
Aluminium (Al)	83.39	83.39	83.39	263.55
Calcium (Ca)	1512.81	1512.81	1512.81	3802.48
Potassium (K)	506.49	506.49	506.49	1587.87
Iron (Fe)	200.33	200.33	200.33	1375.58
Sodium (Na)	106.56	106.56	106.56	521.33
Silicon (Si)	107.82	107.82	107.82	271.87
Magnesium (Mg)	197.34	197.34	197.34	550.12
Phosphorus (P)	0.01	0.01	0.01	0.01
Titanium (Ti)	1.92	1.92	1.92	18.68
Minor elements (mg/kg)				
Arsenic (As)	16.64	28.9	42.0	5.94
Cadmium (Cd)	0.17	0.17	0.17	0.41
Cobalt (Co)	0.1	0.1	0.1	2.11
Chromium (Cr)	11.27	11.27	11.27	66.97
Copper (Cu)	7.34	7.34	7.34	20.61
Manganese (Mn)	62.43	62.43	62.43	182.21
Nickel (Ni)	40.6	103.5	84.5	6.64
Lead (Pb)	0.34	0.34	0.34	60.02
Vanadium (V)	0.19	0.19	0.19	0.66
Zinc (Zn)	14.24	14.24	14.24	111.17
Mercury (Hg)	1	1	1	0.43
Molybdenum (Mo)	0.17	0.17	0.17	1.3
Selenium (Se)	0.07	0.07	0.07	0.1

* Mean value (triplicate sample)

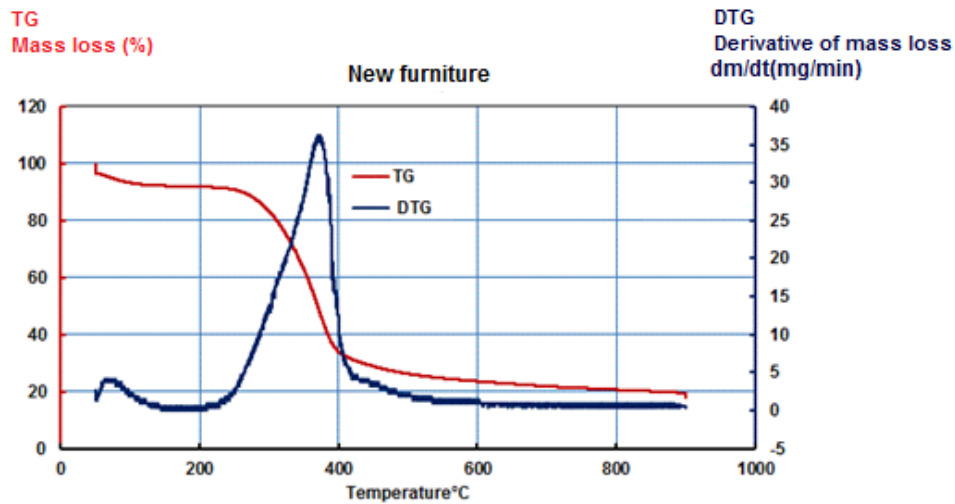
Differential thermogravimetric DTG curves showed that there were three distinct weight loss stages during the thermal decomposition of the samples:

- The dehydration stage occurred because the evaporation of water from both the structure and surface of the samples (Mansaray and Ghaly, 1999; V, 1992). The temperature range for dehydration stage was approx. 30-180°C. These results seem to be in line with those of previous studies under similar conditions (Francisco-fernández et al., 2012; Mayer, Apfelbacher and Hornung, 2012; Poletto et al., 2012).
- The active pyrolysis stage was due to the volatilisation of the inorganic content and the major components (hemicellulose, cellulose, and lignin) of the samples (Poletto et al., 2012; Yang, 2007). The temperature range of this stage was from 200 to 500°C. The DTG curves indicated that the main peak of each sample exhibited a different value, as shown in Figure 6-7b and Table 6-6. This is mainly attributed to the chemical compositions present in the wood species (Kinata et al., 2013; Poletto et al., 2010, 2012).
- The passive pyrolysis stage (also known as the char conversion stage) took place from 500 to 900°C.

In addition, most of the observed differences in the thermal behaviour of the original samples were likely due to the degradation of the major components (Kinata et al., 2013) and the different levels of inorganic compounds present in those samples. This was evident by the temperatures within the active pyrolysis stage, corresponding to the maximum loss weights of the samples (Table 6-6). As a consequence, the descending order of peak temperatures was 425 °C (old furniture) > 419°C (demolition) > 410°C (mixed furniture) > 397°C (pellets) > 394°C (chips) > 385°C (new furniture) > 370°C (L.d.(3-7 m)) > 369°C (L.d. (37.5-39 m)) > 369°C (L.d. (50-51 m)) > 368°C (L.d. (41-43 m)).

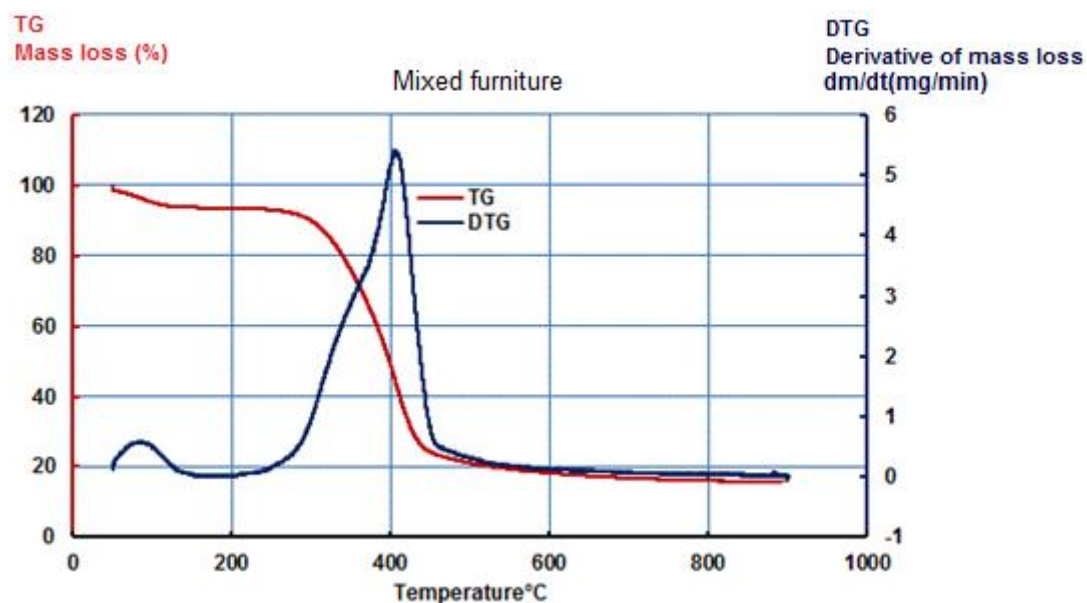


(a) Old furniture.

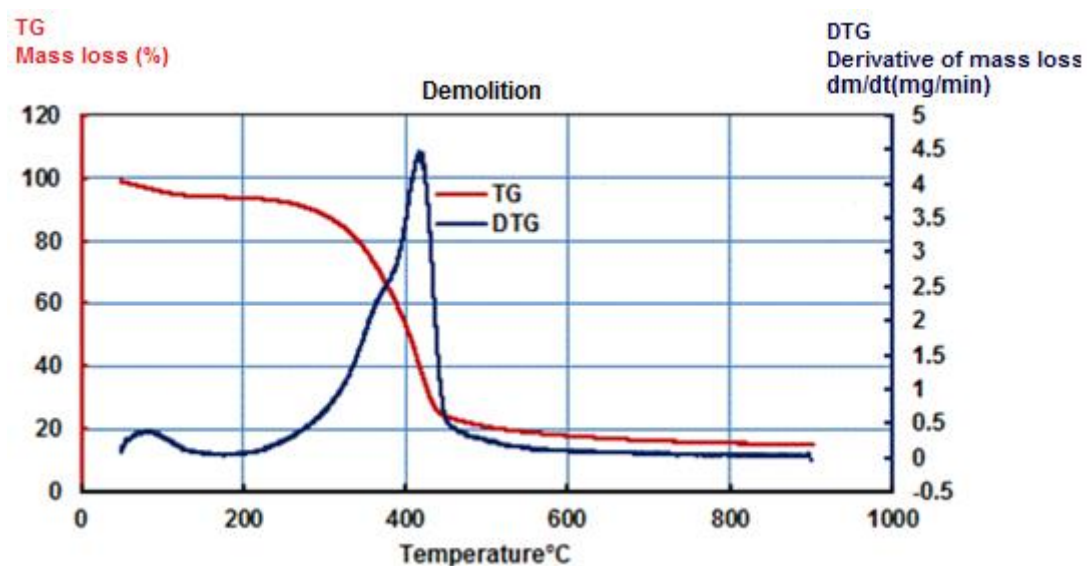


(b) New furniture.

Figure 6-2. TG and DTG curves for waste wood in pyrolysis under heating rate of $50^{\circ}C\ min^{-1}$, (a) old furniture and (b) new furniture.

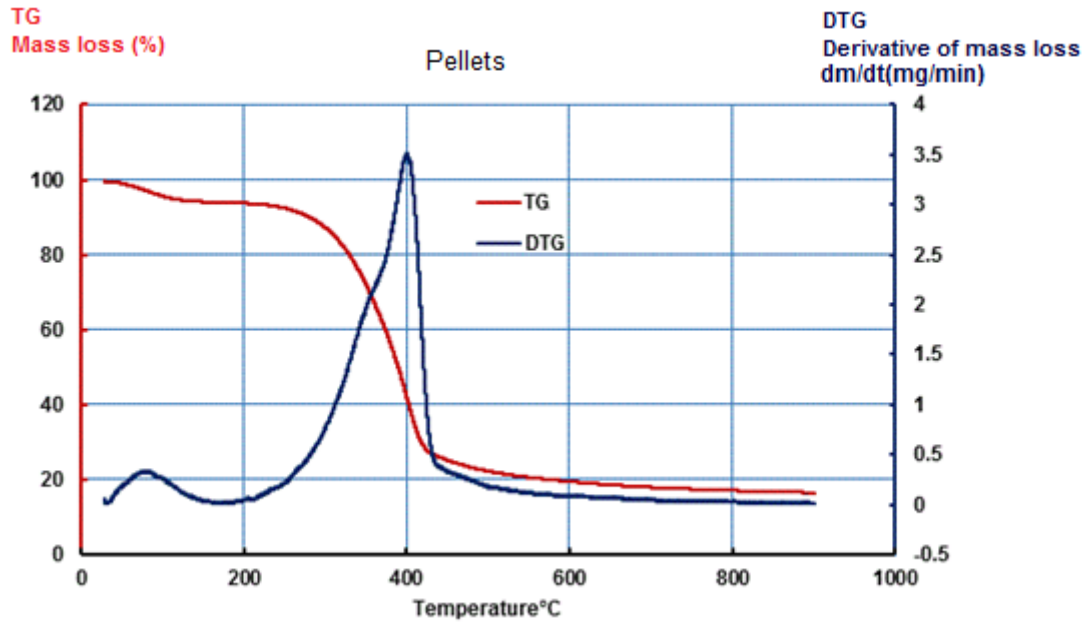


(a) Mixed furniture.

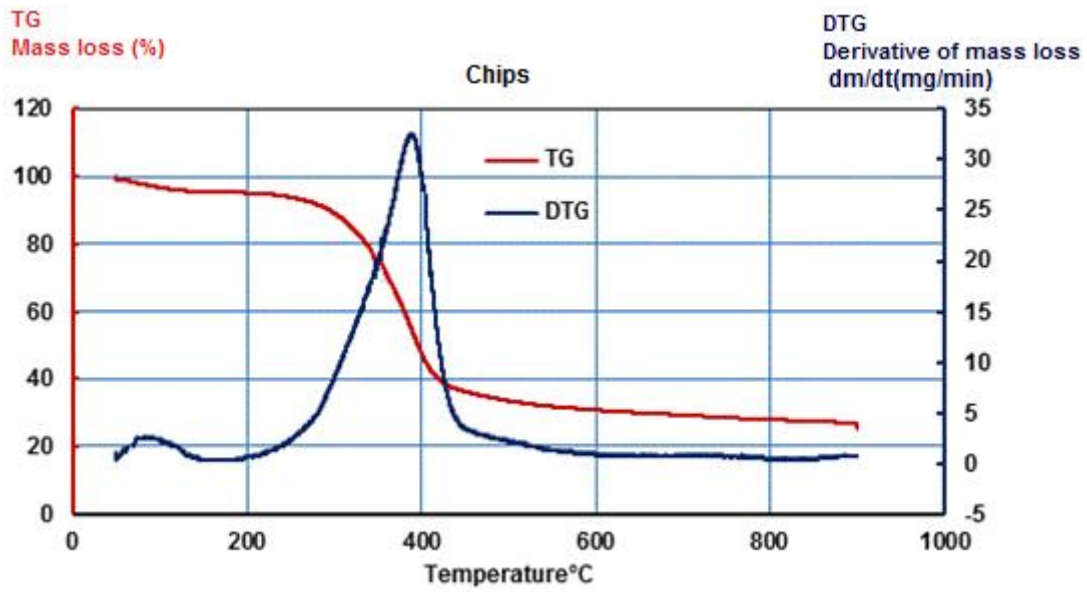


(b) Demolition.

Figure 6-3. TG and DTG curves for waste wood in pyrolysis under heating rate of $50^{\circ}\text{C min}^{-1}$, (a) mixed furniture and (b) demolition.



(a) Pellets.



(b) Chips.

Figure 6-4. TG and DTG curves for waste wood in pyrolysis under heating rate of $50^{\circ}\text{C min}^{-1}$, (a) pellets and (b) chips.

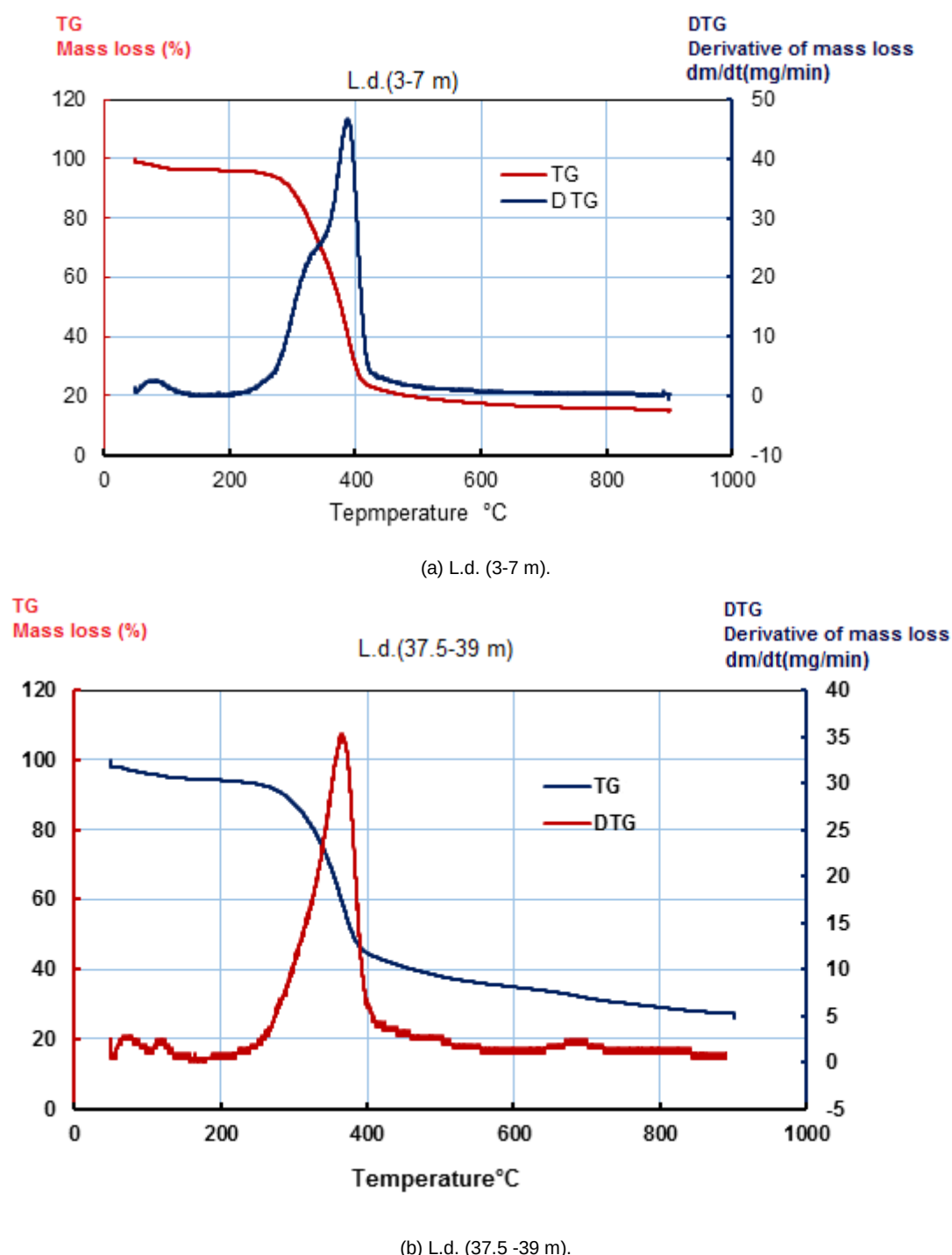
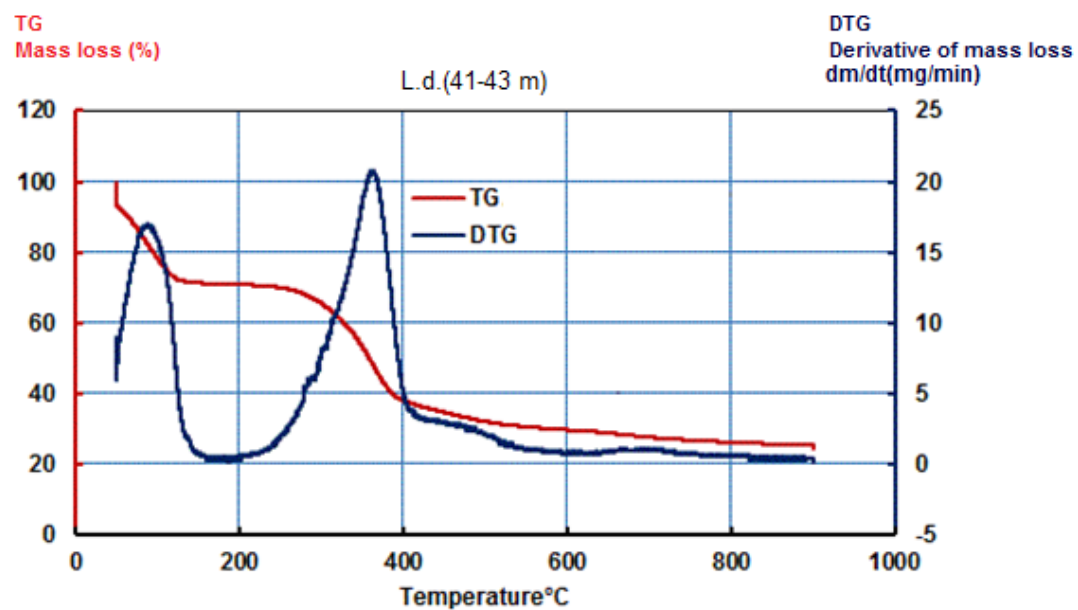
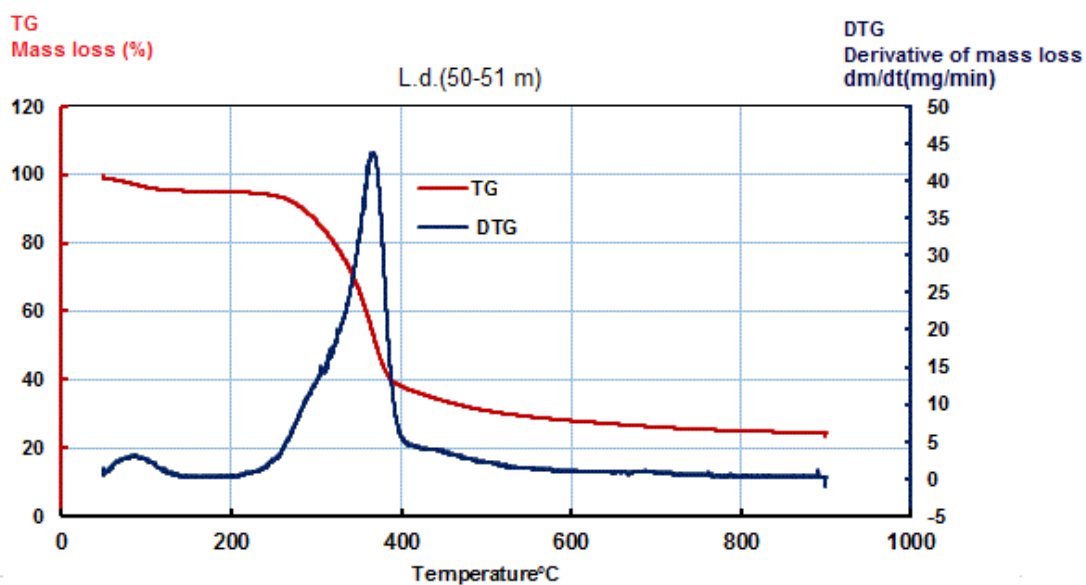


Figure 6-5. TG and DTG curves for waste wood in pyrolysis under heating rate of $50^{\circ}\text{C min}^{-1}$, (a) landfill (3-7 m) and (b) landfill (37.5-39 m).

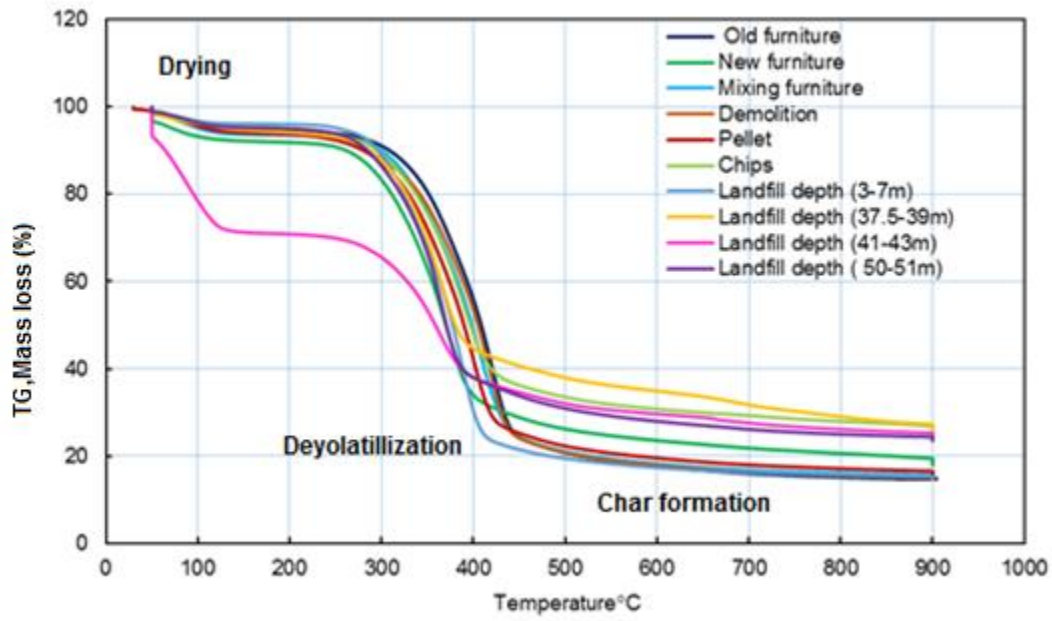


(a) L.d. (41-43 m).

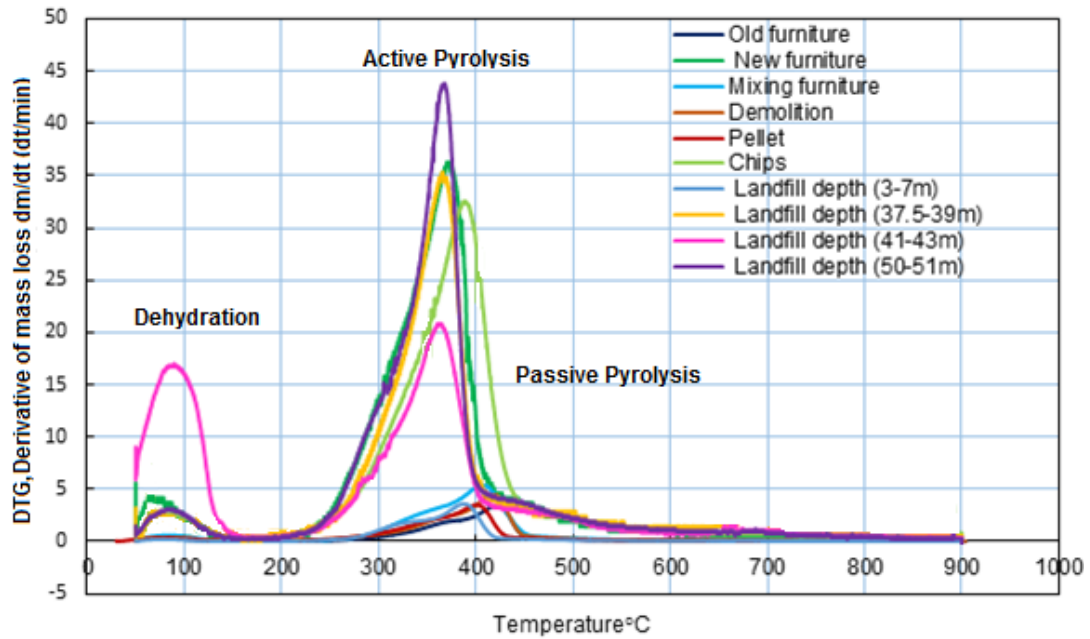


(b) L.d. (50-51 m).

Figure 6-6. TG and DTG curves for waste wood in pyrolysis under heating rate of $50^{\circ}\text{C min}^{-1}$, (a) landfill (41-43 m) and (b) landfill (50-51 m).



(a) TG curves.



(b) DTG curves.

Figure 6-7. Comparison of the thermal behavior of different types of waste wood in pyrolysis under heating rate of $50^{\circ}\text{C min}^{-1}$, (a) TG curves and (b) DTG curves.

Table 6-6. Peak temperatures and amounts of residues of different types of original waste wood at $\beta = 50^\circ\text{C min}^{-1}$ under N_2 (40.0 ml/min).

Types of original waste wood	Temperature of active pyrolysis	Temperature of passive pyrolysis	α max	(dw/dt) max g/min	(da/dt) max min^{-1}	Residue (%)
Old furniture	425	520	0.48	3.29	0.73	14.48
New furniture	385	571	0.87	3.58	0.54	15.26
Mixed furniture	410	540	0.44	5.32	0.701	15.6
Demolition	419	564	0.73	4.39	0.49	15.05
Pellets	397	586	0.86	2.9	0.19	18.35
Chips	394	590	0.80	31.77	0.43	26.71
L.d. (3-7 m)	370	599	0.82	36.30	0.43	19.5
L.d. (37.5-39 m)	369	561	0.74	1.14	0.47	27.20
L.d. (41-43 m)	368	594	0.82	2.02	0.27	24.89
L.d. (50-51m)	369	570	0.80	43.11	0.57	23.99

To support this observation, SEM-EDX analysis was conducted and the results of the L.d (41-43 m) and L.d (50-51 m), respectively, are depicted in Figure 6-8 and Figure 6-9. It is clear that Pb, As, Ti, Cu and Ca covered the surface of L.d (41-43 m) samples and the Cr, As, Fe, Ni, Zn and Ca covered the surface of L.d (50-51 m) samples

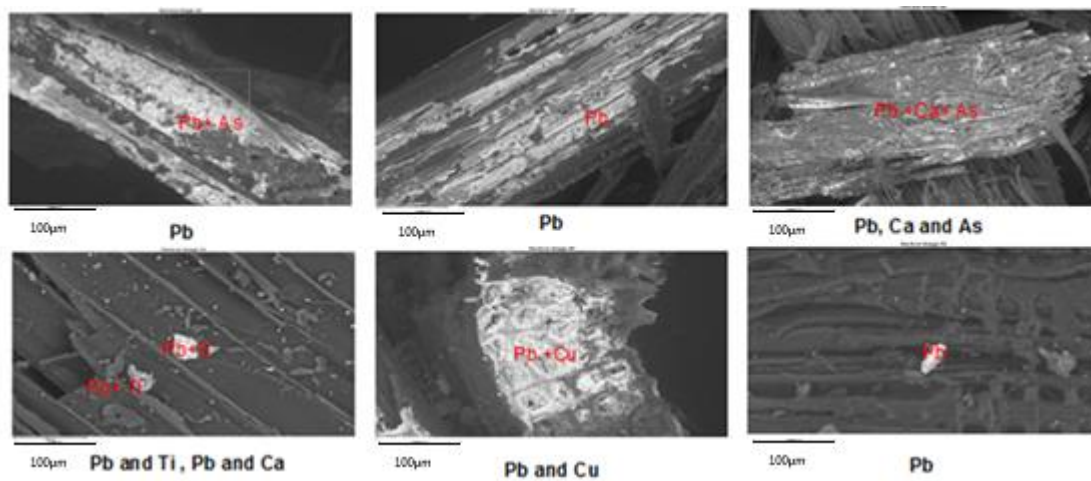


Figure 6-8. SEM-EDX analysis of waste wood from landfill (41-43 m).

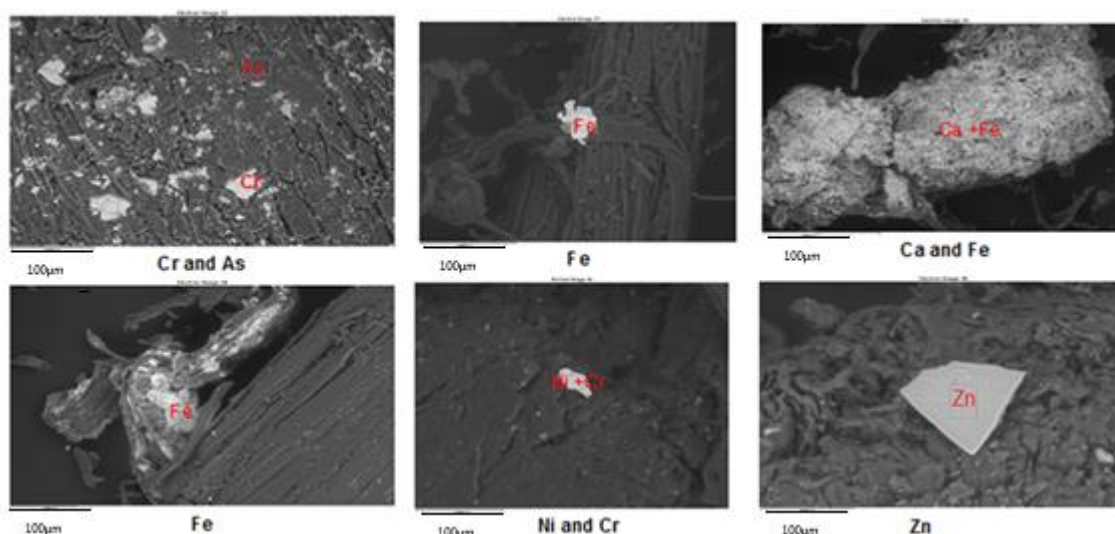
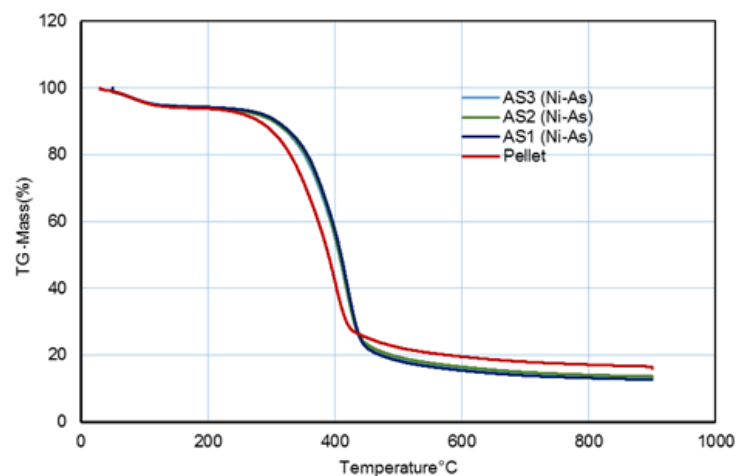


Figure 6-9. SEM-EDX analysis of waste wood from landfill (50-51 m).

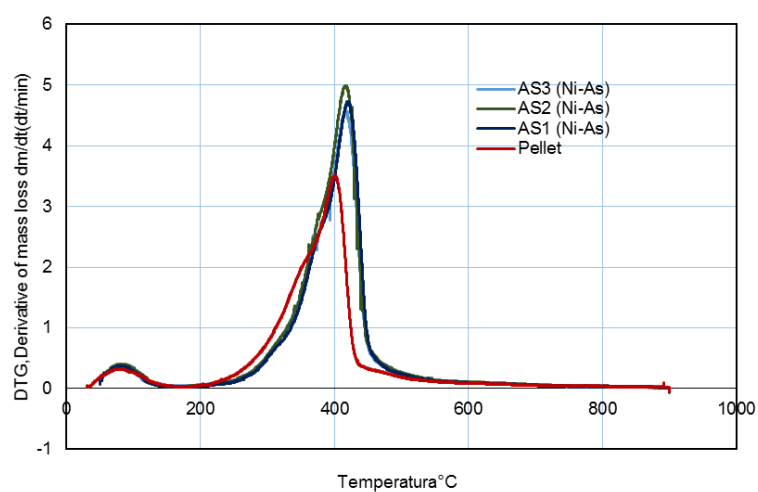
6.5.2.1.2 Artificial waste wood and blend samples

In general, the TG and DTG curves (Figure 6-10a-b) of artificial samples exhibited similar behaviour to that of the original samples. Nevertheless, the maximum weight loss peak of AS₁, AS₂, and AS₃ were, respectively, modified by 1.146, 1.476, and 0.946 compared to the pellet sample, as shown in Table 6-7. This further confirms the influence of metal(loid) content on the thermal decomposition of woody biomass. Figure 6-10c displays the obtained results from the SEM-EDX analysis, which found that As and Ni covered the surface of the artificial sample.

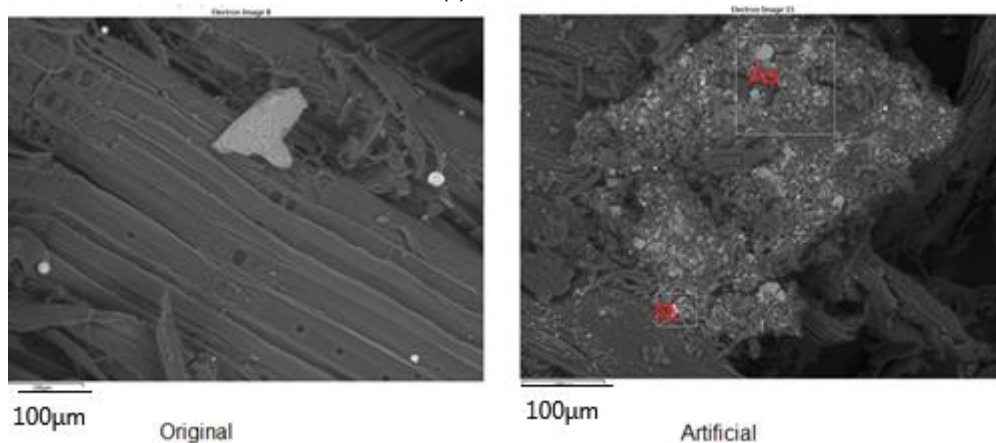
For comparison purposes, the TG and DTG curves of blends, pellets and L.d. samples are shown in Figure 6-11. Quite obviously, the peak weight loss of the blend sample was substantially less than that of the L.d. sample and slightly higher than that of the pellet sample.



(a) TG curves.



(b) DTG curves.

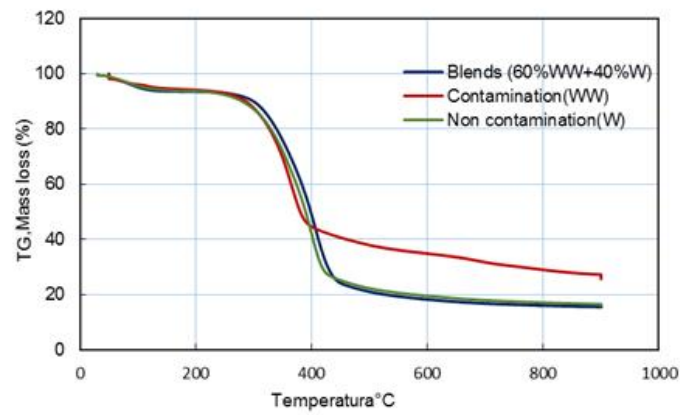


(c) SEM-EDX analysis of original and artificial wood samples.

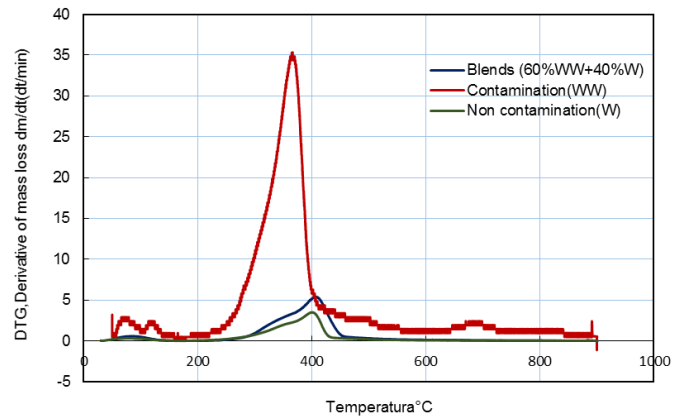
Figure 6-10. Comparison of the thermal behavior of original and artificial samples, (a) TG curves, (b) DTG curves, and (c) SEM-EDX analysis.

Table 6-7. The thermal behaviour of non-contaminated (pellets) sample and contaminated (artificial) samples.

Sample	Temperature of active pyrolysis	Concentration of Contamination elements		(d α /dt) max min ⁻¹
		As mg/kg	Ni mg/kg	
Artificial (AS ₁)	423.22	16.64	40.6	4.63
Artificial (AS ₂)	414.05	28.9	103.5	4.96
Artificial (AS ₃)	426.55	42	84.5	4.43
Original (Pellets)	397	0.04	2.73	3.484



(a) TG curves.



(b) DTG curves.

Figure 6-11. Comparison of the thermal behavior of blends, non-contaminated and contaminated samples, (a) TG curves and (b) DTG curves.

6.5.2.2 Influence of heating rate during thermal treatment of woody biomass samples.

Figure 6-12 and Figure 6-13, respectively, illustrate the thermal behaviour of the pellet sample (non-contaminated) and the landfill wood sample (contaminated) at heating rates of 20, 30, 50, and 80 °C min⁻¹. As shown in Figure 6-12a and Figure 6-13a, the TG curves of both samples possessed similar variation tendencies under pyrolysis conditions with different heating rates. No changes were observed in the final weights of these samples. Thus, the heating rate had an insignificant influence on the final weight of the pellet and landfill samples. These results are in accordance with the observations of previous studies (Duan et al., 2017a; Fidalgo et al., 2019; Poletto et al., 2010). The assessment of DTG curves, Figure 6-12 b and Figure 6-13b shows that the maximum weight loss peak of each sample increased as the heating rate increased.

6.5.2.3 Kinetic analysis

The activation energy (E_a) and pre-exponential factor (A) for each tested wood sample were determined based on model-free methods (KAS and FWO). The Kissinger plot of β versus $1/T$ for pellet and landfill sample decomposition processes is given in Figure 6-14a and b, where the calculation of correlation coefficients (R^2) for the linear-squares fitting is also presented.

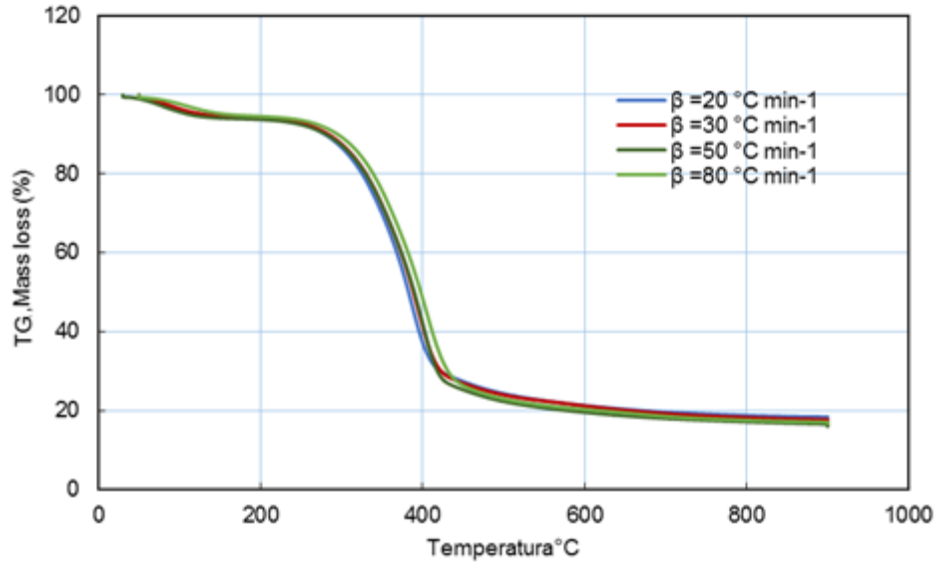
As pointed out in previous studies (Poletto et al., 2010; Slopiecka, Bartocci and Fantozzi, 2011), the FWO and KAS methods are often used in a complementary fashion. In this sense, the kinetic parameters were determined using the FWO method at various degrees of conversion. The FWO plots of pellet and landfill samples for different conversion values (0.1 to 0.9), temperatures ($1000/T$ K⁻¹), and heating rates (20, 30, 50, and 80 °C min⁻¹) are shown in Figure 6-15a and b. Clearly, the fitted lines are approximately parallel, leading to approximate the activation energies at various degrees of conversation, and hence inducing a single reaction mechanism (Poletto, Zattera and Santana, 2012; Slopiecka, Bartocci and Fantozzi, 2011; Yao et al., 2008). The activation energies were then estimated from the slopes of the KAS and FWO plots, while the pre-exponential

values were derived from the intercept of the regression lines and are listed in Table 6-8. The activation energies for landfill wood pyrolysis were higher than for pellet wood pyrolysis. This might be due to the highly bound nature of the chemical compounds present in landfill wood (Edo, 2016; Fidalgo et al., 2019; Helsen and Van Den Bulck, 2000; Issues et al., 2001).

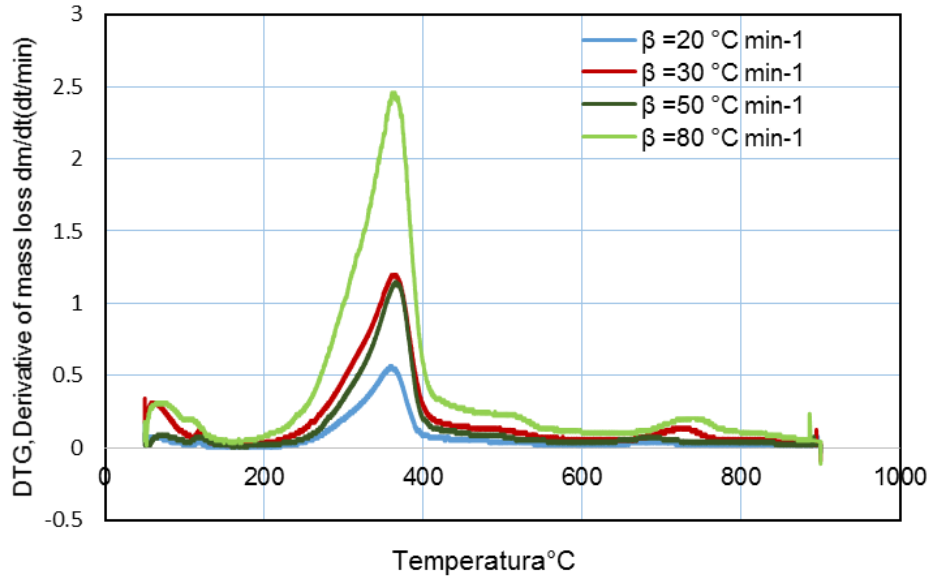
Table 6-8. The resulted Ea and A for a pellets sample (non-contaminated) and landfill wood sample (contaminated) by FWO and Kissinger methods.

α	Contamination (Landfill)			Non-contamination (Pellet)		
	FWO					
	Ea(KJ/mol)	A[min^{-1}]	R ^{2*}	Ea (KJ/mol)	A [min^{-1}]	R ^{2*}
0.1	228.64	2.41	0.999	136.35	2.23	0.999
0.2	226.97	2.40	0.999	135.52	2.22	0.999
0.3	225.31	2.40	0.999	134.69	2.22	0.999
0.4	222.82	2.39	0.999	13.39	2.21	0.999
0.5	221.15	2.38	0.998	133.02	2.21	1.000
0.6	218.66	2.37	0.999	132.19	2.20	0.999
0.7	214.50	2.35	0.998	130.53	2.19	1.000
0.8	210.34	2.33	0.999	128.04	2.18	0.999
0.9	202.86	2.30	0.999	125.54	2.16	0.999
	Kissinger					
	357.31	1.16×10 ²⁵	0.994	276.62	7.09×10 ¹⁷	0.991

R^{2*}: Corresponding to linear fitting in Figure 6-14 and Figure 6-15.

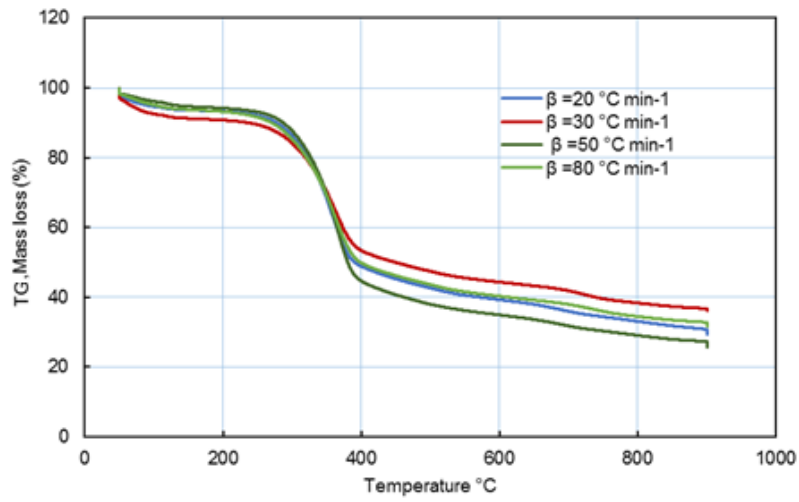


(a) TG curves under four heating rates.

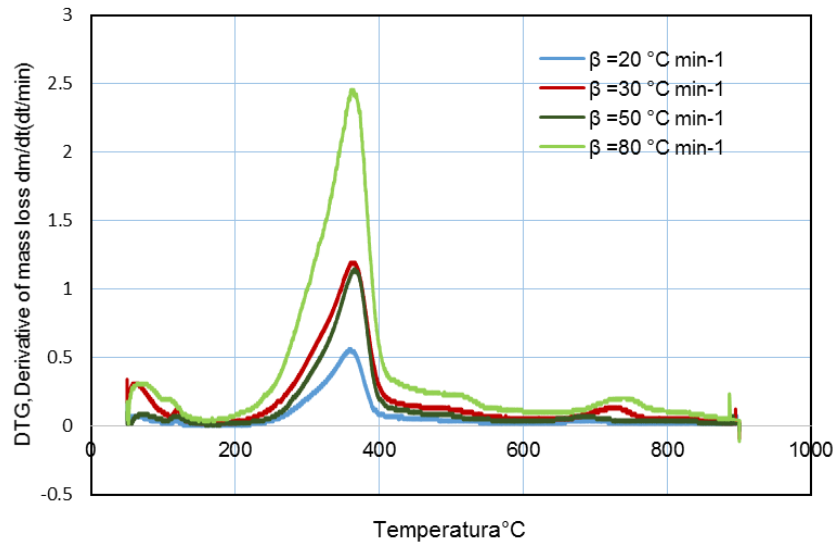


(b) DTG curves under four heating rates.

Figure 6-12. The thermal behavior of pellets sample (non-contaminated) under four heating rates 20, 30, 50, and 80 °C min⁻¹, (a) TG curves and (b) DTG curves.

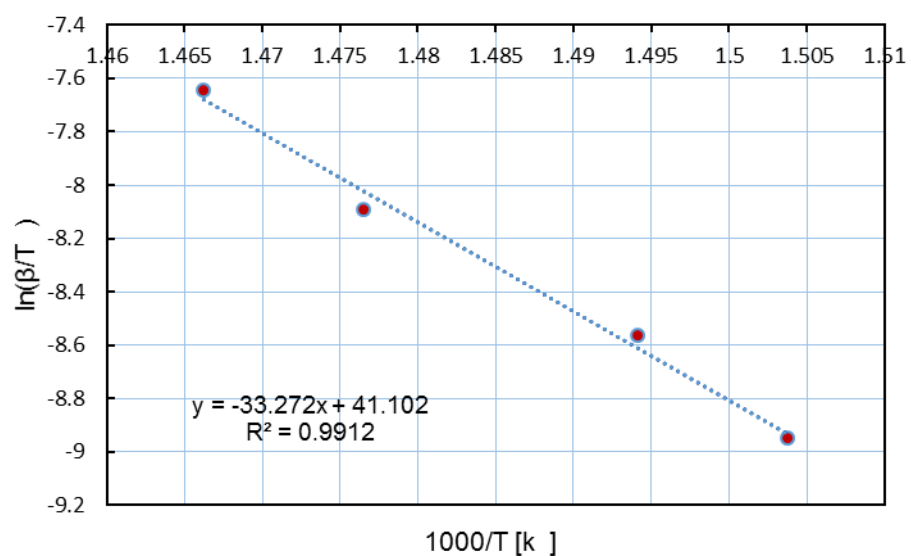


(a) TG curves under four heating rates.

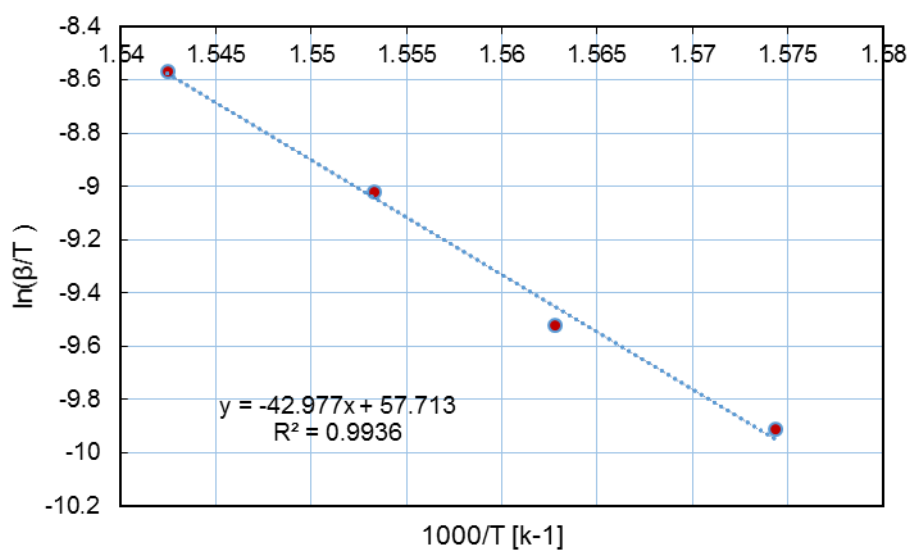


(b) DTG curves under four heating rates.

Figure 6-13. The thermal behavior of landfill sample (contaminated) under four heating rates 20, 30, 50, and 80 °C min⁻¹, (a) TG curves and (b) DTG curves in pyrolysis process.

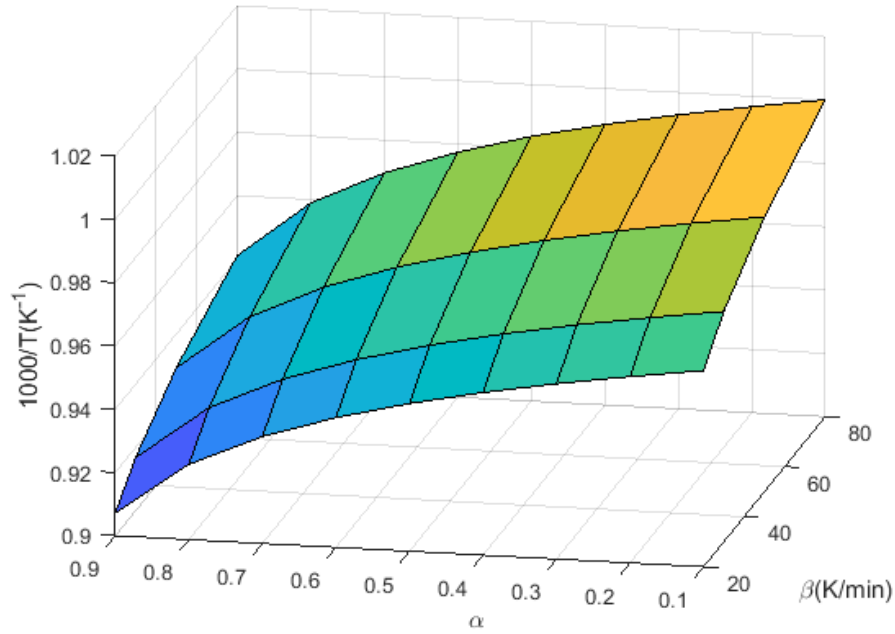


(a) Pellets sample (non-contaminated).

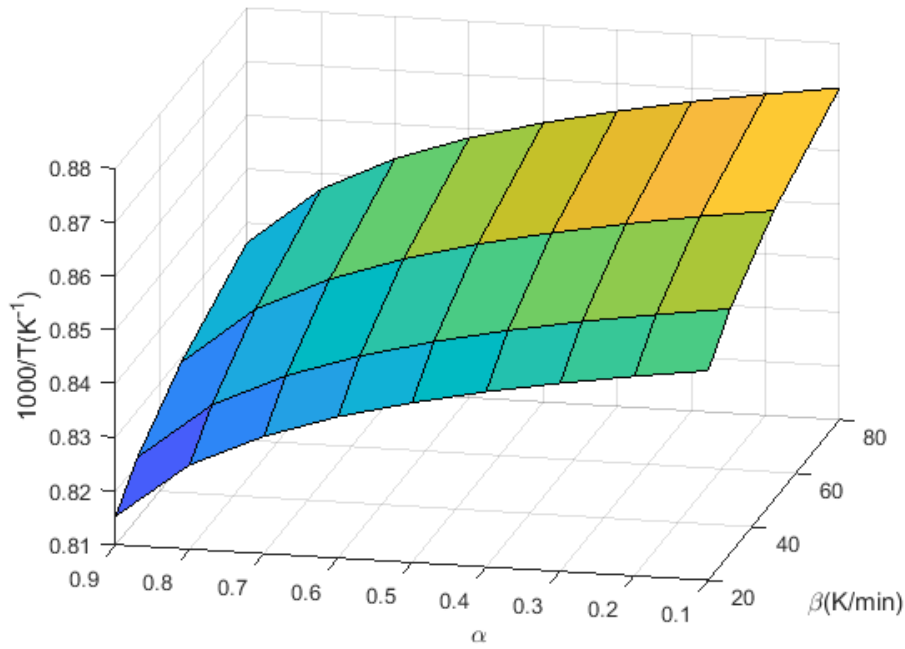


(b) Landfill sample (contaminated).

Figure 6-14. Kissinger plot of (a) pellets sample (non-contaminated) and (b) landfill sample (contaminated).



(a) Pellets sample (non-contaminated).



(b) Landfill sample (contaminated).

Figure 6-15. Surface plot of FWO method: the temperature [$1/T(k)$] as a function of extend of conversion degree (0.1-0.9) and four heat rates 20,30, 50, and 80 $K\ min^{-1}$ of (a) pellets sample (non-contaminated) and (b) landfill sample (contaminated).

6.5.3 Tube furnace pyrolysis

In this study, the experimental works on the pyrolysis of woody biomass in a tube furnace with emphasis on the partitioning of the metal(loid) elements across the bottom and fly ashes. The recovery of each element was calculated by the percentage of the summation of element retained in bottom ash and absorption train solution (Dong et al., 2015; Duan et al., 2017b; Reed, Dugwell and Kandiyoti, 2001b). In general, the results showed that more than 73% recovery ratio was reached. This is in accordance with previous studies (Duan et al., 2017b; Reed, Dugwell and Kandiyoti, 2001b), which showed that the mass balance ratio of $100 \pm 30\%$ was satisfactory for metal(loid) elements in advanced thermochemical conversion processes.

6.5.3.1 Original waste wood samples

In all the experimental trials on the original waste wood samples, the Cd and Hg were recognized as very volatile elements under pyrolysis conditions. These results agree with findings of other studies (Bunt and Waanders, 2008; Dong et al., 2015; Wu, Lin and Zeng, 2014). Further, Al, Co, Cr, Cu, Fe, Mo, Ni, Si, Ti, and V were identified as non-volatile elements, which corresponds with observations in other studies (Bunt and Waanders, 2010; Dong et al., 2015; Jano-Ito, Reed and Millan, 2014; Jiang et al., 2016; Miller, Dugwell and Kandiyoti, 2006). The distributions of As, Mn, Pb, and Zn between the bottom ash and train solution were substantially different across the experimental trials.

6.5.3.1.1 Arsenic (As)

The percentage retention values of As in bottom ash ranged from 12 to 92% at 500°C and 0.0 to 86% at 900°C, as shown in Figure 6-16. Only in the cases of mixed furniture and new furniture, 90% of the As remained in solid phase and was not volatilised at temperatures of 500°C and 900 °C. In contrast, regarding the other samples, the percentage retention values of As at 500°C., in increasing order, were 12% (L.d. 41-43 m) > 62% (L.d. 37.5-39 m) > 65% (L.d. 3-7 m) > 68% (demolition) > 89% (L.d. 50-51 m) > 79% (pellets) > 91% (chips). While at temperature 900°C, the percentage retention values of As, in increasing order,

were 0.00% (L.d. 41-43 m) > 1.0% (L.d. 3-7 m) > 15% (chips) > 25% (L.d. 50-51 m) > 34% (demolition) > 33% (L.d. 37.5-39 m) > 32.9% (pellets). Thus, the concentration of other elements played an important role in the partitioning of As and its speciation formation, as will be discussed later in section 6.5.4.1. The obtained results here are in line with those of previous studies (Contreras, Arostegui and Armesto, 2009; Haynes, Boström and Nordin, 2008; Helsen, 2005; Kartal et al., 2008; Liu et al., 2006a; Lundholm, 2007).

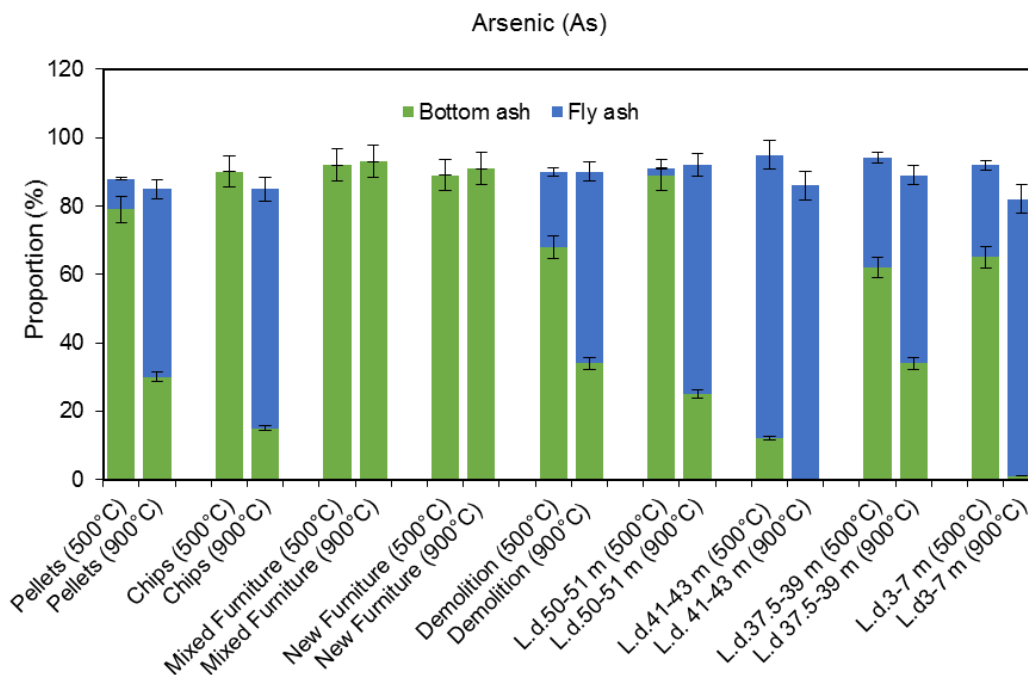


Figure 6-16. Distribution of arsenic between bottom ash and fly ash from pyrolysis furnace experiments of original WW samples.

6.5.3.1.2 Manganese (Mn)

Figure 6-17 presents the percentage retention data of Mn from all samples tested. As expected, the majority of Mn was retained in the bottom ash with percentage retention values ranging from 80% to 90% at both 500°C and 900°C. Conversely, about 86% of Mn was present in the fly ash from the L.d. (50-51 m) sample pyrolysis. Although these results are consistent with the data obtained in (Duan et al., 2016), which showed that Mn completely remained in solid phase, the

results are different than those of (Bunt and Waanders, 2010; Jiang et al., 2016). However, the thermodynamic modelling approach can explain these differences.

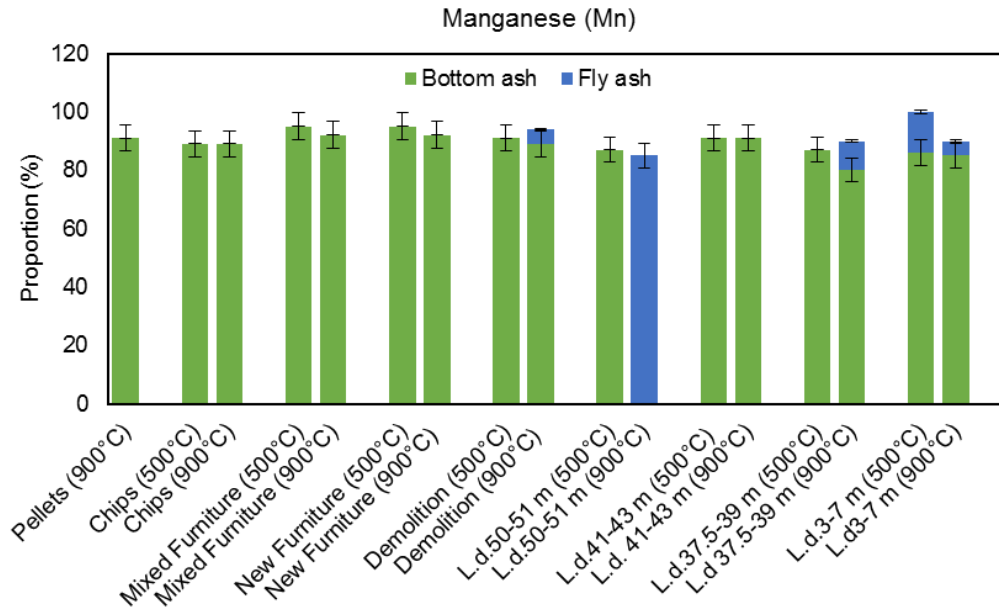


Figure 6-17. Distribution of manganese between bottom ash and fly ash from pyrolysis furnace experiments of original WW samples.

6.5.3.1.3 Lead (Pb)

Figure 6-18 shows the bar chart representation of the partitioning of Pb in bottom ash and fly ash. Obviously, was Pb present in the fly ash of all samples at 900°C, whereas at 500°C, the percentage retention levels were 91% (mixed furniture) > 89% (demolition) > 86% (new furniture) > 85% (pellets) > 82% (L.d. 41-43 m) > 80% (chips) > 74% (L.d. 37.5-39 m) > 66% (L.d. 50-51 m) > 48% (L.d. 3-7 m). These results are in line with those of previous studies (Ange Nzihou and Brian Stanmore, 2013; Dong et al., 2015; Duan et al., 2016; Jano-Ito, Reed and Millan, 2014).

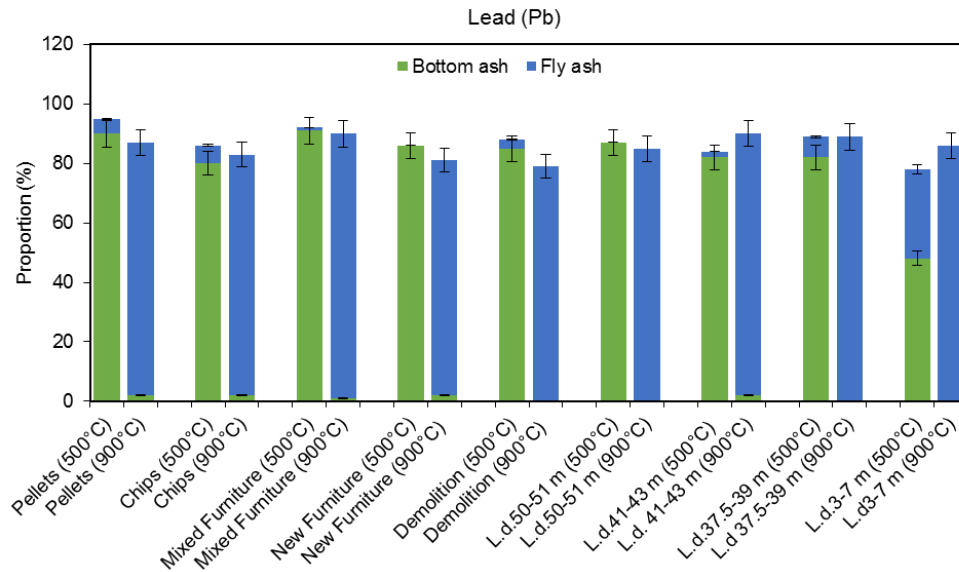


Figure 6-18. Distribution of lead between bottom ash and fly ash from pyrolysis furnace experiments of original WW samples.

6.5.3.1.4 Zinc (Zn)

Nearly complete volatilisation was observed from all the samples at 900°C (Figure 6-19). At 500 °C, the percentage retention values of Zn ranged from 89% to 92% except in the case of the L.d. (50-51 m) sample, where the Zn was completely present in fly ash. Other studies also found that Zn exhibited high volatility under typical operating conditions (Ange Nzihou and Brian Stanmore, 2013; Dong et al., 2015; Sørsum, Frandsen and Hustad, 2003).

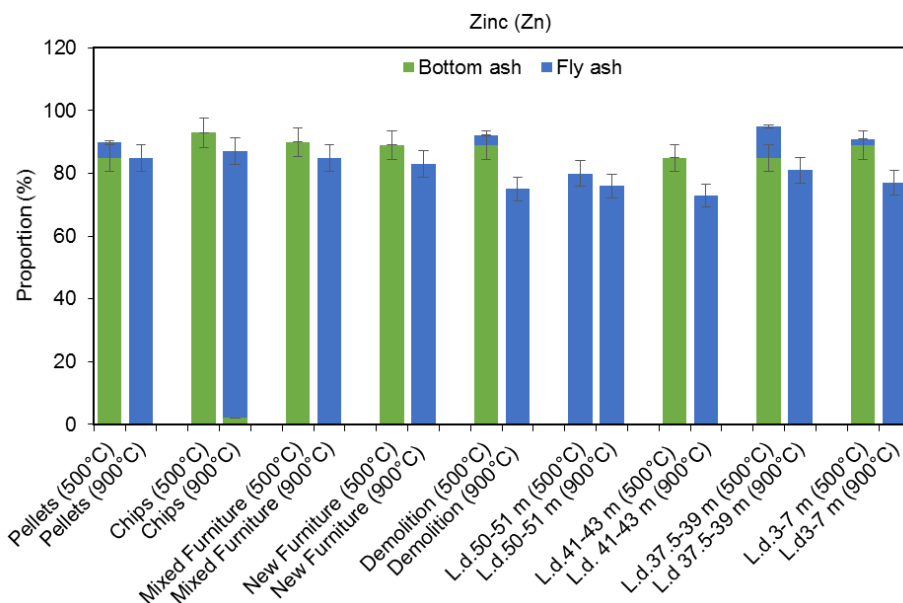


Figure 6-19. Distribution of zinc between bottom ash and fly ash from pyrolysis furnace experiments of original WW samples.

6.5.3.2 Artificial waste wood and blend samples

At 500°C and 700°C, the majority of the As and Ni introduced with AS₁, AS₂, AS₃, and BS were completely retained in the bottom ash. These results support previous research (Reed, Dugwell and Kandiyoti, 2001a) which suggested that the presence of Ni in the fuel samples can capture the As. Most importantly, the current study has provided a unique insight into the behaviour of As linked to Ni; that is, the presence of Ni should be regarded together with its associated concentration profile. Table 6-9 shows the effects of Ni concentrations on the retention of As.

Table 6-9. Comparison of the effect of concentrations of As and Ni on the percentage retention values of As from original, artificial, and blends samples.

Sample	Percentage retention values of As	Concentration	
		As mg/kg	Ni mg/kg
Artificial (AS ₁)	90%	16.64	40.6
Artificial (AS ₂)	90%	28.9	103.5
Artificial (AS ₃)	90%	42	84.5
Blends	84%	5.9	6.64
Original (Pellets)	34%	0.04	2.73
Landfill	29.5%	10.17	5.9

Moreover, at 700°C, the As percentage retention values from BS, pellets, and landfill samples are given in Figure 6-20. The percentage retention values of As from the blend sample increased by around 50% and 54.5%, as compared to those measured under pyrolysis conditions with pellets and landfill, respectively.

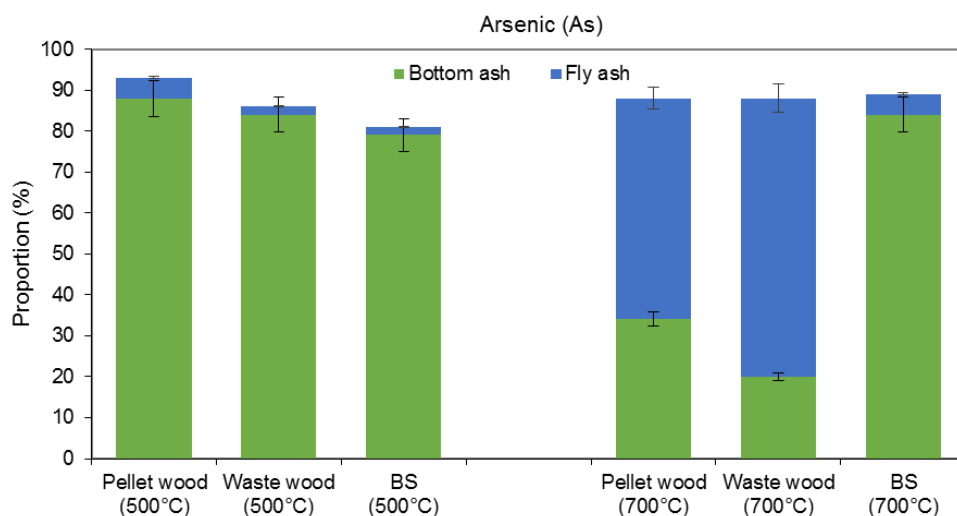


Figure 6-20. The distribution of arsenic across bottom ash and fly ash during pyrolysis furnace experiments on BS, pellet and landfill samples.

6.5.4 Thermodynamic calculations

6.5.4.1 Original waste wood samples

In order to predict the equilibrium partitioning of Al, As, Cd, Co, Cr, Cu, Fe, Hg, Mn, Mo, Ni, Pb, Si, Ti, V, and Zn, along with speciation formation, the equilibrium calculations were carried out with the composition data of the original samples (pellets, chips, mixed furniture, new furniture, demolition, L.d. (50-51 m), L.d. (41-43 m), L.d. (37.5-39 m) and L.d. (3-7 m) and process parameters given in Table 6-4 and Table 6-5. The simulation results revealed that, at the temperature range of 30-900°C, amongst the 16 elements, nine elements (i.e., Al, Co, Cr, Fe, Mo, Ni, Si, Ti, and V) remained in solid phase around 99.99% as dominant species as shown in Table 6-9. The results were consistent with other research (Bunt and Waanders, 2010; Froment et al., 2013; Jiang et al., 2016; Kilgallon, Simms and Oakey, 2002; Miller, Kandiyoti and Dugwell, 2004; Thompson and Argent, 2002), which proved that, under typical thermochemical conditions, these elements were usually non-volatile.

Further, in the present study, the Cl and S content in the samples were minimal, at $\leq 0.1\%$ and 0.01% , respectively. As a result no metal chlorides nor metal

sulphates were released in the gas phase (Bradshaw, Simms and Nicholls, 2008; Dong et al., 2015).

With respect to the sample types, the predictive results indicated that the evolution of elemental speciation strongly depended on the type of woody biomass, as detailed in Table 6-10. This phenomenon (in addition to the characteristics of each type of woody biomass) is common, since different element content in a particular sample can lead to unexpected interactions between them, resulting in different species (Contreras, Arostegui and Armesto, 2009; Jano-Ito, Reed and Millan, 2014; Yan, Gauthier and Flamant, 2000).

Because As, Cd, Cu, Hg, Mn, Pb, and Zn were the main concern, as the largest sources of contaminations (Edo, 2016; Haynes, Boström and Nordin, 2008; Huron et al., 2017; Lundholm, 2007), each will be discussed individually below.

Table 6-10. Partitioning behaviour and main species of Al, Co, Cr, Fe, Mo, Ni, Si, Ti, and V during pyrolysis process of original samples.

Types of wood	Solid species
Aluminium (Al)	
Pellets	$\text{Al}_{14}\text{Ca}_{12}\text{O}_{33}, \text{Al}_2\text{Ca}_2\text{O}_7\text{Si}, \text{Al}_2\text{FeO}_4, \text{Al}_2\text{H}_2\text{O}_4, \text{Al}_2\text{MnO}_4, \text{AlNaO}_2, \text{Al}_2\text{O}_4\text{Zn}$
Chips	$\text{Al}_{14}\text{Ca}_{12}\text{O}_{33}, \text{Al}_2\text{Ca}_2\text{O}_7\text{Si}, \text{Al}_2\text{CuO}_4, \text{Al}_2\text{FeO}_4, \text{Al}_3\text{H}_2\text{KO}_{12}\text{Si}, \text{Al}_2\text{H}_2\text{O}_4, \text{AlKO}_4\text{Si}, \text{Al}_2\text{K}_2\text{O}_8\text{Si}_2, \text{Al}_2\text{MnO}_4, \text{AlNaO}_2, \text{Al}_2\text{Na}_2\text{O}_{16}\text{Si}, \text{Al}_2\text{O}_4\text{Zn}$
Mixed Furniture	$\text{Al}_{14}\text{Ca}_{12}\text{O}_{33}, \text{Al}_2\text{Ca}_2\text{O}_7\text{Si}, \text{Al}_2\text{CuO}_4, \text{Al}_2\text{FeO}_4, \text{Al}_3\text{H}_2\text{KO}_{12}\text{Si}, \text{Al}_2\text{H}_2\text{O}_4, \text{AlKO}_4\text{Si}, \text{Al}_2\text{K}_2\text{O}_8\text{Si}_2, \text{Al}_2\text{MnO}_4, \text{AlNaO}_2, \text{Al}_2\text{O}_4\text{Zn}$
New Furniture	$\text{Al}_{14}\text{Ca}_{12}\text{O}_{33}, \text{Al}_2\text{Ca}_2\text{O}_7\text{Si}, \text{Al}_2\text{CuO}_4, \text{Al}_2\text{FeO}_4, \text{Al}_3\text{H}_2\text{KO}_{12}\text{Si}, \text{Al}_2\text{H}_2\text{O}_4, \text{AlKO}_4\text{Si}, \text{Al}_2\text{K}_2\text{O}_8\text{Si}_2, \text{Al}_2\text{MnO}_4, \text{AlNaO}_2, \text{Al}_2\text{O}_4\text{Zn}$
Demolition	$\text{Al}_{14}\text{Ca}_{12}\text{O}_{33}, \text{Al}_2\text{Ca}_2\text{O}_7\text{Si}, \text{Al}_2\text{FeO}_4, \text{Al}_2\text{H}_2\text{O}_4, \text{Al}_2\text{MnO}_4, \text{AlNaO}_2, \text{Al}_2\text{O}_4\text{Zn}$
L.d. 50-51 m	AlN
L.d. 41-43 m	$\text{Al}_2\text{CuO}_4, \text{Al}_2\text{FeO}_4, \text{Al}_3\text{H}_2\text{KO}_{12}\text{Si}, \text{Al}_2\text{H}_2\text{O}_4, \text{Al}_2\text{MnO}_4, \text{AlNaO}_2, \text{Al}_2\text{Na}_2\text{O}_{16}\text{Si}, \text{Al}_2\text{O}_4\text{Zn}$
L.d. 37.5-39 m	$\text{Al}_{14}\text{Ca}_{12}\text{O}_{33}, \text{Al}_2\text{Ca}_2\text{O}_7\text{Si}, \text{Al}_2\text{FeO}_4, \text{Al}_2\text{H}_2\text{O}_4, \text{Al}_2\text{MnO}_4, \text{AlNaO}_2, \text{Al}_2\text{O}_4\text{Zn}$
L.d. 3-7 m	$\text{Al}_{14}\text{Ca}_{12}\text{O}_{33}, \text{Al}_2\text{Ca}_2\text{O}_7\text{Si}, \text{Al}_2\text{FeO}_4, \text{Al}_2\text{H}_2\text{O}_4, \text{Al}_2\text{MnO}_4, \text{AlNaO}_2, \text{Al}_2\text{O}_4\text{Zn}$
Cobalt (Co)	
Pellets	$\text{Co}, \text{Co}_9\text{S}_8$
Chips	$\text{Co}, \text{CoFe}_2\text{O}_4, \text{Co}_9\text{S}_8$
Mixed Furniture	$\text{Co}, \text{CoFe}_2\text{O}_4$
New Furniture	$\text{Co}, \text{Co}_9\text{S}_8$
Demolition	$\text{Co}, \text{CoFe}_2\text{O}_4$
L.d. 50-51 m	Co
L.d. 41-43 m	Co

Table 6-10. Partitioning behaviour and main species of Al, Co, Cr, Fe, Mo, Ni, Si, Ti, and V during pyrolysis process of original samples.

Types of wood	Solid species
L.d. 37.5-39 m	Co, Co ₉ S ₈ .
L.d. 3-7 m	Co, CoS
Chromium (Cr)	
Pelletd	CaCr ₂ O ₄ , Cr ₂ FeO ₄ .
Chips	CaCr ₂ O ₄ , Cr ₂ FeO ₄ , CrKO ₂ .
Mixed Furniture	CaCr ₂ O ₄ , Cr ₂ FeO ₄ , CrKO ₂
New Furniture	CaCr ₂ O ₄ , Cr ₂ FeO ₄ , CrKO ₂
Demolition	CaCr ₂ O ₄ , Cr ₂ FeO ₄
L.d. 50-51 m	C ₂ Cr ₃ , CrN
L.d. 41-43 m	CaCr ₂ O ₄ , Cr ₂ FeO ₄
L.d. 37.5-39 m	CaCr ₂ O ₄ , Cr ₂ FeO ₄
L.d. 3-7 m	CaCr ₂ O ₄ , Cr ₂ FeO ₄
Iron (Fe)	
Pellets	FeH ₂ O ₂ , Al ₂ FeO ₄ , CaFe ₂ O ₄ , Cr ₂ FeO ₄ , CuFeS ₂ , Cu ₅ FeS ₄ , Fe, Fe ₃ O ₄
Chips	Al ₂ FeO ₄ , CFe ₃ , CaFe ₂ O ₄ , CoFe ₂ O ₄ , Cr ₂ FeO ₄ , Fe, FeO, Fe ₃ O ₄ , FeO ₃ Ti, FeO ₄ V ₂
Mixed Furniture	Al ₂ FeO ₄ , CFe ₃ , CaFe ₂ O ₄ , CoFe ₂ O ₄ , Cr ₂ FeO ₄ , Fe, Fe ₂ NiO ₄ , Fe ₃ O ₄ , FeO ₃ Ti, FeO ₄ V ₂
New Furniture	Al ₂ FeO ₄ , CFe ₃ , CaFe ₂ O ₄ , CoFe ₂ O ₄ , Cr ₂ FeO ₄ , Fe, Fe ₂ NiO ₄ , Fe ₃ O ₄ , FeO ₃ Ti, FeO ₄ V ₂
Demolition	Al ₂ FeO ₄ , CFe ₃ , CaFe ₂ O ₄ , CoFe ₂ O ₄ , Cr ₂ FeO ₄ , FeO, Fe ₃ O ₄ , FeO ₃ Ti, Fe ₂ O ₄ Ti, FeO ₄ V ₂ , FeSe _{0.96}
L.d. 50-51 m	CFe ₃ , Fe
L.d. 41-43 m	Al ₂ FeO ₄ , CFe ₃ , CaFe ₂ O ₄ , Cr ₂ FeO ₄ , Cu ₅ FeS ₄ , Fe, FeO, Fe ₃ O ₄ , FeO ₃ Ti, FeO ₄ V ₂ .
L.d. 37.5-39 m	Al ₂ FeO ₄ , CaFe ₂ O ₄ , Cr ₂ FeO ₄ , CuFeS ₂ , Cu ₅ FeS ₄ , Fe, Fe ₃ O ₄
L.d. 3-7 m	Al ₂ FeO ₄ , CFe ₃ , CaFe ₂ O ₄ , Cr ₂ FeO ₄ , Cu ₅ FeS ₄ , Fe, Fe ₃ O ₄ .
Molybdenum (Mo)	
Pellets	CMo, CMo ₂ , CaMoO ₄ , MoNa ₂ O ₄
Chips	CMo, CMo ₂ , CaMoO ₄ , MoNa ₂ O ₄
Mixed Furniture	CMo, CMo ₂ , CaMoO ₄ , MoNa ₂ O ₄ , MoO ₂
New Furniture	CMo, CMo ₂ , CaMoO ₄ , MoNa ₂ O ₄ , MoO ₂
Demolition	CMo ₂ , CaMoO ₄ , MoNa ₂ O ₄ , Mo ₂ Na ₂ O ₇
L.d. 50-51 m	CMo, Mo
L.d. 41-43 m	CaMoO ₄ , MoO ₂
L.d. 37.5-39 m	CMo ₂ , CaMoO ₄ , MoNa ₂ O ₄
L.d. 3-7 m	CMo, Mo
Nickel (Ni)	
Pellet	As ₂ Ni ₅ , As ₈ Ni ₁₁ , Ni ₃ S ₂
Chips	As ₂ Ni ₅ , As ₈ Ni ₁₁ ,
Mixed Furniture	As ₂ Ni ₅ , Fe ₂ NiO ₄ , Ni, Ni ₃ S ₂
New Furniture	As ₂ Ni ₅ , Fe ₂ NiO ₄ , Ni, Ni ₃ S ₂
Demolition	AsNi, As ₂ Ni ₅ , As ₈ Ni ₁₁
L.d. 50-51 m	As ₂ Ni ₅ , Ni

Table 6-10. Partitioning behaviour and main species of Al, Co, Cr, Fe, Mo, Ni, Si, Ti, and V during pyrolysis process of original samples.

Types of wood	Solid species
L.d. 41-43 m	As ₂ Ni ₅ , As ₈ Ni ₁₁ ,
L.d. 37.5-39 m	As ₂ Ni ₅ , As ₈ Ni ₁₁ , Ni ₃ S ₂
L.d. 3-7 m	As ₂ Ni ₅ , As ₈ Ni ₁₁ ,
Silicon (Si)	
Pellets	Al ₂ Ca ₂ O ₇ Si, Ca ₂ O ₄ Si, Na ₂ O ₃ Si
Chips	Al ₂ Ca ₂ O ₇ Si, Al ₃ H ₂ KO ₁₂ Si, AlKO ₄ Si, Al ₂ K ₂ O ₈ Si ₂ , Al ₂ Na ₂ O ₁₆ Si, CaO ₃ Si, Ca ₂ O ₄ Si, Mn ₂ O ₄ Si,
Mixed Furniture	Al ₂ Ca ₂ O ₇ Si, Al ₃ H ₂ KO ₁₂ Si, AlKO ₄ Si, Al ₂ K ₂ O ₈ Si ₂ , Ca ₂ O ₄ Si, Mn ₂ O ₄ Si
New Furniture	Al ₂ Ca ₂ O ₇ Si, Al ₃ H ₂ KO ₁₂ Si, AlKO ₄ Si, Al ₂ K ₂ O ₈ Si ₂ , Ca ₂ O ₄ Si, Mn ₂ O ₄ Si
Demolition	Al ₂ Ca ₂ O ₇ Si, AlKO ₄ Si, Al ₂ K ₂ O ₈ Si ₂ , Ca ₂ H ₂ Mg ₅ O ₂₄ , CaMgO ₄ Si, Ca ₃ MgO ₈ Si ₂ , Ca ₂ O ₄ Si, H ₂ Mg ₃ O ₁₂ Si ₄ , H ₄ Mg ₃ O ₉ Si ₂ , Mg ₂ O ₄ Si, Mn ₂ O ₄ Si
L.d. 50-51 m	N ₄ Si ₃ , Na ₄ O ₄ Si
L.d. 41-43 m	Al ₃ H ₂ KO ₁₂ Si, Al ₂ Na ₂ O ₁₆ Si.
L.d. 37.5-39 m	Al ₂ Ca ₂ O ₇ Si, Ca ₂ O ₄ Si, Na ₂ O ₃ Si
L.d. 3-7 m	Al ₂ Ca ₂ O ₇ Si, Ca ₂ O ₄ Si, Na ₂ O ₃ Si
Titanium (Ti)	
Pellets	Ca ₄ O ₁₀ Ti ₃ , Na ₂ O ₅ Ti ₂ .
Chips	CaO ₃ Ti, Ca ₄ O ₁₀ Ti ₃ , FeO ₃ Ti, MnO ₃ Ti, Mn ₂ O ₄ Ti, O ₃ PbTi.
Mixed Furniture	CaO ₃ Ti, Ca ₄ O ₁₀ Ti ₃ , FeO ₃ Ti, MnO ₃ Ti, Mn ₂ O ₄ Ti, O ₃ PbTi
New Furniture	CaO ₃ Ti, Ca ₄ O ₁₀ Ti ₃ , FeO ₃ Ti, MnO ₃ Ti, Mn ₂ O ₄ Ti, O ₃ PbTi
Demolition	Ca ₄ O ₁₀ Ti ₃ , CdO ₃ Ti, FeO ₃ Ti, Fe ₂ O ₄ Ti, O ₃ PbTi
L.d. 50-51 m	NTi
L.d. 41-43 m	CaO ₃ Ti, Ca ₄ O ₁₀ Ti ₃ , FeO ₃ Ti.
L.d. 37.5-39 m	Ca ₄ O ₁₀ Ti ₃ , Na ₂ O ₅ Ti ₂
L.d. 3-7 m	CaO ₃ Ti, Ca ₃ O ₇ Ti ₂ , Ca ₄ O ₁₀ Ti ₃ , Na ₂ O ₅ Ti ₂
Vanadium (V)	
Pellets	Ca ₃ O ₈ V ₂ , Na ₄ O ₇ V ₂ , Na ₆ O ₈ V ₂ .
Chips	Ca ₃ O ₈ V ₂ , FeO ₄ V ₂ , Na ₄ O ₇ V ₂ , O ₃ V ₂ .
Mixed Furniture	Ca ₃ O ₈ V ₂ , FeO ₄ V ₂ , Na ₆ O ₈ V ₂
New Furniture	Ca ₃ O ₈ V ₂ , FeO ₄ V ₂ , Na ₆ O ₈ V ₂
Demolition	Ca ₃ O ₈ V ₂ , FeO ₄ V ₂ , O ₃ V ₂
L.d. 50-51 m	NV.
L.d. 41-43 m	Ca ₃ O ₈ V ₂ , FeO ₄ V ₂ , Na ₄ O ₇ V ₂ , O ₃ V ₂ .
L.d. 37.5-39 m	Ca ₃ O ₈ V ₂ , Na ₄ O ₇ V ₂ , Na ₆ O ₈ V ₂ .
L.d. 3-7 m	NV, OV, O ₃ V ₂

6.5.4.1.1 Arsenic (As)

As observed in Figure 6-21 and Table 6-11, there are similarities and differences in the As phase transformation temperatures and types of species during pyrolysis of different original WW samples. For instance, the obtained results from the L.d. (37.5-39 m), L.d. (3-7 m), and demolition WW samples show that the As was first released into gaseous phase from 470°C to 620°C, and then declined as the temperature rose to between 620°C to 720°C. The results from pellet wood, mixed furniture and new furniture WW samples indicated that 99.99% As remained in solid phase at temperature range of 30-900°C. In order to provide a more thorough analysis, the obtained results from each sample will be presented and discussed separately in the subsequent sub-sections.

6.5.4.1.1.1 Arsenic in landfill depth (37.5-39 m) sample

As noted, As was released into gaseous phase first at temperatures between 470°C and 620°C (62.80% SP), and decreased in a temperature range from 620°C-720°C (90.99% SP), as displayed in Figure 6-22a. This was mainly due to the As-Ni interaction, which initially generated the species As^{+5} as AsK_3O_4 and As_2Ni_5 , and as the temperature increased the As^{+3} became As_8Ni_{11} , as shown in Figure 6-22b.

These results agree with the findings of the study by (Duan et al., 2017b). In addition, (Contreras, Arostegui and Armesto, 2009; Haynes, Boström and Nordin, 2008) proved that As remained in solid phase for a temperature range of 100-600°C as the inorganic compound AsK_3O_4 . Also, (Reed, Dugwell and Kandiyoti, 2001a) acknowledged that As remained in solid phase at temperatures $\leq 1027^\circ C$ as As_2Ni_5 and As_8Ni_{11} , and this was further confirmed by (Oakey, Simms and Kilgallon, 2004).

6.5.4.1.1.2 Arsenic in landfill depth (3-7 m) sample

Here, the phase transformation and speciation formation of As were similar to those obtained with the L.d. (37.5-39 m) sample (Figure 6-22). However, a slight

1.07% difference in the remaining As in solid phase (as As_2Ni_5) was found at 920°C.

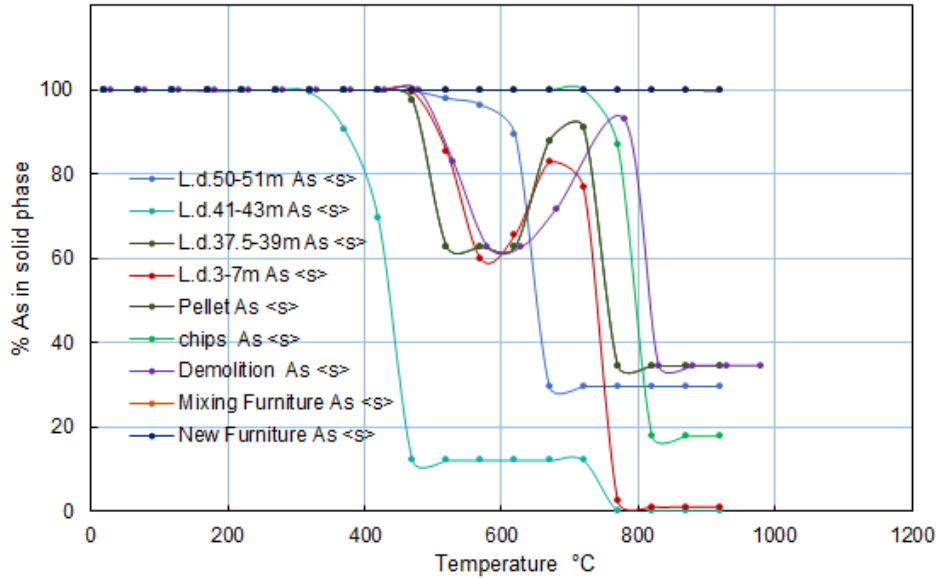
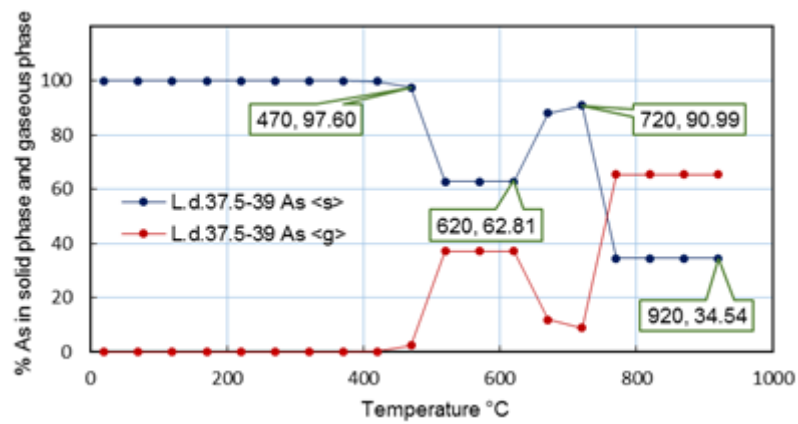


Figure 6-21. Arsenic retention in solid phases during the pyrolysis of original waste wood samples.

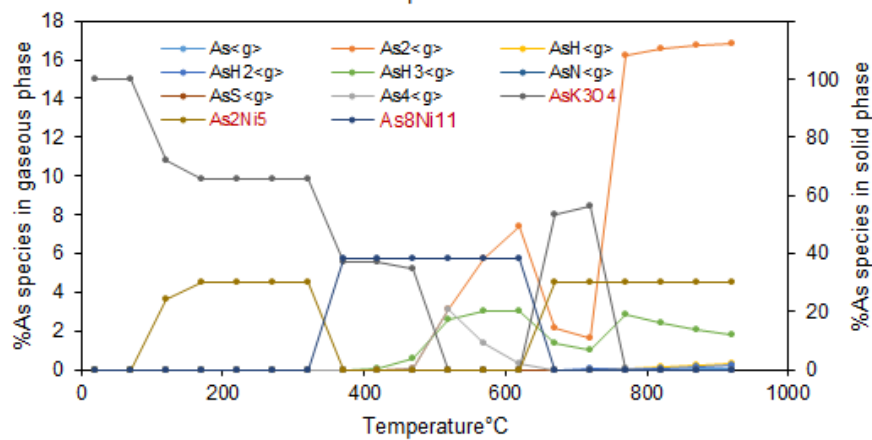
Table 6-11. Partitioning behaviour and main species of arsenic during pyrolysis of different original woody biomass samples.

Types of wood	Solid species	Gaseous species	Phase transformation temperature °C Solid → gaseous Under 1 atm (101325Pa) (30-920°C)
Pellets	$\text{As}_2\text{Ni}_5, \text{As}_8\text{Ni}_{11}$	AsH_3	900→920 (99.91% SP)
Chips	$\text{AsK}_3\text{O}_4, \text{As}_2\text{Ni}_5, \text{As}_8\text{Ni}_{11}$	$\text{As}, \text{As}_2, \text{As}_4, \text{AsH}, \text{AsH}_2, \text{AsH}_3, \text{AsN},$	770→920 (17.85% SP)
Mixed furniture	As_2Ni_5	AsH_3	870→920 (99.91% SP)
New furniture	As_2Ni_5	AsH_3	870→920 (99.91% SP)
Demolition	$\text{AsK}_3\text{O}_4, \text{As}_2\text{Ni}_5, \text{As}_8\text{Ni}_{11}$	$\text{As}, \text{As}_2, \text{As}_4, \text{AsH}, \text{AsH}_2, \text{AsH}_3,$ $\text{AsN}, \text{AsS}, \text{AsSe}$	580→680 (71.75% SP) 680→780 (92.86% SP) 830→920 (34.54% SP)
L.d. 50-51 m	$\text{AsMn}, \text{AsNa}_3, \text{As}_2\text{Ni}_5$	$\text{As}, \text{As}_2, \text{AsH}, \text{AsH}_2, \text{AsH}_3, \text{AsN}$	520→920 (29.63% SP)
L.d. 41-43 m	$\text{AsCu}_3, \text{AsK}_3\text{O}_4, \text{As}_2\text{Ni}_5, \text{As}_8\text{Ni}_{11},$ AsS	$\text{As}, \text{As}_2, \text{As}_3, \text{As}_4, \text{AsH}, \text{AsH}_2,$ $\text{AsH}_3, \text{AsN}, \text{AsS}, \text{AsSe}$	400→780 (100% GP)
L.d. 37.5-39 m	$\text{AsK}_3\text{O}_4, \text{As}_2\text{Ni}_5, \text{As}_8\text{Ni}_{11}$	$\text{As}, \text{As}_2, \text{As}_4, \text{AsH}, \text{AsH}_2, \text{AsH}_3, \text{AsN},$ AsS	470→620 (62.80% SP) 620→720 (90.99% SP) 720→920 (34.54% SP)
L.d. 3-7 m	$\text{AsK}_3\text{O}_4, \text{As}_2\text{Ni}_5, \text{As}_8\text{Ni}_{11}$	$\text{As}, \text{As}_2, \text{As}_3, \text{As}_4, \text{AsH}, \text{AsH}_2,$ $\text{AsH}_3, \text{AsN}, \text{AsS}$	470→570 (59.89% SP) 570→670 (82.84% SP) 670→820 (1.06 % SP)

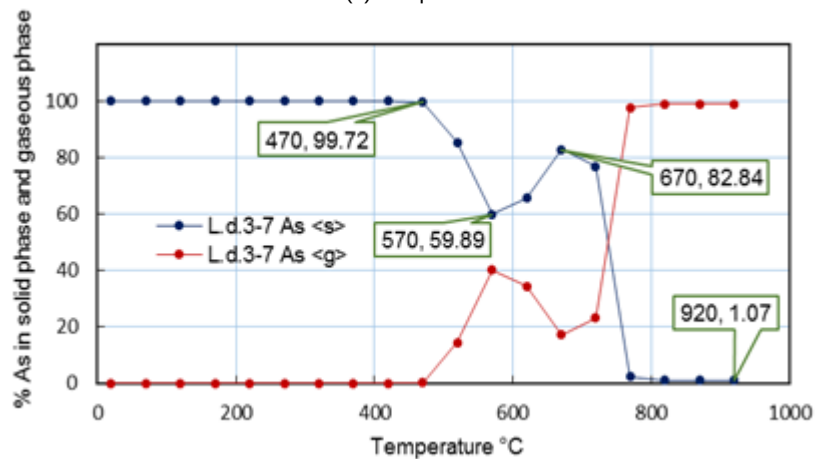
SP (Mass percentage in solid phase) and GP (Mass percentage in gaseous phase).



(a) As phase transformation in landfill depth (37.5-39 m)



(b) As species.



(c) As phase transformation in landfill depth (3-7 m).

Figure 6-22. Phase transition and equilibrium speciation of As in waste wood from landfill depth (37.5-39 m) and landfill depth (3-7 m) during pyrolysis process.

6.5.4.1.1.3 Arsenic in demolition sample

With this type of WW, for a temperature range of 480-630°C, 62.81% of the As remained in solid phase, and then increased to 92.86% at a temperature 780°C, as shown in Figure 6-23. The identified species were similar to those formed during the pyrolysis of L.d. (37.5-39 m) and L.d. (3-7 m) samples.

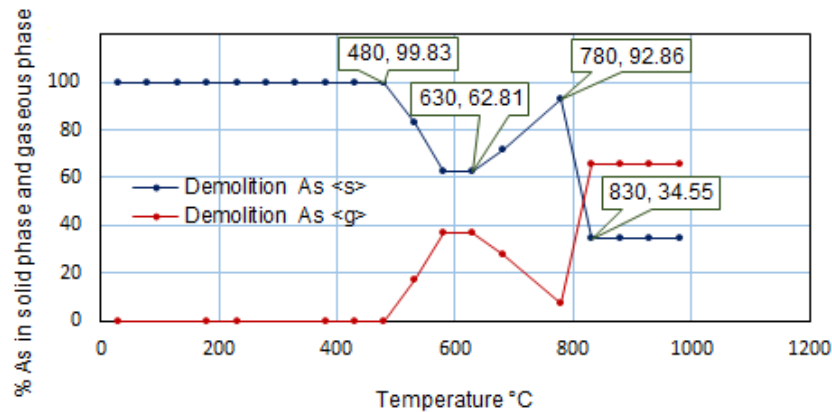


Figure 6-23. Phase transition and equilibrium speciation of As in waste wood from demolition during pyrolysis process.

6.5.4.1.1.4 Arsenic in landfill depth (50-51 m) sample

In this case, the As solid/gaseous phase transformation dropped from 99.77% to 29.63% at temperatures between 470°C and 920°C, and ended up as gaseous about 70.37%, as shown in Figure 6-24a. This is can be attributed to the presence of Na, Ni, and Mn. Figure 6-24b shows that the dominant species of As were AsNa_3 and As_2Ni_5 , which resulted from the As-Na interaction and As-Ni interaction, respectively. The species were stable in the solid phase until a temperature of 520°C. These results are in line with the previous study by (Lundholm et al., 2007), which reported that the As and Na in wood samples could form stable species in solid phase as AsNa_3O_4 at temperatures of 850-1000°C. Also, (Reed, Dugwell and Kandiyoti, 2001a) proved that when both Ni and As present in the system, they can interact and form the solid species As_2Ni_5 . With regard to the presence of Mn, a solid dominant species (AsMn) was formed at temperatures between 520°C and 670°C. While this finding was unexpected, it is

possible, since Mn can interact with As (Nascimento, Oliveira and Campos, 2006).

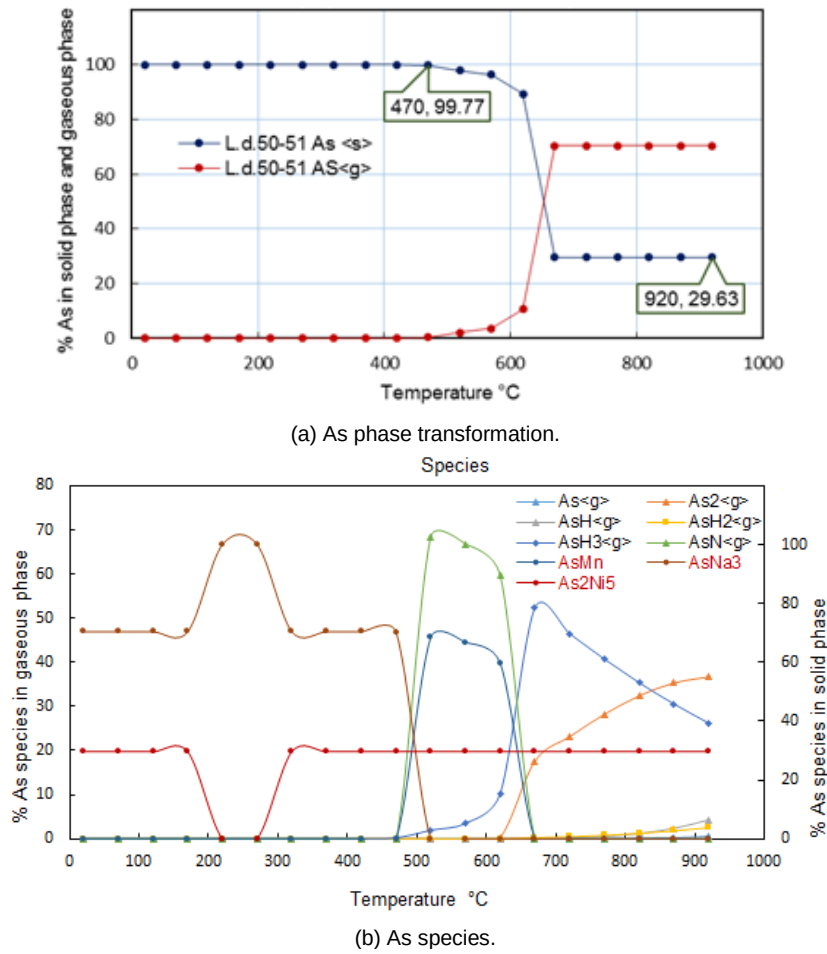
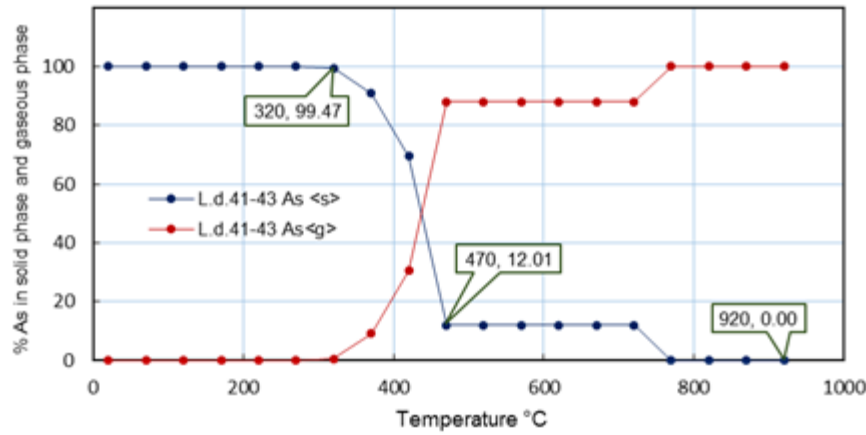


Figure 6-24. Phase transition and equilibrium speciation of As in waste wood from landfill depth (50-51 m) during pyrolysis process.

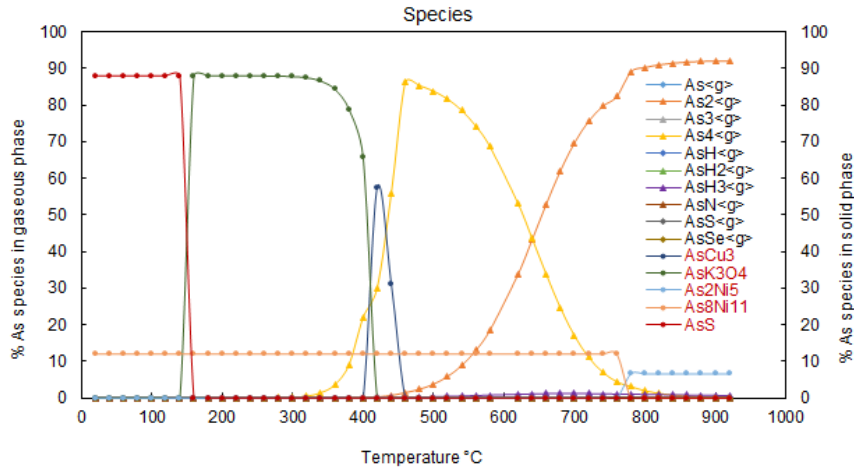
6.5.4.1.1.5 Arsenic in landfill depth (41-43 m) sample

Figure 6-25a exhibits the solid/gaseous phase transformation of As during the pyrolysis of the L.d. (41-43 m) sample. Obviously, when the temperature was $\leq 320^{\circ}\text{C}$, As presented as a solid in the form of AsS , AsK_3O_4 and $\text{As}_8\text{Ni}_{11}$. Above 320°C , it turned into AsCu_3 , As_2Ni_5 and $\text{As}_8\text{Ni}_{11}$, whilst starting to gradually emerge as gaseous species up until 920°C , as shown in Figure 6-25b. Furthermore, the presence of S and Se increased the volatility of As. This was also observed in the literature (Contreras, Arostegui and Armesto, 2009;

Lundholm, 2007; Vassilev, Baxter and Vassileva, 2014; Yan, Gauthier and Flamant, 2000).



(a) As phase transformation.



(b) As species.

Figure 6-25. Phase transition and equilibrium speciation of As in waste wood from landfill depth (41-43 m) during pyrolysis process.

6.5.4.1.1.6 Arsenic in chips sample

Arsenic partitioning under pyrolysis conditions was strongly impacted by the presence of K and Ni. As expected, about 100% of As remained as solid species AsK_3O_4 and As_8Ni_{11} at 720°C, as shown in Figure 6-26a. With the increasing temperature, As compounds gradually turned into As_2Ni_5 and emerged as gaseous species (Figure 6-26b).

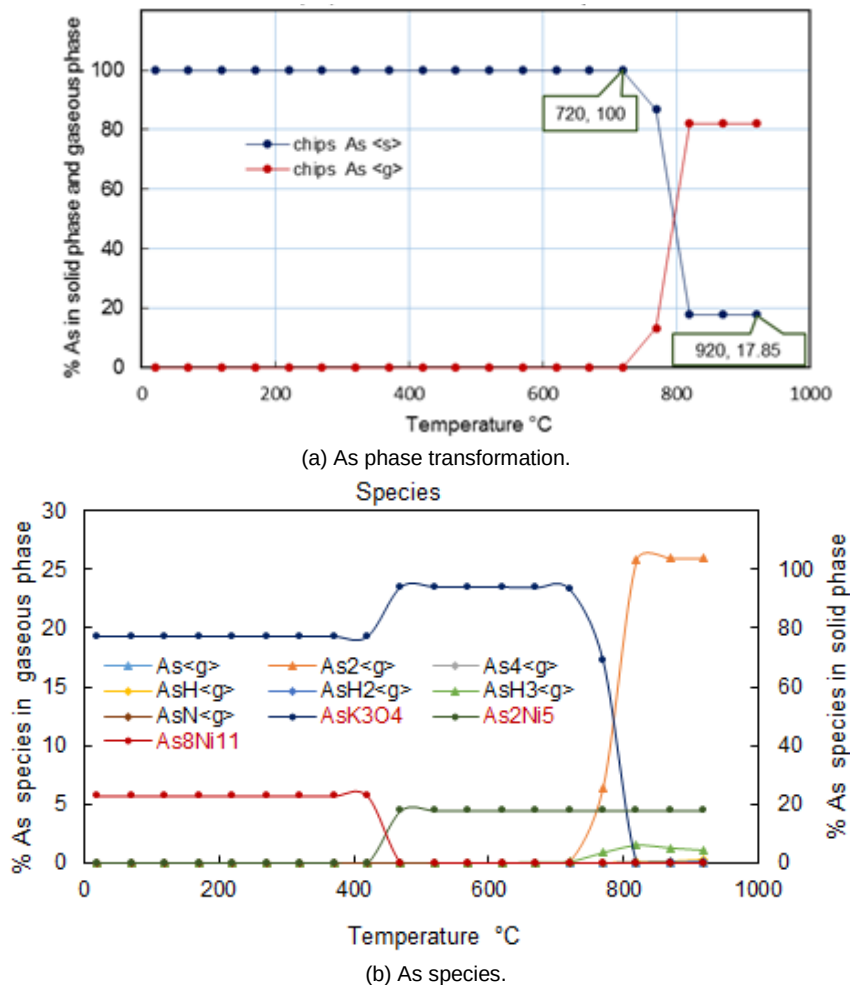


Figure 6-26. Phase transition and equilibrium speciation of As in chips wood during pyrolysis process.

6.5.4.1.1.7 Arsenic in pellet, mixed furniture, and new furniture samples

As noted already (Figure 6-16 and Table 6-11), 99.91% of As remained in solid from 0 to 920°C. This may be due to the Ni-As interaction during the pyrolysis of each sample. The formation of the solid species As_2Ni_5 and $\text{As}_8\text{Ni}_{11}$ has been predicted for pellet wood pyrolysis, whereas As_2Ni_5 has been predicted for mixed furniture and new furniture wood pyrolysis. The AsH_3 (0.09%) was observed as a gaseous species in all cases. These results further confirmed that the presence of Ni was useful in capturing As.

6.5.4.1.2 Cadmium (Cd)

Figure 6-27 and Table 6-12 demonstrate the partitioning profile of Cd during the pyrolysis of different WW samples. In the case of pellet wood, Cd was predicted in gaseous phase at temperatures higher than 320°C. In the case of mixed furniture and new furniture woods, Cd was released into gaseous phase at 270°C. For the pyrolysis of demolition, L.d. (41-43 m), L.d. (37.5-39 m), and L.d. (3-7 m) woods, the predictive results showed that Cd was entirely released into gaseous phase at 175°C. At 50°C and 70°C, Cd started to release into gaseous phase during the pyrolysis of L.d. (50-51 m) and chips, respectively, respectively.

The results here indicated that Cd has a higher volatilisation potential, which was consistent with the literature (Bradshaw, Simms and Nicholls, 2008; Cotton, Patchigolla and Oakey, 2014; Jano-Ito, Reed and Millan, 2014; Kilgallon, Simms and Oakey, 2002; Liu et al., 2006b; Oakey, Simms and Kilgallon, 2004; Reed, Dugwell and Kandiyoti, 2001a).

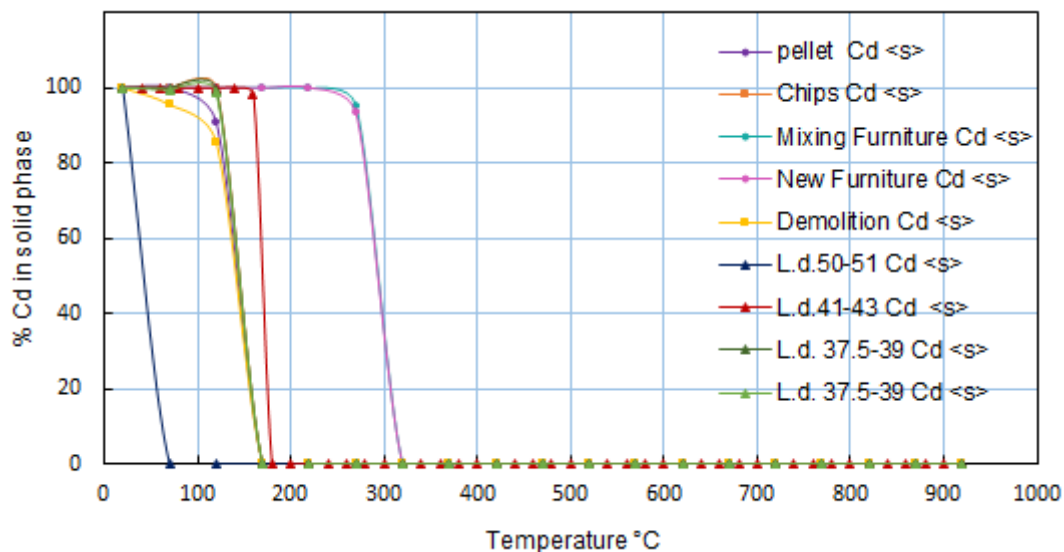


Figure 6-27. Cadmium retention in solid phases during the pyrolysis of original waste wood samples.

Table 6-12. Partitioning behaviour and main species of cadmium during pyrolysis of different original wood samples.

Types of wood	Solid species	Gaseous species	Phase transformation temperature °C (30-920°C) Solid →gaseous Under 1 atm (101325Pa)
Pellets	CCdO ₃ , CdS	Cd	270→320 (100% GP)
Chips	Cd	Cd	70→120 (100% GP)
Mixed furniture	CCdO ₃ , CdS	Cd	270→320 (100% GP)
New furniture	CCdO ₃ , CdS	Cd	270→320 (100% GP)
Demolition	Cd,CdH ₂ O ₂	Cd	70→170 (100% GP)
L.d. 50-51 m	Cd	Cd, CdH	50→70 (100% GP)
L.d. 41-43 m	CCdO ₃ ,Cd,CdO	Cd	160→180 (100% GP)
L.d. 37.5-39 m	Cd,CdH ₂ O ₂	Cd	70→170 (100% GP)
L.d. 3-7 m	Cd,CdH ₂ O ₂	Cd	120→170 (100% GP)

SP (Mass percentage in solid phase) and GP (Mass percentage in gaseous phase).

6.5.4.1.3 Copper (Cu)

A substantial amount (99%) of Cu was observed in the solid phase below the 920°C, except in the case of L.d. (50-51 m) wood, where around 83.42% remained in the solid phase below the same temperature, as shown in Table 6-13. Interestingly, the predictive calculations showed that there were different types of solid species in each case. For example, the dominant species of Cu in the case of L.d. (41-43 m) wood were Al₂CuO₄, AsCu₃, Cu, Cu₅FeS₄, Cu₂S, and Cu₂Se, and each was formed at a specific temperature, as detailed in Figure 6-28. In general, these results are in line with those of previous studies (Cotton, Patchigolla and Oakey, 2014; Haynes, Boström and Nordin, 2008; Jano-Ito, Reed and Millan, 2014; Lundholm, 2007; Oakey, Simms and Kilgallon, 2004), and, for instance, (Lundholm, 2007), indicated that Cu was present in bottom ash at temperatures above 900°C.

Table 6-13. Partitioning behaviour and main species of copper during pyrolysis of different original wood samples.

Types of wood	Solid species	Gaseous species	Phase transformation temperature °C (30-920°C) Solid →gaseous Under 1 atm (101325Pa)
Pellets	CuFeS_2 , Cu_5FeS_4 , Cu_2S , Cu	ClCu , Cu, CuH	820→920 (99.52% SP)
Chips	Al_2CuO_4 , Cu, Cu_2S	Cu, CuH	820→920 (99.99% SP)
Mixed furniture	Al_2CuO_4 , Cu	Cu, CuH	820→920 (99.23% SP)
New furniture	Al_2CuO_4 , Cu	Cu, CuH	820→920 (99.23% SP)
Demolition	Al_2CuO_4 , Cu, Cu_2Se	ClCu , Cu, CuH, CuSe	820→920 (99.99% SP)
L.d. 50-51 m	Cu	ClCu , Cu, CuH	820→920 (83.42% SP)
L.d. 41-43 m	Al_2CuO_4 , AsCu_3 , Cu, Cu_5FeS_4 , Cu_2S , Cu_2Se	ClCu , Cu, CuH	820→920 (99.95% SP)
L.d. 37.5-39 m	CuFeS_2 , Cu_5FeS_4 , Cu_2S , Cu	ClCu , Cu, CuH	820→920 (99.99% SP)
L.d. 3-7 m	Cu, Cu_5FeS_4	Cu, CuH	820→920 (99.73% SP)

SP (Mass percentage in solid phase) and GP (Mass percentage in gaseous phase).

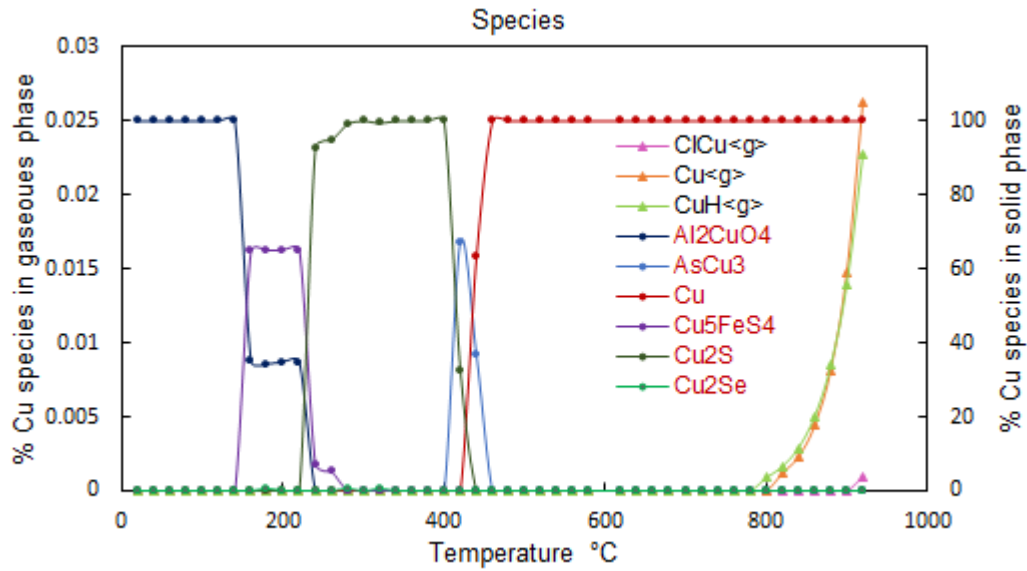


Figure 6-28. Equilibrium speciation of Cu in chips wood during pyrolysis process.

6.5.4.1.4 Mercury (Hg)

Here almost complete volatilisation was noted for all tested woods in the temperature range of 50-80°C, as shown in Table 6-14. These results agree with the finding of other studies (Bunt and Waanders, 2008; Froment et al., 2013; Jano-Ito, Reed and Millan, 2014; Konttinen et al., 2013; Miller, Dugwell and Kandiyoti, 2006; Yan, Gauthier and Flamant, 2000), which reported that Hg had a high volatilisation rate regardless of the type of wood.

Table 6-14. Partitioning behaviour and main species of mercury during pyrolysis of different original wood samples.

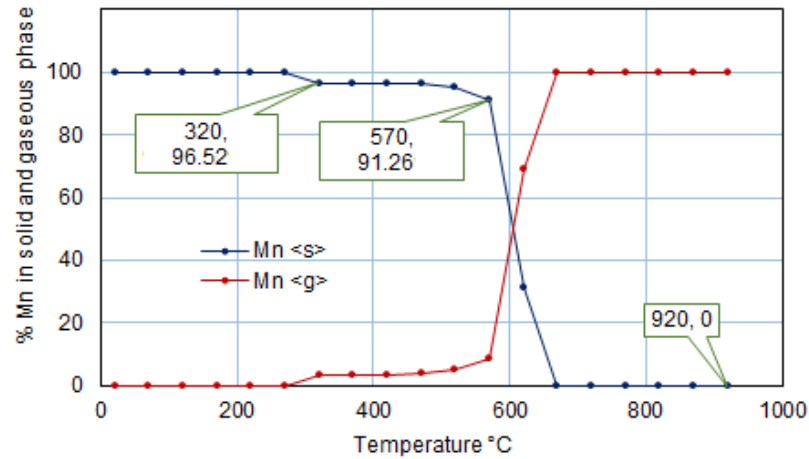
Types of wood	Solid species	Gaseous species	Phase transformation temperature °C (30-920°C) Solid →gaseous Under 1 atm (101325Pa)
Pellets	Hg	Hg	50→120 (100% GP)
Chips	Hg	Hg, HgSe	50→220 (100% GP)
Mixed furniture		Hg	50 (100% GP)
New furniture		Hg	50 (100% GP)
Demolition	Hg	Hg, HgSe	80→230 (100% GP)
L.d. 50-51 m	-	-	-
L.d. 41-43 m	HgSe	Hg	50→70 (100% GP)
L.d. 37.5-39 m		Hg	50 (100% GP)
L.d. 3-7 m		HHg, Hg	50 (100% GP)

SP (Mass percentage in solid phase) and GP (Mass percentage in gaseous phase).

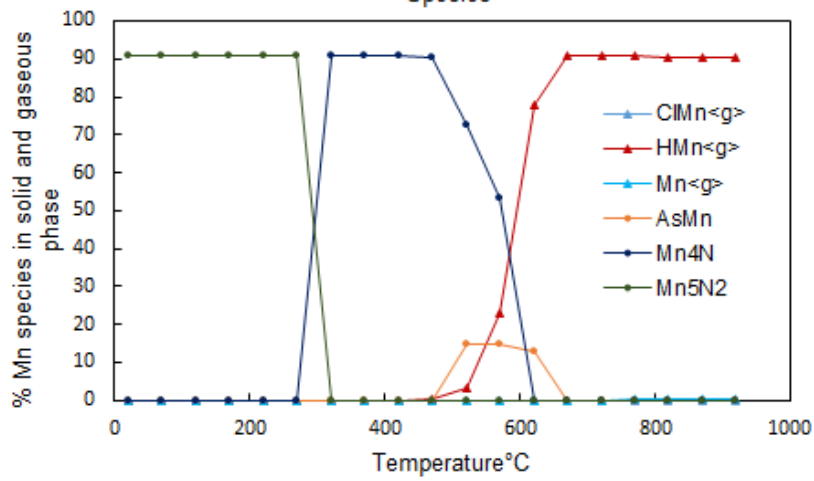
6.5.4.1.5 Manganese (Mn)

As observed, Mn tended to transform to its gaseous form at relatively high temperatures (720 to 780°C), as shown in Table 6-15. However, in the case of L.d. (50-51 m) wood, the Mn phase transformation temperature was 570°C, as shown in Figure 6-29. The solid dominant species of Mn were Mn₄N, and Mn₅N₂ at temperatures between 320°C and 570°C. When the temperature increased, new solid species (AsMn) and gaseous species (MnCl) were formed due to As-Mn and Cl-Mn interactions. At temperatures above 600°C, Mn completely transformed into its gaseous form, as shown in Figure 6-29. The obtained results showed agreement with the literature (Jano-Ito, Reed and Millan, 2014; Miller,

Dugwell and Kandiyoti, 2006), specifically in terms of the formation of solid species.



(a) Mn phase transformation.
Species



(b) Mn species.

Figure 6-29. Phase transition and equilibrium speciation of Mn in chips wood during pyrolysis process.

Table 6-15. Partitioning behaviour and main species of manganese during pyrolysis of different original wood samples.

Types of wood	Solid species	Gaseous species	Phase transformation temperature °C Solid →gaseous Under 1 atm (101325Pa) (30-920°C)
Pellets	Al ₂ MnO ₄ , H ₂ MnO ₂ , MnO	MnCl, HMn, Mn	720→920 (86.52% SP)
Chips	Al ₂ MnO ₄ , CMnO ₃ , MnO, Mn ₂ O ₄ Si, MnO ₃ Ti, Mn ₂ O ₄ Ti	MnCl, HMn, Mn	720→920 (93.42% SP)
Mixed furniture	Al ₂ MnO ₄ , CMnO ₃ , MnO, Mn ₂ O ₄ Si, MnO ₃ Ti, Mn ₂ O ₄ Ti	MnCl, HMn, Mn	770→920 (95.99% SP)
New furniture	Al ₂ MnO ₄ , CMnO ₃ , MnO, Mn ₂ O ₄ Si, MnO ₃ Ti, Mn ₂ O ₄ Ti	MnCl, HMn, Mn	770→920 (95.99% SP)
Demolition	Al ₂ MnO ₄ , CMnO ₃ , MnO, Mn ₂ O ₄ Si, MnSe	MnCl, HMn, Mn	780→920 (99.85% SP)
L.d. 50-51 m	AsMn, Mn ₄ N, Mn ₅ N ₂ ,	MnCl, HMn, Mn	320→670 (100% GP)
L.d. 41-43 m	Al ₂ MnO ₄ , CMnO ₃ , MnO.	MnCl, HMn, Mn	760→920 (95.39% SP)
L.d. 37.5-39 m	Al ₂ MnO ₄ , H ₂ MnO ₂ , MnO	MnCl, HMn, Mn	720→920 (86.52% SP)
L.d. 3-7 m	Al ₂ MnO ₄ , H ₂ MnO ₂ , MnO	MnCl, HMn, Mn	720→920 (86.52% SP)

SP (Mass percentage in solid phase) and GP (Mass percentage in gaseous phase).

6.5.4.1.6 Lead (Pb)

In all cases, the solid/gaseous phase transformation of Pb started at temperatures between 420 and 770°C, as depicted in Figure 6-30. At temperatures $\leq 420^\circ\text{C}$, Pb was predicted to be a stable solid species, at 99.98%. As the temperature increased from 420°C to 570°C, the mass percentage of Pb decreased gradually in the solid phase, and it reformed as a set of new gaseous species, as shown in Table 6-16.

Other studies (Bunt and Waanders, 2008; Froment et al., 2013) reported similar types of species in both solid and gaseous phases. For example, (Bunt and Waanders, 2008) showed that Pb, PbS, and PbSe were the solid and gaseous species of Pb. Furthermore, (Kontinen et al., 2013) indicated that the phase transformation threshold of Pb was 500-650 °C, which is close to that predicted in the current study.

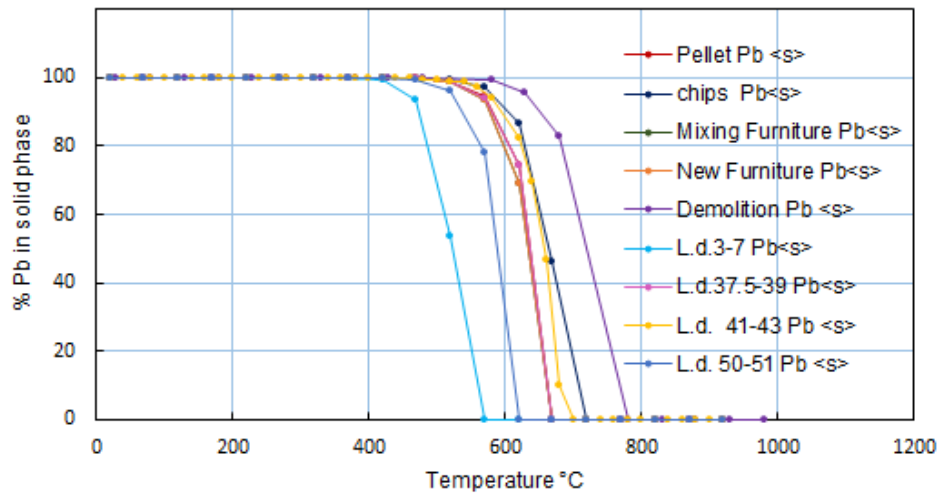


Figure 6-30. Lead retention in solid phases during the pyrolysis of original wood samples.

Table 6-16. Partitioning behaviour and main species of lead during pyrolysis of different original wood samples.

Types of wood	Solid species	Gaseous species	Phase transformation
			temperature °C (30-920°C) Solid →gaseous Under 1 atm (101325Pa)
Pellets	Pb, PbS, PbSe	ClPb,HPb,Pb,Pb ₂ ,PbS,PbSe	570→670 (100% GP)
Chips	O3PbTi,Pb,PbS	ClPb, HPb, Pb, PbS	570→720 (100% GP)
Mixed furniture	O3PbTi,PbPbS,PbSe	ClPb, HPb, Pb, PbS	570→670 (100% GP)
New furniture	O3PbTi,Pb,PbS,PbSe	ClPb, HPb, Pb, PbS	570→670 (100% GP)
Demolition	O3PbTi,Pb,	ClPb,HPb,Pb,Pb ₂ ,PbS, PbSe	570→670 (100% GP)
L.d. 50-51 m	Pb	ClPb, HPb, Pb,	520→780 (100% GP)
L.d. 41-43 m	Pb ,PbS, PbSe	ClPb, HPb, Pb, PbS, PbSe.	560→520 (100% GP)
L.d. 37.5-39 m	Pb, PbS, PbSe	ClPb,HPb,Pb,Pb ₂ ,PbS,PbSe	520→670 (100% GP)
L.d. 3-7 m	Pb,PbS	ClPb,Pb,PbS.	420→570 (100% GP)

SP (Mass percentage in solid phase) and GP (Mass percentage in gaseous phase).

6.5.4.1.7 Zinc (Zn)

The predicted phase transformations of Zn for all samples are shown in Figure 6-31. Generally, Zn starts to transform to its gaseous form between 520°C and 570°C. However, in the case of L.d. (50-51 m) wood, it started at 220°C. Although Zn species in the gaseous phases were mostly identical, however, they were substantially different in the solid phases, as detailed in Table 6-17.

The obtained results are in accordance with previous studies that have observed the solid/gaseous phase transformation of Zn starting between 500°C and 650°C (Konttinen et al., 2013; M. Diaz-Somoano, 2003), and between 200°C to 500°C (Cui et al., 2013). Additionally, the predicted species of Zn in this study agreed with the findings of other studies (Bunt and Waanders, 2008; Froment et al., 2013; Konttinen et al., 2013; M. Diaz-Somoano, 2003; Miller, Dugwell and Kandiyoti, 2006).

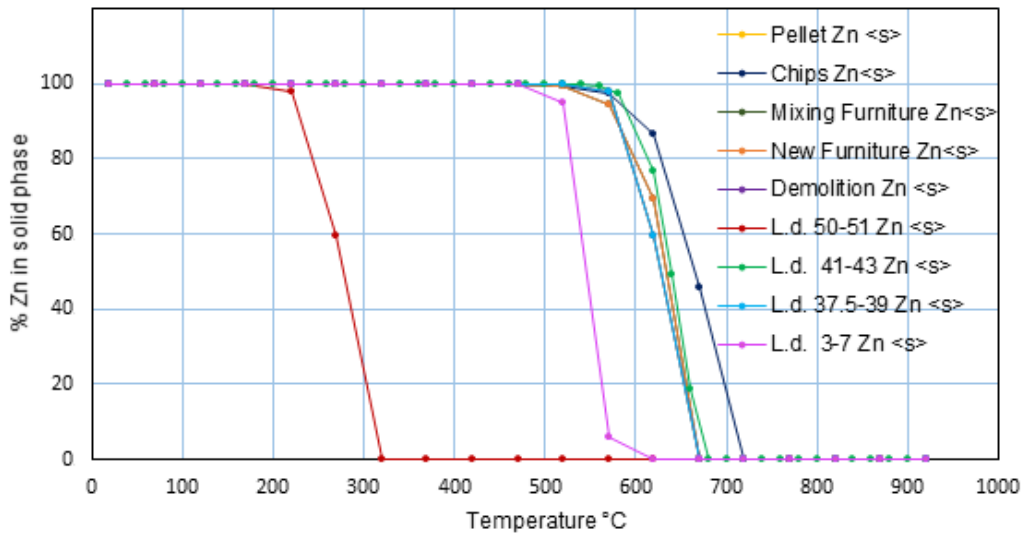


Figure 6-31. Zinc retention in solid phases during the pyrolysis of original wood samples.

Table 6-17. Partitioning behaviour and main species of zinc during pyrolysis of different original wood samples.

Types of wood	Solid species	Gaseous species	Phase transformation temperature °C (0-920°C)
			Solid →gaseous Under 1 atm (101325Pa)
Pellets	$\text{Al}_2\text{O}_4\text{Zn}$, ZnS .	Zn	570→670 (100% GP)
Chips	$\text{Al}_2\text{O}_4\text{Zn}$, ZnS .	Zn	570→620 (100% GP)
Mixed furniture	$\text{Al}_2\text{O}_4\text{Zn}$, ZnS .	Zn	570→670 (100% GP)
New furniture	$\text{Al}_2\text{O}_4\text{Zn}$, ZnS .	Zn	570→670 (100% GP)
Demolition	$\text{Al}_2\text{O}_4\text{Zn}$, ZnS .	Zn	570→620 (100% GP)
L.d. 50-51 m	Zn	Zn	220→320 (100% GP)
L.d. 41-43 m	$\text{Al}_2\text{O}_4\text{Zn}$, SZn , SeZn	Zn	570→670 (100% GP)
L.d. 37.5-39 m	$\text{Al}_2\text{O}_4\text{Zn}$, SZn , SeZn	Zn	570→670 (100% GP)
L.d. 3-7 m	$\text{Al}_2\text{O}_4\text{Zn}$, SZn	Zn	520→620 (100% GP)

SP (Mass percentage in solid phase) and GP (Mass percentage in gaseous phase).

6.5.4.2 Artificial wood and blends samples

6.5.4.2.1 Artificial samples

The predictive calculations for the three artificial wood samples (AS_1 , AS_2 and AS_3) showed that the As solid/gaseous transformation started at 920°C. Additional results indicated that, for both AS_2 and AS_3 samples, the As condensed species and gaseous species were similar, as shown in Figure 6-32. These results are in line with those obtained by (Reed, Dugwell and Kandiyoti, 2001a) as well as the presented results in section 6.5.4.1.1., where the presence of Ni was shown to be beneficial for capturing As.

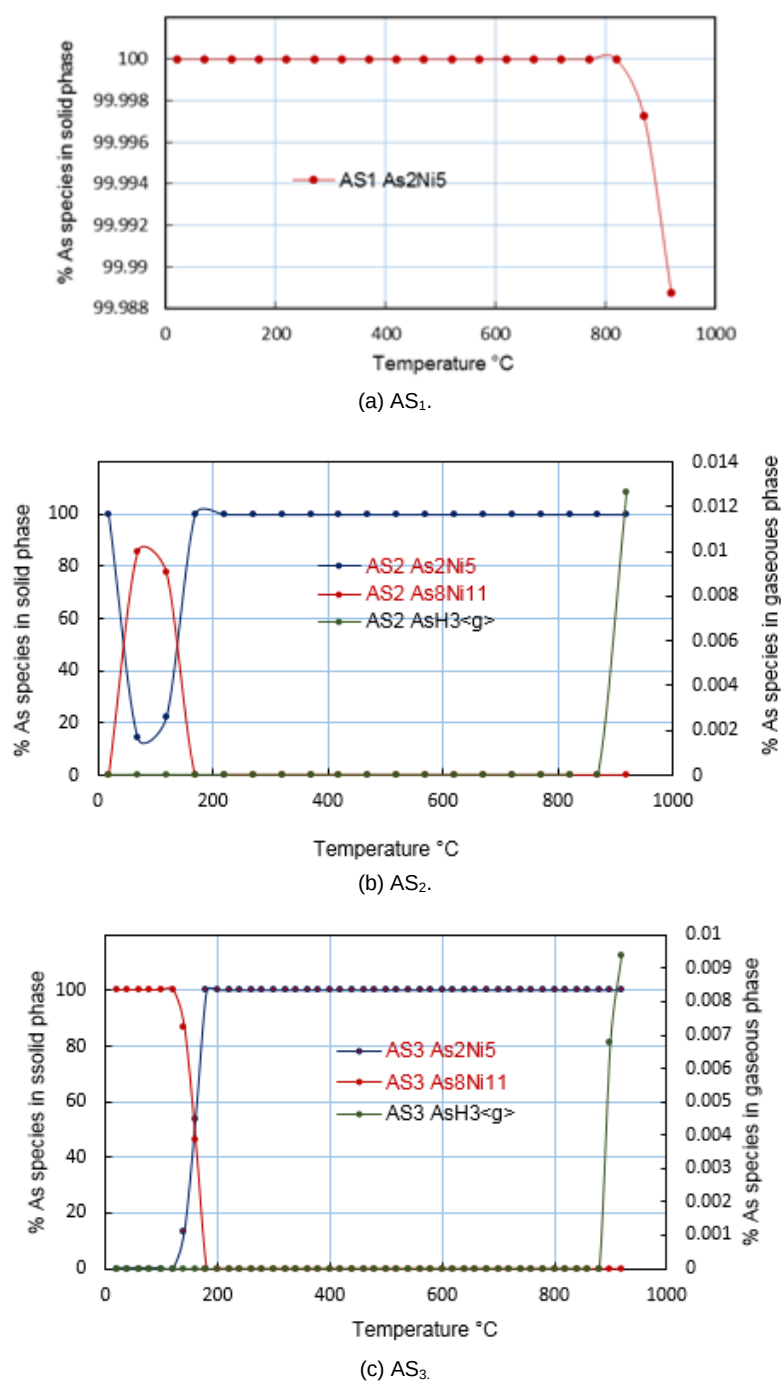


Figure 6-32. Phase transition and equilibrium speciation of As in artificial samples during pyrolysis process.

6.5.4.2.2 Blend sample

The simulation results of blended woody biomass during pyrolysis showed that the threshold temperatures of As were improved by 430°C as compared to those obtained during the pyrolysis of pellet wood and landfill wood, as demonstrated in Figure 6-33. This might be as a result of the increased concentrations of As and Ni, which, in turn, improved the phase transformation threshold of As, as shown in Table 6-18. As such, blending landfill wood with pellet wood could be a promising approach to increasing the phase transformation temperature of As.

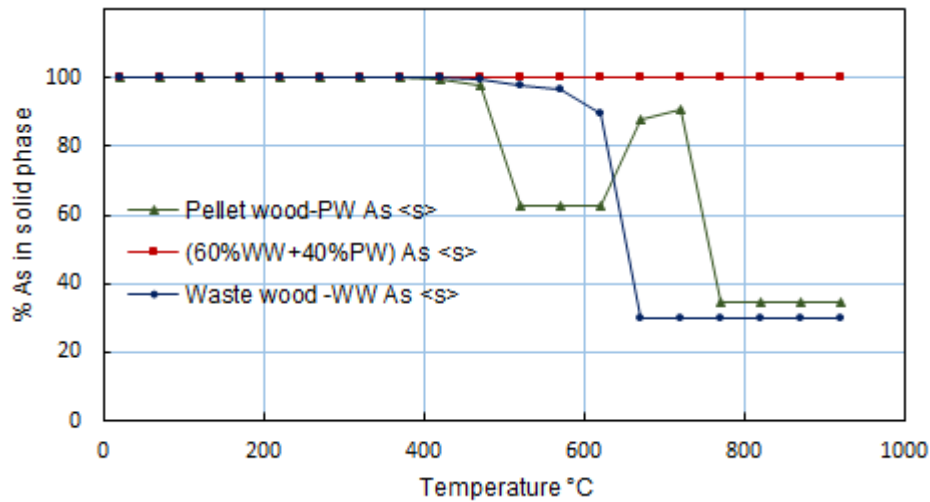


Figure 6-33. Comparison of phase transition of As in artificial, blends, pellet, and landfill samples during pyrolysis process.

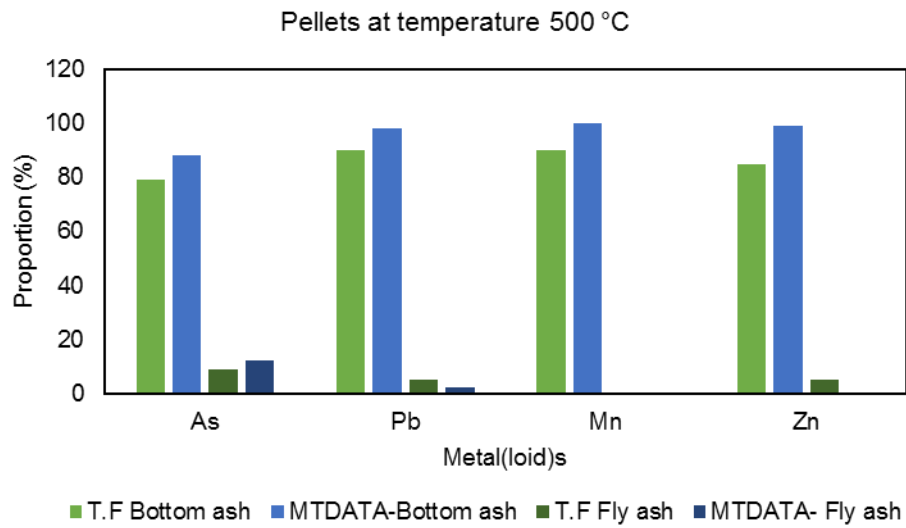
Table 6-18. Comparison of phase transition and species of arsenic in blends, pellet, and landfill samples during pyrolysis process.

Types of wood	Solid species	Gaseous species	Phase transformation temperature (30-920°C) Solid →gaseous Under 1 atm (101325Pa)
Pellets (PW)	As ₂ Ni ₅ , As ₈ Ni ₁₁	AsH ₃	900→920 (99.91% SP)
Waste wood (WW)	AsMn, AsNa ₃ , As ₂ Ni ₅	As, As ₂ , AsH, AsH ₂ , AsH ₃ , AsN	520→920 (29.63% SP)
Mixing (60%WW+40%PW)	As ₂ Ni ₅	AsH ₃	870→920 (99.91% SP)

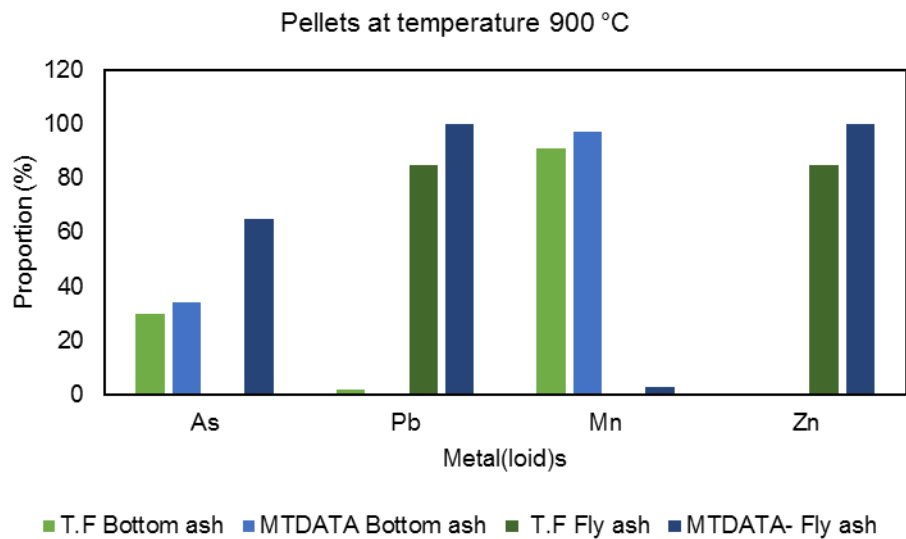
SP (Mass percentage in solid phase) and GP (Mass percentage in gaseous phase).

6.5.5 Comparison between experimental data and simulation results

- The results obtained from experimental works showed good agreement with those obtained by predictive models.
- Both experimental data and simulation results revealed that Al, Co, Cr, Cu, Fe, Mo, Ni, Si, Ti, and V were non-volatile, and that both Hg and Cd were very volatile.
- The phase transformation and partitioning behaviour of As, Mn, Pb, and Zn, estimated by thermodynamic modeling were in line with those of experimental works, as shown in Figure 6-34 to Figure 6-42. Only insignificant differences were observed, generally due to unavoidable analytical errors caused by dilution as well as experimental errors attributed to the preparing the samples and collecting the fly ash.
- The experimental data and the simulation results are complementary rather than being competitive each other. Consequently, the overall experimental results were within acceptable validation limits.

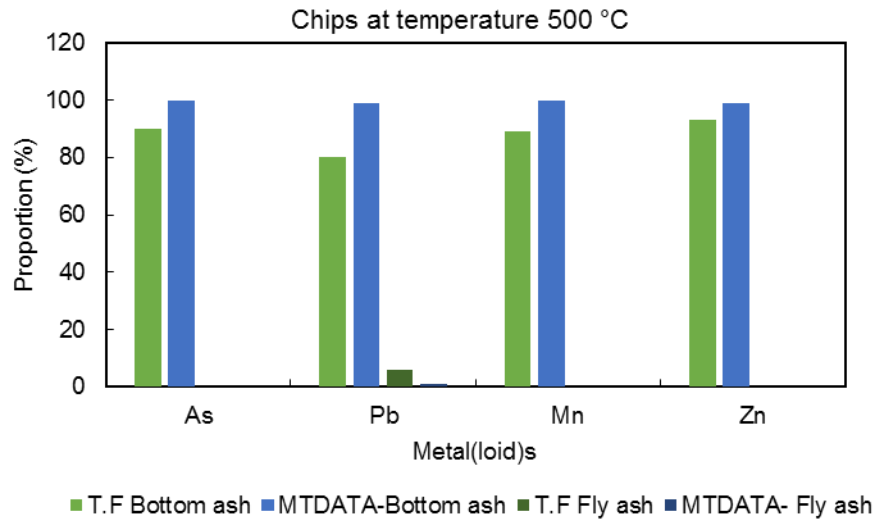


(a) Temperature 500°C.

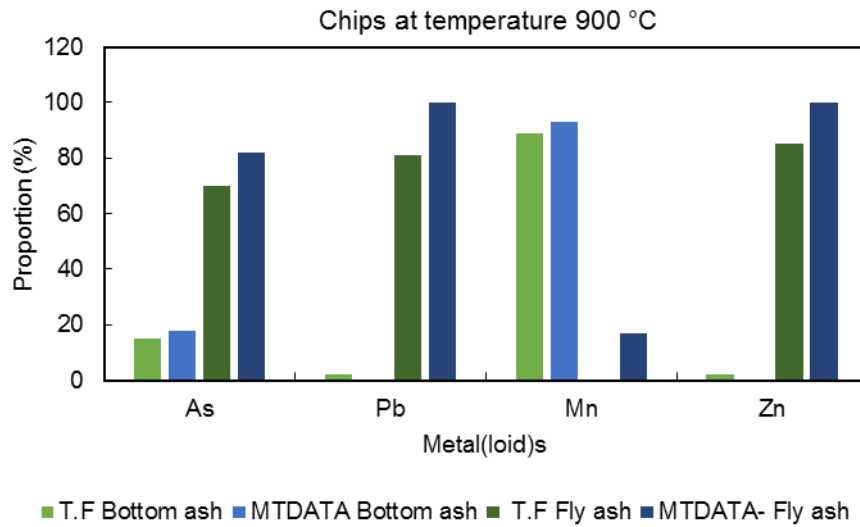


(b) Temperature 900°C.

Figure 6-34. Comparison of predicted results (MTDATA) and experimental (T.F) results for pellets wood at temperature 500 and 900°C.

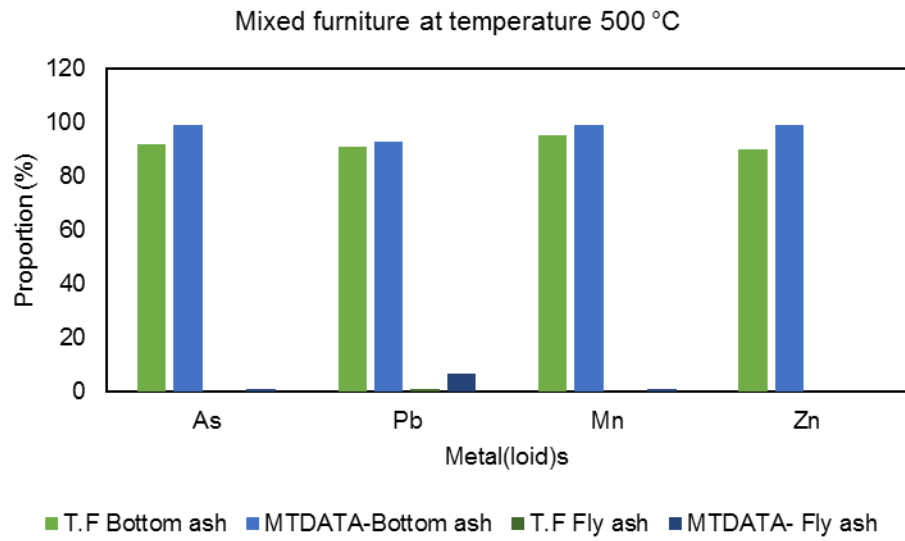


(a) Temperature 500°C.

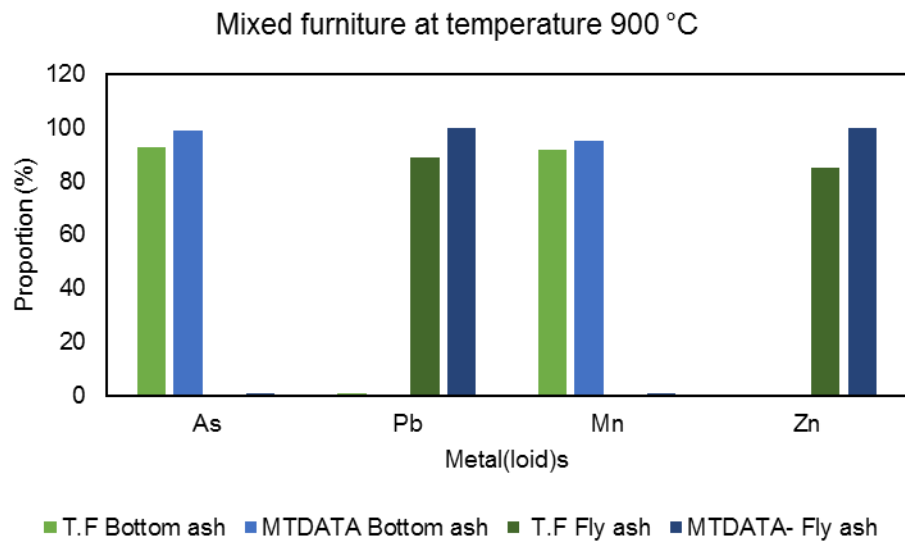


(b) Temperature 900°C.

Figure 6-35. Comparison of predicted results (MTDATA) and experimental (T.F) results for chips WW at temperature 500 and 900°C.

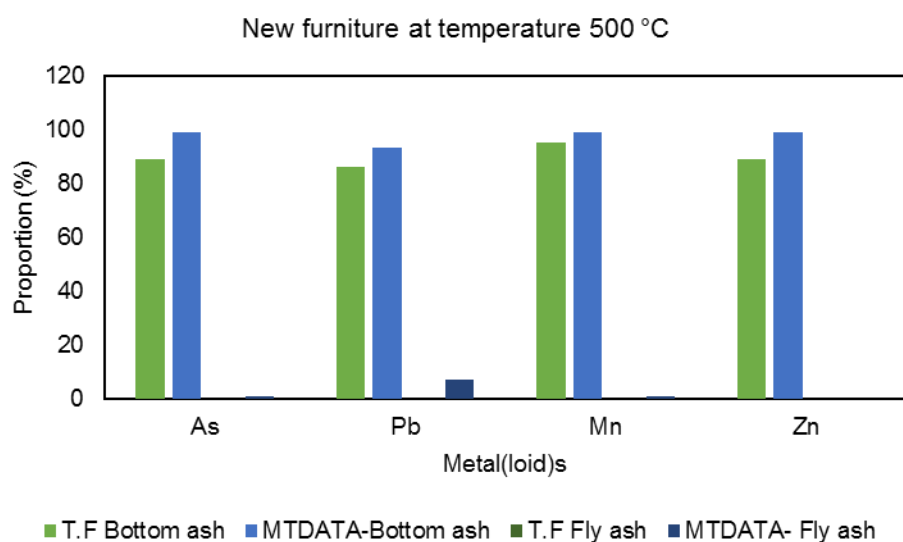


(a) Temperature 500°C.

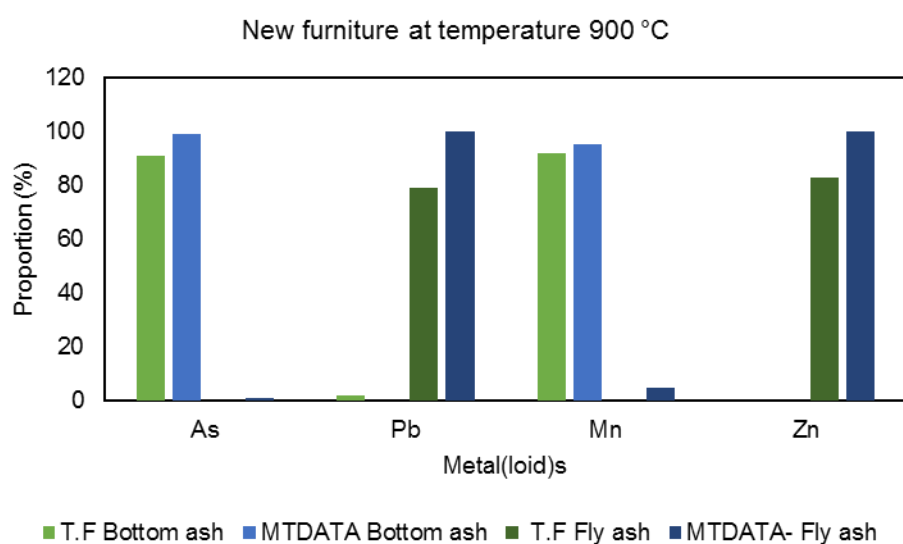


(b) Temperature 900°C.

Figure 6-36. Comparison of predicted results (MTDATA) and experimental (T.F) results for mixed furniture WW at temperature 500 and 900°C.

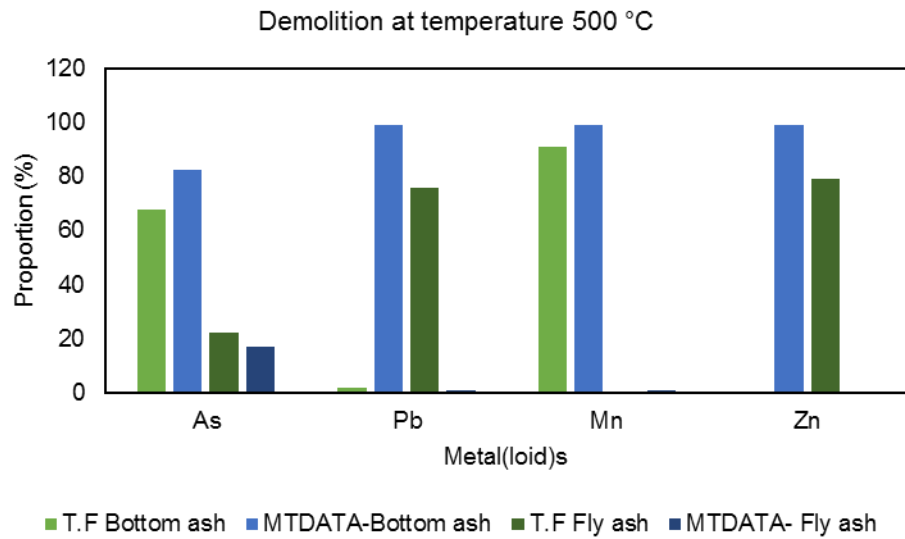


(a) Temperature 500°C.

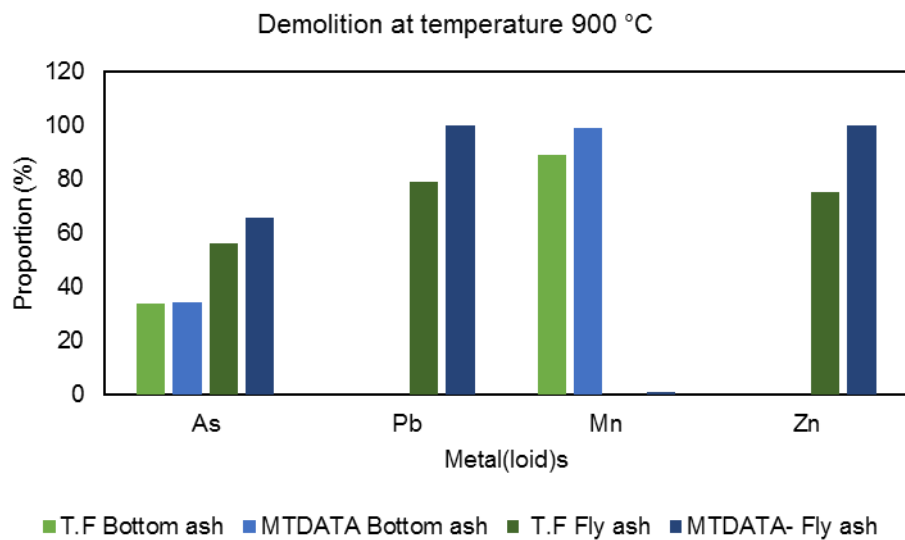


(b) Temperature 900°C.

Figure 6-37. Comparison of predicted results (MTDATA) and experimental (T.F) results for new furniture WW at temperature 500 and 900°C.

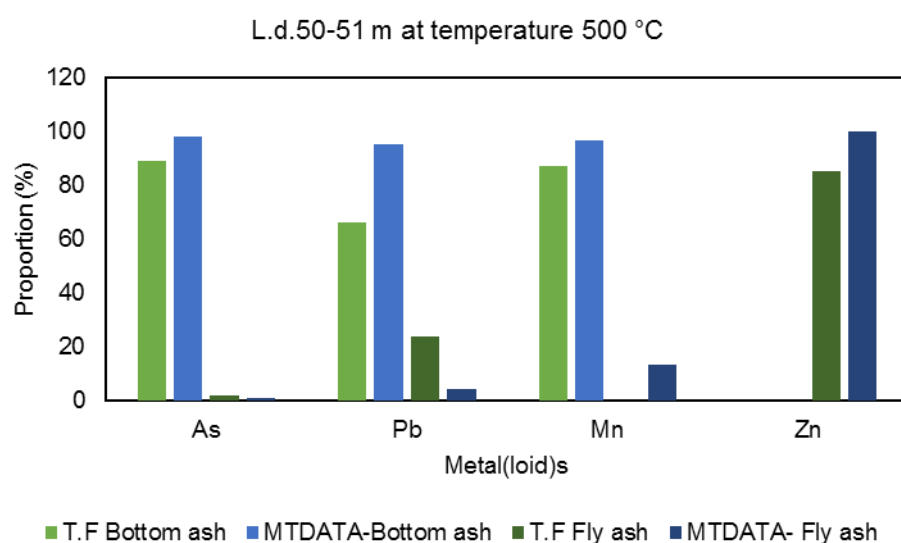


(a) Temperature 500°C.

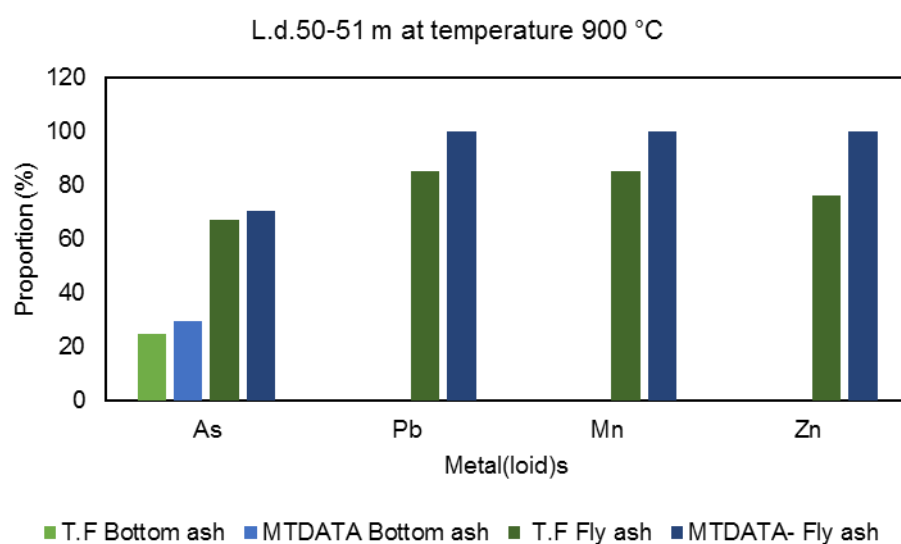


(b) Temperature 900°C.

Figure 6-38. Comparison of predicted results (MTDATA) and experimental (T.F) results for demolition WW at temperature 500 and 900°C.

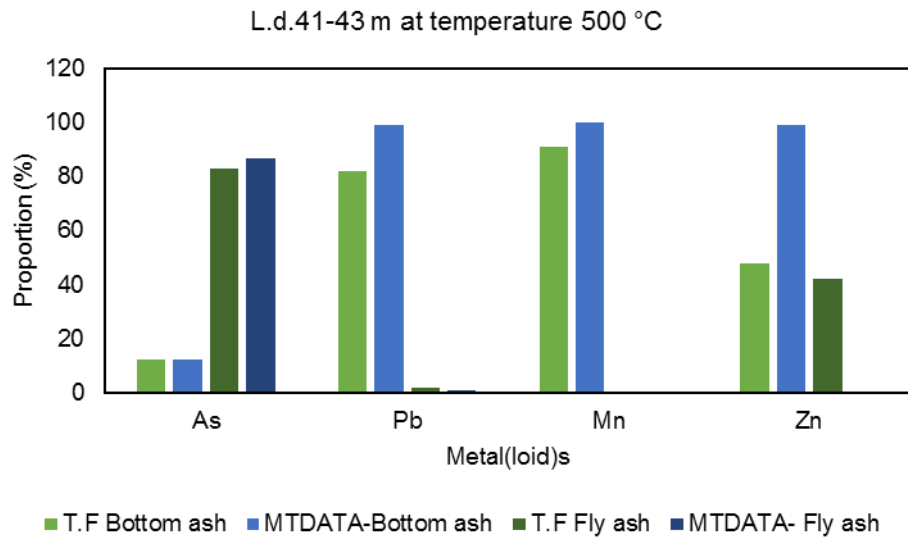


(a) Temperature 500°C.

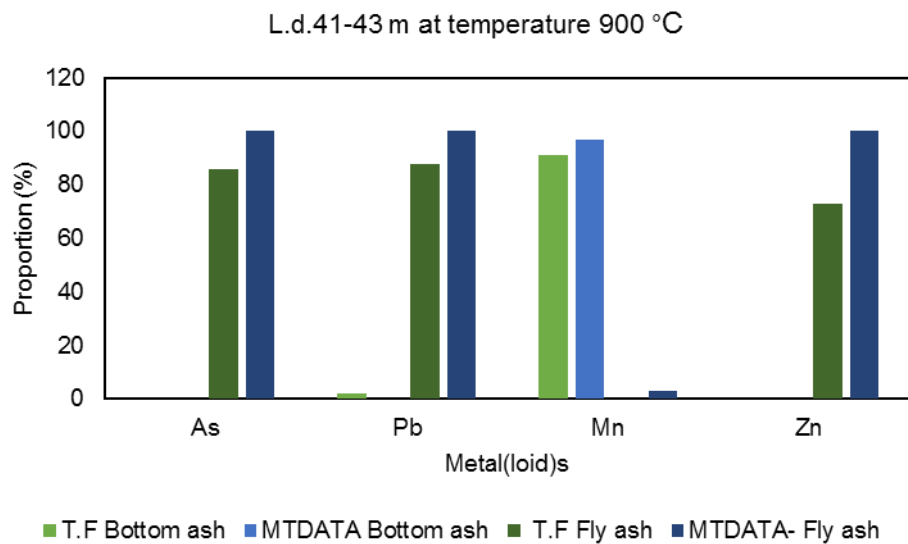


(b) Temperature 900°C.

Figure 6-39. Comparison of predicted results (MTDATA) and experimental (T.F) results for landfill WW (L.d.50-51m) at temperature 500 and 900°C.

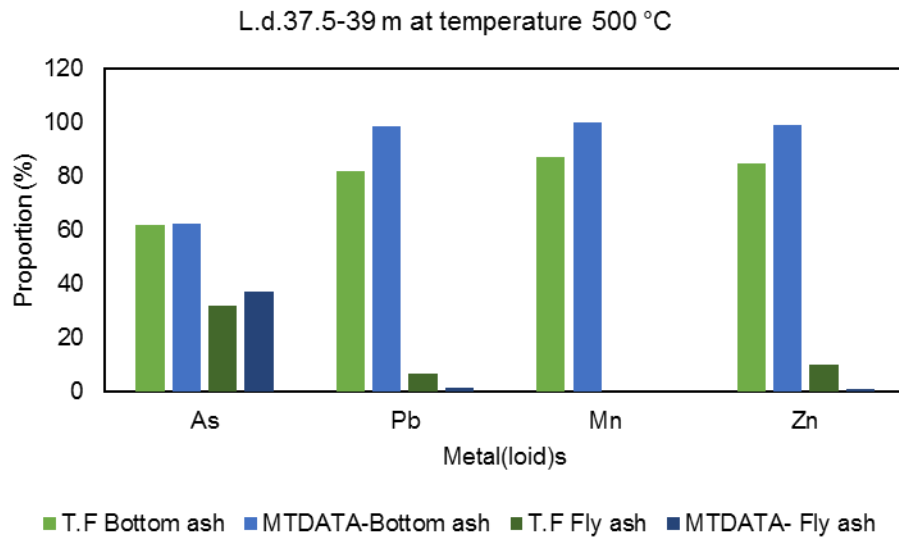


(a) Temperature 500°C.

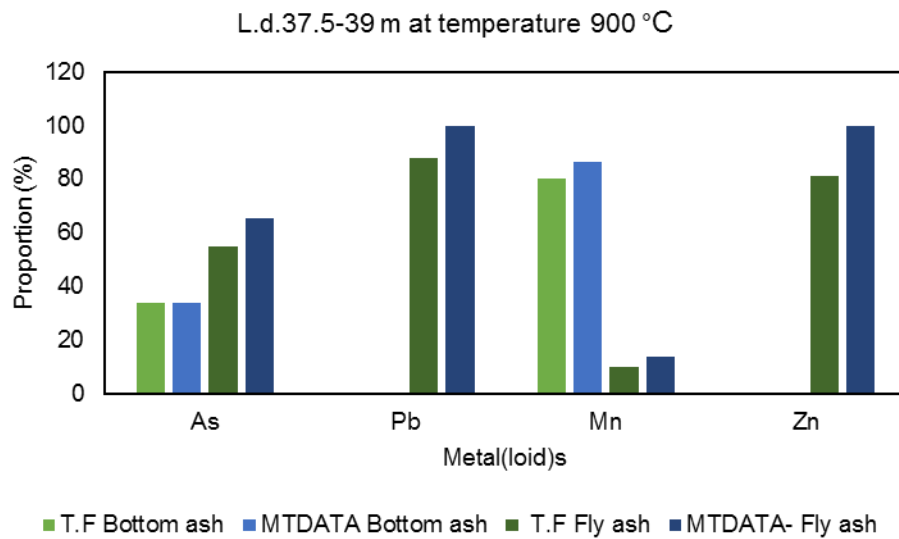


(b) Temperature 900°C.

Figure 6-40. Comparison of predicted results (MTDATA) and experimental (T.F) results for landfill WW (L.d.41-43 m) at temperature 500 and 900°C.

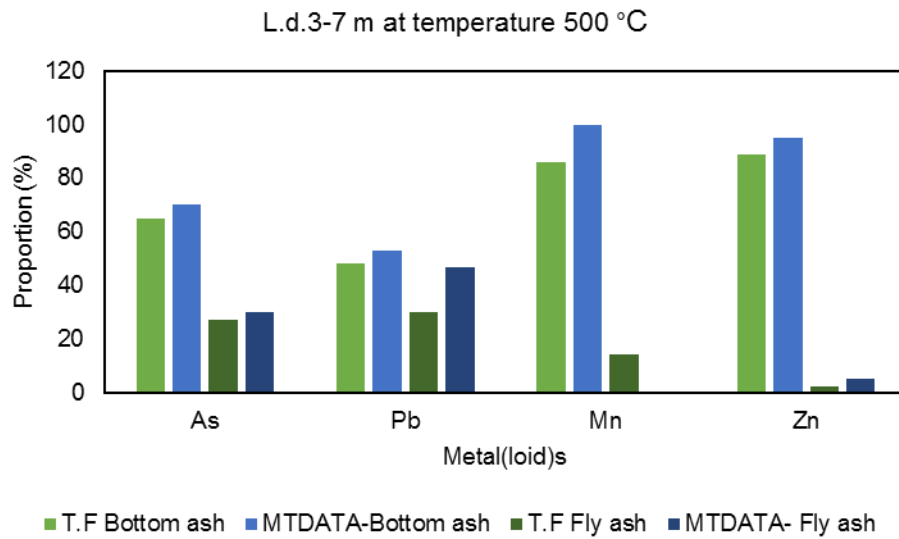


(a) Temperature 500°C.

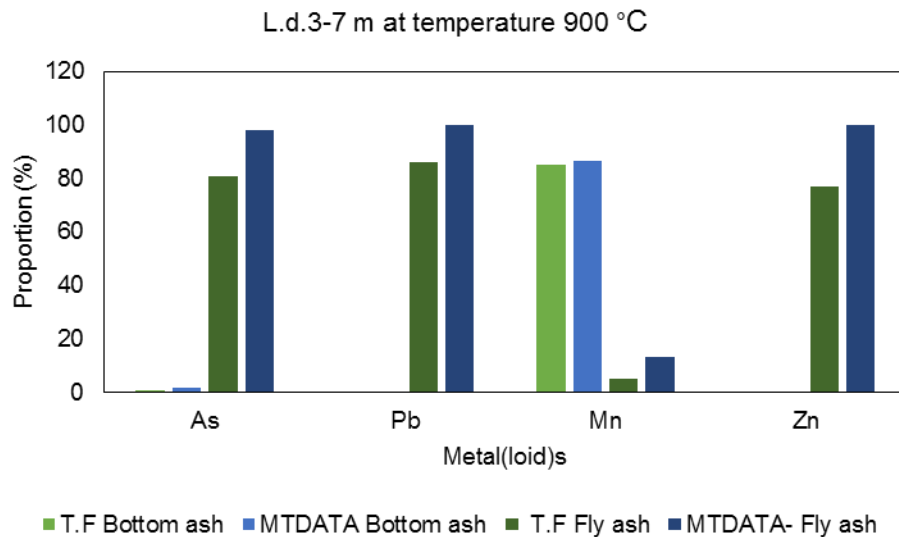


(b) Temperature 900°C.

Figure 6-41. Comparison of predicted results (MTDATA) and experimental (T.F) results for landfill WW (L.d. 37.5-39 m) at temperature 500 and 900°C.



(a) Temperature 500°C.



(b) Temperature 900°C.

Figure 6-42. Comparison of predicted results (MTDATA) and experimental (T.F) results for landfill WW (L.d. 3-7 m) at temperature 500 and 900°C.

6.6 Conclusions

In this chapter, two approaches, i.e. experimental works and thermodynamic equilibrium calculations, were applied to understand the behaviour of metal(loid) elements present in different woody biomass samples (original, artificial, and blends) during pyrolysis. The experimental works were conducted to optimise the operational conditions of the pyrolysis process. In doing so, thermogravimetric analyses (TG and DTG curves), SEM-EDX analyses, kinetic studies, and tube furnace experiments were performed. Further, thermodynamic equilibrium calculations (MTDATA-based) were used to predict the fate of the meta(loid)s under the optimised operational conditions.

Overall, the results regarding the behaviour and partitioning profile of the targeted metal(loid)s can be summarized as follows:

- Cd and Hg were recognized as very volatile elements in all tested samples
- Al, Co, Cr, Cu Fe, Mo, Ni, Si, Ti, and V were identified as non-volatile in all tested samples
- As, Mn, Pb, and Zn showed differences in partitioning across all tested samples

Eventually, despite the analytical and experimental errors, the obtained results from experimental works showed good agreement with those predicted by thermodynamic modelling.

Chapter 7 Conclusions and Future Work

This chapter summarises the findings of this PhD thesis, highlighting the significant contribution to science and suggesting further work to build on these findings.

7.1 Conclusions

The research undertaken for this thesis contributes to the current understanding of the behaviour of identified key metal(loid) elements in woody biomass. Indeed, integrating information from thermogravimetric experiments, tube furnace pyrolysis experiments, and model predictions generated supportive information regarding the profile distribution of these elements during thermal conversion processes.

The first step in this project was described in chapter 2, where insights into woody biomass and types of contaminations gained, as well as the gap of knowledge identified. The results showed that waste wood (WW) is a highly homogeneous solid fuel, but it very often contaminated with metal(loid)s at concentrations leading to toxicity emissions and damages to facilities during thermal conversion. As such, procedures for preventing and/or alleviating the negative impacts of metal(loid) elements during the thermal conversion of WW require further improvement, since, there are still some shortcomings in relation to the fate of these elements need to be addressed, such as the limitations on the available information about the key metal(loid)s contaminations in WW alongside their phase transformation and speciation in terms of interactions and interferences among. Also, there is still uncertainty regarding the effects of blending different types of WW on the behaviour of metal(loid)s.

The thermodynamic equilibrium modelling was carried out based on 78 scenarios to investigate the effect of the process parameters of gasification and pyrolysis on the fate of key metal(loid)s in groups CCA and CCB preservatives in chapter 3. The simulation results indicated that no significant differences were observed

in relation to the considered agents in terms of phase transformation temperature and speciation.

Additionally, thermodynamic equilibrium calculations were carried out to identify the possible interactions and interferences among the CCA-elements and Ca, Na, S, Cl, Fe, and Ni in contaminated WW during gasification and pyrolysis. Moreover, the influences of types of wood (chip, beech, and pin) on the fate of CCA elements in terms of interactions and interferences were also investigated in chapter 4. The most importantly, results indicated that the Na and Ni content in WW played a vital role in remaining As in solid phase at temperatures $\leq 800^{\circ}\text{C}$. This would aid in mitigating the negative impacts of toxicity emissions associated with CCA elements through systematically mixing different types of woody biomass.

Moreover, in chapter 5, a new dataset comprises the detailed elemental composition of 28 WW samples from different sources.

Chapter 6 involved the optimisation of pyrolysis operational conditions through TGA, the experimental investigation of the distributions of metal(loid)s in tube furnace pyrolysis experiments, and the validation of modelling predictions using the experimental data. The main contribution of this chapter is to show that pyrolysis of blends of different types of waste woods can return potential advantages over the pyrolysis of a single type. It follows that the contaminated waste wood can be utilised for clean energy production or simply disposed.

7.2 Research overview

In Chapter 1, the overall objectives of this works were provided and were met throughout the delivery of the research. These objectives and an explanation of how they were achieved is provided.

1. To critically review the literature to identify the key metal(loid)s in waste wood materials and their sources; discuss the gaps in the scientific understanding to enable the development of a programme of work leading to a significant contribution to knowledge.

Chapter 2 presents a literature review of waste wood (sources, demands, classification, and the contaminations on it), thermal biomass conversion (combustion, gasification and pyrolysis), the behaviour of metal(loid)s during thermochemical conversion and their interactions and interferences. It was concluded that:

- The key metal(loid)s contaminants in waste wood are As, B, Co, Cr, Cu, Fe, Ni, Pb and Ti.
- The gathered information from previous studies and standard databases were integrated and utilised for setting up the modelling to ensure reliable and accurate predictions.
- Interactions and interferences between metal(loid)s during the thermal treatment of woody biomass, together with their relevant impacts, are still not understood and thus require further research.
- With the use of thermodynamic equilibrium models, elemental partitioning behaviour can be quantified under optimised operational conditions, which provides substantial support to the pyrolysis experimental works.
- Integrating both modelling results and experimental data can generate insight into the fate of key metal(loid) elements during advanced thermochemical conversion processes, and thus provide an understanding of how to control the emissions and dispositions of these elements.

2. To develop biomass waste wood gasification and pyrolysis models using specialised software to predict the fate of the key metal(loid)s in terms of the compositions of phase transition during these processes.

In the development of the models in chapter 3, the initial elemental composition data was selected based on the findings of the literature review and subsequent experiments. The most probable concentration ranges of the composition data that drawing from the literature review were estimated via the Risk Analysis and Simulation Add-In for Microsoft Excel. The actual elemental compositions were obtained using mass balances of the gasification and pyrolysis. Then, the thermodynamic equilibrium of gasification (ASR and CR) and pyrolysis was carried out using a multiphase module of the MTDATA software to assess the partitioning and speciation of the metal(loid) elements As, B, Cr, Co, Cu, Fe, Pb, Ni and Ti, which were classified into two groups (CCA and CCB) according the types of wood. The modelling revealed the percentages of the chemical species and the relationship between the threshold temperatures of phase transition and operational parameters. These findings suggest that the predictive information can be useful for experimental works, particularly in determining process operation conditions and parameters. The results also suggest that systematically blending WW with willow wood can enhance the retention of some metal(loid)s in the solid phase.

3. To investigate the possible interactions and interferences between the key metal(loid)s using the developed model.

The interactions and interferences were investigated in Chapter 4. The calculations were performed to study the effects of the occurred interactions and interferences on the fate of metal(loid)s as consequence of various contents of the metal(loid)s themselves and other elements in WW samples. Thus, 94 different scenarios were assumed and simulated. Chapter 4 further introduces three predictive models for contaminated WW gasification (ASR₁ and CR₁) and pyrolysis (P₁), to better understand the behaviour of CCA elements in terms of interactions and interferences. Chapter 4 also demonstrated the Na and Ni content in WW plays a vital role in the maintenance of As in its solid state at temperatures $\leq 800^{\circ}\text{C}$. This aids in mitigating the negative impacts of toxicity

emissions associated with CCA elements by systematically mixing different types of woody biomass.

4. Develop and undertake valid waste wood sample collection from a range of sources including those with high levels of contamination. Complete a comprehensive analysis of the samples using standard methods for proximate, ultimate and elemental content.

Chapter 5 presented the collected WW samples from different sources, including a landfill site, waste streams, and industrial locations. Chapter 5 also discussed how each sample was prepared and analysed. These procedures include a full chemical characterisation and the determination of each sample's elemental composition. The analysis results were considered as reference profiles for the thermodynamic equilibrium modelling and experiments.

5. To validate the developed pyrolysis models using experimental data, including thermal degradation behaviours, and optimise the operational parameters of the models.

The models were optimised and validated in chapter 6. A thermogravimetric analyser was used to study the thermal behaviour of WW under pyrolysis operation conditions at temperatures ranging from 30-900°C with N₂ pure gas at 40.0 mL/min. Also, artificial fuel samples contain species and concentrations of only metal(loid)s were prepared to better understand, and subsequently validate, the simulation results. The main conclusions of chapter 6 are as follows:

- This study confirmed the necessity of using the TGA analysis to design a suitable energy system for the thermal treatment of contaminated waste wood and related materials.
- The activation energy for contaminated wood and non-contaminated wood was determined using FWO and KSA methods. The average activation

energy for non-contaminated wood was lower than that for contaminated wood.

- The experimental works were conducted to optimise the operational conditions of the pyrolysis process. Thermogravimetric analyses (TG and DTG curves), SEM-EDX analyses, kinetic studies, and tube furnace experiments were performed. Furthermore, thermodynamic equilibrium calculations (MTDATA-based) were used to predict the fate of the metal(loid)s under the optimised operational conditions.

Nonetheless, the current limitations include:

- The created dataset did not cover the information of woody biomass contaminated with oil and organic materials.
- The effect of metal(loid) elements on the syngas content was not addressed.
- The economic benefit from using contaminated woody biomass as fuel was not quantified.

7.3 Contribution to knowledge

The core intellectual contributions of this PhD project are as follows:

- Novel datasets containing comprehensive elemental analysis of waste wood samples collected from different sites were established. These datasets offer a significant amount of information towards appropriate thermodynamic equilibrium modelling.
- A new pre-processing scheme was developed for calculating the best fit of the composition data. This type of statistic give an important opportunity to support thermodynamic equilibrium modelling and experimental works.
- New insights were generated onto the fate of metal(loid)s during the gasification and pyrolysis of waste wood, mainly regarding behaviour of As in terms of As-Ni interaction. That is, the presence of Ni should be regarded in combination with its associated concentration profile.

- New ways of further understanding the behaviour of metal(oids)s, in terms of interactions and interferences, were realised. This study explained the effect of interactions and interferences on the elemental phase transformation and speciation formation. For instance, the Ca-Cr interaction forms C_3Cr_7 ; meanwhile, the absence of Ca creates instability in the Cr phase transformation due to the generation of the species $\text{Cr}_2\text{Na}_2\text{O}_4$.
- For the first time, the kinetic triple was incorporated into the thermal decomposition of contaminated waste wood, enriching the understating of metal(loid)s behaviour. The results indicate that the activation energies for landfill wood pyrolysis were higher than those for pellet wood pyrolysis. This due to the highly bound nature of the chemical compounds present in the landfill wood and was further confirmed by using artificial samples.
- Toxicity emissions were improved during the gasification and pyrolysis of contaminated waste wood through the systematic blending of different contaminated waste wood prior to gasification and pyrolysis. This study found the solid/gaseous phase transition of As and Cr in willow wood decreased by around 11% and 16% compared to those predicted under same reaction when dealing with demolition WW. Besides that, results of blended woods revealed improvement in the phase transformation temperatures of As and Cr about 150°C and 100°C , respectively, compared to those obtained when gasifying willow wood.

7.4 Future work

- It would be necessary to investigate the behaviours of elements during tube furnace experiments under further temperature ranges and increased pressures.
- Potential studies must first establish datasets that contain a comprehensive elemental analysis of the contamination of waste wood samples with oil and organic materials, and subsequently test these during gasification and pyrolysis. In this case, it is recommended to determine the

pH of the materials as well as the solution of train in the tube furnace experiments.

- Future studies should be conducted to investigate the possible interactions and interferences of metal(loid)s during gasification and pyrolysis of wood waste and bed materials. Here, systematic blending of wood waste and bed materials can give new view on the elemental phase transformation and speciation formation.
- Future studies can also investigate the effect of increased concentrations of Se on capturing Cd and Hg.
- An in-depth study should be undertaken to fully understand the possible interactions and interferences of metal(loid)s. More specifically, considering different elemental groups according to the periodic table.

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Appendices

This section presents five appendices: published papers, detailed information about the analysis methods, scenarios of the composition data introduced to MDTATA, and the results of waste wood samples analysis.

Appendix A Chapter 1 list of publications

- Al-Badri S, Jiang Y & Wagland S (2018) Possible interactions and interferences of copper, chromium, and arsenic during the gasification of contaminated waste wood, *Energies*, 11 (8) Article No. 1966.
- Al-Badri SB, Jiang Y & Wagland ST (2018) Interactions and interferences of Cu, Cr and As during contaminated waste wood gasification: A thermodynamic equilibrium study. In: 9th International Renewable Energy Congress (IREC 2018), Hammamet, 20-22 March 2018.
- Al-Badri S, Jiang Y & Wagland ST (2018) Reduce toxic emissions of As, Cr, and Cu phases during woody biomass gasification: A thermodynamic equilibrium study. In: 5th International Conference on Environment and Renewable Energy (ICERE 2018), Vienna, 18-19 May 2018.

Appendix B Chapter 3

B.1. Willow wood composition data obtained from energy technologies institute UK (www.eti.co.uk)

B.2. Statistical analysis of the WW samples (PHYLLIS2)

B.3. Statistical analysis of the willow wood samples (www.eti.co.uk)

B.4. Examples of the conversion procedure

B.5. Molar composition to be fed to MTDATA for gasification (ASR and CR)

B.5.1.The total moles of the major and minor elements (ASR)

B.5.2.The total moles of the major and minor elements (CR)

B.5.3.The total moles of major and minor elements in WW, willow wood, and their blends (WW 60% and willow wood 40%) during ASR₁

B.5.4.The total moles of major and minor elements in WW, willow wood, and their blends (WW 60% and willow wood 40%) during ASR₁

B.6. Molar composition to be fed to MTDATA for pyrolysis

B.1 Willow wood composition data obtained from energy technologies institute UK (www.eti.co.uk)

Composition data from energy technologies institute UK (www.eti.co.uk)

Sample No.	Ultimate Analysis				Proximate Analysis						
	Moisture	Volatile matter	Fixed carbon	Ash	C	H	N	S	Cl	O	F
1	54.4	37.6	7.3	0.8	49.51	6.18	0.32	0.01	0.01	43.99	1.95
2	51.3	40.9	7.3	0.6	50.64	6.18	0.32	0.01	0.01	42.87	1.928
3	52.3	39.6	7.4	0.7	50.57	6.16	0.43	0.01	0.02	42.82	2.005
4	57.1	35.5	6.7	0.7	49.83	6.19	0.45	0.01	0.01	43.54	1.975
5	51.9	40.2	7.4	0.5	50.66	6.19	0.32	0.01	0.02	42.81	1.985
6	49.4	41.8	8	0.8	50.3	6.17	0.54	0.01	0.01	42.99	1.927
7	56.7	35.3	7.2	0.9	50.2	6.27	0.51	0.01	0.01	43.02	1.964
8	52.8	39.5	7.2	0.6	50.52	6.19	0.33	0.01	0.02	42.94	1.973
9	51.7	39.9	7.7	0.7	50.32	6.15	0.61	0.01	0.01	42.92	1.999
10	56	36.5	6.8	0.7	49.56	6.14	0.4	0.01	0.01	43.91	2.08
11	50.9	40.8	7.7	0.6	50.53	6.17	0.35	0.01	0.02	42.92	1.945
12	51.6	40.1	7.6	0.8	50.47	6.16	0.54	0.01	0.01	42.83	2.011
13	54.9	37.2	7.1	0.8	50.06	6.12	0.4	0.01	0.01	43.42	1.979
14	52.7	39.2	7.4	0.6	50.58	6.18	0.37	0.01	0.01	42.87	2.03
15	52.5	39.2	7.6	0.7	50.25	6.16	0.73	0.01	0.01	42.86	1.978
16	54.8	37.2	7.1	0.8	50.26	6.27	0.4	0.01	0.01	43.07	1.986
17	54.7	37.2	7.5	0.6	50.37	6.18	0.46	0.01	0.01	42.98	2.076
18	50.7	40.5	8	0.7	50.67	6.15	0.48	0.01	0.01	42.7	2.004
19	55.4	36.9	6.9	0.8	50.26	6.27	0.45	0.01	0.01	43.02	1.963
20	50.7	40.8	7.9	0.6	49.69	6.15	0.43	0.01	0.01	43.73	2.009
21	50.1	41.1	8	0.8	50.61	6.16	0.52	0.01	0.01	42.71	2.031
22	55.7	36.7	6.9	0.8	50.24	6.25	0.43	0.01	0.01	43.07	1.955
23	52.4	39.5	7.5	0.6	49.79	6.31	0.42	0.01	0.01	43.48	1.967
24	50.5	40.7	7.9	0.9	50.7	6.14	0.51	0.01	0.01	42.64	4.247
25	53.5	38.5	7.2	0.8	50.22	6.29	0.41	0.01	0.01	43.08	2.01
26	52.5	39.3	7.6	0.6	50.27	6.31	0.39	0.01	0.04	42.99	2.007
27	51.7	39.7	7.8	0.8	50.72	6.18	0.5	0.01	0.01	42.6	2.035
28	56.1	36.3	6.9	0.8	49.84	6.25	0.43	0.01	0.01	43.47	2.037
29	53.1	39	7.3	0.6	50.04	6.19	0.41	0.01	0.01	43.37	1.979
30	52.5	39.1	7.6	0.8	50.21	6.09	0.56	0.01	0.01	43.13	2.066
31	56.5	36	6.8	0.7	49.53	6.03	0.25	0.01	0.01	44.18	1.949
32	52.1	39.6	7.7	0.6	50.13	6.26	0.44	0.01	0.01	43.17	1.937
33	54	38.2	7.2	0.7	49.97	6.07	0.57	0.01	0.01	43.4	1.997
34	53.7	38	7.5	0.8	50.22	6.27	0.42	0.01	0.01	43.09	1.969
35	53.7	38.3	7.3	0.7	50.79	6.12	0.43	0.01	0.01	42.67	1.972
36	51.3	40.2	7.8	0.7	50.12	6.13	0.54	0.01	0.01	43.22	2.002
37	55.3	37.5	6.6	0.7	49.46	6.08	0.22	0.01	0.01	44.25	1.987
38	52	39.9	7.6	0.6	49.65	6.31	0.44	0.01	0.01	43.6	13.647
39	50.6	41.9	6.7	0.9	51.16	6.15	0.43	0.01	0.02	42.24	2.003
40	55.7	36.8	6.7	0.7	50.27	6.23	0.41	0.01	0.01	43.08	1.946
41	53	38.6	7.6	0.8	51.12	6.11	0.39	0.01	0.01	42.38	2.009
42	51.9	40.1	7.3	0.7	50.01	6.14	0.54	0.01	0.01	43.3	2.041
43	56.8	35.8	6.7	0.7	49.49	6.02	0.29	0.01	0.01	44.2	1.97
45	50.2	41.6	7.7	0.6	50.45	6.13	0.36	0.01	0.02	43.04	1.947
46	51.4	40.2	7.5	0.9	50.17	6.12	0.57	0.01	0.01	43.14	1.938
47	56	36.7	6.7	0.6	49.1	6.24	0.37	0.01	0.01	44.28	1.99
48	52.4	39.4	7.6	0.6	50.71	6.1	0.36	0.01	0.01	42.83	1.968
49	51.2	40.5	7.5	0.9	50.32	6.11	0.68	0.01	0.02	42.88	1.939
50	55.4	36.8	7	0.8	50.14	6.27	0.41	0.01	0.01	43.18	1.98
51	51.3	40.3	7.7	0.7	50.44	6.13	0.34	0.01	0.01	43.1	1.985
52	52.9	39.2	7.1	0.9	50.15	6.07	0.53	0.01	0.01	43.25	1.965
53	55.8	36.6	6.9	0.7	49.45	6.14	0.4	0.01	0.01	44.01	2.028
54	54.6	37.4	7.3	0.7	50.57	6.17	0.4	0.01	0.01	42.86	1.925
55	49.8	41.5	7.9	0.8	50.92	6.15	0.44	0.01	0.02	42.46	1.976
56	56.9	35.8	6.6	0.7	50.04	6.12	0.4	0.01	0.01	43.44	2.059
57	53.7	37.8	7.5	1	50.98	6.13	0.33	0.01	0.02	42.54	1.987
58	49.9	41.2	8.1	0.8	49.88	6.15	0.51	0.01	0.02	43.45	1.963
59	56.3	36	6.8	0.8	49.63	6.13	0.43	0.01	0.01	43.81	2.036
60	64.6	25.9	7.2	2.4	54.31	6.53	2.99	0.39	0.18	35.59	3.892
61	62.6	26.8	7.8	2.8	54.68	6.51	2.7	0.4	0.14	35.57	1.947
62	62.9	26.7	6.7	3.7	54.53	6.54	3.3	0.66	0.18	34.79	3.778
63	65.6	25	6.5	2.9	54.25	6.51	2.94	0.48	0.16	35.66	1.984
64	64	25.6	7.5	2.9	54.22	6.47	2.9	0.36	0.18	35.86	4.008
65	64.3	26.4	6.8	2.5	53.61	6.62	3.55	0.48	0.15	35.58	1.982
66	54.6	32.6	9	3.9	53.54	6.28	2.11	0.41	0.17	37.49	4.057
67	68.5	22.6	6.5	2.4	53.72	6.29	2.97	0.5	0.14	36.39	2.003
68	52.64	38.76	7.69	0.91	50.14	6.21	0.4	0.01	0.03	43.23	1.87
69	52.96	38.52	7.8	0.72	50.23	6.22	0.64	0.02	0.01	42.87	1.894
70	55.03	36.81	7.45	0.71	50.19	6.18	0.59	0.01	0.01	43.01	1.961
71	53.35	38.24	7.64	0.77	50.75	6.16	0.64	0.01	0.01	42.4	1.921
72	58.39	33.46	7.36	0.8	50.49	6.2	0.81	0.03	0.01	42.45	1.935
73	53.81	38.04	7.33	0.82	50.09	6.21	0.42	0.01	0.02	43.25	1.936
74	53.69	38.47	7.24	0.6	50.14	6.22	0.55	0.01	0.02	43.07	1.963
75	54.96	37.22	7.24	0.58	50.44	6.23	0.45	0.01	0.02	42.87	2.021
76	54.7	37.14	7.39	0.77	50.3	6.2	0.53	0.02	0.01	42.95	1.947
77	56.79	35.3	7.15	0.76	50.13	6.13	0.52	0.02	0.01	43.19	1.932
78	54.82	36.15	8.14	0.89	50.79	6.14	0.75	0.02	0.02	42.27	1.967
79	52.88	38.21	7.91	1	49.91	6.21	0.43	0.02	0.02	43.4	1.977
80	55.45	35.82	7.87	0.86	50.19	6.24	0.57	0.05	0.02	42.94	1.908
81	54.56	36.92	7.66	0.86	50.09	6.27	0.5	0.02	0.02	43.1	1.938

Composition data from energy technologies institute UK (www.eti.co.uk)

Sample No.	Ultimate Analysis				Proximate Analysis						
	Moisture	Volatile matter	Fixed carbon	Ash	C	H	N	S	Cl	O	F
82	50.38	40.53	8.31	0.78	49.17	6.22	0.4	0.04	0.02	44.14	1.886
83	57.79	34.03	7.39	0.8	50.26	6.19	0.69	0.02	0.02	42.8	1.932
69	52.96	38.52	7.8	0.72	50.23	6.22	0.64	0.02	0.01	42.87	1.894
70	55.03	36.81	7.45	0.71	50.19	6.18	0.59	0.01	0.01	43.01	1.961
71	53.35	38.24	7.64	0.77	50.75	6.16	0.64	0.01	0.01	42.4	1.921
72	58.39	33.46	7.36	0.8	50.49	6.2	0.81	0.03	0.01	42.45	1.935
73	53.81	38.04	7.33	0.82	50.09	6.21	0.42	0.01	0.02	43.25	1.936
74	53.69	38.47	7.24	0.6	50.14	6.22	0.55	0.01	0.02	43.07	1.963
75	54.96	37.22	7.24	0.58	50.44	6.23	0.45	0.01	0.02	42.87	2.021
76	54.7	37.14	7.39	0.77	50.3	6.2	0.53	0.02	0.01	42.95	1.947
77	56.79	35.3	7.15	0.76	50.13	6.13	0.52	0.02	0.01	43.19	1.932
78	54.82	36.15	8.14	0.89	50.79	6.14	0.75	0.02	0.02	42.27	1.967
79	52.88	38.21	7.91	1	49.91	6.21	0.43	0.02	0.02	43.4	1.977
80	55.45	35.82	7.87	0.86	50.19	6.24	0.57	0.05	0.02	42.94	1.908
81	54.56	36.92	7.66	0.86	50.09	6.27	0.5	0.02	0.02	43.1	1.938
82	50.38	40.53	8.31	0.78	49.17	6.22	0.4	0.04	0.02	44.14	1.886
83	57.79	34.03	7.39	0.8	50.26	6.19	0.69	0.02	0.02	42.8	1.932

Sample No.	Elements (dry sample)													
	Ba	Be	Cr	Co	Cu	Mo	Ni	V	Zn	Sb	As	Hg	Br	Se
1	3.61	0.1	0.1	0.1	4.3	0.1	0.32	0.1	51.79	0.02	0.02	0.005	1.95	0.39
2	41.11	0.07	0.17	0.29	3.44	0.07	0.58	0.07	74.75	0.03	0.01	0.004	1.928	0.386
3	6	0.09	0.27	0.11	4.79	0.09	0.69	0.09	107.95	0.02	0.06	0.004	2.005	0.4
4	3.12	0.09	0.09	0.13	3.55	0.09	0.54	0.09	50.48	0.02	0.02	0.005	1.975	0.395
5	66.92	0.09	0.27	0.55	3.29	0.09	0.97	0.15	128.27	1.27	0.07	0.009	1.985	0.397
6	7.34	0.08	0.28	0.1	4.76	0.08	0.74	0.11	91.55	0.02	0.03	0.004	1.927	0.395
7	3.64	0.11	0.11	0.17	4.42	0.11	0.68	0.11	61.16	0.02	0.02	0.005	1.964	0.393
8	26.99	0.08	0.12	0.37	3.2	0.08	0.55	0.08	81.92	0.02	0.04	0.004	1.973	0.395
9	10.17	0.09	0.27	0.12	5.02	0.09	1.4	0.09	117.31	0.02	0.03	0.004	1.999	0.398
10	3.12	0.1	0.1	0.1	3.51	0.1	0.43	0.12	53.66	0.02	0.02	0.004	2.08	0.416
11	54.82	0.07	0.19	0.31	3.46	0.07	0.49	0.11	73.53	0.02	0.02	0.004	1.945	0.389
12	12.47	0.1	0.18	0.1	4.72	0.1	1.05	0.1	105.95	0.02	0.02	0.004	2.011	0.402
13	1.85	0.1	0.1	0.1	3.86	0.1	0.24	0.1	47	0.02	0.02	0.004	1.969	0.396
14	59.07	0.07	0.15	0.4	3.53	0.07	0.42	0.08	86.85	0.01	0.07	0.004	2.03	0.406
15	5.13	0.08	0.3	0.11	4.62	0.08	0.8	0.08	87.01	0.02	0.19	0.004	1.978	0.393
16	2.08	0.11	0.11	0.11	4.38	0.11	0.33	0.11	56.97	0.02	0.02	0.005	1.986	0.397
17	58.1	0.08	0.2	0.43	3.83	0.08	0.44	0.08	96.92	0.02	0.02	0.004	2.076	0.415
18	5.22	0.08	0.23	0.1	4.41	0.08	0.75	0.1	78.75	0.02	0.03	0.004	2.004	0.388
19	2.61	0.1	0.1	0.1	4.17	0.1	0.67	0.1	52.69	0.02	0.02	0.006	1.963	0.393
20	39.54	0.08	0.14	0.38	4.33	0.08	0.47	0.08	130.58	0.02	0.04	0.004	2.009	0.402
21	8.83	0.09	0.27	0.11	4.43	0.09	1.59	0.18	92.34	0.02	0.03	0.004	2.031	0.398
22	2.98	0.09	0.09	0.12	3.44	0.09	0.55	0.09	49.79	0.02	0.02	0.004	1.955	0.391
23	77.26	0.08	0.14	0.17	3.4	0.08	0.29	0.08	85.17	0.02	0.05	0.004	1.967	0.393
24	14.17	0.12	0.7	0.26	5.26	0.12	1.68	0.65	120.37	0.03	0.07	0.004	2.123	0.398
25	3.22	0.09	0.11	0.16	3.53	0.09	0.58	0.09	47.3	0.02	0.02	0.005	2.01	0.402
26	58.61	0.1	1.47	0.76	17.5	0.18	23.4	0.1	1054.96	0.29	0.09	0.004	2.007	0.401
27	9.34	0.1	0.35	0.17	5.78	0.1	1.78	0.19	134.55	0.02	0.03	0.004	2.035	0.399
28	3.39	0.1	0.1	0.11	3.69	0.1	0.57	0.1	52.07	0.02	0.02	0.004	2.037	0.407
29	62.01	0.08	0.27	0.39	3.66	0.08	0.35	0.17	96.64	0.02	0.02	0.004	1.979	0.396
30	8.7	0.09	0.35	0.14	4.5	0.09	1.35	0.23	91.41	0.02	0.03	0.004	2.066	0.399
31	3.48	0.11	0.11	0.11	3.9	0.11	0.49	0.11	54.32	0.02	0.02	0.005	1.949	0.39
32	65.37	0.09	0.18	0.36	3.61	0.09	0.27	0.09	94.44	0.02	0.08	0.004	1.937	0.387
33	8.29	0.08	0.15	0.08	3.56	0.08	0.83	0.08	83.42	0.02	0.02	0.004	1.997	0.401
34	2.42	0.11	0.11	0.11	4.21	0.11	0.39	0.11	53.36	0.02	0.02	0.004	1.969	0.394
35	58.75	0.08	0.22	0.21	3.32	0.08	0.27	0.08	94.45	0.02	0.15	0.004	1.972	0.394
36	9.32	0.09	0.27	0.11	4.51	0.09	1.42	0.12	100.38	0.02	0.06	0.004	2.002	0.397
37	2.26	0.09	0.09	0.09	3.77	0.09	0.53	0.09	45.51	0.02	0.02	0.004	1.987	0.397
38	60.83	0.08	0.18	0.37	3.73	0.08	0.4	0.08	89.05	0.02	0.07	0.004	1.95	0.39
39	8.8	0.08	0.25	0.13	14.09	0.08	1.18	0.12	96.6	0.02	0.06	0.004	2.003	0.407
40	4.18	0.09	0.15	0.15	3.16	0.09	0.69	0.1	54.15	0.02	0.02	0.012	1.946	0.389
41	64.38	0.1	0.18	0.52	4.45	0.1	0.52	0.1	114.83	0.02	0.07	0.004	2.009	0.402
42	9.13	0.09	0.22	0.11	4.93	0.09	1.38	0.09	95.11	0.03	0.02	0.004	2.041	0.391
43	4.41	0.1	0.12	0.13	3.37	0.1	0.5	0.1	61.41	0.02	0.02	0.004	1.97	0.394
45	40.83	0.07	0.15	0.15	3.03	0.07	0.25	0.07	70.28	0.02	0.07	0.004	1.947	0.389
46	6.92	0.09	0.45	0.18	4.95	0.09	1.04	0.31	89.96	0.02	0.07	0.004	1.938	0.387
47	2.7	0.08	0.09	0.11	3.19	0.08	0.6	0.08	40.83	0.02	0.02	0.004	1.99	0.398
48	51.57	0.08	0.14	0.38	3.67	0.08	0.67	0.08	78.14	0.02	0.04	0.004	1.968	0.394

Sample No.	Elements (dry sample)															
	Ba	Be	Cr	Co	Cu	Mo	Ni	V	Zn	Sb	As	Hg	Br	Se	Cd	Pb
49	14.01	0.1	0.23	0.1	4.91	0.1	2.2	0.1	115.05	0.02	0.03	0.004	1.939	0.401	1.863	0.508
50	2.53	0.1	0.1	0.1	3.9	0.1	0.39	0.1	54.09	0.02	0.02	0.004	1.98	0.396	2.066	0.094
51	61.25	0.09	0.16	0.28	4.01	0.09	0.49	0.09	89.31	0.02	0.04	0.004	1.985	0.397	0.428	6.242
52	7.79	0.11	0.37	0.23	5.4	0.11	1.08	0.24	102.15	0.03	0.04	0.004	1.965	0.4	0.955	0.429
53	3.5	0.09	0.1	0.13	3.17	0.09	0.62	0.09	56.29	0.02	0.02	0.004	2.028	0.406	2.153	0.274
54	41.28	0.08	0.19	0.15	3.32	0.08	0.24	0.08	80.79	0.02	0.05	0.004	1.925	0.385	1.478	0.309
55	7.14	0.09	0.4	0.18	4.84	0.09	0.99	0.26	96.24	0.03	0.04	0.004	1.976	0.399	0.755	0.475
56	3.32	0.09	0.11	0.11	3.66	0.09	0.52	0.11	50.88	0.02	0.02	0.006	2.059	0.412	2.554	0.076
57	16.52	0.13	0.18	0.16	4	0.13	0.13	0.13	74.81	0.03	0.06	0.004	1.987	0.397	0.794	0.239
58	11.92	0.09	0.25	0.16	4.49	0.09	1.3	0.09	89.28	0.05	0.03	0.004	1.963	0.391	1.413	0.707
3	2.35	0.11	0.11	0.11	4.01	0.11	0.28	0.11	58.84	0.02	0.02	0.004	2.002	0.407	0.431	0.068
60	24.89	0.35	0.38	1.42	7.08	0.35	15.55	0.35	56.24	0.07	0.07	0.018	19.461	0.389	0.893	0.404
61	49.7	0.38	0.99	0.68	7.15	0.42	1.9	0.38	191.53	0.08	0.13	0.018	27.258	0.389	2.292	0.422
62	22.14	0.53	0.8	1.02	10.8	0.91	19.9	0.53	424.74	0.11	0.11	0.019	18.892	0.378	4.59	0.672
63	22.55	0.42	0.83	1.21	8.03	0.42	6.7	0.42	155.84	0.08	0.08	0.02	19.84	0.397	5.067	0.354
64	60.67	0.41	0.74	0.41	9.81	1.44	4.9	0.41	351.05	0.26	0.08	0.015	20.039	0.401	4.059	0.64
65	4.27	0.37	0.4	0.48	8.58	0.37	9.5	0.37	188.98	0.11	0.07	0.02	19.816	0.396	2.259	0.476
66	18.22	0.46	0.6	1.58	7.76	0.46	9.94	0.46	220.41	0.15	0.09	0.022	20.283	0.406	8.881	1.643
67	32.61	0.4	0.57	0.4	7.37	0.4	6.76	0.4	232.93	0.09	0.08	0.013	19.872	0.457	7.947	0.783
68	3.96	0.1	0.19	0.14	3.57	0.1	0.41	0.1	51.9	0.03	0.05	0.004	1.87	0.374	2.268	1.48
69	28.82	0.06	0.08	0.22	3.03	0.06	1.01	0.06	56.37	0.05	0.01	0.004	1.894	0.379	1.093	0.3
70	7.99	0.07	0.11	0.14	3.03	0.07	0.28	0.07	83.73	0.03	0.02	0.004	1.961	0.392	0.953	0.39
71	11.04	0.09	0.12	0.09	4.15	0.09	0.25	0.09	78.72	0.02	0.03	0.004	1.921	0.384	0.13	0.3
72	4.96	0.09	0.09	0.11	3.96	0.09	2.29	0.09	76.44	0.02	0.02	0.004	1.935	0.387	1.222	0.26
73	3.93	0.11	0.19	0.11	4.29	0.11	0.55	0.11	63.67	0.02	0.02	0.004	1.936	0.387	3.403	0.21
74	34.18	0.06	0.23	0.03	3.13	0.06	1.16	0.06	58.94	0.03	0.04	0.004	1.963	0.393	1.145	1.02
75	9.95	0.08	0.11	0.08	3.65	0.08	0.26	0.08	68.04	0.02	0.03	0.004	2.021	0.404	1.375	0.08
76	8.11	0.08	0.12	0.12	3.32	0.08	0.26	0.08	135.6	0.02	0.02	0.004	1.947	0.389	1.435	0.39
77	4.66	0.07	0.22	0.25	3.98	0.07	0.7	0.07	73.64	0.07	0.02	0.004	1.932	0.386	3.554	7.34
78	4.14	0.07	0.11	0.11	4.11	0.07	1.86	0.07	61.01	0.02	0.01	0.004	1.967	0.393	0.982	0.14
79	5.02	0.11	0.33	0.13	4.28	0.11	0.46	0.11	61.66	0.2	0.07	0.005	1.977	0.395	2.404	2.09
80	12.51	0.1	0.24	0.1	5.04	0.1	0.43	0.1	89.86	0.06	0.04	0.006	1.908	0.382	1.378	1.71
81	11.29	0.1	0.21	0.14	3.05	0.1	0.23	0.1	126.87	0.05	0.02	0.004	1.938	0.388	1.356	0.5
82	4.65	0.1	0.21	0.2	3.68	0.1	0.94	0.1	105.35	0.02	0.02	0.004	1.886	0.377	3.732	0.25
83	5.64	0.11	0.12	0.12	3.95	0.11	2.26	0.11	89.26	0.02	0.02	0.004	1.932	0.386	1.295	0.12
83	5.64	0.11	0.12	0.12	3.95	0.11	2.26	0.11	89.26	0.02	0.02	0.004	1.932	0.386	1.295	0.12

Composition data from energy technologies institute UK (www.eti.co.uk)

Sample No.	Elements (dry ash)									
	Al	Ca	Fe	K	Mg	Mn	Na	P	Si	Ti
1	9.91	5295	15.47	1628	204	20.81	26.42	514.6	75	1.02
2	10.81	2334	31.92	1387	367.2	73.44	35.52	648.9	60	5.04
3	26.71	3528	27.44	2288	349.44	19.15	36.26	770	106	7.56
4	7.21	5125	13.09	1781	237.66	56.3	31.45	614.9	51	1.02
5	11.66	2413	20.02	1246	357.06	76.03	29.3	415.3	86	7.92
6	78.71	4026	56.7	2454	406.8	15.12	43.29	802.6	265	9
7	11.66	5880	18.2	1975	254.4	47.52	41.44	704	75	1.2
8	13.78	3256	23.66	1958	432.9	50.54	48.1	710.4	78	3.9
9	56.45	3668	44.1	2110	379.8	21.6	36.63	814.4	245	8.1
10	6.78	4879	13.44	1575	203.52	33.41	36.7	539.3	44	0.96
11	11.02	2934	20.93	1617	489.06	78.62	38.48	690.4	67	4.68
12	27.14	4221	26.88	1991	417.6	25.34	40.26	731.5	129	6.72
13	7.21	5293	13.09	1432	186.66	12.24	27.68	463.8	53	1.02
14	11.71	2731	23.66	1778	470.34	124.49	28.86	640.1	46	3.9
15	24.65	3790	29.4	2099	413.1	12.96	43.29	893.6	123	8.1
16	7.05	5991	15.96	1766	210.9	15.05	30.93	538.4	46	1.14
17	11.13	2914	29.4	1870	502.32	122.98	56.98	683.8	65	4.2
18	33.39	3674	33.6	2339	374.4	9.72	35.52	851.4	145	9
19	27.67	5371	13.86	1794	241.92	36.29	34.63	614.6	94	1.08
20	9.54	2817	20.16	1955	405.36	71.71	40.85	576	39	3.6
21	90.1	3948	58.31	2602	423.3	12.24	41.51	941	320	13.26
22	7.21	5159	14.28	1819	230.52	56.3	39	592.4	78	1.02
23	10.18	2507	20.16	2375	386.64	101.09	47.06	601.9	99	5.76
24	341.53	3512	176.4	2099	368.28	23.33	46.62	742.1	1122	27
25	7.63	5432	15.12	1700	252.72	69.98	39.96	595.6	41	1.08
26	66.14	2682	41.86	1705	483.6	109.51	108.71	490.2	290	60.84

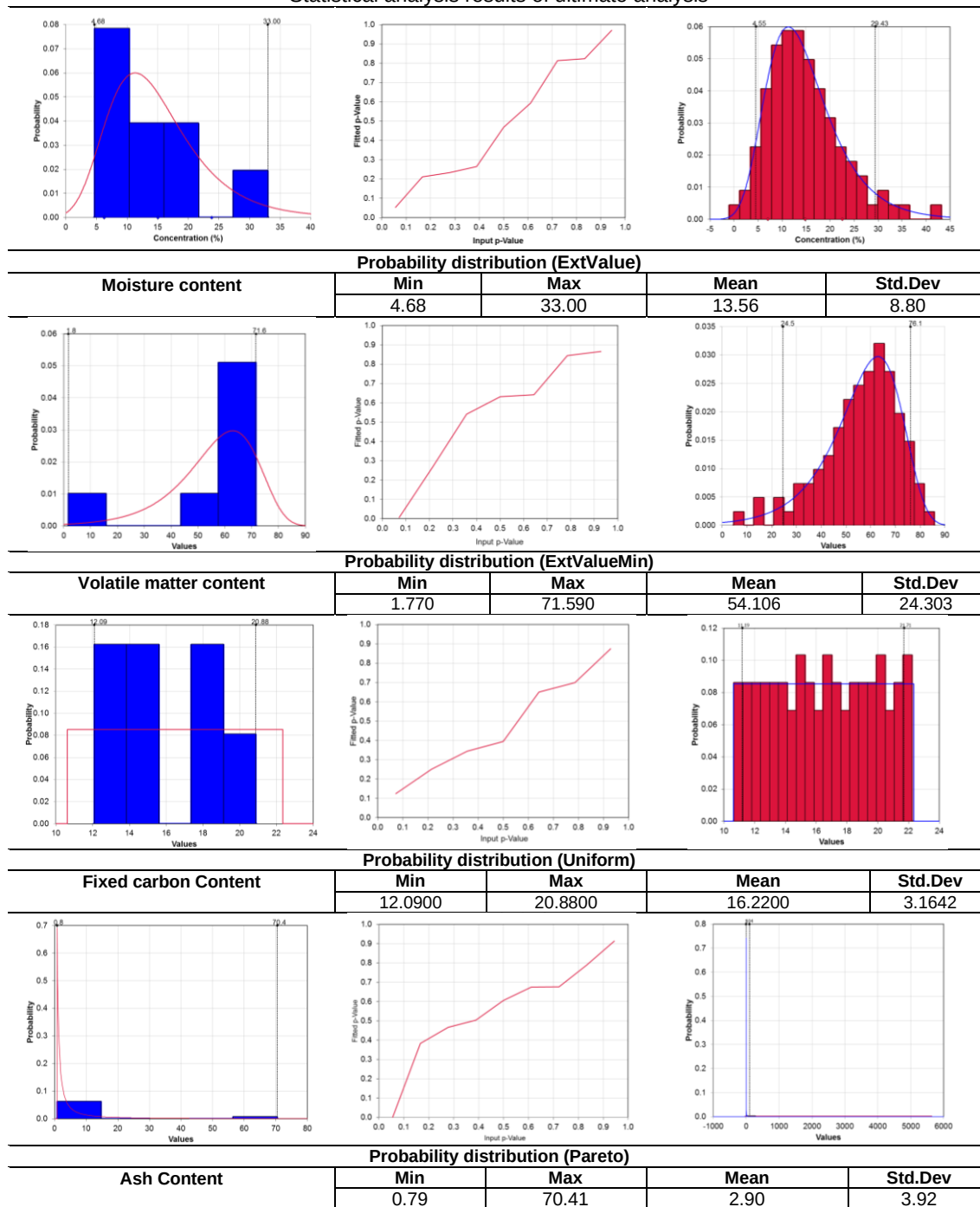
Composition data from energy technologies institute UK (www.eti.co.uk)										
Sample No.	Elements (dry ash)									
	Al	Ca	Fe	K	Mg	Mn	Na	P	Si	Ti
27	121.16	4343	75.6	2683	462.24	25.92	53.28	976.5	402	14.04
28	6.68	5374	16.38	1739	240.84	50.54	38.63	618.6	53	1.08
29	11.45	2715	24.36	1466	445.68	101.09	39.96	548.6	68	3.6
30	159.48	3889	91.63	2859	429.42	12.24	41.51	967.2	545	16.32
31	5.94	5001	12.32	1473	196.8	33.41	34.34	514.6	56	0.96
32	10.34	3194	25.48	1672	442.26	114.19	42.33	520.5	42	3.9
33	23.74	3534	19.6	1872	356.16	7.06	24.86	789.7	105	7.56
34	6.31	5407	11.9	1497	192.78	18.36	32.71	467.5	69	1.02
35	13.36	2913	47.04	1781	444.36	212.69	43.51	693	69	10.08
36	91.43	3519	57.75	2176	341.1	14.04	29.97	813.1	357	11.7
37	7.95	4478	12.6	1536	202.5	33.48	26.64	531.3	38	0.9
38	13.36	2867	28.56	1695	395.28	133.06	34.63	569.2	50	3.6
39	72.08	4179	48.79	2888	455.94	22.03	40.26	981.4	330	11.22
40	11.02	4687	15.68	1742	240.96	85.25	41.44	617.4	65	0.96
41	14.42	4273	30.94	1995	501.84	141.98	61.64	685.9	63	5.1
42	51.2	3471	37.24	1720	366.24	13.1	32.12	823	190	9.24
43	10.18	4845	14.56	1572	232.32	71.42	29.6	566.7	56	0.96
45	9.54	2834	21.84	2022	404.64	84.67	55.94	649.4	90	3.6
46	242.69	4145	129.01	2246	461.7	25.99	52.02	1020.8	816	21.66
47	7.42	4102	11.76	1535	203.28	43.34	32.12	527.3	51	0.84
48	11.02	2916	21.84	1912	419.64	117	45.21	618.9	45	3.9
49	41.98	4702	35.28	2053	435.24	18.14	43.96	925.8	165	9.72
50	16.22	5575	13.86	1643	214.92	20.74	33.3	530.6	55	1.08
51	11.87	3592	23.52	2194	432.6	92.74	63.2	580.3	72	6.72
52	144	4386	2037.56	2416	487.92	32.83	46.4	925.5	504	15.96
53	10.18	4808	15.68	1752	241.92	69.12	44.99	622.3	94	0.96
54	16.11	3886	29.12	2052	450.24	72.58	65.12	811	67	5.76
55	171.3	3519	90.72	1950	351.36	19.58	37.89	730.8	550	16.32
56	7.63	4650	13.44	1607	214.08	43.78	36.7	601.9	52	0.96
57	13.36	6137	26.46	1848	307.44	22.68	71.48	604.3	111	6.3
58	48.34	3876	36.96	1741	432	32.26	50.91	777.2	182	13.44
59	7.05	6072	11.97	1563	217.74	6.84	33.74	534.2	67	1.14
60	60.37	12168	89.11	12051	4289.34	381.1	153.7	2576.6	438	4.02
61	87.45	12439	115.5	14012	3181.5	453.6	144.3	3507.9	497	4.5
62	73.46	25136	103.95	11183	2215.62	249.48	197.8	5218.5	563	17.82
63	87.98	17001	133.63	11952	4043.76	609.55	202.69	3107.9	456	14.94
64	99.96	18363	137.76	10767	3168.48	236.16	175.97	6386.2	844	19.68
65	51.2	13526	91.77	13000	2235.6	114.26	127.65	2371.1	302	4.14
66	113.95	22830	132.44	6132	3947.4	173.38	235.47	3757.5	521	15.48
67	174.9	13526	162.75	10470	2619	97.2	210.9	3006.3	959	31.5
68	30.53	5680	37.63	1809	246.5	42.85	25.57	646.3	129	2.3
69	14.5	3303	28.73	1610	767.9	64.57	35.99	863.4	6	0.91
70	12.56	3982	25.44	1818	357.4	86.46	21.05	904.5	71	0.95
71	22.87	4012	26.73	2061	503	78.88	29.48	913	317	1
72	9.16	4886	17.47	2214	395.1	29.03	19.89	1131.2	42	1.15
73	34.71	4940	30.98	1660	241.1	32.11	28.82	626.2	240	5.31
74	36.1	2862	34.85	883	592.6	60.46	33.93	624.2	188	8.65
75	21.03	3084	17.02	1118	390.1	62.3	19.89	745.1	120	3.07
76	15.32	4715	24.99	2282	371.3	93.39	27.68	918.5	113	1.02
77	0	0	0	0	0	0	0	0	0	0
78	14.62	4835	22.06	2577	471.6	32.34	27.7	1374.7	98	1.18
79	78.65	5906	66.78	2236	276	31.29	47.06	657.6	447	11.45
80	29.66	4807	39.18	1306	581.3	97.69	65.7	1013.1	169	4.63
81	14.02	5321	41.01	1349	356.1	92.13	32.17	881.5	93	2.27
82	16.64	4187	23.08	1069	355.1	14.02	25.56	650.7	111	1.88
83	8.97	4917	17.11	1326	351.9	21.25	30.61	1005	80	1.13

Notes: the references according to <http://www.eti.co.uk/programmes/bioenergy/characterisation-of-feedstocks>

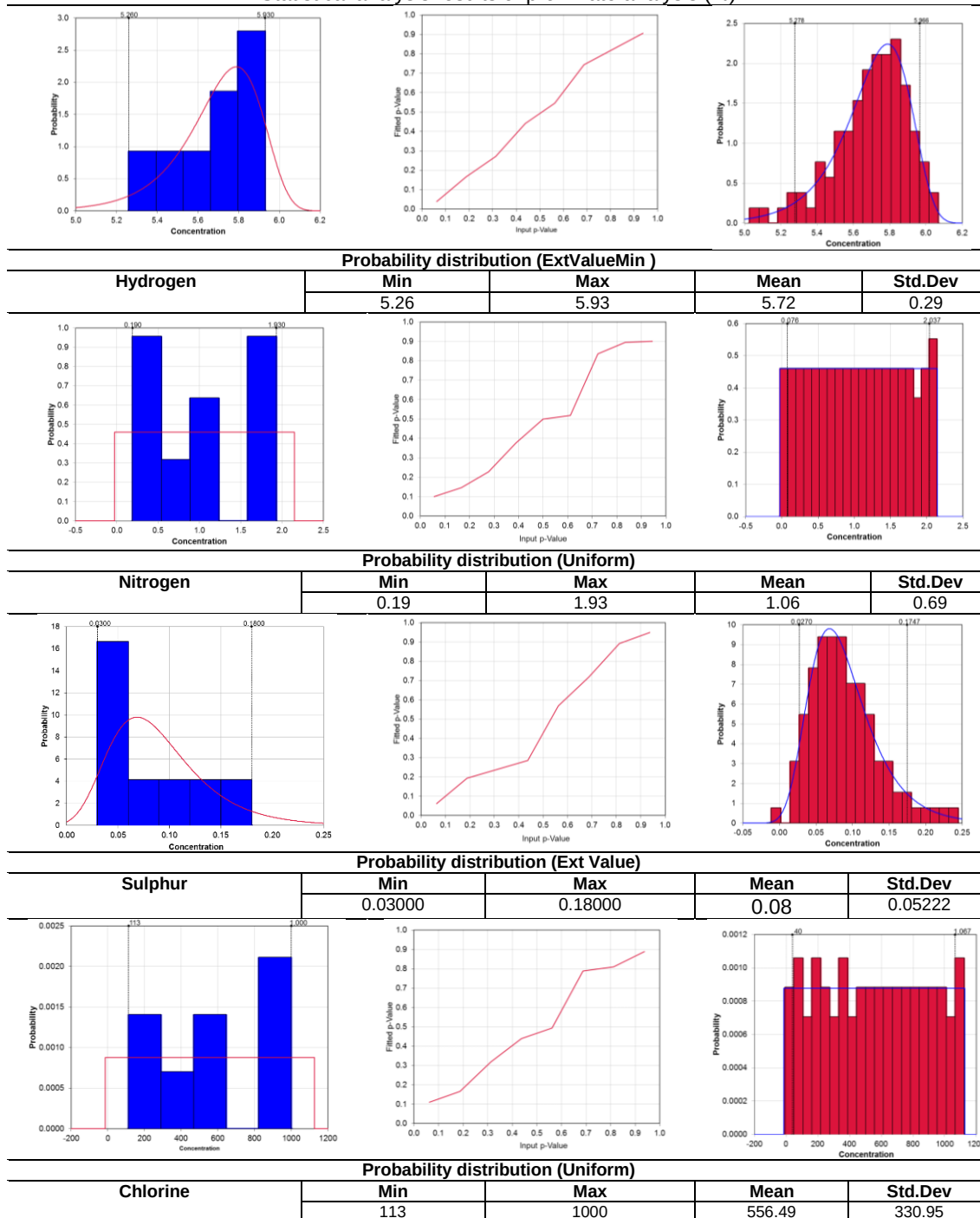
Sample	FR Reference code	Sample	FR Reference code	Sample	FR Reference code
1	048/SRC-W/1/IF	29	046/SRC-W/11/IF	58	047/SRC-W/20/IF
2	046/SRC-W/2/IF	30	047/SRC-W/11/IF	59	048/SRC-W/20/IF
3	047/SRC-W/2/IF	31	048/SRC-W/11/IF	60	103/Leaves
4	048/SRC-W/2/IF	32	046/SRC-W/12/IF	61	104/Leaves
5	046/SRC-W/3/IF	33	047/SRC-W/12/IF	62	105/Leaves
6	047/SRC-W/3/IF	34	048/SRC-W/12/IF	63	106/Leaves
7	048/SRC-W/3/IF	35	046/SRC-W/13/IF	64	107/Leaves
8	046/SRC-W/4/IF	36	047/SRC-W/13/IF	65	108/Leaves
9	047/SRC-W/4/IF	37	048/SRC-W/13/IF	66	109/Leaves
10	048/SRC-W/4/IF	38	046/SRC-W/14/IF	67	110/Leaves
11	046/SRC-W/5/IF	39	047/SRC-W/14/IF	68	111/Leaves
12	047/SRC-W/5/IF	40	048/SRC-W/14/IF	69	048B/SRC-W/Nov15
13	048/SRC-W/5/IF	41	046/SRC-W/15/IF	70	103B/SRC-W/Nov15
14	046/SRC-W/6/IF	42	047/SRC-W/15/IF	71	113B/SRC-W/Nov15
15	047/SRC-W/6/IF	43	048/SRC-W/15/IF	72	114B/SRC-W/Nov15
16	048/SRC-W/6/IF	45	046/SRC-W/16/IF	73	017B/SRC-W/Nov15
17	046/SRC-W/7/IF	46	047/SRC-W/16/IF	74	048B/SRC-W/Jan16
18	047/SRC-W/7/IF	47	048/SRC-W/16/IF	75	103B/SRC-W/Jan16
19	048/SRC-W/7/IF	48	046/SRC-W/17/IF	76	112B/SRC-W/Jan16
20	046/SRC-W/8/IF	49	047/SRC-W/17/IF	77	113B/SRC-W/Jan16
21	047/SRC-W/8/IF	50	048/SRC-W/17/IF	78	114B/SRC-W/Jan16
22	048/SRC-W/8/IF	51	046/SRC-W/18/IF	79	017B/SRC-W/Jan16
23	046/SRC-W/9/IF	52	047/SRC-W/18/IF	80	048B/SRC-W/Mar16
24	047/SRC-W/9/IF	53	048/SRC-W/18/IF	81	112B/SRC-W/Mar16
25	048/SRC-W/9/IF	54	046/SRC-W/19/IF	82	113B/SRC-W/Mar16
26	046/SRC-W/10/IF	55	047/SRC-W/19/IF	83	114B/SRC-W/Mar16
27	047/SRC-W/10/IF	56	048/SRC-W/19/IF		
28	048/SRC-W/10/IF	57	046/SRC-W/20/IF		

B.2 Statistical analysis of the WW samples (PHYLLIS2)

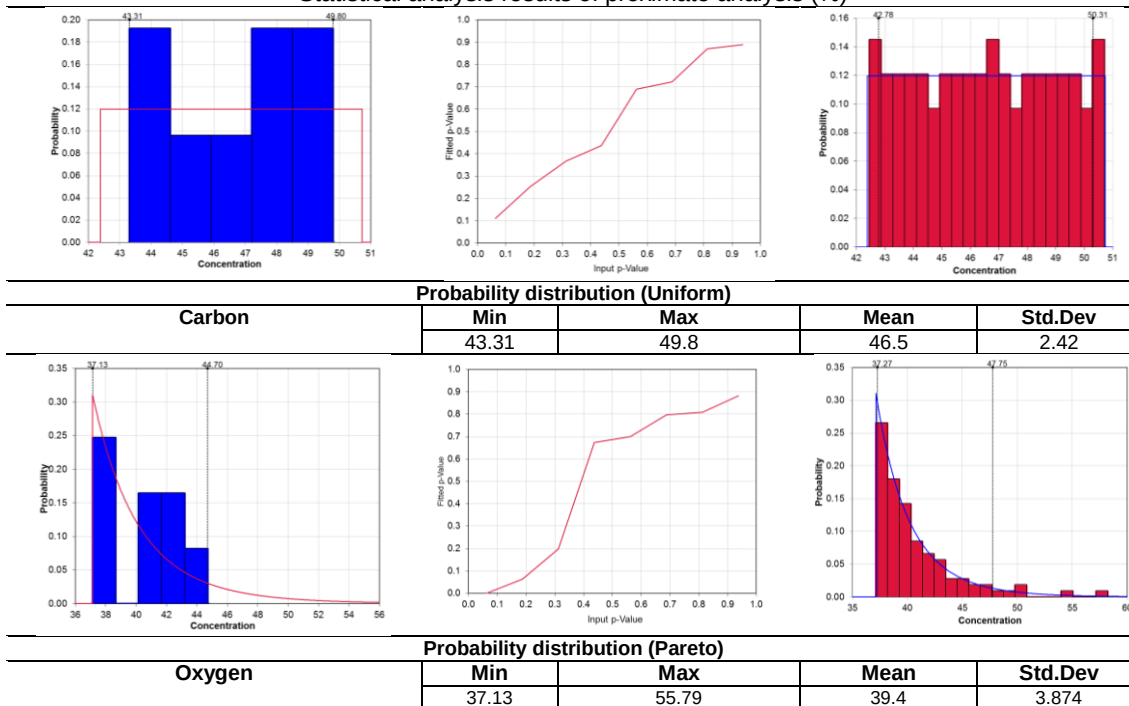
Statistical analysis results of ultimate analysis



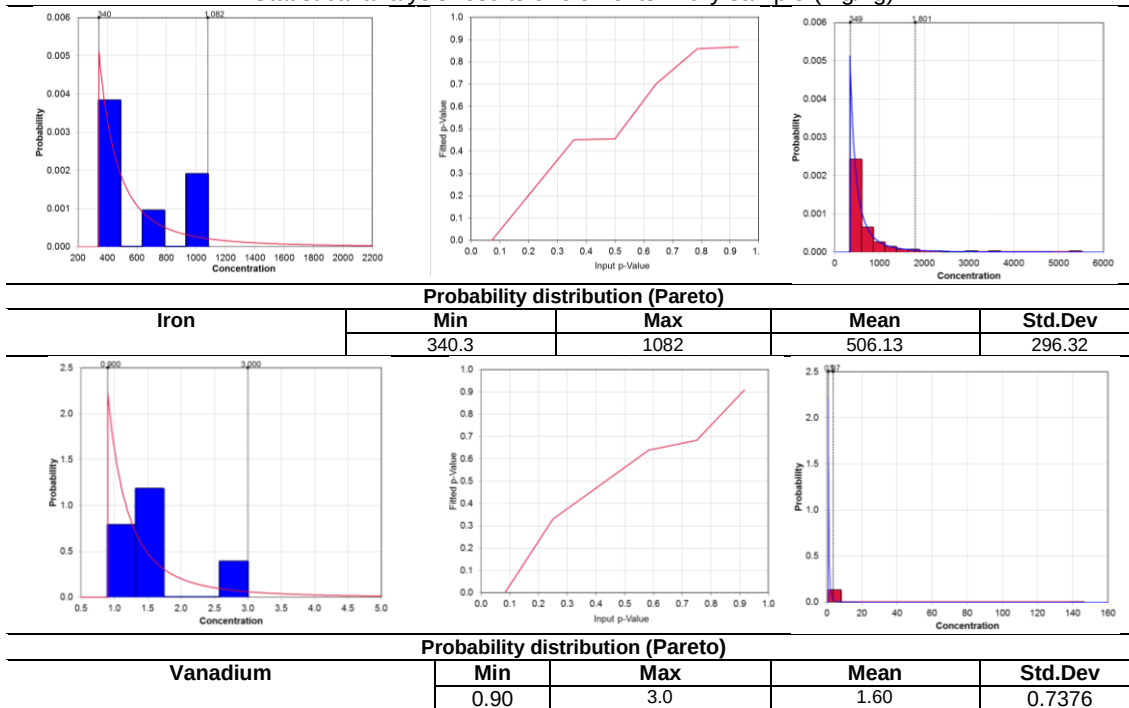
Statistical analysis results of proximate analysis (%)



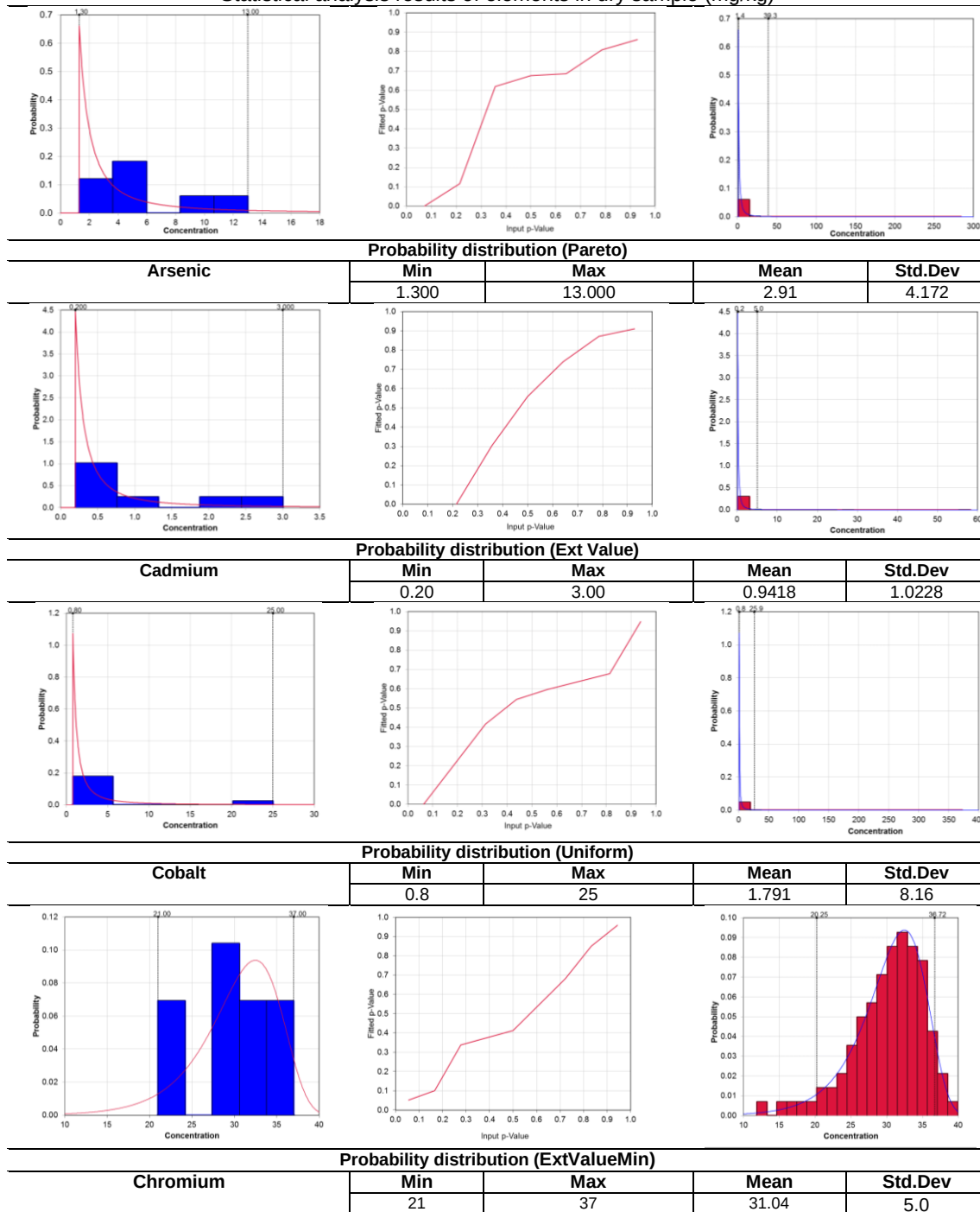
Statistical analysis results of proximate analysis (%)



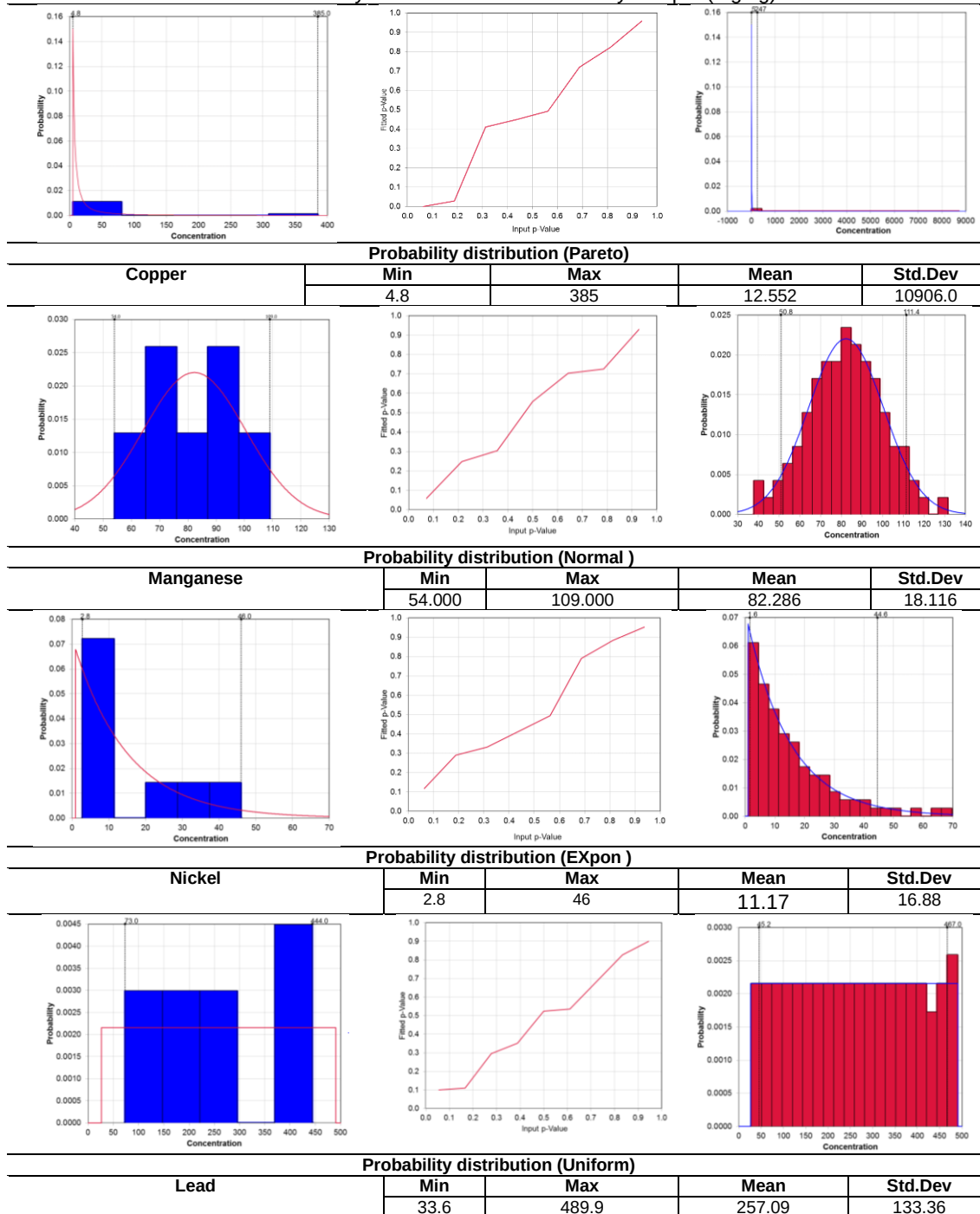
Statistical analysis results of elements in dry sample (mg/kg)



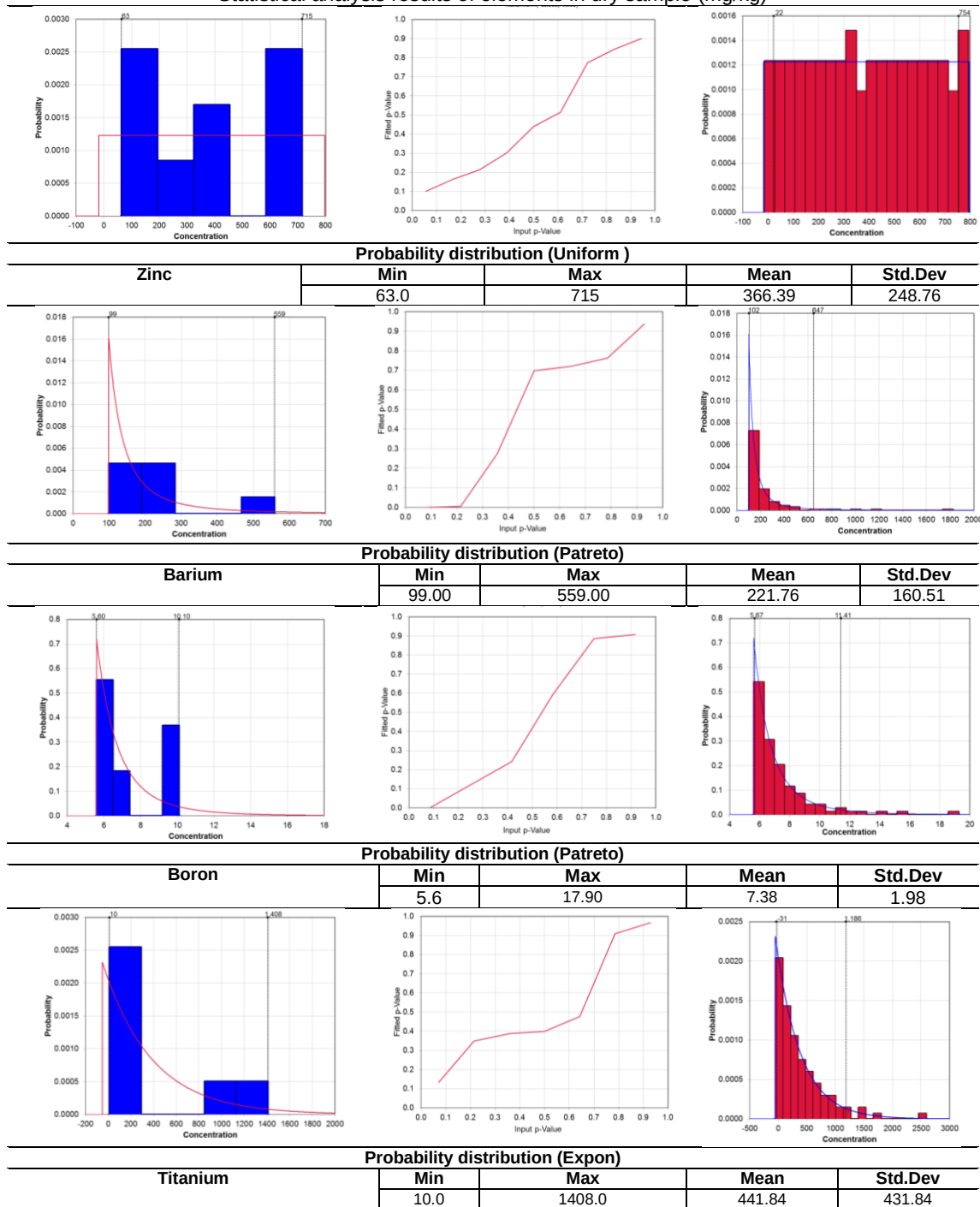
Statistical analysis results of elements in dry sample (mg/kg)



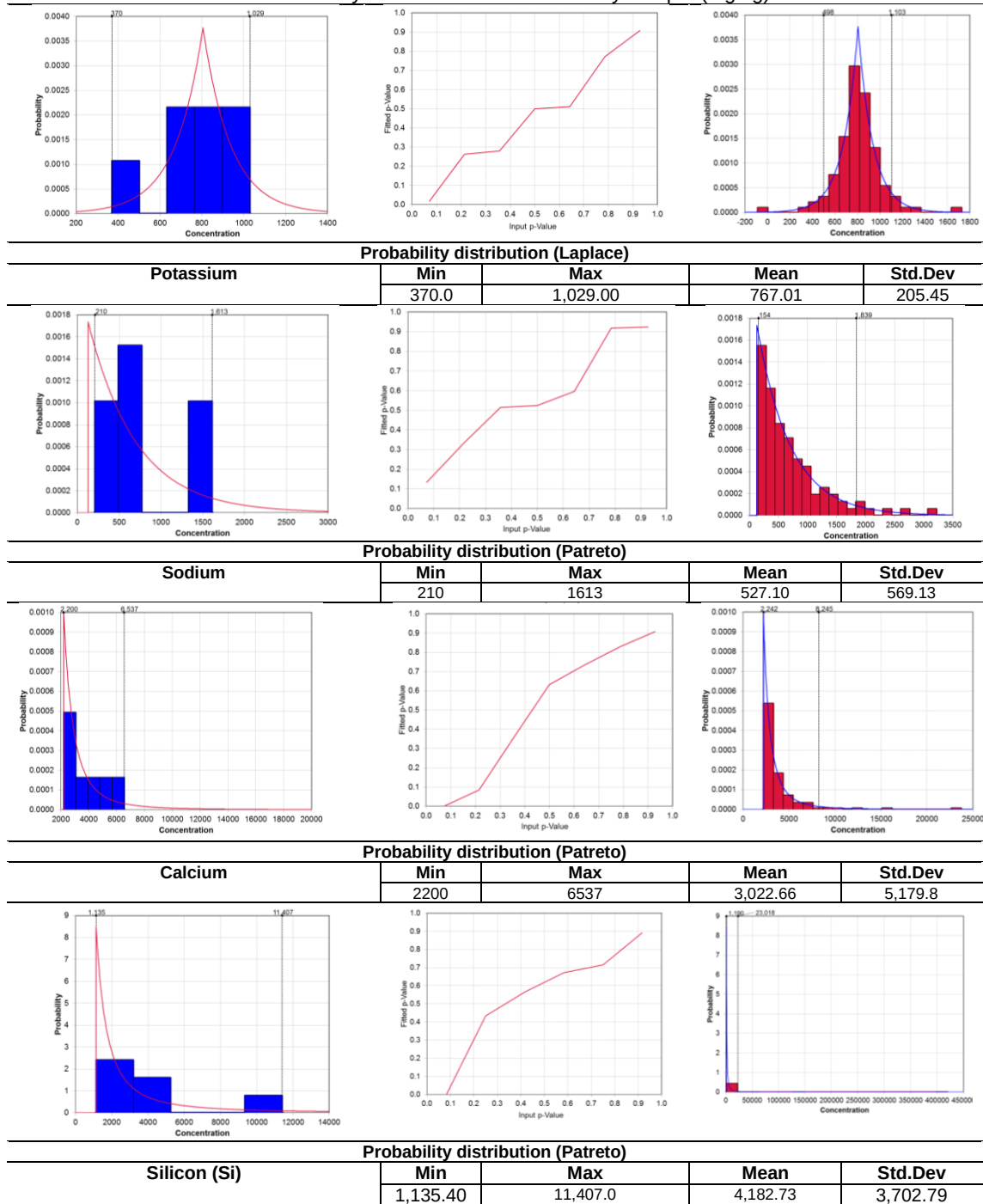
Statistical analysis results of elements in dry sample (mg/kg)



Statistical analysis results of elements in dry sample (mg/kg)

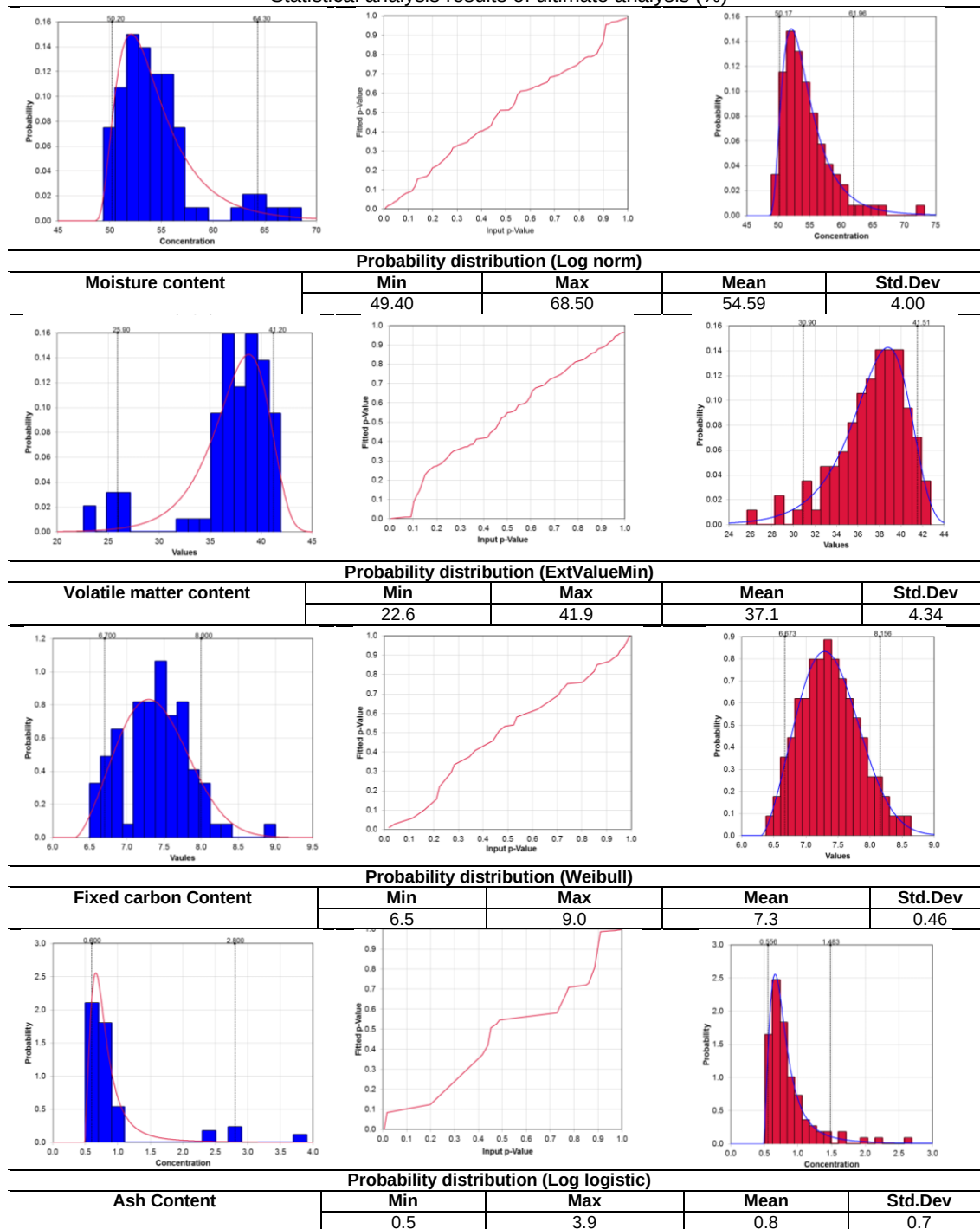


Statistical analysis results of elements in dry sample (mg/kg)

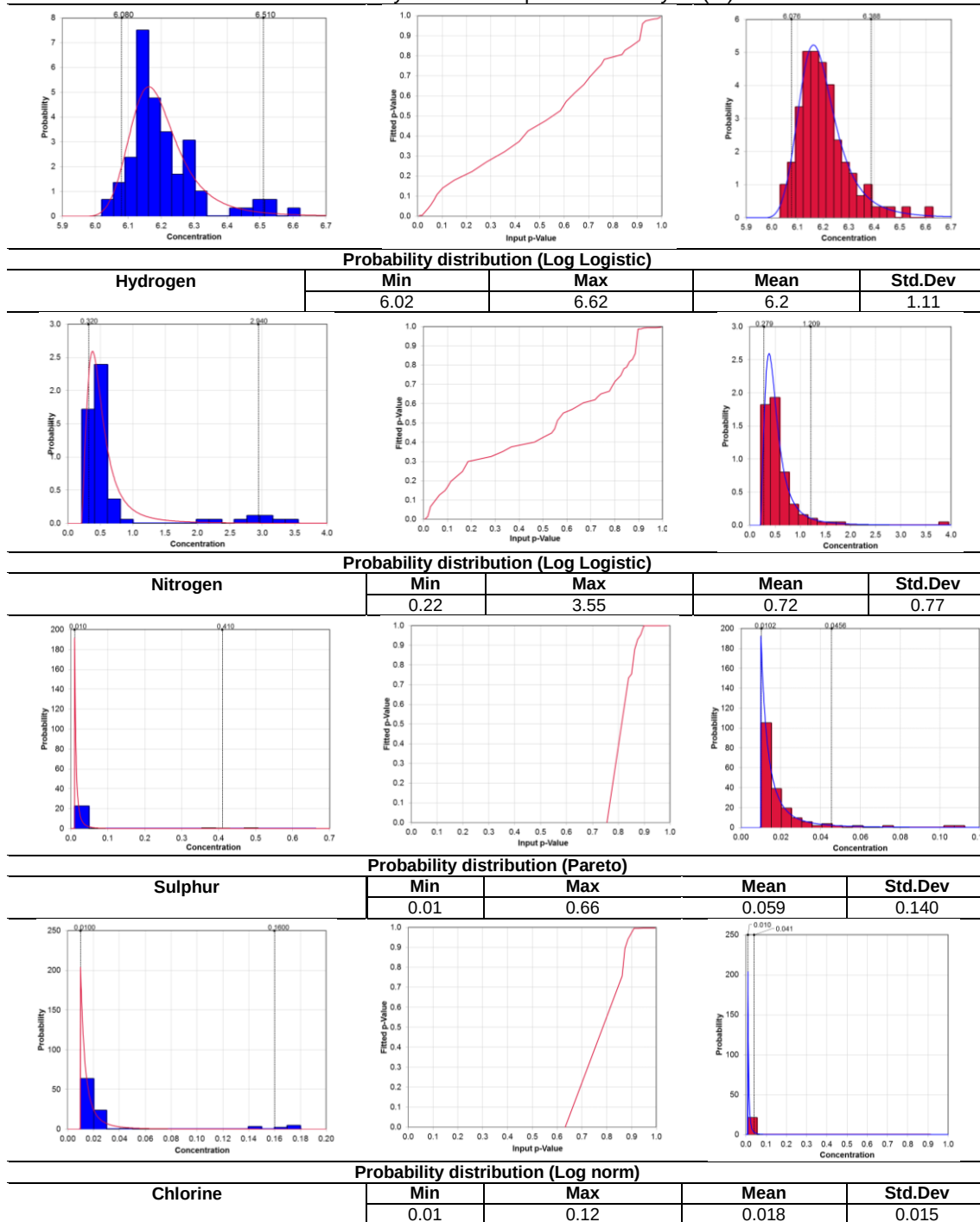


B.3 Statistical analysis of the willow wood samples (www.eti.co.uk)

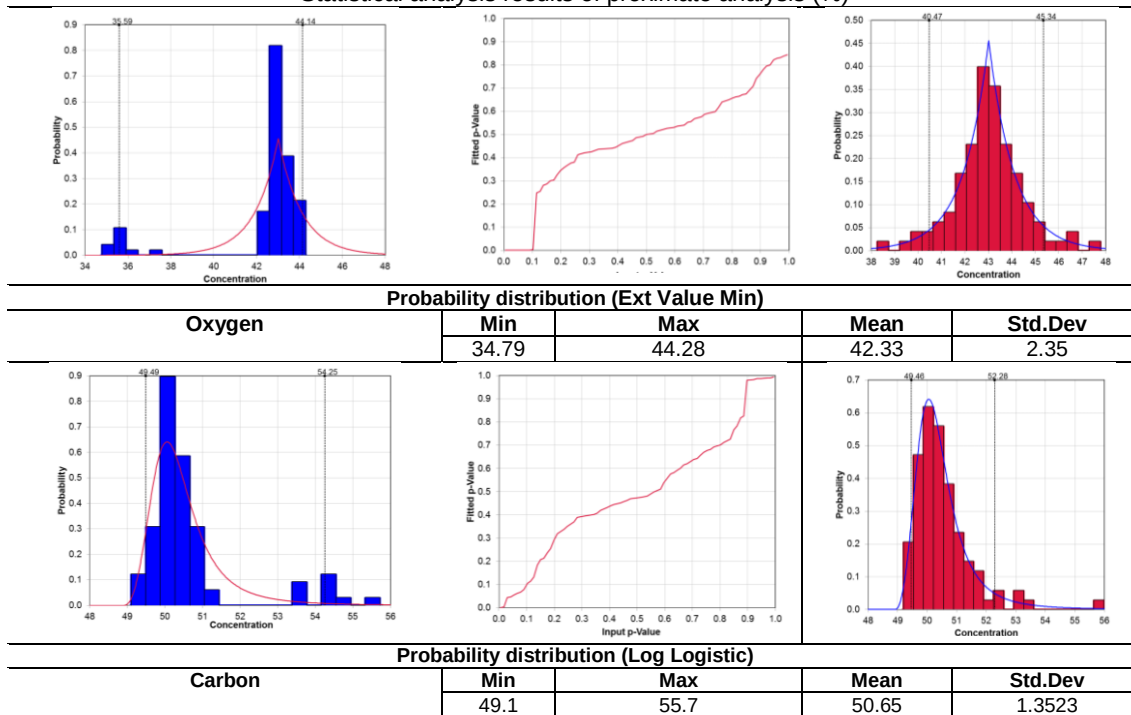
Statistical analysis results of ultimate analysis (%)



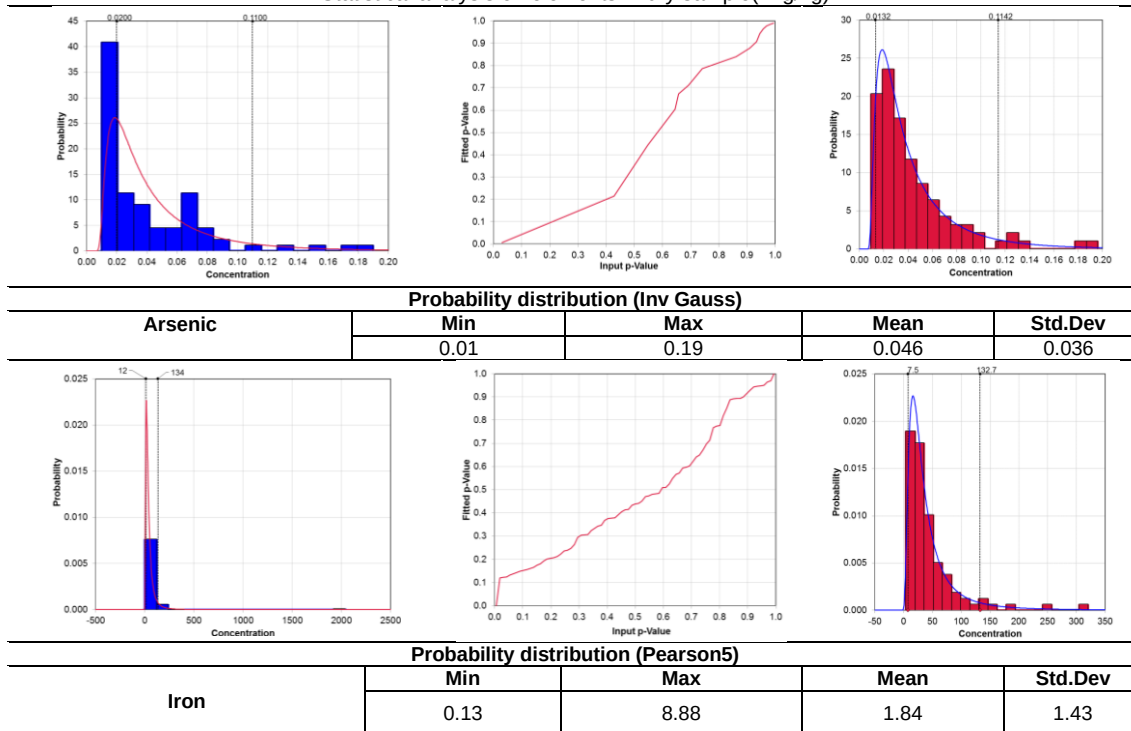
Statistical analysis results of proximate analysis (%)



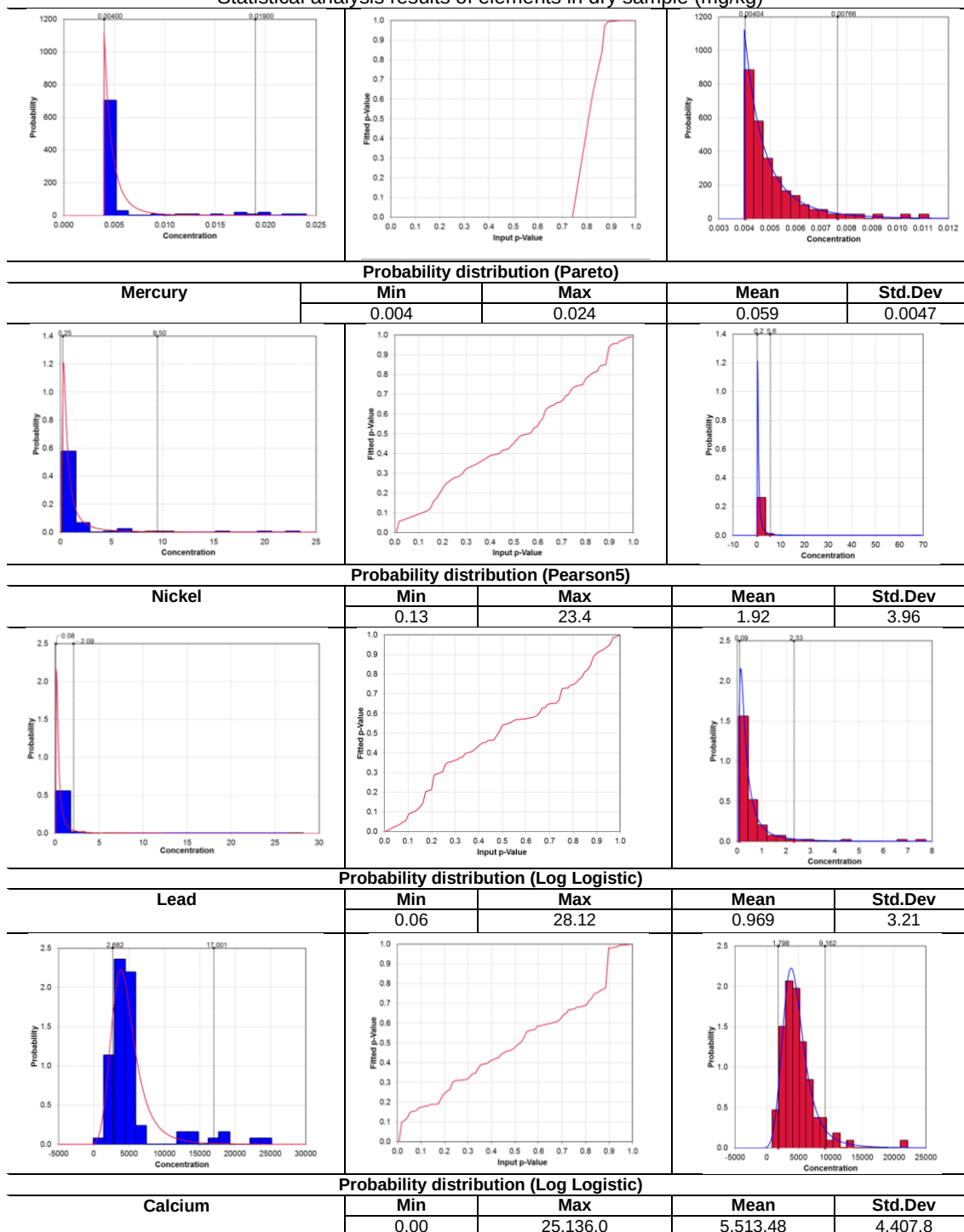
Statistical analysis results of proximate analysis (%)



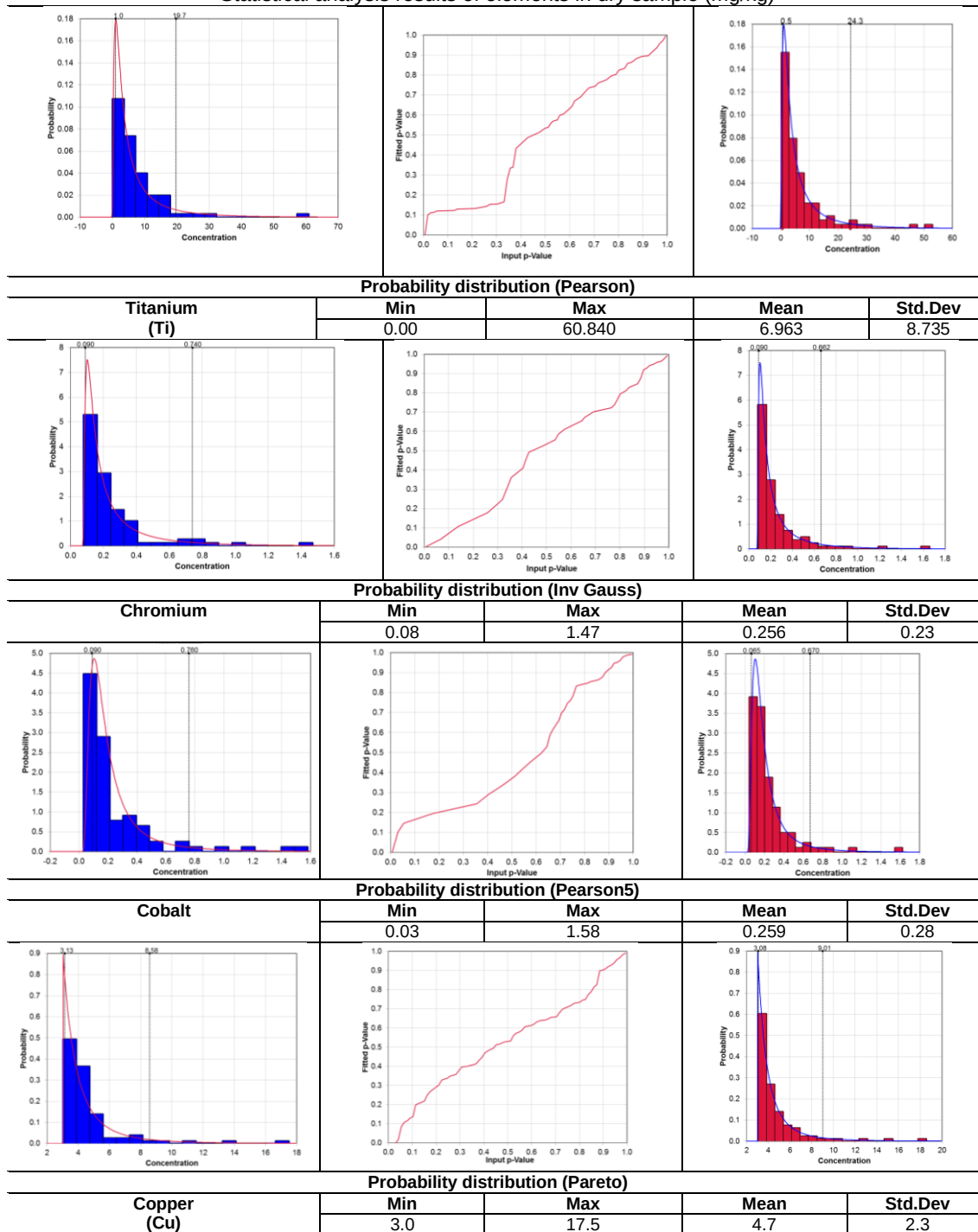
Statistical analysis of elements in dry sample (mg/kg)



Statistical analysis results of elements in dry sample (mg/kg)



Statistical analysis results of elements in dry sample (mg/kg)



B.4 Examples of the conversion procedure

Fuel Composition (as analysed)			Actual Fuel Composition (Basis ar)		
Fuel Composition		Weight from @Risk Analysis Simulation	Weight %	Conversion factor	Actual Fuel Composition (ar Basis)
Component	Basis				Weight %
Moisture (H ₂ O)	ar	13.56%	13.56	None	13.56
Ash	ar	2.93%	2.93	None	2.93
C	Dry	46.5%	46.5	46.555*0.86437	40.19321
H	Dry	5.72%	5.72	5.7287*0.86437	4.944196
N	Dry	1.06%	1.06	1.060*0.86437	0.916232
O	Dry	39.4%	39.4	39.4299*0.86437	34.05618
S	Dry	0.08%	0.08	0.08228*0.86437	0.06915
Cl	Dry	556.49 mg/kg	0.055649	0.055649*0.86437	0.048101
Cu	Daf	12.552 mg/Kg	0.0012552	0.0012552*0.83507	0.001048
Ni	Daf	11.17 mg/Kg	0.001117	0.001117*0.83507	0.000933
As	Daf	2.91 mg/Kg	0.000291	0.000291*0.83507	0.000243
Co	Daf	1.791 mg/Kg	0.0001791	0.0001791*0.83507	0.00015
Cr	Daf	31.04 mg/kg	0.003104	0.003104*0.83507	0.002592
Na	Daf	527.10 mg/Kg	0.05271	0.05271*0.83507	0.044017
Ca	Daf	3,022.66 mg/kg	0.302266	0.302266*0.83507	0.252413
Fe	Daf	506.13 mg/kg	0.050613	0.050613*0.83507	0.042265
B	Daf	7.38 mg/kg	0.000738	0.000738*0.83507	0.000616
Ti	Daf	441.84 mg/kg	0.044184	0.044184*0.83507	0.036897
Pb	Daf	257.09 mg/Kg	0.025709	0.025709*0.83507	0.021469

$$\text{Dry } E = \frac{E \text{ content (ar\%wt)} * 100}{(100 - \text{water content\%})}$$

$$\text{ar } E \% \text{ wt} = \frac{\text{Dry } E * (100 - \text{water content\%})}{100}$$

$$\text{Daf } E = \frac{E \text{ content (ar\%wt)} * 100}{(100 - \text{ASH} - \text{water content\%})}$$

$$\text{ar } E \% \text{ wt} = \frac{\text{Daf } E * (100 - \text{ASH} - \text{water content\%})}{100}$$

Calculation of moles per hour for solid fuel (biomass rate 1 (kg/h))

Atomic mass unit of element	Element	Calculation	moles/hour
14	N	$(0.916232/100) \times 1 \times (1000/14)$	6.544516
16	O	From Fuel $(34.05618/100) \times 1 \times (1000/16)$ From H ₂ O $(13.56/100) \times 1 \times (1000/((2 \times 1) + 16))$	32.6838
12	C	$(40.19321/100) \times 1 \times (1000/12)$	33.49434
1	H	From Fuel $(4.944196/100) \times 1 \times (1000/1)$ From H ₂ O $(13.56/100) \times 1 \times (1000/(2/(2 \times 1) + 16))$	64.58383
32	S	$(0.06915/100) \times 1 \times (1000/32)$	0.2160925
35.5	Cl	$(0.048101/100) \times 1 \times (1000/35.5)$	0.135496693
63.54	Cu	$(0.001048/100) \times 1 \times (1000/63.54)$	0.001649638
58.69	Ni	$(0.000933/100) \times 1 \times (1000/58.69)$	0.001589322
74.92	As	$(0.000243/100) \times 1 \times (1000/74.92)$	0.000324353
58.93	Co	$(0.00015/100) \times 1 \times (1000/58.93)$	0.000253794
51.996	Cr	$(0.002592/100) \times 1 \times (1000/51.996)$	0.004985109
23	Na	$(0.044017/100) \times 1 \times (1000/23)$	0.19137626
40	Ca	$(0.252413/100) \times 1 \times (1000/40)$	0.631033172
55.84	Fe	$(0.042265/100) \times 1 \times (1000/55.84)$	0.075690183
10.81	B	$(0.000616/100) \times 1 \times (1000/10.81)$	0.005701033
47.86	Ti	$(0.036897/100) \times 1 \times (1000/47.86)$	0.077093048
207.2	Pb	$(0.021469/100) \times 1 \times (1000/207.2)$	0.010361397

B.5 Molar composition to be fed to MTDATA for gasification (ASR and CR)

B.5.1 The total moles of the major and minor elements (ASR)

The total moles of the elements to be fed to MTDATA (ASR)

Element	CCA-Group (mole/h)				
	Test1 (ASR ₁)	Test2 (ASR ₂)	Test3 (ASR ₃)	Test4 (ASR ₄)	Test5 (ASR ₅)
Ar	0.25	0.43	0.12	0.07	0.41
N	41.65	70.18	19.17	11.19	67.79
O	142.01	150.67	51.84	38.31	196.5
C	139.39	127.18	47.72	37.63	184.8
H	743.1	1075.86	315.07	199.98	1140.75
S	0.09	0.08	0.03	0.02	0.122
Cl	563.2	513.83	192.81	152.05	746.66
Cu	6.85	6.25	2.34	1.84	9.08
Cr	20.71	18.9	7.09	5.59	27.46
Co	1.03	0.94	0.35	0.27	1.37
Ni	6.57	5.99	2.25	1.77	8.71
As	1.34	1.22	0.46	0.36	1.78
Na	796	726.22	272.51	214.9	1055.3
Ca	2617.15	2387.74	895.98	706.58	3469.7
Fe	314.48	286.92	107.66	84.91	416.93
Element	CCB-Group (mole/h)				
	Test6 (ASR ₁)	Test7 (ASR ₂)	Test8 (ASR ₃)	Test9 (ASR ₄)	Test10 (ASR ₅)
Ar	0.25	0.43	0.12	0.07	0.41
N	41.65	70.18	19.17	11.19	67.79
O	142.01	150.67	51.84	38.31	196.5
C	139.39	127.18	47.72	37.63	184.8
H	743.1	1075.86	315.07	199.98	1140.75
S	0.09	0.08	0.03	0.02	0.122
Cl	563.2	513.83	192.81	152.05	746.66
Cu	6.85	6.25	2.34	1.84	9.08
Cr	20.71	18.9	7.09	5.59	27.46
Ni	6.57	5.99	2.25	1.77	8.71
Na	796	726.22	272.51	214.9	1055.3
Ca	2617.15	2387.74	895.98	706.58	3469.7
B	23.67	21.63	8.113	6.391	31.39
Ti	320	292.4	109.66	86.48	424.39
Pb	43.00	39.2944	14.735	11.62	57.62

B.5.2 The total moles of the major and minor elements (CR)

The total moles of the elements to be fed to MTDATA (CR)					
Element	CCA-Group (moles/h)				
	Test1 (CR ₁)	Test2 (CR ₂)	Test3 (CR ₃)	Test4 (CR ₄)	Test5 (CR ₅)
Ar	0.00	0.00	0.00	0.00	0.00
N	2.72	2.48	0.93	0.73	3.606
O	116.70	106.5	40.00	31.67	154.64
C	139.50	127.30	47.83	37.74	184.90
H	261.71	238.77	89.6	70.66	346.96
S	0.09	0.08	0.03	0.02	0.122
Cl	563.2-E03	513.83	192.81	152.05	746.66
Cu	6.85	6.25	2.34	1.84	9.08
Cr	20.71	18.9	7.09	5.59	27.46
Co	1.03	0.94	0.35	0.27	1.37
Ni	6.57	5.99	2.25	1.77	8.71
As	1.34	1.22	0.46	0.36	1.78
Na	796	726.28	272.51	214.9	1055.3
Ca	2617.15	2387.74	895.98	706.58	3469.7
Fe	314.48	286.92	107.66	84.91	416.93
	CCB-Group (moles/h)				
	Test6 (CR ₁)	Test7 (CR ₂)	Test8 (CR ₃)	Test9 (CR ₄)	Test10 (CR ₅)
Ar	0.00	0.00	0.00	0.00	0.00
N	2.72	2.48	0.93	0.73	3.606
O	116.70	106.5	40.00	31.67	154.64
C	139.50	127.30	47.83	37.74	184.90
H	261.71	238.77	89.6	70.66	346.96
S	0.09	0.08	0.03	0.02	0.122
Cl	563.2	513.83	192.81	152.05	746.66
Cu	6.85	6.25	2.34	1.84	9.08
Cr	20.71	18.9	7.09	5.59	27.46
Ni	6.57	5.99	2.25	1.77	8.71
Na	796	726.28	272.51	214.9	1055.3
Ca	2617.15	2387.74	895.98	706.58	3469.7
B	23.67	21.63	8.113	6.391	31.39
Ti	320	292.4	109.66	86.48	424.39
Pb	43.00	39.2944	14.735	11.62	57.62

B.5.3 The total moles of major and minor elements in WW, willow wood, and their blends (WW 60% and willow wood 40%) during ASR₁

The total moles of the elements to be fed to MTDATA

Element	Test 1 Demolition Waste Wood (WW)	Test 2 Willow Wood	Test 3 Mix 60WW+40Willow
Ar	0.25	0.248328	0.248328
N	41.65	40.26196	41.00986
O	142.01	228.8363	176.0572
C	139.39	149.645	142.7304
H	743.1	694.976	721.5533
S	0.09	0.02136	0.063466
Cl	563.2	0.02136	334.843
Cu	6.85	2.67	5.141779
Cr	20.71	0.17088	12.3856
Co	1.03	0.150944	0.676614
Ni	6.57	1.3884	4.464454
As	1.34	0.020292	0.80933
Na	796	85.12672	507.289
Ca	2617.15	42443.39	18533.3
Fe	314.48	2985.665	1381.236

B.5.4 The total moles of major and minor elements in WW, willow wood, and their blends (WW 60% and willow wood 40%) during CR₁

The total moles of the elements to be fed to MTDATA

Element	Test 1 Demolition Waste Wood (WW)	Test 2 Willow Wood	Test 3 Mix 60WW+40Willow
Ar	0.00	0.00	0.00
N	2.72	1.44892	1.947519
O	116.70	203.6028	168.4168
C	139.50	149.74748	145.1377
H	261.71	215.024	232.7422
S	0.09	0.02136	0.049431
Cl	563.2	0.02136	223.2358
Cu	6.85	2.67	4.317853
Cr	20.71	0.17088	8.314024
Co	1.03	0.150944	0.50139
Ni	6.57	1.3884	3.439102
As	1.34	0.020292	0.546318
Na	796	85.12672	366.5682
Ca	2617.15	42443.388	26503.33
Fe	314.48	2985.6652	1916.046

B.6 Molar composition to be fed to MTDATA for pyrolysis

The total moles of the elements to be fed to MTDATA (pyrolysis)

CCA-Group (moles/h)		
Element	Test1 (P ₁)	Test2 (P ₂)
Ar	0	0
N	62.0614	56.62513
O	349.1709	116.3903
C	417.8311	139.277
H	784.5143	261.5048
S	0.276924	0.092308
Cl	1688.28	562.7601
Cu	20.54054	6.846848
Cr	62.10521	20.70174
Co	3.107145	1.035715
Ni	19.71018	6.570059
As	4.039827	1.346609
Na	2386.131	795.3771
Ca	7845.305	2615.102
Fe	942.7272	314.2424

CCB-Group (moles/h)		
Element	Test3 (P ₁)	Test4 (P ₂)
Ar	0	0
N	62.0614	56.62513
O	349.1709	116.3903
C	417.8311	139.277
H	784.5143	261.5048
S	0.276924	0.092308
Cl	1688.28	562.7601
Cu	20.54054	6.846848
Cr	62.10521	20.70174
Ni	3.107145	1.035715
Na	19.71018	6.570059
Ca	7845.305	2615.102
B	71.03892	23.67964
Ti	960.2317	320.0772
Pb	129.0246	43.0082

Appendix C Chapter 4

C.1. The total moles of the major and minor elements: Influence of CCA elements during ASR₁

C.2. The total moles of the major and minor elements: Influence of CCA elements during CR₁

C.3. The total moles of the major and minor elements (P₁) Influences on CCA elements

C.4. The total moles of the major and minor elements: Influences of Ca, Na, S, Cl, Fe, and Ni on CCA elements during ASR₁

C.5. The total moles of the major and minor elements: Influences of Ca, Na, S, Cl, Fe, and Ni on CCA elements during CR₁

C.6. The total moles of the major and minor elements: Influences of Ca, Na, S, Cl, Fe, and Ni on CCA elements during P₁

C.7. The total moles of the major and minor elements: Assessing CCA elements reactivity during ASR₁

C.8. The total moles of the major and minor elements: Assessing CCA elements reactivity during CR₁

C.9. The total moles of the major and minor elements: Assessing CCA elements reactivity during P₁

C.10. The total moles of the major and minor elements: Effect of type of wood on CCA elements during ASR₁

C.11. The total moles of the major and minor elements: Effect of type of wood on CCA elements during CR₁

C.12. The total moles of the major and minor elements: Effect of type of wood on CCA elements during P₁

C.1 The total moles of the major and minor elements: Influence of CCA elements during ASR₁

The total moles of the elements to be fed to MTDATA

Input	Elemental Molar flow (mole/h)													
	Ar	N	O	C	H	S	Cl	Cu	Cr	Ni	As	Na	Ca	Fe
Test 1	0.25	41.65	142.01	139.39	743.1	0.09	563.2	6.85	20.71	6.57	1.34	796.00	2617.00	315.00
Test 2	0.25	41.65	142.01	139.39	743.1	0.09	563.2	6.85	20.71	6.57	0.00	796.00	2617.00	315.00
Test 3	0.25	41.65	142.01	139.39	743.1	0.09	563.2	6.85	20.71	6.57	0.70	796.00	2617.00	315.00
Test 4	0.25	41.65	142.01	139.39	743.1	0.09	563.2	6.85	20.71	6.57	1.50	796.00	2617.00	315.00
Test 5	0.25	41.65	142.01	139.39	743.1	0.09	563.2	6.85	20.71	6.57	5.00	796.00	2617.00	315.00
Test 6	0.25	41.65	142.01	139.39	743.1	0.09	563.2	0.00	20.71	6.57	1.34	796.00	2617.00	315.00
Test 7	0.25	41.65	142.01	139.39	743.1	0.09	563.2	4.00	20.71	6.57	1.34	796.00	2617.00	315.00
Test 8	0.25	41.65	142.01	139.39	743.1	0.09	563.2	6.00	20.71	6.57	1.34	796.00	2617.00	315.00
Test 9	0.25	41.65	142.01	139.39	743.1	0.09	563.2	8.00	20.71	6.57	1.34	796.00	2617.00	315.00
Test 10	0.25	41.65	142.01	139.39	743.1	0.09	563.2	6.85	0.00	6.57	1.34	796.00	2617.00	315.00
Test 11	0.25	41.65	142.01	139.39	743.1	0.09	563.2	6.85	5.00	6.57	1.34	796.00	2617.00	315.00
Test 12	0.25	41.65	142.01	139.39	743.1	0.09	563.2	6.85	10.00	6.57	1.34	796.00	2617.00	315.00
Test 13	0.25	41.65	142.01	139.39	743.1	0.09	563.2	6.85	20.00	6.57	1.34	796.00	2617.00	315.00
Test 14	0.25	41.65	142.01	139.39	743.1	0.09	563.2	6.85	30.00	6.57	1.34	796.00	2617.00	315.00

C.2 The total moles of the major and minor elements: Influence of CCA elements during CR₁

The total moles of the elements to be fed to MTDATA

Input	Elemental molar flow (mole/h)													
	Ar	N	O	C	H	S	Cl	Cu	Cr	Ni	As	Na	Ca	Fe
Test 1	0.00	2.72	116.48	139.39	261.71	0.09	563.2	6.85	20.71	6.57	1.34	796.00	2617.00	315.00
Test 2	0.00	2.72	116.48	139.39	261.71	0.09	563.2	6.85	20.71	6.57	0.00	796.00	2617.00	315.00
Test 3	0.00	2.72	116.48	139.39	261.71	0.09	563.2	6.85	20.71	6.57	0.70	796.00	2617.00	315.00
Test 4	0.00	2.72	116.48	139.39	261.71	0.09	563.2	6.85	20.71	6.57	1.50	796.00	2617.00	315.00
Test 5	0.00	2.72	116.48	139.39	261.71	0.09	563.2	6.85	20.71	6.57	5.00	796.00	2617.00	315.00
Test 6	0.00	2.72	116.48	139.39	261.71	0.09	563.2	0.00	20.71	6.57	1.34	796.00	2617.00	315.00
Test 7	0.00	2.72	116.48	139.39	261.71	0.09	563.2	4.00	20.71	6.57	1.34	796.00	2617.00	315.00
Test 8	0.00	2.72	116.48	139.39	261.71	0.09	563.2	6.00	20.71	6.57	1.34	796.00	2617.00	315.00
Test 9	0.00	2.72	116.48	139.39	261.71	0.09	563.2	8.00	20.71	6.57	1.34	796.00	2617.00	315.00
Test 10	0.00	2.72	116.48	139.39	261.71	0.09	563.2	6.85	0.00	6.57	1.34	796.00	2617.00	315.00
Test 11	0.00	2.72	116.48	139.39	261.71	0.09	563.2	6.85	5.00	6.57	1.34	796.00	2617.00	315.00
Test 12	0.00	2.72	116.48	139.39	261.71	0.09	563.2	6.85	10.00	6.57	1.34	796.00	2617.00	315.00
Test 13	0.00	2.72	116.48	139.39	261.71	0.09	563.2	6.85	20.00	6.57	1.34	796.00	2617.00	315.00
Test 14	0.00	2.72	116.48	139.39	261.71	0.09	563.2	6.85	30.00	6.57	1.34	796.00	2617.00	315.00

C.3 The total moles of the major and minor elements: Influence of CCA elements during P₁

The total moles of the elements to be fed to MTDATA

Input	Elemental molar flow (mole/h)													
	Ar	N	O	C	H	S	Cl	Cu	Cr	Ni	As	Na	Ca	Fe
Test 1	0.00	62.07	349.17	139.39	261.71	0.09	563.2	6.85	20.71	6.57	1.34	796.00	2617.00	315.00
Test 2	0.00	62.07	349.17	139.39	261.71	0.09	563.2	6.85	20.71	6.57	0.00	796.00	2617.00	315.00
Test 3	0.00	62.07	349.17	139.39	261.71	0.09	563.2	6.85	20.71	6.57	0.70	796.00	2617.00	315.00
Test 4	0.00	62.07	349.17	139.39	261.71	0.09	563.2	6.85	20.71	6.57	1.50	796.00	2617.00	315.00
Test 5	0.00	62.07	349.17	139.39	261.71	0.09	563.2	6.85	20.71	6.57	5.00	796.00	2617.00	315.00
Test 6	0.00	62.07	349.17	139.39	261.71	0.09	563.2	0.00	20.71	6.57	1.34	796.00	2617.00	315.00
Test 7	0.00	62.07	349.17	139.39	261.71	0.09	563.2	4.00	20.71	6.57	1.34	796.00	2617.00	315.00
Test 8	0.00	62.07	349.17	139.39	261.71	0.09	563.2	6.00	20.71	6.57	1.34	796.00	2617.00	315.00
Test 9	0.00	62.07	349.17	139.39	261.71	0.09	563.2	8.00	20.71	6.57	1.34	796.00	2617.00	315.00
Test 10	0.00	62.07	349.17	139.39	261.71	0.09	563.2	6.85	0.00	6.57	1.34	796.00	2617.00	315.00
Test 11	0.00	62.07	349.17	139.39	261.71	0.09	563.2	6.85	5.00	6.57	1.34	796.00	2617.00	315.00
Test 12	0.00	62.07	349.17	139.39	261.71	0.09	563.2	6.85	10.00	6.57	1.34	796.00	2617.00	315.00
Test 13	0.00	62.07	349.17	139.39	261.71	0.09	563.2	6.85	20.00	6.57	1.34	796.00	2617.00	315.00
Test 14	0.00	62.07	349.17	139.39	261.71	0.09	563.2	6.85	30.00	6.57	1.34	796.00	2617.00	315.00

C.4 The total moles of the major and minor elements: Influences of Ca, Na, S, Cl, Fe, and Ni on CCA elements during ASR₁

The total moles of the elements to be fed to MTDATA

Input	Elemental molar flow (mole/h)													
	Ar	N	O	C	H	Cu	Cr	As	Ni	Fe	Cl	S	Na	Ca
Test 1	0.25	41.65	142.01	139.39	743.1	6.85	20.71	1.34	6.57	315.00	563.2	0.09	796.00	2617.00
Test 2	0.25	41.65	142.01	139.39	743.1	6.85	20.71	1.34	6.57	315.00	563.2	0.09	796.00	0.00
Test 3	0.25	41.65	142.01	139.39	743.1	6.85	20.71	1.34	6.57	315.00	563.2	0.09	796.00	100.00
Test 4	0.25	41.65	142.01	139.39	743.1	6.85	20.71	1.34	6.57	315.00	563.2	0.09	796.00	250.00
Test 5	0.25	41.65	142.01	139.39	743.1	6.85	20.71	1.34	6.57	315.00	563.2	0.09	796.00	500.00
Test 6	0.25	41.65	142.01	139.39	743.1	6.85	20.71	1.34	6.57	315.00	563.2	0.09	796.00	1000.00
Test 7	0.25	41.65	142.01	139.39	743.1	6.85	20.71	1.34	6.57	315.00	563.2	0.09	796.00	3000.00
Test 8	0.25	41.65	142.01	139.39	743.1	6.85	20.71	1.34	6.57	315.00	563.2	0.09	0.00	2617.00
Test 9	0.25	41.65	142.01	139.39	743.1	6.85	20.71	1.34	6.57	315.00	563.2	0.09	200.00	2617.00
Test 10	0.25	41.65	142.01	139.39	743.1	6.85	20.71	1.34	6.57	315.00	563.2	0.09	500.00	2617.00
Test 11	0.25	41.65	142.01	139.39	743.1	6.85	20.71	1.34	6.57	315.00	563.2	0.09	800.00	2617.00
Test 12	0.25	41.65	142.01	139.39	743.1	6.85	20.71	1.34	6.57	315.00	563.2	0.09	900.00	2617.00
Test 13	0.25	41.65	142.01	139.39	743.1	6.85	20.71	1.34	6.57	315.00	563.2	0.00	796.00	2617.00
Test 14	0.25	41.65	142.01	139.39	743.1	6.85	20.71	1.34	6.57	315.00	563.2	0.05	796.00	2617.00
Test o15	0.25	41.65	142.01	139.39	743.1	6.85	20.71	1.34	6.57	315.00	563.2	0.10	796.00	2617.00
Test 16	0.25	41.65	142.01	139.39	743.1	6.85	20.71	1.34	6.57	315.00	563.2	0.20	796.00	2617.00
Test 17	0.25	41.65	142.01	139.39	743.1	6.85	20.71	1.34	6.57	315.00	563.2	0.80	796.00	2617.00
Test 18	0.25	41.65	142.01	139.39	743.1	6.85	20.71	1.34	6.57	315.00	0.00	0.09	796.00	2617.00
Test 9	0.25	41.65	142.01	139.39	743.1	6.85	20.71	1.34	6.57	315.00	100.00	0.09	796.00	2617.00
Test 20	0.25	41.65	142.01	139.39	743.1	6.85	20.71	1.34	6.57	315.00	300.00	0.09	796.00	2617.00
Test 21	0.25	41.65	142.01	139.39	743.1	6.85	20.71	1.34	6.57	315.00	500.00	0.09	796.00	2617.00
Test 22	0.25	41.65	142.01	139.39	743.1	6.85	20.71	1.34	6.57	315.00	700.00	0.09	796.00	2617.00
Test 23	0.25	41.65	142.01	139.39	743.1	6.85	20.71	1.34	6.57	0.00	563.2	0.09	796.00	2617.00
Test24	0.25	41.65	142.01	139.39	743.1	6.85	20.71	1.34	6.57	50.00	563.2	0.09	796.00	2617.00
Test25	0.25	41.65	142.01	139.39	743.1	6.85	20.71	1.34	6.57	100.00	563.2	0.09	796.00	2617.00
Test 26	0.25	41.65	142.01	139.39	743.1	6.85	20.71	1.34	6.57	150.00	563.2	0.09	796.00	2617.00
Test 27	0.25	41.65	142.01	139.39	743.1	6.85	20.71	1.34	6.57	250.00	563.2	0.09	796.00	2617.00
Test 28	0.25	41.65	142.01	139.39	743.1	6.85	20.71	1.34	6.57	300.00	563.2	0.09	796.00	2617.00
Test 29	0.25	41.65	142.01	139.39	743.1	6.85	20.71	1.34	6.57	500.00	563.2	0.09	796.00	2617.00
Test 30	0.25	41.65	142.01	139.39	743.1	6.85	20.71	1.34	0.00	315.00	563.2	0.09	796.00	2617.00
Test 31	0.25	41.65	142.01	139.39	743.1	6.85	20.71	1.34	5.00	315.00	563.2	0.09	796.00	2617.00
Test 32	0.25	41.65	142.01	139.39	743.1	6.85	20.71	1.34	10.0	315.00	563.2	0.09	796.00	2617.00
Test 33	0.25	41.65	142.01	139.39	743.1	6.85	20.71	1.34	20.0	315.00	563.2	0.09	796.00	2617.00

C.5 The total moles of the major and minor elements: Influences of Ca, Na, S, Cl, Fe, and Ni on CCA elements during CR₁

The total moles of the elements to be fed to MTDATA

Elemental molar flow (mole/h)														
Input	Ar	N	O	C	H	Cu	Cr	As	Ni	Fe	Cl	S	Na	Ca
Test 1	0.00	2.72	116.48	139.39	261.71	6.85	20.71	1.34	6.57	315.00	563.2	0.09	796.00	2617.00
Test 2	0.00	2.72	116.48	139.39	261.71	6.85	20.71	1.34	6.57	315.00	563.2	0.09	796.00	0.00
Test 3	0.00	2.72	116.48	139.39	261.71	6.85	20.71	1.34	6.57	315.00	563.2	0.09	796.00	100.00
Test 4	0.00	2.72	116.48	139.39	261.71	6.85	20.71	1.34	6.57	315.00	563.2	0.09	796.00	250.00
Test 5	0.00	2.72	116.48	139.39	261.71	6.85	20.71	1.34	6.57	315.00	563.2	0.09	796.00	500.00
Test 6	0.00	2.72	116.48	139.39	261.71	6.85	20.71	1.34	6.57	315.00	563.2	0.09	796.00	1000.00
Test 7	0.00	2.72	116.48	139.39	261.71	6.85	20.71	1.34	6.57	315.00	563.2	0.09	796.00	3000.00
Test 8	0.00	2.72	116.48	139.39	261.71	6.85	20.71	1.34	6.57	315.00	563.2	0.09	0.00	2617.00
Test 9	0.00	2.72	116.48	139.39	261.71	6.85	20.71	1.34	6.57	315.00	563.2	0.09	200.00	2617.00
Test 10	0.00	2.72	116.48	139.39	261.71	6.85	20.71	1.34	6.57	315.00	563.2	0.09	500.00	2617.00
Test 11	0.00	2.72	116.48	139.39	261.71	6.85	20.71	1.34	6.57	315.00	563.2	0.09	800.00	2617.00
Test 12	0.00	2.72	116.48	139.39	261.71	6.85	20.71	1.34	6.57	315.00	563.2	0.09	900.00	2617.00
Test 13	0.00	2.72	116.48	139.39	261.71	6.85	20.71	1.34	6.57	315.00	563.2	0.00	796.00	2617.00
Test 14	0.00	2.72	116.48	139.39	261.71	6.85	20.71	1.34	6.57	315.00	563.2	0.05	796.00	2617.00
Test 15	0.00	2.72	116.48	139.39	261.71	6.85	20.71	1.34	6.57	315.00	563.2	0.10	796.00	2617.00
Test 16	0.00	2.72	116.48	139.39	261.71	6.85	20.71	1.34	6.57	315.00	563.2	0.20	796.00	2617.00
Test 17	0.00	2.72	116.48	139.39	261.71	6.85	20.71	1.34	6.57	315.00	563.2	0.80	796.00	2617.00
Test 18	0.00	2.72	116.48	139.39	261.71	6.85	20.71	1.34	6.57	315.00	0.00	0.09	796.00	2617.00
Test 19	0.00	2.72	116.48	139.39	261.71	6.85	20.71	1.34	6.57	315.00	100.00	0.09	796.00	2617.00
Test 20	0.00	2.72	116.48	139.39	261.71	6.85	20.71	1.34	6.57	315.00	300.00	0.09	796.00	2617.00
Test 21	0.00	2.72	116.48	139.39	261.71	6.85	20.71	1.34	6.57	315.00	500.00	0.09	796.00	2617.00
Test 22	0.00	2.72	116.48	139.39	261.71	6.85	20.71	1.34	6.57	315.00	700.00	0.09	796.00	2617.00
Test 23	0.00	2.72	116.48	139.39	261.71	6.85	20.71	1.34	6.57	0.00	563.2	0.09	796.00	2617.00
Test 24	0.00	2.72	116.48	139.39	261.71	6.85	20.71	1.34	6.57	50.00	563.2	0.09	796.00	2617.00
Test 25	0.00	2.72	116.48	139.39	261.71	6.85	20.71	1.34	6.57	100.00	563.2	0.09	796.00	2617.00
Test 26	0.00	2.72	116.48	139.39	261.71	6.85	20.71	1.34	6.57	150.00	563.2	0.09	796.00	2617.00
Test 27	0.00	2.72	116.48	139.39	261.71	6.85	20.71	1.34	6.57	250.00	563.2	0.09	796.00	2617.00
Test 28	0.00	2.72	116.48	139.39	261.71	6.85	20.71	1.34	6.57	300.00	563.2	0.09	796.00	2617.00
Test 29	0.00	2.72	116.48	139.39	261.71	6.85	20.71	1.34	6.57	500.00	563.2	0.09	796.00	2617.00
Test 30	0.00	2.72	116.48	139.39	261.71	6.85	20.71	1.34	0.00	315.00	563.2	0.09	796.00	2617.00
Test 31	0.00	2.72	116.48	139.39	261.71	6.85	20.71	1.34	5.00	315.00	563.2	0.09	796.00	2617.00
Test 32	0.00	2.72	116.48	139.39	261.71	6.85	20.71	1.34	10.0	315.00	563.2	0.09	796.00	2617.00
Test 33	0.00	2.72	116.48	139.39	261.71	6.85	20.71	1.34	20.0	315.00	563.2	0.09	796.00	2617.00

C.6 The total moles of the major and minor elements: Influences of Ca, Na, S, Cl, Fe, and Ni on CCA elements during P₁

The total moles of the elements to be fed to MTDATA

Elemental molar flow (mole/h)														
Input	Ar	N	O	C	H	Cu	Cr	As	Ni	Fe	Cl	S	Na	Ca
Test 1	0.00	62.07	349.17	139.39	261.71	6.85	20.71	1.34	6.57	315.00	563.2	0.09	796.00	2617.00
Test 2	0.00	62.07	349.17	139.39	261.71	6.85	20.71	1.34	6.57	315.00	563.2	0.09	796.00	0.00
Test 3	0.00	62.07	349.17	139.39	261.71	6.85	20.71	1.34	6.57	315.00	563.2	0.09	796.00	100.00
Test 4	0.00	62.07	349.17	139.39	261.71	6.85	20.71	1.34	6.57	315.00	563.2	0.09	796.00	250.00
Test 5	0.00	62.07	349.17	139.39	261.71	6.85	20.71	1.34	6.57	315.00	563.2	0.09	796.00	500.00
Test 6	0.00	62.07	349.17	139.39	261.71	6.85	20.71	1.34	6.57	315.00	563.2	0.09	796.00	1000.00
Test 7	0.00	62.07	349.17	139.39	261.71	6.85	20.71	1.34	6.57	315.00	563.2	0.09	796.00	3000.00
Test 8	0.00	62.07	349.17	139.39	261.71	6.85	20.71	1.34	6.57	315.00	563.2	0.09	0.00	2617.00
Test 9	0.00	62.07	349.17	139.39	261.71	6.85	20.71	1.34	6.57	315.00	563.2	0.09	200.00	2617.00
Test 10	0.00	62.07	349.17	139.39	261.71	6.85	20.71	1.34	6.57	315.00	563.2	0.09	500.00	2617.00
Test 11	0.00	62.07	349.17	139.39	261.71	6.85	20.71	1.34	6.57	315.00	563.2	0.09	800.00	2617.00
Test 12	0.00	62.07	349.17	139.39	261.71	6.85	20.71	1.34	6.57	315.00	563.2	0.09	900.00	2617.00
Test 13	0.00	62.07	349.17	139.39	261.71	6.85	20.71	1.34	6.57	315.00	563.2	0.00	796.00	2617.00
Test 14	0.00	62.07	349.17	139.39	261.71	6.85	20.71	1.34	6.57	315.00	563.2	0.05	796.00	2617.00
Test 15	0.00	62.07	349.17	139.39	261.71	6.85	20.71	1.34	6.57	315.00	563.2	0.10	796.00	2617.00
Test 16	0.00	62.07	349.17	139.39	261.71	6.85	20.71	1.34	6.57	315.00	563.2	0.20	796.00	2617.00
Test 17	0.00	62.07	349.17	139.39	261.71	6.85	20.71	1.34	6.57	315.00	563.2	0.80	796.00	2617.00
Test 18	0.00	62.07	349.17	139.39	261.71	6.85	20.71	1.34	6.57	315.00	0.00	0.09	796.00	2617.00
Test 9	0.00	62.07	349.17	139.39	261.71	6.85	20.71	1.34	6.57	315.00	100.00	0.09	796.00	2617.00
Test 20	0.00	62.07	349.17	139.39	261.71	6.85	20.71	1.34	6.57	315.00	300.00	0.09	796.00	2617.00
Test 21	0.00	62.07	349.17	139.39	261.71	6.85	20.71	1.34	6.57	315.00	500.00	0.09	796.00	2617.00
Test 22	0.00	62.07	349.17	139.39	261.71	6.85	20.71	1.34	6.57	315.00	700.00	0.09	796.00	2617.00
Test 23	0.00	62.07	349.17	139.39	261.71	6.85	20.71	1.34	6.57	0.00	563.2	0.09	796.00	2617.00
Test 24	0.00	62.07	349.17	139.39	261.71	6.85	20.71	1.34	6.57	50.00	563.2	0.09	796.00	2617.00
Test 25	0.00	62.07	349.17	139.39	261.71	6.85	20.71	1.34	6.57	100.00	563.2	0.09	796.00	2617.00
Test 26	0.00	62.07	349.17	139.39	261.71	6.85	20.71	1.34	6.57	150.00	563.2	0.09	796.00	2617.00
Test 27	0.00	62.07	349.17	139.39	261.71	6.85	20.71	1.34	6.57	250.00	563.2	0.09	796.00	2617.00
Test 28	0.00	62.07	349.17	139.39	261.71	6.85	20.71	1.34	6.57	300.00	563.2	0.09	796.00	2617.00
Test 29	0.00	62.07	349.17	139.39	261.71	6.85	20.71	1.34	6.57	500.00	563.2	0.09	796.00	2617.00
Test 30	0.00	62.07	349.17	139.39	261.71	6.85	20.71	1.34	0.00	315.00	563.2	0.09	796.00	2617.00
Test 31	0.00	62.07	349.17	139.39	261.71	6.85	20.71	1.34	5.00	315.00	563.2	0.09	796.00	2617.00
Test 32	0.00	62.07	349.17	139.39	261.71	6.85	20.71	1.34	10.0	315.00	563.2	0.09	796.00	2617.00
Test 33	0.00	62.07	349.17	139.39	261.71	6.85	20.71	1.34	20.0	315.00	563.2	0.09	796.00	2617.00

C.7 The total moles of the major and minor elements: Assessing CCA elements reactivity during ASR₁

The total moles of the elements to be fed to MTDATA

Input	Elemental molar flow (mole/h)													
	Ar	N	O	C	H	Cu	Cr	As	Ni	Fe	Cl	S	Na	Ca
Test 1	0.2 5	41.6 5	142.0 1	139.3 9	743. 1	6.8 5	20.7 1	1.3 4	6.5 7	315.0 0	563. 2	0.0 9	796.0 0	2617.0 0
Test 2	0.2 5	41.6 5	142.0 1	139.3 9	743. 1	6.8 5	20.7 1	1.3 4	0.0 0	0.00	563. 2	0.0 9	0.00	0.00
Test 3	0.2 5	41.6 5	142.0 1	139.3 9	743. 1	6.8 5	20.7 1	1.3 4	0.0 0	0.00	0.00	0.0 0	0.00	0.00
Test 4	0.2 5	41.6 5	142.0 1	139.3 9	743. 1	0.2 5	0.25	0.2 5	0.2 5	0.25	0.25	0.2 5	0.25	0.25

Notes:

Test1	As, Cu, Cr, Na, Ca, Fe, S, Cl and Ni	Test 2	As, Cu, Cr, S, and Cl
Test 3	As, Cu, and Cr		
Test 4	As, Cu, Cr, Na, Ca, Fe, S, Cl and Ni		

C.8 The total moles of the major and minor elements: Assessing CCA elements reactivity during CR₁

The total moles of the elements to be fed to MTDATA

Input	Elemental molar flow (mole/h)													
	Ar	N	O	C	H	Cu	Cr	As	Ni	Fe	Cl	S	Na	Ca
Test 1	0.0 0	2.7 2	116.4 8	139.3 9	261.7 1	6.8 5	20.7 1	1.3 4	6.5 7	315.0 0	563. 2	0.0 9	796.0 0	2617.0 0
Test2	0.0 0	2.7 2	116.4 8	139.3 9	261.7 1	6.8 5	20.7 1	1.3 4	0.0 0	0.00	563. 2	0.0 9	0.00	0.00
Test3	0.0 0	2.7 2	116.4 8	139.3 9	261.7 1	6.8 5	20.7 1	1.3 4	0.0 0	0.00	0.00	0.0 0	0.00	0.00
Test 4	0.0 0	2.7 2	116.4 8	139.3 9	261.7 1	0.2 5	0.25	0.2 5	0.2 5	0.25	0.25	0.2 5	0.25	0.25

Notes:

Test1	As, Cu, Cr, Na, Ca, Fe, S, Cl and Ni	Test 2	As, Cu, Cr, S, and Cl
Test 3	As, Cu, and Cr		
Test 4	As, Cu, Cr, Na, Ca, Fe, S, Cl and Ni		

C.9 The total moles of the major and minor elements: Assessing CCA elements reactivity during P₁

The total moles of the elements to be fed to MTDATA

	Elemental molar flow (mole/h)													
Input	Ar	N	O	C	H	Cu	Cr	As	Ni	Fe	Cl	S	Na	Ca
Test 1	0.25	62.07	349.17	139.39	743.1	6.85	20.71	1.34	6.57	315.00	563.2	0.09	796.00	2617.00
Test 2	0.25	62.07	349.17	139.39	743.1	6.85	20.71	1.34	0.00	0.00	563.2	0.09	0.00	0.00
Test 3	0.25	62.07	349.17	139.39	743.1	6.85	20.71	1.34	0.00	0.00	0.00	0.00	0.00	0.00
Test 4	0.25	62.07	349.17	139.39	743.1	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
Notes:														
Test1			As, Cu, Cr, Na, Ca, Fe, S, Cl and Ni					Test 2			As, Cu, Cr, S, and Cl			
Test 3								As, Cu, and Cr						
Test 4								As, Cu, Cr, Na, Ca, Fe, S, Cl and Ni						

C.10 The total moles of the major and minor elements: Effect of type of wood on CCA elements during ASR₁

The total moles of the elements to be fed to MTDATA

Elemental molar flow (mole/h)														
Wood Type	Ar	N	O	C	H	Cu	Cr	As	Ni	Fe	Cl	S	Na	Ca
Test 1 Chip	0.25	43.3	143.48	143.15	758.71	6.85	20.71	1.34	6.57	315.00	563.2	0.09	796.00	2617.00
Test 2 Beech	0.25	44.4	144.01	144.8	764.32	6.85	20.71	1.34	6.57	315.00	563.2	0.09	796.00	2617.00
Test 3 Pin	0.25	44.6	142.12	144.7	757.45	6.85	20.71	1.34	6.57	315.00	563.2	0.09	796.00	2617.00

C.11 The total moles of the major and minor elements: Effect of type of wood on CCA elements during CR₁

The total moles of the elements to be fed to MTDATA

Elemental molar flow (mole/h)														
Input	Ar	N	O	C	H	Cu	Cr	As	Ni	Fe	Cl	S	Na	Ca
Test 1 Chip	0.00	2.68	113.48	153.15	258.71	6.85	20.71	1.34	6.57	315.00	563.2	0.09	796.00	2617.00
Test 2 Beech	0.00	2.72	114.01	154.8	264.32	6.85	20.71	1.34	6.57	315.00	563.2	0.09	796.00	2617.00
Test 3 Pin	0.00	2.88	112.12	164.7	257.45	6.85	20.71	1.34	6.57	315.00	563.2	0.09	796.00	2617.00

C.12 The total moles of the major and minor elements: Effect of type of wood on CCA elements during P₁

The total moles of the elements to be fed to MTDATA

Elemental molar flow (mole/h)														
Input	Ar	N	O	C	H	Cu	Cr	As	Ni	Fe	Cl	S	Na	Ca
Test 1 Chip	0.00	65.63	113.48	153.15	258.71	6.85	20.71	1.34	6.57	315.00	563.2	0.09	796.00	2617.00
Test 2 Beech	0.00	65.63	114.01	154.8	264.32	6.85	20.71	1.34	6.57	315.00	563.2	0.09	796.00	2617.00
Test 3 Pin	0.00	65.63	112.12	164.7	257.45	6.85	20.71	1.34	6.57	315.00	563.2	0.09	796.00	2617.00

Appendix D Chapter 5

D.1 The full dataset of samples from landfill

D.2 Proximate analysis

D.2.1 Moisture content

D.2.2 Ash content

D.2.3 Volatile matter

D.2.4 Fixed carbon content

D.3 Ultimate analysis

D.3.1 Carbon content

D.3.2 Nitrogen content

D.3.3 Hydrogen content

D.3.4 C/N Ratio content

D.3.5 Sulphur content

D.3.6 Oxygen content

D.4 Calorific value (CV), TCV and HHV

D.4.1 Calorific value (CV)

D.4.2 TCV and HHV

D.5 Total Cl, Br, F, and P analysis by Bomb Combustion and Ion Chromatogra

D.6 Elements content from ICP-MS analysis

D.1 The full dataset of wastes samples from Landfill

Total solid waste in Landfill site (55-3 m) by material, 2018

Waste fraction from landfill (Weight %)											
Depth (m)	Wood	Plastics	Paper/ cardboard	Metals	Glass/ ceramic	Textile	Soil/fine fraction between 20-6.30 mm	Soil/fine fraction <6.30 mm	Batteries	WEEE	Other
53-55	8.1	12.1	14.8	0	0.7	3.3	10.7	10.4	0	0	40.2
50-51	6.2	11	10.6	3.1	1	7.7	13.6	13.8	0	0	33
48-50.5	11.5	6.3	0.1	3.1	1.4	0	50.2	4.6	0	0	22.9
46-48	46.7	1.9	0.6	11.4	0.7	1.6	15.7	17.9	0	0	3.5
44.5-46	1.5	2.2	16.9	3.2	1.1	11.4	34.9	21.4	0	0	7.3
41-43	1.7	3.9	0	0.1	0.1	0.1	48.5	1.2	0	0	44.2
40-41.5	9.9	2.6	22.75	0.2	0.2	2.9	45.1	13.2	0	0.3	2.9
37.5-39	2.8	2.6	3.2	5.1	0.6	5.6	33.7	22.8	0	0	23.6
36-37.5	7.2	9.5	16.9	3.3	0.5	28	6.5	7	0	16.1	4.9
35-36.5	5.1	4.8	7.5	6.7	0.5	0.2	46.8	24.6	0	0	3.8
32.5-35	45.1	1.2	6.4	1.2	0.1	0.1	40.6	2.7	0	0	2.5
29-30.5	10.4	0.8	5	11.7	0.3	0	53.1	16.2	0	0	2.6
25-27	1.3	17.5	21.9	2.1	0.1	0	25.5	5.4	0	0	26.1
23-25	11.2	6.3	5.8	0	0	14.7	14.4	16.4	0	0	31.2
20-23	26.7	6.8	13.1	0.9	0.5	22.2	10.7	10.4	0	0	8.6
17-20	1.7	6.6	35.9	0	0.2	1.2	20.4	10.8	0	0	23.1
13.5-17	4.8	4.5	14.8	4	2	10.4	28.8	28.1	0	0	2.7
11-13.5	3.8	6.3	14.5	6.7	0.5	11.3	7.8	5.7	0	0	43.5
9-11	23.6	15.7	13.1	7.4	0.6	7.2	11.9	9.7	0	0.7	10.1
7-9	6.9	5.1	30.1	4.3	0.9	1.3	27.8	14.4	0	0	9.2

D.2 Proximate analysis

D.2.1 Moisture content

Moisture content (%) determined using the standard method E-871 and statistical analysis.

Type of waste wood sample	Wt.(g) T1	Wt.(g) T2	Wt.(g) T3	Moisture (%)T1	Moisture (%)T2	Moisture (%)T3	M	STD	RSD
Streams									
Mixed furniture	1.002	1.0004	1.005	8.935	8.789	9.079	8.935	0.145	1.621
Demolition	1.003	1.001	1.004	11.277	11.100	11.186	11.188	0.089	0.792
Mixed stream (unknown)	1.002	1.0006	1.008	8.919	8.792	8.360	8.690	0.293	3.373
New furniture	1.001	1.0008	1.004	9.727	9.709	10.131	9.856	0.238	2.419
Old furniture	1.001	1.0012	1.009	9.506	9.524	9.618	9.549	0.060	0.627
Industrial									
Pellets	1.002	1.0002	1.005	9.141	8.977	9.119	9.079	0.089	0.977
Chips wood	1.002	1.0004	1.005	8.867	8.721	8.607	8.732	0.130	1.492
L.d.									
L.d. (3-7 m)	1.0030	1.0016	1.0060	33.4098	33.3209	34.4454	33.7254	0.6251	1.8536
L.d. (7-9 m)	1.003	1.0012	1.009	28.010	27.881	27.915	27.935	0.067	0.240
L.d. (9-11 m)	1.0010	1.0016	1.0020	38.2930	39.7810	37.0435	38.3725	1.3705	3.5715
L.d. (11-13.5 m)	1.002	1.0006	1.008	39.275	39.190	38.697	39.054	0.312	0.800
L.d. (13.5-17 m)	1.002	1.0004	1.005	45.687	45.600	46.401	45.896	0.439	0.957
L.d. (17-20 m)	1.002	1.0012	1.004	38.470	38.421	38.491	38.461	0.036	0.094
L.d. (20-23 m)	1.002	1.0008	1.004	27.779	27.693	27.490	27.654	0.148	0.536
L.d. (23-25 m)	1.003	1.0002	1.005	37.015	36.839	37.929	37.261	0.585	1.570
L.d. (25-27 m)	1.002	1.0012	1.003	26.293	26.234	26.835	26.454	0.331	1.253
L.d. (29-32.5 m)	1.0020	1.0016	1.0060	22.4941	22.4632	21.8753	22.2775	0.3487	1.5653
L.d. (32.5-35 m)	1.002	1.0004	1.005	52.422	52.345	51.996	52.254	0.227	0.434
L.d. (35-36.5 m)	1.001	1.0004	1.007	39.549	39.513	38.563	39.208	0.559	1.426
L.d. (36-37.5 m)	1.001	1.0014	1.004	38.819	38.844	38.600	38.754	0.134	0.347
L.d. (37.5-39 m)	1.003	1.0004	1.005	32.285	32.109	31.753	32.049	0.271	0.846
L.d. (40-41.5 m)	1.0020	1.0014	1.0080	41.2624	41.2272	41.3892	41.2930	0.0852	0.2064
L.d. (41-43 m)	1.001	1.001	1.004	45.461	45.461	45.729	45.5503	0.1547	0.3397
L.d. (44.5-46 m)	1.002	1.0006	1.006	38.555	38.470	38.019	38.348	0.288	0.752
L.d. (46-48 m)	1.001	1.0006	1.007	45.872	45.850	46.291	46.004	0.248	0.540
L.d. (48-50.5 m)	1.0020	1.0006	1.0060	41.3649	41.2940	41.7785	41.4791	0.2616	0.6308
L.d. (50-51 m)	1.003	1.0016	1.002	9.882	9.756	10.025	9.888	0.135	2.757
L.d. (53-55 m)	1.002	1.0014	1.004	7.634	7.578	7.972	7.728	0.213	1.012

Wt. (g): weight of sample; M: Mean; STD: Standard deviation; RSD: Relative standard deviation

D.2.2 Ash content

ASH content (%) determined by standard method E-1755-01 and statistical analysis.

Name of waste wood sample	Wt.(g) T1	Wt.(g) T2	Wt.(g) T3	%Ash T1	%Ash T2	%Ash T3	M	STD	RSD
Streams									
Mixed furniture	1.002	1.002	1.0935	0.5133	0.4991	0.5112	0.5079	0.0077	1.54
Demolition	1.0026	1.003	1.1434	1.5916	1.9222	1.8562	1.7900	0.1750	9.78
Mixed stream (unknown)	1.0024	1.002	1.0706	1.9883	1.3905	1.7895	1.7228	0.3045	17.68
New furniture	1.0024	1.001	1.1065	0.6042	0.7590	0.7052	0.6895	0.0786	11.40
Old furniture	1.0012	1.001	1.0543	0.6314	0.5722	0.6259	0.6098	0.0327	5.36
Industrial									
Pellets	1.002	1.002	1.1756	0.9069	0.9198	0.9016	0.9094	0.0094	1.04
Chips wood	1.0005	1.002	1.0561	2.6253	2.9083	2.7897	2.7744	0.1421	5.12
L.d.									
L.d. (3-7 m)	1.0096	1.003	1.0069	1.3985	1.2104	1.5680	1.3923	0.1789	12.85
L.d. (7-9 m)	1.0001	1.003	1.0736	2.5359	2.6499	2.5689	2.5849	0.0587	2.27
L.d. (9-11 m)	1.0012	1.001	1.0193	5.0993	4.9603	5.2586	5.1060	0.1493	2.93
L.d. (11-13.5 m)	1.0011	1.002	1.0081	11.1801	10.8194	11.2350	11.0782	0.2258	2.04
L.d. (13.5-17 m)	1.0034	1.002	1.0946	16.1894	19.0621	18.2350	17.8288	1.4788	8.30
L.d. (17-20 m)	1.0065	1.002	1.0844	11.3099	14.9454	12.5680	12.9411	1.8462	14.27
L.d. (20-23 m)	1.0003	1.002	1.0731	6.0726	6.7252	6.3250	6.3743	0.3290	5.16
L.d. (23-25 m)	1.0019	1.003	1.0111	9.5947	12.9304	10.2590	10.9280	1.7657	16.16
L.d. (25-27 m)	1.006	1.002	1.0041	12.7302	14.3614	13.3250	13.4722	0.8255	6.13
L.d. (29-32.5 m)	1.005	1.002	1.1625	10.0425	12.0429	11.2358	11.1071	1.0064	9.06
L.d. (32.5-35 m)	1.005	1.002	1.0195	8.0716	7.2775	7.5862	7.6451	0.4003	5.24
L.d. (35-36.5 m)	1.0002	1.001	1.0046	9.2801	9.6415	9.1256	9.3491	0.2648	2.83
L.d. (36-37.5 m)	1.009	1.001	1.0184	9.0504	7.3981	8.2350	8.2278	0.8262	10.04
L.d. (37.5-39 m)	1.0018	1.003	1.0358	7.9026	8.9808	8.5236	8.4690	0.5411	6.39
L.d. (40-41.5 m)	1.009	1.002	1.0063	5.6884	5.9691	5.6890	5.7822	0.1619	2.80
L.d. (41-43 m)	1.003	1.001	1.0662	12.6490	13.9323	13.2350	13.2721	0.6425	4.85
L.d. (44.5-46 m)	1.0044	1.002	1.0003	10.2123	11.9836	12.5600	11.5853	1.2235	10.56
L.d. (46-48 m)	1.0059	1.001	1.0231	6.0813	6.2183	6.2350	6.1782	0.0843	1.37
L.d. (48-50.5 m)	1.0027	1.002	1.1059	10.5958	10.5664	10.6234	10.5952	0.0285	0.27
L.d. (50-51 m)	1.0012	1.001	1.0025	4.0762	3.5961	3.6126	3.7616	0.2726	7.25
L.d. (53-55 m)	1.0021	1.003	1.0725	4.3055	6.6022	5.3560	5.4212	1.1497	21.21

Wt. (g): weight of sample; M: Mean; STD: Standard deviation; RSD: Relative standard deviation

D.2.3 Volatile matter

Volatile matter content (%) determined by standard method E-872 and statistical analysis.

Name of waste wood sample	Wt.(g) T1	Wt.(g) T2	Wt.(g) T3	%VM T1	%VM T2	%VM T3	M	STD	RSD
Streams									
Mixed furniture	1.0010	1.0020	1.0020	86.4562	86.7453	86.5963	86.5993	0.1446	0.1670
Demolition	1.0006	1.0026	1.0030	85.0362	85.3690	85.2360	85.2137	0.1675	0.1966
Mixed stream (unknown)	1.0008	1.0024	1.0020	84.6446	85.0020	85.3260	84.9909	0.3408	0.4010
New furniture	1.0012	1.0024	1.0010	83.8028	84.2360	83.5020	83.8469	0.3690	0.4401
Old furniture	1.0004	1.0012	1.0010	86.3863	86.2350	86.3259	86.3157	0.0762	0.0883
Industrial									
Pellets	1.0004	1.0020	1.0020	86.9555	85.9963	87.0025	86.6514	0.5678	0.6553
Chips wood	1.0016	1.0005	1.0020	80.6856	80.2360	80.3650	80.4289	0.2315	0.2879
L.d.									
L.d. (3-7 m)	1.0006	1.0096	1.0030	63.4404	63.2150	63.2680	63.3078	0.1178	0.1861
L.d. (7-9 m)	1.0004	1.0001	1.0030	63.2667	63.2580	63.2580	63.2609	0.0050	0.0079
L.d. (9-11 m)	1.0014	1.0012	1.0010	54.0037	54.2360	54.4236	54.2211	0.2103	0.3879
L.d. (11-13.5 m)	1.0008	1.0011	1.0020	35.1190	35.1245	35.3690	35.2042	0.1428	0.4055
L.d. (13.5-17 m)	1.0010	1.0034	1.0020	25.4885	26.0020	26.3580	25.9495	0.4371	1.6846
L.d. (17-20 m)	1.0002	1.0065	1.0020	48.5951	48.2560	48.3560	48.4024	0.1743	0.3600
L.d. (20-23 m)	1.0012	1.0003	1.0020	42.1756	42.0124	42.1235	42.1038	0.0834	0.1980
L.d. (23-25 m)	1.0004	1.0019	1.0030	49.8316	49.2350	48.9900	49.3522	0.4329	0.8772
L.d. (25-27 m)	1.0004	1.0060	1.0020	47.2272	46.9953	46.2350	46.8192	0.5190	1.1086
L.d. (29-32.5 m)	1.0006	1.0050	1.0020	56.2377	57.0250	57.0230	56.7619	0.4540	0.7998
L.d. (32.5-35 m)	1.0016	1.0050	1.0020	35.7065	35.2630	35.2680	35.4125	0.2546	0.7190
L.d. (35-36.5 m)	1.0006	1.0002	1.0010	30.0661	30.0246	30.0568	30.0492	0.0218	0.0725
L.d. (36-37.5 m)	1.0014	1.0090	1.0010	52.7900	52.3690	52.6840	52.6143	0.2190	0.4162
L.d. (37.5-39 m)	1.0012	1.0018	1.0030	48.9492	45.0237	45.2360	46.4029	2.2076	4.7575
L.d. (40-41.5 m)	1.0016	1.0090	1.0020	55.5133	55.5210	55.6840	55.5728	0.0964	0.1735
L.d. (41-43 m)	1.0006	1.0030	1.0010	36.8831	37.0250	37.2450	37.0510	0.1824	0.4922
L.d. (44.5-46 m)	1.0050	1.0044	1.0020	36.6774	36.9850	36.8520	36.8381	0.1543	0.4188
L.d. (46-48 m)	1.0012	1.0059	1.0010	47.4518	47.2368	47.2360	47.3082	0.1244	0.2170
L.d. (48-50.5 m)	1.0004	1.0027	1.0020	46.6287	47.0235	47.3200	46.9907	0.3468	0.7381
L.d. (50-51 m)	1.0014	1.0012	1.0010	67.3418	67.2150	67.2350	67.2639	0.0682	0.1013
L.d. (53-55 m)	1.0014	1.0021	1.0030	80.9111	80.1236	80.1235	80.3861	0.4547	0.5656

Wt. (g): weight of sample; M: Mean; STD: Standard deviation; RSD: Relative standard deviation

D.2.4 Fixed carbon (FC) content

Fixed carbon content (%) determined by difference and statistical analysis.

Name of waste wood sample	M* %	ASH* %	VM*%	FC%
Streams				
Mixed furniture	8.9350	0.5079	86.5993	3.9578
Demolition	11.1880	1.7900	85.2137	1.8083
Mixed stream (unknown)	8.6900	1.7228	84.9909	4.5963
New furniture	9.8560	0.6895	83.8469	5.6076
Old furniture	9.5490	0.6098	86.3157	3.5255
Industrial				
Pellets	9.0790	0.9094	86.6514	3.3602
Chips wood	8.7320	2.7744	80.4289	8.0647
L.d.				
L.d. (3-7 m)	33.7254	1.3923	63.3078	1.5745
L.d. (7-9 m)	27.9350	2.5849	63.2609	6.2192
L.d. (9-11 m)	38.3725	5.1060	54.2211	2.3004
L.d. (11-13.5 m)	39.0540	11.0782	35.2042	14.6636
L.d. (13.5-17 m)	45.8960	17.8288	25.9495	10.3257
L.d. (17-20 m)	38.4610	12.9411	48.4024	0.1955
L.d. (20-23 m)	27.6540	6.3743	42.1038	23.8679
L.d. (23-25 m)	37.2610	10.9280	49.3522	2.4588
L.d. (25-27 m)	26.4540	13.4722	46.8192	13.2546
L.d. (29-32.5 m)	22.2780	11.1071	56.7619	9.8530
L.d. (32.5-35 m)	52.2540	7.6451	35.4125	4.6884
L.d. (35-36.5 m)	39.2080	9.3491	30.0492	21.3937
L.d. (36-37.5 m)	38.7540	8.2278	52.6143	0.4039
L.d. (37.5-39 m)	32.0490	8.4690	46.4029	13.0791
L.d. (40-41.5 m)	38.2874	5.7822	55.5728	0.3576
L.d. (41-43 m)	45.5503	13.2721	37.051	4.1266
L.d. (44.5-46 m)	38.3480	11.5853	36.8381	13.2286
L.d. (46-48 m)	46.0040	6.1782	47.3082	0.5096
L.d. (48-50.5 m)	41.4790	10.5952	46.9907	0.9351
L.d. (50-51 m)	9.8880	3.7616	67.2639	19.0865
L.d. (53-55 m)	7.7280	5.4212	80.3861	6.4647

* Mean; M: Moisture; ASH: Ash content; VM: Volatile matter; FC: Fixed carbon;

D.3 Ultimate analysis.

D.3.1 Carbon content

Carbon (%) determined by CHNS analyser and statistical analysis.

Name of waste wood sample	Wt.(mg) T1	Wt.(mg) T2	Wt.(mg) T3	Carbon Total (%) T1	Carbon Total (%) T2	Carbon Total (%) T3	M	STD	RSD
Streams									
Mixed furniture	30.4370	29.6220	26.6160	49.5724	49.5423	55.2486	51.4544	3.2859	6.3860
Demolition	29.6410	29.8500	31.3320	50.3475	49.5691	50.8077	50.2414	0.6261	1.2461
Mixed stream (unknown)	29.6220	30.4960	29.5650	51.6240	49.5483	49.2470	50.1398	1.2942	2.5812
New furniture	30.6170	29.8860	31.7830	49.0119	48.9511	49.2167	49.0599	0.1392	0.2837
Old furniture	29.3780	29.8180	30.5570	49.9739	50.0792	50.0020	50.0184	0.0545	0.1090
Industrial									
Pellets	30.3860	29.0930	29.7990	50.6812	50.9051	50.4689	50.6851	0.2181	0.4304
Chips wood	33.4060	29.4400	30.1430	48.7008	47.3077	48.8482	48.2856	0.8501	1.7605
L.d.									
L.d. (3-7 m)	30.6330	30.8550	30.0770	49.4917	48.9330	49.6632	49.3626	0.3818	0.7735
L.d. (7-9 m)	30.2390	30.1830	30.8550	47.1556	49.4534	47.3636	47.9909	1.2708	2.6481
L.d. (9-11 m)	30.3930	30.6510	30.1760	45.1735	43.7689	44.2494	44.3973	0.7139	1.6080
L.d. (11-13.5 m)	30.2900	30.8880	30.5440	44.3968	37.1404	40.3131	40.6168	3.6377	8.9562
L.d. (13.5-17 m)	30.6920	30.4520	30.3680	42.4582	43.5099	41.8715	42.6132	0.8301	1.9481
L.d. (17-20 m)	30.4020	30.6370	30.8350	42.5805	46.6502	44.8196	44.6834	2.0382	4.5615
L.d. (20-23 m)	30.6600	30.6300	30.2990	53.6093	47.2796	47.2594	49.3828	3.6603	7.4120
L.d. (23-25 m)	30.2270	30.5770	30.6220	41.4250	46.2964	39.7561	42.4925	3.3983	7.9975
L.d. (25-27 m)	30.0200	30.4350	30.1620	42.2193	44.7766	39.0873	42.0277	2.8495	6.7800
L.d. (29-32.5 m)	30.6210	30.1200	30.1640	46.6160	47.7611	44.1592	46.1787	1.8403	3.9852
L.d. (32.5-35 m)	30.2200	30.4300	30.7510	44.1786	47.4667	45.4602	45.7018	1.6573	3.6263
L.d. (35-36.5 m)	30.0290	30.5310	30.5040	43.0468	46.3369	46.2552	45.2129	1.8764	4.1501
L.d. (36-37.5 m)	30.7150	30.8480	30.6680	48.1023	47.4923	47.1749	47.5898	0.4713	0.9904
L.d. (37.5-39 m)	30.2080	30.7370	30.7350	41.1809	45.7747	46.0319	44.3291	2.7295	6.1574
L.d. (40-41.5 m)	30.6400	30.6090	30.3010	49.6451	48.9969	49.0702	49.2374	0.3550	0.7209
L.d. (41-43 m)	30.4900	30.2810	30.1040	42.6523	42.5076	41.5659	42.2419	0.5899	1.3965
L.d. (44.5-46 m)	30.2570	30.7860	30.4700	39.4109	38.9742	36.2474	38.2108	1.7143	4.4865
L.d. (46-48 m)	30.4800	30.8460	30.8570	47.6501	46.7314	46.0395	46.8070	0.8080	1.7262
L.d. (48-50.5 m)	30.6640	30.3900	30.1940	44.0401	43.6745	43.6520	43.7889	0.2179	0.4976
L.d. (50-51 m)	30.1120	30.4270	30.0310	46.3193	38.1157	52.2322	45.5557	7.0892	15.5615
L.d. (53-55 m)	30.0930	30.0210	30.0550	47.4017	47.5394	47.2454	47.3955	0.1471	0.3104

Wt. (g): weight of sample; M: Mean; STD: Standard deviation; RSD: Relative standard deviation

D.3.2 Nitrogen content

Nitrogen (%) determined by CHNS analyser and statistical analysis.

Name of waste wood sample	Wt.(mg) T1	Wt.(mg) T2	Wt.(mg) T3	Nitrogen total (%) T1	Nitrogen total (%) T2	Nitrogen total (%) T3	M	STD	RSD
Streams									
Mixed furniture	30.4370	29.6220	26.6160	0.0843	0.0743	0.1045	0.0877	0.0154	17.5236
Demolition	29.6410	29.8500	31.3320	0.0639	0.0550	0.0617	0.0602	0.0046	7.6969
Mixed stream (unknown)	29.6220	30.4960	29.5650	0.6576	0.3266	0.3520	0.4454	0.1842	41.3551
New furniture	30.6170	29.8860	31.7830	0.1184	0.1047	0.1609	0.1280	0.0293	22.8777
Old furniture	29.3780	29.8180	30.5570	0.0613	0.0575	0.0514	0.0568	0.0050	8.7845
Industrial									
Pellets	30.3860	29.0930	29.7990	0.0891	0.0845	0.0984	0.0907	0.0071	7.8034
Chips wood	33.4060	29.4400	30.1430	1.9064	2.1245	1.8905	1.9738	0.1307	6.6242
L.d.									
L.d. (3-7 m)	30.6330	30.8550	30.0770	0.1873	0.2094	0.1747	0.1905	0.0176	9.2255
L.d. (7-9 m)	30.2390	30.1830	30.8550	0.3262	0.2497	0.2989	0.2916	0.0387	13.2826
L.d. (9-11 m)	30.3930	30.6510	30.1760	1.0246	0.9863	0.7478	0.9196	0.1500	16.3136
L.d. (11-13.5 m)	30.2900	30.8880	30.5440	1.4301	1.3973	1.4833	1.4369	0.0434	3.0195
L.d. (13.5-17 m)	30.6920	30.4520	30.3680	0.7362	0.7430	0.7871	0.7554	0.0276	3.6567
L.d. (17-20 m)	30.4020	30.6370	30.8350	1.2739	1.3669	1.2981	1.3130	0.0482	3.6747
L.d. (20-23 m)	30.6600	30.6300	30.2990	0.6282	0.6971	0.6873	0.6709	0.0373	5.5589
L.d. (23-25 m)	30.2270	30.5770	30.6220	0.9593	1.0642	0.8975	0.9737	0.0843	8.6546
L.d. (25-27 m)	30.0200	30.4350	30.1620	0.5922	0.5272	0.4851	0.5348	0.0540	10.0885
L.d. (29-32.5 m)	30.6210	30.1200	30.1640	0.6282	0.2210	0.6647	0.5047	0.2463	48.8075
L.d. (32.5-35 m)	30.2200	30.4300	30.7510	0.7488	0.6578	0.6770	0.6945	0.0480	6.9051
L.d. (35-36.5 m)	30.0290	30.5310	30.5040	0.8863	0.9506	0.8033	0.8801	0.0738	8.3869
L.d. (36-37.5 m)	30.7150	30.8480	30.6680	0.8656	0.8408	0.8387	0.8484	0.0149	1.7605
L.d. (37.5-39 m)	30.2080	30.7370	30.7350	0.5773	0.4800	0.3802	0.4792	0.0986	20.5669
L.d. (40-41.5 m)	30.6400	30.6090	30.3010	0.4373	0.4546	0.4294	0.4404	0.0129	2.9205
L.d. (41-43 m)	30.4900	30.2810	30.1040	0.7249	0.6829	0.6380	0.6819	0.0435	6.3768
L.d. (44.5-46 m)	30.2570	30.7860	30.4700	0.7252	0.6348	0.6897	0.6832	0.0455	6.6643
L.d. (46-48 m)	30.4800	30.8460	30.8570	0.7669	0.8974	0.7561	0.8068	0.0787	9.7508
L.d. (48-50.5 m)	30.6640	30.3900	30.1940	0.6204	0.6012	0.5893	0.6036	0.0157	2.6031
L.d. (50-51 m)	30.1120	30.4270	30.0310	0.3269	0.2641	0.2828	0.2913	0.0323	11.0760
L.d. (53-55 m)	30.0930	30.0210	30.0550	0.4127	0.3556	0.4071	0.3918	0.0315	8.0346

Wt. (g): weight of sample; M: Mean; STD: Standard deviation; RSD: Relative standard deviation

D.3.3 Hydrogen content

Hydrogen (%) determined by CHNS analyser and statistical analysis.									
Name of waste wood sample	Wt.(mg) T1	Wt.(mg) T2	Wt.(mg) T3	H total (%)T1	H total (%)T2	H total (%) T3	M	STD	RSD
Streams									
Mixed furniture	30.437	29.622	26.616	7.0886	7.0828	7.8908	7.355	0.464	6.32
Demolition	29.641	29.850	31.332	7.1535	7.0483	7.2067	7.1362	0.080	1.13
Mixed stream (unknown)	29.622	30.496	29.565	7.3770	7.0465	6.9924	7.1386	0.208	2.92
New furniture	30.617	29.886	31.783	7.0362	6.9788	7.0644	7.0265	0.043	0.63
Old furniture	29.378	29.818	30.557	7.1756	7.1710	7.1560	7.1675	0.010	0.15
Industrial									
Pellets	30.386	29.093	29.799	7.1749	7.1818	7.1378	7.165	0.023	0.33
Chips wood	33.406	29.440	30.143	6.9615	6.7658	7.0010	6.9095	0.126	1.83
L.d.	30.633	30.855	30.077	7.5516	7.4557	7.4432	7.4835	0.059	0.798
L.d. (3-7 m)	30.239	30.183	30.855	7.6112	7.4829	7.2704	7.4548	0.172	2.4
L.d. (7-9 m)	30.393	30.651	30.176	6.7968	6.5338	6.8224	6.7177	0.159	2.38
L.d. (9-11 m)	30.290	30.888	30.544	6.6267	7.0522	No result	6.8395	3.954	57.82
L.d. (11-13.5 m)	30.692	30.452	30.368	6.2157	6.3670	6.0827	6.2218	0.142	2.29
L.d. (13.5-17 m)	30.402	30.637	30.835	6.2061	6.8243	6.5879	6.5394	0.312	4.78
L.d. (17-20 m)	30.660	30.630	30.299	6.9017	7.1357	7.1795	7.0723	0.149	2.12
L.d. (20-23 m)	30.227	30.577	30.622	5.9177	6.6351	5.7835	6.1121	0.457	7.49
L.d. (23-25 m)	30.020	30.435	30.162	6.2506	6.5549	5.7391	6.1815	0.412	6.66
L.d. (25-27 m)	30.621	30.120	30.164	6.7964	7.0191	6.3525	6.7227	0.3394	5.05
L.d. (29-32.5 m)	30.220	30.430	30.751	6.6146	7.2762	6.8862	6.9257	0.332	4.81
L.d. (32.5-35 m)	30.029	30.531	30.504	6.1071	6.5723	6.6244	6.4346	0.284	4.43
L.d. (35-36.5 m)	30.715	30.848	30.668	7.1940	7.1605	7.1019	7.1521	0.046	0.65
L.d. (36-37.5 m)	30.208	30.737	30.735	5.9840	6.6399	6.7805	6.4682	0.425	6.57
L.d. (37.5-39 m)	30.640	30.609	30.301	7.4483	7.3935	7.3923	7.4114	0.032	0.43
L.d. (40-41.5 m)	30.490	30.281	30.104	6.2531	6.1783	6.0862	6.1725	0.083	1.35
L.d. (41-43 m)	30.257	30.786	30.470	6.3435	5.9944	5.5675	5.9685	0.388	6.51
L.d. (44.5-46 m)	30.480	30.846	30.857	6.9043	6.7246	6.6628	6.7639	0.125	1.85
L.d. (46-48 m)	30.664	30.390	30.194	6.5994	6.5524	6.5045	6.5521	0.047	0.72
L.d. (48-50.5 m)	30.112	30.427	30.031	6.9307	6.9520	7.0204	6.9677	0.046	0.67
L.d. (50-51 m)	30.093	30.021	30.055	7.0271	7.0060	6.9707	7.0012	0.028	0.40

Wt. (g): weight of sample; M: Mean; STD: Standard deviation; RSD: Relative standard deviation

D.3.4 Carbon/Nitrogen ratio

C/N Ratio									
Name of waste wood sample	Wt.(mg) T1	Wt.(mg) T2	Wt.(mg) T3	C/N Ratio T1	C/N Ratio T2	C/N Ratio T3	M	STD	RSD
Streams									
Mixed furniture	30.4370	29.6220	26.6160	587.9944	666.4378	528.6506	594.3610	69.113	11.6283
Demolition	29.6410	29.8500	31.3320	787.9573	901.2473	823.4709	837.5585	57.944	6.9182
Mixed stream (unknown)	29.6220	30.4960	29.5650	78.5042	151.7045	139.8994	123.3693	39.300	31.8557
New furniture	30.6170	29.8860	31.7830	413.7943	467.6081	305.9518	395.7847	82.319	20.7990
Old furniture	29.3780	29.8180	30.5570	814.9551	870.8953	972.1366	885.9957	79.671	8.9923
Industrial									
Pellets	30.3860	29.0930	29.7990	569.0984	602.1020	512.8072	561.3359	45.150	8.0434
Chips wood	33.4060	29.4400	30.1430	25.5462	22.2679	25.8389	24.5510	1.9826	8.0755
L.d.	30.6330	30.8550	30.0770	264.1965	280.1345	284.3146	276.2152	10.616	3.8435
L.d. (3-7 m)	30.2390	30.1830	30.8550	144.5706	165.4523	158.4608	156.1612	10.629	6.8065
L.d. (7-9 m)	30.3930	30.6510	30.1760	44.0881	58.5339	59.1765	53.9328	8.5318	15.8193
L.d. (9-11 m)	30.2900	30.8880	30.5440	31.0456	25.0398	27.1789	27.7548	3.0440	10.9676
L.d. (11-13.5 m)	30.6920	30.4520	30.3680	57.6755	55.2815	53.1998	55.3856	2.2397	4.0438
L.d. (13.5-17 m)	30.4020	30.6370	30.8350	33.4254	35.9364	34.5262	34.6293	1.2587	3.6347
L.d. (17-20 m)	30.6600	30.6300	30.2990	85.3434	68.7879	68.7585	74.2966	9.5668	12.8765
L.d. (20-23 m)	30.2270	30.5770	30.6220	43.1813	51.5825	44.2954	46.3530	4.5630	9.8439
L.d. (23-25 m)	30.0200	30.4350	30.1620	71.2973	92.3133	80.5840	81.3982	10.531	12.9384
L.d. (25-27 m)	30.6210	30.1200	30.1640	74.2006	71.8516	66.4330	70.8284	3.9836	5.6243
L.d. (29-32.5 m)	30.2200	30.4300	30.7510	58.9989	70.1175	67.1535	65.4233	5.7577	8.8007
L.d. (32.5-35 m)	30.0290	30.5310	30.5040	48.5704	57.6803	57.5786	54.6098	5.2305	9.5780
L.d. (36-37.5 m)	30.7150	30.8480	30.6680	55.5739	56.6278	56.2493	56.1503	0.5339	0.9509
L.d. (37.5-39 m)	30.2080	30.7370	30.7350	71.3322	120.3928	121.0694	104.2648	28.522	27.3558
L.d. (40-41.5 m)	30.6400	30.6090	30.3010	113.5363	114.0995	114.2701	113.9686	0.3840	0.3369
L.d. (41-43 m)	30.4900	30.2810	30.1040	58.8381	66.6306	65.1546	63.5411	4.1392	6.5143
L.d. (44.5-46 m)	30.2570	30.7860	30.4700	54.3466	56.5117	52.5580	54.4721	1.9798	3.6346
L.d. (46-48 m)	30.4800	30.8460	30.8570	62.1324	61.8089	60.8937	61.6117	0.6425	1.0428
L.d. (48-50.5 m)	30.6640	30.3900	30.1940	70.9843	74.1150	74.0767	73.0586	1.7966	2.4591
L.d. (50-51 m)	30.1120	30.4270	30.0310	141.6734	134.7706	184.6842	153.7094	27.046	17.5956
L.d. (53-55 m)	30.0930	30.0210	30.0550	114.8461	116.7672	116.0450	115.8861	0.9704	0.8374

Wt. (g): weight of sample; M: Mean; STD: Standard deviation; RSD: Relative standard deviation

D.3.5 Sulphur content

Sulphur (%) determined by ICP-MS.						
Name of waste wood sample	Wt. (%) T1	Wt. (%) T2	Wt. (%) T3	M	STD	RSD
Streams						
Mixed furniture	0.0013	0.0019	0.0024	0.0019	0.0005	27.8499
Demolition	0.0021	0.0017	0.0015	0.0018	0.0003	16.0628
Mixed stream (unknown)	0.0006	0.0008	0.0008	0.0007	0.0001	20.5091
New furniture	0.0004	0.0012	0.0012	0.0009	0.0005	50.5653
Old furniture	0.0007	0.0010	0.0017	0.0011	0.0005	49.0735
Industrial						
Pellets	0.0024	0.0028	0.0023	0.0025	0.0002	9.7406
Chips wood	0.0038	0.0012	0.0017	0.0022	0.0014	60.7141
L.d.						
L.d. (3-7 m)	0.0030	0.0040	0.0039	0.0036	0.0006	15.9172
L.d. (7-9 m)	0.0008	0.0011	0.0009	0.0009	0.0001	15.4478
L.d. (9-11 m)	0.0023	0.0034	0.0043	0.0033	0.0010	30.2085
L.d. (11-13.5 m)	0.0066	0.0064	0.0064	0.0065	0.0001	1.4265
L.d. (13.5-17 m)	0.0045	0.0050	0.0043	0.0046	0.0004	7.9820
L.d. (17-20 m)	0.0044	0.0036	0.0064	0.0048	0.0014	30.0683
L.d. (20-23 m)	0.0047	0.0048	0.0049	0.0048	0.0001	2.1828
L.d. (23-25 m)	0.0178	0.0166	0.0145	0.0163	0.0017	10.1378
L.d. (25-27 m)	0.0102	0.0080	0.0148	0.0110	0.0035	31.3584
L.d. (29-32.5 m)	0.0105	0.0104	0.0109	0.0106	0.0002	2.1390
L.d. (32.5-35 m)	0.0050	0.0062	0.0057	0.0056	0.0006	10.8748
L.d. (35-36.5 m)	0.0057	0.0066	0.0078	0.0067	0.0011	16.1526
L.d. (36-37.5 m)	0.0023	0.0024	0.0023	0.0023	0.0000	1.9158
L.d. (37.5-39 m)	0.0120	0.0128	0.0112	0.0120	0.0008	6.4250
L.d. (40-41.5 m)	0.0053	0.0041	0.0034	0.0043	0.0010	22.9964
L.d. (41-43 m)	0.0072	0.0050	0.0057	0.0060	0.0011	19.0900
L.d. (44.5-46 m)	0.0067	0.0069	0.0077	0.0071	0.0005	7.0942
L.d. (46-48 m)	0.0098	0.0088	0.0102	0.0096	0.0007	7.2460
L.d. (48-50.5 m)	0.0109	0.0061	0.0101	0.0090	0.0026	28.3501
L.d. (50-51 m)	0.0177	0.0165	0.0049	0.0130	0.0071	54.4993
L.d. (53-55 m)	0.0064	0.0165	0.0115	0.0115	0.0050	43.8182

Wt. (g): weight of sample; M: Mean; STD: Standard deviation; RSD: Relative standard deviation

D.3.6 Oxygen content

Oxygen (%)					
Name of waste wood sample	M.N (%)	M.C (%)	M.H (%)	M.S (%)	O* (%)
Streams					
Mixed furniture	0.0877	51.4544	7.3541	0.0019	41.1019
Demolition	0.0602	50.2414	7.1362	0.0018	42.5604
Mixed stream (unknown)	0.4454	50.1398	7.1386	0.0007	42.2754
New furniture	0.1280	49.0599	7.0265	0.0009	43.7847
Old furniture	0.0568	50.0184	7.1675	0.0011	42.7562
Industrial					
Pellets	0.0907	50.6851	7.1649	0.0025	42.0569
Chips wood	1.9738	48.2856	6.9095	0.0022	42.8290
L.d.					
L.d. (3-7 m)	0.1905	49.3626	7.4835	0.0036	42.9598
L.d. (7-9 m)	0.2916	47.9909	7.4548	0.0009	44.2618
L.d. (9-11 m)	0.9196	44.3973	6.7177	0.0033	47.9622
L.d. (11-13.5 m)	1.4369	40.6168	6.8395	0.0065	51.1005
L.d. (13.5-17 m)	0.7554	42.6132	6.2218	0.0046	50.4050
L.d. (17-20 m)	1.3130	44.6834	6.5394	0.0048	47.4594
L.d. (20-23 m)	0.6709	49.3828	7.0723	0.0048	42.8693
L.d. (23-25 m)	0.9737	42.4925	6.1121	0.0163	50.4054
L.d. (25-27 m)	0.5348	42.0277	6.1815	0.0110	51.2449
L.d. (29-32.5 m)	0.5047	46.1787	6.7227	0.0106	46.5833
L.d. (32.5-35 m)	0.6945	45.7018	6.9257	0.0056	46.6724
L.d. (35-36.5 m)	0.8801	45.2129	6.4346	0.0067	47.4657
L.d. (36-37.5 m)	0.8484	47.5898	7.1521	0.0023	44.4073
L.d. (37.5-39 m)	0.4792	44.3291	6.4682	0.0120	48.7115
L.d. (40-41.5 m)	0.4404	49.2374	7.4114	0.0043	42.9065
L.d. (41-43 m)	0.6819	42.2419	6.1725	0.0060	50.8977
L.d. (44.5-46 m)	0.6832	38.2108	5.9685	0.0071	55.1304
L.d. (46-48 m)	0.8068	46.8070	6.7639	0.0096	45.6127
L.d. (48-50.5 m)	0.6036	43.7889	6.5521	0.0090	49.0464
L.d. (50-51 m)	0.2913	45.5557	6.9677	0.0130	47.1723
L.d. (53-55 m)	0.3918	47.3955	7.0012	0.0115	45.2000

M: Mean; *calculation

D.4 Calorific value (CV), TCV and HHV

D.4.1 Calorific value (CV)

Calorific value (MJ g⁻¹) measured using Bomb Combustion.

Name of waste wood sample	Wt.(g) T1	Wt.(g) T2	Wt.(g) T3	Experimenta- l CVT1 (MJ g ⁻¹)	Experiment- al CVT2 (MJ g ⁻¹)	Experiment- al CVT3 (MJ g ⁻¹)	Mean	STD	RSD
Streams									
Mixed furniture	0.6006	0.6034	0.6030	18.6300	18.6886	18.4575	18.592	0.12	0.6462
Demolition	0.6023	0.6011	0.6005	17.8332	17.7950	17.9539	17.860	0.08	0.4644
Mixed stream (unknown)	0.6030	0.6024	0.6057	19.2441	17.9276	17.9831	18.384	0.74	4.0499
New furniture	0.6057	0.6053	0.6041	17.5129	18.5473	17.7877	17.949	0.53	2.9851
Old furniture	0.6075	0.6003	0.6075	18.7368	18.3568	18.2217	18.438	0.26	1.4485
Industrial									
Pellets	0.6037	0.6057	0.6016	17.5948	17.8282	18.2687	17.897	0.34	1.9121
Chips wood	0.6095	0.6012	0.6067	18.164	18.1663	18.2921	18.207	0.07	0.4026
L.d.									
L.d. (3-7 m)	0.5009	0.5043	0.5078	18.7002	18.5858	18.6465	18.644	0.05	0.3070
L.d. (7-9 m)	0.5079	0.5068	0.5042	18.4948	18.3471	18.4073	18.416	0.07	0.4033
L.d. (9-11 m)	0.5027	0.5072	0.5029	18.1924	17.9033	17.7462	17.947	0.22	1.2611
L.d. (11-13.5 m)	0.6009	0.6040	0.6010	17.3885	16.7639	16.5734	16.908	0.42	2.5217
L.d. (13.5-17 m)	0.5027	0.5033	0.5015	17.4879	16.4064	16.4768	16.790	0.60	3.6039
L.d. (17-20 m)	0.5016	0.5032	0.5056	16.6298	17.6783	17.8217	17.376	0.65	3.7447
L.d. (20-23 m)	0.5039	0.4006	0.4009	18.545	18.151	18.1472	18.281	0.22	1.2504
L.d. (23-25 m)	0.50076	0.503	0.5002	17.9296	18.1951	16.8328	17.652	0.72	4.0911
L.d. (25-27 m)	0.5011	0.5079	0.5090	18.9818	18.1013	17.3196	18.134	0.83	4.5857
L.d. (29-32.5 m)	0.5003	0.5027	0.6002	16.598	17.8944	18.0588	17.517	0.80	4.5679
L.d. (32.5-35 m)	0.5062	0.5018	0.5085	18.2859	18.4013	17.7943	18.160	0.32	1.7750
L.d. (35-36.5 m)	0.5049	0.5016	0.5016	18.3476	18.2452	17.0749	17.889	0.70	3.9526
L.d. (36-37.5 m)	0.5056	0.5034	0.5074	18.5152	19.315	19.0044	18.944	0.40	2.1283
L.d. (37.5-39 m)	0.4035	0.4052	0.4092	18.0214	18.2582	17.4744	17.918	0.40	2.2436
L.d. (40-41.5 m)	0.5500	0.5087	0.5008	19.742	19.7164	19.5338	19.664	0.11	0.5774
L.d. (41-43 m)	0.4061	0.4066	0.4076	15.4152	13.8599	14.3458	14.540	0.79	5.4723
L.d. (44.5-46 m)	0.4045	0.4080	0.4078	17.8703	17.6615	17.1993	17.577	0.34	1.9536
L.d. (46-48 m)	0.5080	0.5087	0.5072	18.1445	18.5345	18.2761	18.318	0.19	1.0831
L.d. (48-50.5 m)	0.6447	0.6065	0.60436	17.733	17.2096	17.7244	17.555	0.29	1.7073
L.d. (50-51 m)	0.54915	0.5704	0.58137	18.2397	18.3818	19.1119	18.577	0.46	2.5190
L.d. (53-55 m)	0.6035	0.6008	0.6047	17.8377	17.473	17.6473	17.652	0.18	1.0333

Wt. (g): weight of sample; M: Mean; STD: Standard deviation; RSD: Relative standard deviation

D.4.2 TCV and HHV

Name of waste wood sample	M C (%)	M H (%)	M N (%)	Oxygen *(%)	M S (%)	TCV *(MJ g ⁻¹)	HHVd*(MJ g ⁻¹)
Streams							
Mixed furniture	51.4544	7.3541	0.0877	41.1019	0.0019	21.1880	22.3663
Demolition	50.2414	7.1362	0.0602	42.5604	0.0018	20.3048	21.5086
Mixed stream (unknown)	50.1398	7.1386	0.4454	42.2754	0.0007	19.5082	21.5010
New furniture	49.0599	7.0265	0.1280	43.7847	0.0009	19.4218	20.8624
Old furniture	50.0184	7.1675	0.0568	42.7562	0.0011	20.2518	21.4723
Industrial							
Pellets	50.6851	7.1649	0.0907	42.0569	0.0025	20.5077	21.7675
Chips wood	48.2856	6.9095	1.9738	42.8290	0.0022	15.2623	20.4815
L.d.							
L.d. (3-7 m)	49.3626	7.4835	0.1905	42.9598	0.0036	20.1692	21.5342
L.d. (7-9 m)	47.9909	7.4548	0.2916	44.2618	0.0009	19.2557	20.9021
L.d. (9-11 m)	44.3973	6.7177	0.9196	47.9622	0.0033	15.1128	18.2911
L.d. (11-13.5 m)	40.6168	6.8395	1.4369	51.1005	0.0065	12.4487	16.6998
L.d. (13.5-17 m)	42.6132	6.2218	0.7554	50.4050	0.0046	13.7784	16.6085
L.d. (17-20 m)	44.6834	6.5394	1.3130	47.4594	0.0048	14.2053	18.1048
L.d. (20-23 m)	49.3828	7.0723	0.6709	42.8693	0.0048	18.5948	20.9960
L.d. (23-25 m)	42.4925	6.1121	0.9737	50.4054	0.0163	13.1229	16.5806
L.d. (25-27 m)	42.0277	6.1815	0.5348	51.2449	0.0110	13.8594	16.3657
L.d. (29-32.5 m)	46.1787	6.7227	0.5047	46.5833	0.0106	16.8014	18.9847
L.d. (32.5-35 m)	45.7018	6.9257	0.6945	46.6724	0.0056	16.5175	19.1179
L.d. (35-36.5 m)	45.2129	6.4346	0.8801	47.4657	0.0067	15.1428	18.2480
L.d. (36-37.5 m)	47.5898	7.1521	0.8484	44.4073	0.0023	17.4977	20.2632
L.d. (37.5-39 m)	44.3291	6.4682	0.4792	48.7115	0.0120	15.5454	17.8753
L.d. (40-41.5 m)	49.2374	7.4114	0.4404	42.9065	0.0043	19.5073	21.3569
L.d. (41-43 m)	42.2419	6.1725	0.6819	50.8977	0.0060	13.6626	16.4040
L.d. (44.5-46 m)	38.2108	5.9685	0.6832	55.1304	0.0071	11.3672	14.4176
L.d. (46-48 m)	46.8070	6.7639	0.8068	45.6127	0.0096	16.5847	19.4524
L.d. (48-50.5 m)	43.7889	6.5521	0.6036	49.0464	0.0090	15.1706	17.7039
L.d. (50-51 m)	45.5557	6.9677	0.2913	47.1723	0.0130	17.2993	19.1535
L.d. (53-55 m)	47.3955	7.0012	0.3918	45.2000	0.0115	18.0556	20.0025

M: Mean; *calculation

D.5 Total Cl, Br, F, and P analysis by Bomb Combustion and Ion Chromatography

Total Cl, Br, F, and P concentration by bomb and IC analysis-waste wood samples				
Name of waste wood sample	M Cl (%)	M Br (%)	M F (%)	M P (%)
Streams				
Mixed furniture	0.03	0.00	0.00	0.01
Demolition	0.03	0.00	0.01	0.01
Mixed stream (unknown)	0.03	0.00	0.01	0.01
New furniture	0.03	0.00	0.00	0.01
Old furniture	0.03	0.00	0.02	0.01
Industrial				
Pellets	0.09	0.00	0.00	0.01
Chips wood	0.04	0.00	0.01	0.01
L.d.				
L.d. (3-7 m)	0.06	0.00	0.00	0.01
L.d. (7-9 m)	0.12	0.04	0.00	0.00
L.d. (9-11 m)	0.23	0.06	0.00	0.00
L.d. (11-13.5 m)	0.15	0.06	0.00	0.01
L.d. (13.5-17 m)	0.24	0.05	0.00	0.00
L.d. (17-20 m)	0.09	0.05	0.00	0.01
L.d. (20-23 m)	0.10	0.05	0.00	0.00
L.d. (23-25 m)	0.09	0.04	0.00	0.01
L.d. (25-27 m)	0.12	0.04	0.00	0.00
L.d. (29-32.5 m)	0.17	0.05	0.00	0.01
L.d. (32.5-35 m)	0.17	0.06	0.00	0.01
L.d. (35-36.5 m)	0.17	0.05	0.00	0.00
L.d. (36-37.5 m)	0.25	0.04	0.00	0.00
L.d. (37.5-39 m)	0.11	0.04	0.00	0.00
L.d. (40-41.5 m)	0.18	0.04	0.00	0.00
L.d. (41-43 m)	0.13	0.04	0.00	0.01
L.d. (44.5-46 m)	0.10	0.04	0.00	0.00
L.d. (46-48 m)	0.11	0.04	0.00	0.01
L.d. (48-50.5 m)	0.12	0.04	0.00	0.01
L.d. (50-51 m)	0.12	0.04	0.00	0.01
L.d. (53-55 m)	0.05	0.00	0.00	0.00
M: Mean				

D.6 Elements content measured by ICP-MS

D.6.1 Streams

Elements content measured by ICP-MS analysis (mixed furniture)						
Element (ppm)	C1	C2	C3	M	STD	RSD
Na	90.15	90.98	95.40	92.18	2.82	3.06
Mg	148.71	153.57	163.40	155.23	7.48	4.82
Al	34.98	29.99	40.60	35.19	5.31	15.08
Si	58.56	58.39	69.80	62.25	6.54	10.50
S	13.37	19.08	23.80	18.75	5.22	27.85
K	587.65	601.88	644.00	611.18	29.30	4.79
Ca	881.47	965.81	1224.00	1023.76	178.47	17.43
Fe	211.87	181.16	202.00	198.35	15.68	7.90
Ti	1.25	1.60	1.60	1.48	0.20	13.52
V	0.12	0.12	0.12	0.12	0.00	1.58
Cr	13.53	16.38	12.52	14.14	2.00	14.14
Mn	43.97	43.79	47.20	44.99	1.92	4.26
Co	1.18	1.08	1.22	1.16	0.07	6.26
Ni	11.19	9.80	12.36	11.12	1.28	11.54
Cu	24.59	2.70	3.02	10.10	12.54	124.18
Zn	75.15	61.19	58.20	64.85	9.05	13.96
As	0.04	0.03	0.04	0.04	0.01	23.20
Se	0.09	-0.08	-0.02	-0.01	0.09	-1459.70
Mo	0.41	0.34	0.38	0.38	0.03	9.01
Cd	0.15	0.15	0.16	0.16	0.01	4.19
Pb	1.78	0.57	0.55	0.97	0.70	72.84
Hg	0.45	0.38	0.31	0.38	0.07	18.94

C:concentration; M: Mean ; STD: Standard deviation; RSD: Relative standard deviation

Elements content measured by ICP-MS analysis (demolition)						
Element (ppm)	C1	C2	C3	M	STD	RSD
Na	247.01	149.45	169.45	188.64	51.53	27.32
Mg	181.47	161.84	171.64	171.65	9.82	5.72
Al	258.96	207.79	187.35	218.04	36.89	16.92
Si	116.73	100.50	91.09	102.77	12.97	12.62
S	20.72	16.50	15.37	17.53	2.82	16.06
K	284.86	225.77	246.62	252.42	29.97	11.87
Ca	1521.91	1268.73	1306.68	1365.78	136.54	10.00
Fe	1669.32	2897.10	2267.30	2277.91	613.96	26.95
Ti	14.26	10.39	9.39	11.35	2.57	22.69
V	0.42	0.35	0.34	0.37	0.04	12.01
Cr	62.95	52.15	45.74	53.61	8.70	16.22
Mn	111.35	107.49	114.56	111.14	3.54	3.18
Co	1.28	1.12	1.15	1.18	0.08	7.18
Ni	33.07	25.57	25.66	28.10	4.30	15.31
Cu	7.99	5.09	7.40	6.83	1.53	22.39
Zn	30.68	25.77	28.44	28.30	2.45	8.67
As	0.23	0.16	0.19	0.19	0.03	16.39
Se	-0.05	0.02	0.15	0.04	0.10	247.38
Mo	1.32	1.13	1.17	1.21	0.10	8.00
Cd	0.14	0.12	0.12	0.13	0.01	6.69
Pb	5.42	4.06	4.40	4.62	0.71	15.34
Hg	0.25	0.21	0.18	0.22	0.03	15.63

C:concentration; M: Mean ; STD: Standard deviation; RSD: Relative standard deviation

Elements content measured by ICP-MS analysis (mixed stream)

Element (ppm)	C1	C2	C3	M	STD	RSD
Na	208.99	144.27	168.06	521.33	32.73	6.28
Mg	188.29	170.67	191.16	550.12	11.09	2.02
Al	100.55	83.15	79.85	263.55	11.12	4.22
Si	105.48	82.36	84.03	271.87	12.89	4.74
S	5.60	7.82	8.44	21.86	1.49	6.84
K	544.16	500.10	543.61	1587.87	25.28	1.59
Ca	1267.74	1208.57	1326.16	3802.48	58.80	1.55
Fe	475.16	474.30	426.13	1375.58	28.06	2.04
Ti	8.30	4.11	6.27	18.68	2.10	11.22
V	0.27	0.18	0.21	0.66	0.05	7.38
Cr	26.22	15.66	25.09	66.97	5.80	8.66
Mn	58.95	58.74	64.52	182.21	3.28	1.80
Co	0.75	0.68	0.68	2.11	0.04	1.97
Ni	13.43	10.52	22.70	46.64	6.36	13.64
Cu	6.07	4.54	10.00	20.61	2.81	13.64
Zn	42.98	33.14	35.05	111.17	5.22	4.69
As	0.90	0.93	4.10	5.94	1.84	30.98
Se	0.04	-0.03	0.09	0.10	0.06	56.68
Mo	0.49	0.36	0.44	1.30	0.06	4.98
Cd	0.14	0.13	0.14	0.41	0.01	2.12
Pb	6.05	4.98	48.98	60.02	25.10	41.82
Hg	0.16	0.14	0.13	0.43	0.02	4.62

C:concentration; M: Mean ; STD: Standard deviation; RSD: Relative standard deviation

Elements content measured by ICP-MS analysis (new furniture)

Element (ppm)	C1	C2	C3	M	STD	RSD
Na	122.28	64.63	75.52	87.48	30.6	35.01
Mg	178.76	188.74	192.27	186.59	7.01	3.76
Al	44.79	36.08	43.21	41.36	4.64	11.21
Si	83.63	100.12	104.06	95.94	10.8	11.30
S	3.75	11.70	11.56	9.00	4.55	50.57
K	1084.03	1145.92	1147.67	1125.87	36.25	3.22
Ca	949.27	981.36	1104.06	1011.56	81.7	8.08
Fe	241.78	348.93	408.33	333.01	84.1	25.35
Ti	0.81	0.73	0.95	0.83	0.11	13.22
V	0.10	0.13	0.18	0.14	0.04	30.83
Cr	12.52	17.70	28.15	19.46	7.96	40.89
Mn	59.45	61.86	62.44	61.25	1.58	2.58
Co	0.60	0.65	0.73	0.66	0.06	9.79
Ni	20.02	21.21	24.38	21.87	2.26	10.31
Cu	2.68	3.37	3.77	3.27	0.55	16.88
Zn	12.13	12.31	13.64	12.69	0.82	6.49
As	0.13	0.05	0.06	0.08	0.04	56.62
Se	0.05	-0.07	0.13	0.04	0.10	278.79
Mo	0.58	0.65	0.74	0.66	0.08	12.09
Cd	0.13	0.12	0.13	0.13	0.00	3.78
Pb	0.52	0.59	0.62	0.58	0.05	9.19
Hg	0.12	0.11	0.10	0.11	0.01	10.20

C:concentration; M: Mean ; STD: Standard deviation; RSD: Relative standard deviation

Elements content measured by ICP-MS analysis (old furniture)

Element (ppm)	C1	C2	C3	M	STD	RSD
Na	111.50	77.84	127.69	317.04	25.43	8.02
Mg	115.24	120.16	120.32	355.72	2.89	0.81
Al	36.18	31.74	35.46	103.38	2.39	2.31
Si	71.98	56.09	60.36	188.42	8.22	4.36
S	6.61	9.60	17.21	33.42	5.47	16.36
K	92.23	96.61	96.02	284.85	2.37	0.83
Ca	882.99	944.11	958.17	2785.27	39.97	1.44
Fe	273.35	132.93	149.20	555.49	76.81	13.83
Ti	3.54	3.21	2.63	9.38	0.46	4.92
V	0.27	0.10	0.11	0.48	0.10	19.92
Cr	45.43	7.88	7.83	61.14	21.69	35.48
Mn	25.17	27.94	28.49	81.60	1.78	2.18
Co	1.60	1.56	1.62	4.79	0.03	0.72
Ni	5.78	2.61	2.71	11.11	1.80	16.22
Cu	2.85	3.43	3.21	9.49	0.29	3.09
Zn	88.30	91.02	92.63	271.95	2.19	0.80
As	0.06	0.03	0.09	0.18	0.03	15.68
Se	-0.06	0.03	0.07	0.05	0.07	141.76
Mo	0.40	0.20	0.27	0.86	0.10	11.70
Cd	0.17	0.17	0.19	0.53	0.01	2.29
Pb	0.60	0.62	0.70	1.93	0.05	2.55
Hg	0.09	0.08	1.56	1.72	0.85	49.46

C:concentration; M: Mean ; STD: Standard deviation; RSD: Relative standard deviation

D.6.2 Industrial

Elements content measured by ICP-MS analysis (pellets)						
Element (ppm)	C1	C2	C3	M	STD	RSD
Na	123.60	115.19	80.87	106.56	22.64	21.24
Mg	192.29	205.63	194.09	197.34	7.24	3.67
Al	81.27	89.24	79.67	83.39	5.12	6.15
Si	105.83	109.60	108.03	107.82	1.89	1.76
S	24.16	27.95	23.36	25.16	2.45	9.74
K	553.12	481.13	485.22	506.49	40.43	7.98
Ca	1433.71	1567.18	1537.54	1512.81	70.09	4.63
Fe	188.90	217.61	194.49	200.33	15.22	7.60
Ti	1.90	2.16	1.71	1.92	0.22	11.66
V	0.18	0.21	0.19	0.19	0.01	7.40
Cr	9.44	10.84	13.54	11.27	2.08	18.46
Mn	61.50	64.68	61.10	62.43	1.96	3.14
Co	0.10	0.10	0.10	0.10	0.00	2.47
Ni	2.60	1.87	3.71	2.73	0.93	34.06
Cu	8.95	6.63	6.45	7.34	1.39	18.97
Zn	14.72	14.71	13.28	14.24	0.83	5.82
As	0.04	0.04	0.05	0.04	0.01	11.89
Se	0.06	0.13	0.01	0.07	0.06	85.78
Mo	0.21	0.14	0.15	0.17	0.04	23.45
Cd	0.25	0.13	0.11	0.17	0.08	46.94
Pb	0.45	0.31	0.27	0.34	0.09	27.52
Hg	1.52	0.86	0.61	1.00	0.47	46.93
C:concentration; M: Mean ; STD: Standard deviation; RSD: Relative standard deviation						

Elements content measured by ICP-MS analysis (chips)						
Element (ppm)	C1	C2	C3	M	STD	RSD
Na	533.89	737.49	598.05	623.15	104.09	16.70
Mg	349.93	330.88	296.05	325.62	27.32	8.39
Al	335.93	251.15	156.17	247.75	89.93	36.30
Si	169.77	187.56	147.82	168.38	19.90	11.82
S	37.59	12.08	17.11	22.26	13.51	60.71
K	523.90	667.73	548.38	580.00	76.95	13.27
Ca	2719.46	2910.11	3854.56	3161.37	607.84	19.23
Fe	23195.36	619.89	407.31	8074.19	13095.75	162.19
Ti	22.40	16.34	10.87	16.54	5.77	34.87
V	1.01	0.63	0.54	0.73	0.25	33.86
Cr	37.39	48.04	42.52	42.65	5.32	12.48
Mn	235.95	63.98	55.24	118.39	101.91	86.08
Co	3.48	1.16	0.85	1.83	1.44	78.49
Ni	9.40	4.66	3.66	5.91	3.07	51.91
Cu	21.60	28.70	21.06	23.79	4.27	17.93
Zn	62.39	79.33	59.21	66.98	10.82	16.15
As	13.34	22.12	14.86	16.77	4.70	27.99
Se	0.08	0.17	0.00	0.08	0.09	104.38
Mo	0.83	0.42	0.31	0.52	0.27	52.65
Cd	0.30	0.28	0.29	0.29	0.01	2.57
Pb	166.57	213.27	74.11	151.32	70.82	46.80
Hg	1.00	0.67	0.47	0.71	0.27	37.60
C:concentration; M: Mean ; STD: Standard deviation; RSD: Relative standard deviation						

D.6.3 Landfill

Elements content measured by ICP-MS analysis (L.d. 3-7 m), 2018

Element (ppm)	C1	C2	C3	M	STD	RSD
Na	772.45	751.30	759.99	761.24	10.63	1.40
Mg	294.64	277.00	267.77	279.81	13.66	4.88
Al	161.26	78.52	96.87	112.22	43.45	38.72
Si	194.70	108.01	129.75	144.16	45.11	31.29
S	29.66	40.45	38.59	36.24	5.77	15.92
K	832.17	793.14	777.71	801.01	28.07	3.50
Ca	3583.52	3208.45	3032.09	3274.69	281.62	8.60
Fe	710.73	530.09	490.25	577.03	117.49	20.36
Ti	2.77	1.50	1.73	2.00	0.67	33.72
V	0.52	0.28	0.33	0.38	0.13	33.78
Cr	262.79	247.11	206.73	238.88	28.92	12.11
Mn	36.23	35.67	31.70	34.53	2.47	7.16
Co	1.05	0.97	1.02	1.01	0.04	3.71
Ni	3.58	1.89	4.63	3.37	1.38	41.00
Cu	152.90	142.09	113.61	136.20	20.30	14.90
Zn	21.30	17.30	20.08	19.56	2.05	10.49
As	176.59	176.56	129.75	160.97	27.04	16.80
Se	0.07	0.04	0.23	0.12	0.10	90.07
Mo	0.19	0.14	0.70	0.34	0.31	89.46
Cd	0.08	0.07	0.06	0.07	0.01	9.88
Pb	4.56	2.61	2.74	3.30	1.09	33.02
Hg	0.33	0.23	0.24	0.27	0.06	20.92

C:concentration; M: Mean; STD: Standard deviation; RSD: Relative standard deviation

Elements content measured by ICP-MS analysis (L.d. 7-9 m), 2018

Element (ppm)	C1	C2	C3	M	STD	RSD
Na	1454.73	1420.05	1504.28	1459.69	42.34	2.90
Mg	308.46	306.28	308.83	307.86	1.37	0.45
Al	228.86	246.62	280.93	252.14	26.47	10.50
Si	256.72	242.64	241.08	246.81	8.61	3.49
S	8.14	10.98	9.05	9.39	1.45	15.45
K	700.50	698.09	739.19	712.59	23.07	3.24
Ca	3601.99	3639.62	3526.60	3589.40	57.55	1.60
Fe	1094.53	1081.94	1046.03	1074.16	25.17	2.34
Ti	5.19	5.45	5.24	5.29	0.14	2.57
V	0.78	0.81	0.71	0.76	0.05	6.41
Cr	3.84	15.06	6.73	8.54	5.82	68.15
Mn	20.30	21.88	21.32	21.16	0.80	3.78
Co	1.42	1.41	1.38	1.41	0.02	1.40
Ni	3.28	3.84	3.09	3.40	0.39	11.44
Cu	3.72	7.76	6.04	5.84	2.02	34.68
Zn	25.47	23.87	20.12	23.15	2.74	11.85
As	1.78	4.93	3.69	3.47	1.59	45.78
Se	0.12	0.14	0.14	0.13	0.01	10.48
Mo	0.25	0.25	0.20	0.23	0.03	13.09
Cd	0.04	0.05	0.04	0.04	0.00	3.24
Pb	9.27	9.11	7.93	8.77	0.73	8.36
Hg	0.35	0.27	0.21	0.28	0.07	26.48

C:concentration; M: Mean ; STD: Standard deviation; RSD: Relative standard deviation

Elements content measured by ICP-MS analysis (L.d. 9-11 m), 2018

Element (ppm)	C1	C2	C3	M	STD	RSD
Na	2146.69	2273.63	2249.41	2223.24	67.39	3.03
Mg	284.24	386.92	282.16	317.77	59.89	18.85
Al	310.08	305.15	284.14	299.79	13.78	4.60
Si	204.73	207.42	196.72	202.96	5.56	2.74
S	22.86	33.51	42.82	33.06	9.99	30.21
K	763.27	811.73	795.19	790.06	24.63	3.12
Ca	3875.97	5345.03	3630.62	4283.88	927.14	21.64
Fe	2544.23	2433.19	2071.82	2349.75	247.01	10.51
Ti	8.71	11.71	10.93	10.45	1.56	14.91
V	1.67	2.09	1.81	1.86	0.22	11.63
Cr	7.63	16.69	21.11	15.15	6.87	45.37
Mn	36.18	30.71	28.41	31.77	3.99	12.55
Co	1.75	3.27	1.78	2.26	0.87	38.49
Ni	3.92	14.12	4.62	7.55	5.70	75.49
Cu	12.20	12.92	13.02	12.72	0.45	3.51
Zn	27.83	30.12	44.20	34.05	8.87	26.04
As	2.09	2.25	1.91	2.08	0.17	8.15
Se	0.57	0.34	0.50	0.47	0.12	24.73
Mo	0.33	1.13	0.65	0.70	0.40	56.97
Cd	0.08	0.11	0.10	0.10	0.01	12.64
Pb	13.83	16.93	22.30	17.69	4.28	24.21
Hg	0.05	0.04	1.86	0.65	1.05	161.29

C:concentration; M: Mean ; STD: Standard deviation; RSD: Relative standard deviation

Elements content measured by ICP-MS analysis (L.d. 11-13.5 m), 2018

Element (ppm)	C1	C2	C3	M	STD	RSD
Na	1178.89	1193.46	1146.17	1172.84	24.22	2.07
Mg	511.97	529.99	529.15	523.70	10.17	1.94
Al	572.77	677.43	712.86	654.35	72.84	11.13
Si	451.16	589.76	571.09	537.33	75.21	14.00
S	65.52	64.36	63.70	64.52	0.92	1.43
K	594.35	607.69	599.04	600.36	6.77	1.13
Ca	6296.59	5399.48	6050.32	5915.46	463.51	7.84
Fe	6139.66	6156.60	5910.54	6068.94	137.43	2.26
Ti	21.77	24.71	22.56	23.01	1.52	6.59
V	2.96	3.11	3.00	3.02	0.08	2.54
Cr	13.63	13.55	15.75	14.31	1.25	8.74
Mn	56.30	57.78	55.91	56.66	0.99	1.74
Co	3.22	4.76	2.88	3.62	1.01	27.78
Ni	35.50	15.72	12.10	21.11	12.60	59.68
Cu	15.32	18.63	15.36	16.43	1.90	11.56
Zn	56.89	48.81	44.93	50.21	6.10	12.15
As	3.83	3.45	3.71	3.66	0.19	5.31
Se	0.10	0.30	0.55	0.31	0.23	72.11
Mo	0.71	0.84	0.66	0.74	0.09	12.37
Cd	0.19	0.17	0.20	0.19	0.02	9.19
Pb	165.36	167.96	165.54	166.29	1.45	0.87
Hg	0.97	0.66	0.48	0.70	0.25	35.17

C:concentration; M: Mean ; STD: Standard deviation; RSD: Relative standard deviation

Elements content measured by ICP-MS analysis (L.d. 13.5-17 m), 2018

Element (ppm)	C1	C2	C3	M	STD	RSD
Na	2159.57	2358.95	2372.41	2296.98	119.19	5.19
Mg	623.88	672.30	576.16	624.11	48.07	7.70
Al	2299.54	2103.40	1951.75	2118.23	174.37	8.23
Si	441.91	430.51	562.20	478.21	72.96	15.26
S	45.39	49.93	42.66	46.00	3.67	7.98
K	857.83	896.40	897.13	883.79	22.48	2.54
Ca	13477.30	12423.83	10885.17	12262.10	1303.61	10.63
Fe	9578.08	6840.97	6618.82	7679.29	1648.15	21.46
Ti	40.99	36.96	35.09	37.68	3.02	8.01
V	6.82	5.88	5.94	6.21	0.53	8.47
Cr	49.19	57.20	50.04	52.14	4.40	8.44
Mn	74.19	66.44	62.60	67.74	5.90	8.71
Co	5.86	6.86	8.03	6.92	1.09	15.74
Ni	10.66	16.49	10.89	12.68	3.31	26.07
Cu	43.59	65.46	47.05	52.03	11.76	22.59
Zn	169.17	212.31	164.67	182.05	26.30	14.45
As	3.80	4.01	3.51	3.77	0.25	6.67
Se	0.90	0.95	0.70	0.85	0.13	15.30
Mo	1.66	2.10	1.63	1.80	0.26	14.72
Cd	0.46	0.53	0.39	0.46	0.07	15.20
Pb	82.98	92.79	78.55	84.77	7.29	8.59
Hg	0.41	0.34	0.27	0.34	0.07	19.84

C:concentration; M: Mean ; STD: Standard deviation; RSD: Relative standard deviation

Elements content measured by ICP-MS analysis (L.d. 17-20 m), 2018

Element (ppm)	C1	C2	C3	M	STD	RSD
Na	980.16	1078.04	966.79	1008.33	60.74	6.02
Mg	438.03	374.46	422.48	411.66	33.14	8.05
Al	1060.70	733.15	1049.32	947.72	185.91	19.62
Si	461.60	421.76	508.94	464.10	43.65	9.40
S	43.61	35.87	63.67	47.71	14.35	30.07
K	638.38	593.22	593.44	608.35	26.01	4.28
Ca	8289.14	8080.41	9157.01	8508.85	570.94	6.71
Fe	4340.99	3685.46	4558.85	4195.10	454.61	10.84
Ti	26.32	18.01	22.79	22.38	4.17	18.63
V	3.61	3.63	3.85	3.70	0.13	3.61
Cr	12.59	12.93	22.79	16.10	5.80	35.99
Mn	54.80	53.02	53.65	53.82	0.91	1.68
Co	1.17	0.81	1.07	1.02	0.19	18.28
Ni	3.75	3.53	4.11	3.80	0.29	7.69
Cu	12.32	7.04	9.35	9.57	2.65	27.66
Zn	90.94	79.03	98.64	89.54	9.88	11.04
As	7.44	3.90	5.31	5.55	1.78	32.14
Se	0.65	0.62	0.63	0.64	0.02	2.50
Mo	0.62	0.68	0.76	0.68	0.07	10.23
Cd	0.13	0.11	0.20	0.15	0.04	29.41
Pb	41.64	40.60	53.45	45.23	7.14	15.78
Hg	0.05	0.04	1.76	0.62	0.99	160.89

C:concentration; M: Mean; STD: Standard deviation; RSD: Relative standard deviation

Elements content measured by ICP-MS analysis (L.d. 20-23 m), 2018

Element (ppm)	C1	C2	C3	M	STD	RSD
Na	1218.00	1178.12	1132.34	1176.15	42.87	3.64
Mg	355.42	373.40	372.14	366.99	10.04	2.74
Al	449.26	509.19	658.71	539.05	107.87	20.01
Si	79.27	108.83	535.32	241.14	255.20	105.83
S	46.52	47.92	48.56	47.67	1.04	2.18
K	692.86	708.87	710.45	704.06	9.73	1.38
Ca	5391.16	5890.58	5253.73	5511.82	335.13	6.08
Fe	4033.39	4233.23	3681.59	3982.73	279.28	7.01
Ti	19.31	20.97	24.88	21.72	2.86	13.16
V	2.70	2.80	2.79	2.76	0.06	2.00
Cr	142.37	152.96	129.35	141.56	11.82	8.35
Mn	37.74	39.74	36.42	37.96	1.67	4.40
Co	4.63	4.55	4.44	4.54	0.10	2.15
Ni	3.91	5.31	5.53	4.92	0.88	17.84
Cu	42.73	53.71	38.81	45.08	7.73	17.14
Zn	102.03	105.63	91.94	99.87	7.10	7.11
As	32.95	34.15	27.06	31.39	3.79	12.07
Se	0.36	0.61	0.46	0.47	0.13	26.98
Mo	0.59	0.62	0.77	0.66	0.10	14.80
Cd	0.20	0.20	0.20	0.20	0.00	1.16
Pb	95.24	136.58	86.17	106.00	26.87	25.35
Hg	0.09	0.07	1.75	0.64	0.96	151.44

C:concentration; M: Mean ; STD: Standard deviation; RSD: Relative standard deviation

Elements content measured by ICP-MS analysis (L.d. 23-25 m), 2018

Element (ppm)	C1	C2	C3	M	STD	RSD
Na	1147.48	1038.65	1251.74	1145.96	106.55	9.30
Mg	574.74	622.40	588.12	595.08	24.58	4.13
Al	1049.69	1217.05	1194.12	1153.62	90.73	7.86
Si	554.78	473.74	578.18	535.57	54.81	10.23
S	178.21	165.71	145.44	163.12	16.54	10.14
K	736.38	703.67	792.77	744.27	45.07	6.06
Ca	12033.53	12249.75	10768.93	11684.07	799.88	6.85
Fe	3372.58	2477.70	3198.89	3016.39	474.53	15.73
Ti	34.52	48.56	32.98	38.69	8.59	22.19
V	4.23	5.13	4.41	4.59	0.48	10.41
Cr	23.95	15.74	39.54	26.41	12.09	45.78
Mn	40.11	39.64	40.73	40.16	0.55	1.36
Co	2.27	2.12	2.66	2.35	0.28	11.86
Ni	9.62	9.12	11.46	10.07	1.24	12.28
Cu	53.08	38.85	72.52	54.82	16.90	30.83
Zn	80.62	58.87	74.71	71.40	11.25	15.75
As	4.75	4.30	19.55	9.53	8.68	91.02
Se	0.50	0.65	0.29	0.48	0.18	38.31
Mo	1.45	1.14	1.46	1.35	0.18	13.58
Cd	0.13	0.10	0.14	0.12	0.02	14.32
Pb	28.14	25.17	41.53	31.61	8.71	27.56
Hg	0.16	0.11	0.09	0.12	0.04	28.97

C:concentration; M: Mean; STD: Standard deviation; RSD: Relative standard deviation

Elements content measured by ICP-MS analysis (L.d. 25-27 m), 2018

Element (ppm)	C1	C2	C3	M	STD	RSD
Na	1745.80	1590.34	1487.57	1607.90	130.01	8.09
Mg	909.99	866.10	1128.65	968.25	140.63	14.52
Al	3016.82	1408.66	2205.41	2210.29	804.09	36.38
Si	581.11	552.51	480.00	537.87	52.12	9.69
S	102.37	80.14	147.89	110.14	34.54	31.36
K	942.14	776.51	918.92	879.19	89.68	10.20
Ca	14812.07	14609.26	20454.05	16625.13	3317.50	19.95
Fe	6132.54	4181.18	6789.19	5700.97	1356.51	23.79
Ti	34.87	28.37	47.35	36.86	9.65	26.17
V	4.72	3.88	6.38	4.99	1.27	25.43
Cr	10.76	12.37	16.45	13.19	2.94	22.26
Mn	56.38	50.02	62.27	56.22	6.12	10.89
Co	3.09	3.53	3.83	3.48	0.37	10.64
Ni	7.02	13.17	10.03	10.07	3.07	30.49
Cu	29.67	24.32	39.57	31.19	7.74	24.81
Zn	336.30	154.06	296.22	262.19	95.77	36.53
As	4.25	3.78	8.56	5.53	2.63	47.61
Se	0.87	0.81	0.80	0.83	0.04	4.57
Mo	0.74	0.62	0.85	0.74	0.11	15.53
Cd	0.34	0.26	0.38	0.33	0.06	18.55
Pb	4055.39	2613.24	3545.95	3404.86	731.35	21.48
Hg	1.11	0.77	0.48	0.79	0.32	40.07
C:concentration; M: Mean; STD: Standard deviation; RSD: Relative standard deviation						

Elements content measured by ICP-MS analysis (L.d. 29-32.5 m), 2018

Element (ppm)	C1	C2	C3	M	STD	RSD
Na	1829.13	1842.22	1932.98	1868.11	56.56	3.03
Mg	590.77	509.86	553.91	551.52	40.51	7.35
Al	997.50	952.58	1062.23	1004.10	55.12	5.49
Si	520.34	585.40	533.39	546.38	34.42	6.30
S	105.20	104.49	108.73	106.14	2.27	2.14
K	949.78	952.58	1016.64	973.00	37.82	3.89
Ca	8861.62	7343.68	7978.12	8061.14	762.37	9.46
Fe	6362.19	6798.15	7294.28	6818.21	466.37	6.84
Ti	23.63	17.31	22.18	21.04	3.31	15.74
V	4.64	3.76	5.84	4.74	1.04	22.01
Cr	23.18	20.50	32.60	25.42	6.35	24.99
Mn	55.67	46.79	51.06	51.17	4.44	8.68
Co	2.84	2.27	2.69	2.60	0.30	11.46
Ni	15.56	15.15	41.03	23.91	14.82	61.99
Cu	32.95	59.38	23.02	38.45	18.79	48.88
Zn	493.07	167.23	248.46	302.92	169.61	55.99
As	3.61	3.78	4.13	3.84	0.26	6.83
Se	0.72	0.29	0.49	0.50	0.21	42.41
Mo	1.82	1.77	2.55	2.05	0.44	21.39
Cd	0.34	0.22	0.29	0.28	0.06	19.82
Pb	1554.19	386.07	784.13	908.13	593.85	65.39
Hg	0.44	0.30	0.27	0.34	0.09	25.76
C:concentration; M: Mean ; STD: Standard deviation; RSD: Relative standard deviation						

Elements content measured by ICP-MS analysis (L.d. 32.5-35 m), 2018

Element (ppm)	C1	C2	C3	M	STD	RSD
Na	1671.97	1583.03	1579.37	1611.46	52.44	3.25
Mg	354.30	360.41	306.71	340.48	29.40	8.63
Al	716.56	410.20	310.70	479.15	211.54	44.15
Si	240.84	256.87	244.97	247.56	8.32	3.36
S	49.76	61.93	56.76	56.15	6.11	10.87
K	740.45	700.92	687.11	709.49	27.68	3.90
Ca	6011.15	4540.02	3306.11	4619.09	1354.25	29.32
Fe	2826.43	5057.75	3963.35	3949.18	1115.72	28.25
Ti	14.25	10.23	8.54	11.01	2.93	26.63
V	1.70	1.70	1.27	1.56	0.25	15.86
Cr	6.59	5.73	4.94	5.75	0.82	14.33
Mn	29.26	26.48	19.40	25.05	5.08	20.30
Co	4.94	2.77	2.45	3.38	1.35	39.98
Ni	9.39	7.69	21.11	12.73	7.31	57.40
Cu	40.80	43.41	32.86	39.03	5.49	14.08
Zn	441.88	332.54	390.36	388.26	54.70	14.09
As	2.05	1.89	1.55	1.83	0.26	14.12
Se	0.58	0.45	0.22	0.41	0.18	44.18
Mo	0.41	0.38	0.45	0.41	0.03	7.99
Cd	0.16	0.32	0.10	0.19	0.12	61.17
Pb	26.87	27.88	20.51	25.09	3.99	15.91
Hg	1.03	0.68	0.48	0.73	0.28	37.89

C:concentration; M: Mean ; STD: Standard deviation; RSD: Relative standard deviation

Elements content measured by ICP-MS analysis (L.d. 35-36.5 m), 2018

Element (ppm)	C1	C2	C3	M	STD	RSD
Na	2293.85	2185.47	2146.26	2208.53	76.45	3.46
Mg	624.88	590.67	828.70	681.41	128.69	18.89
Al	2194.98	10750.15	2623.21	5189.45	4820.47	92.89
Si	105.79	74.62	437.20	205.87	200.94	97.61
S	56.56	65.96	78.10	66.87	10.80	16.15
K	1170.65	1141.96	1408.98	1240.53	146.59	11.82
Ca	9590.67	10356.37	9101.75	9682.93	632.38	6.53
Fe	4310.86	4016.54	6001.59	4776.33	1071.26	22.43
Ti	20.37	18.96	41.73	27.02	12.76	47.23
V	5.70	6.54	8.05	6.76	1.19	17.64
Cr	10.74	13.31	14.55	12.86	1.94	15.11
Mn	31.05	28.16	41.14	33.45	6.82	20.38
Co	1.64	1.90	1.83	1.79	0.13	7.45
Ni	34.41	16.72	10.06	20.39	12.59	61.72
Cu	23.14	22.64	31.20	25.66	4.80	18.72
Zn	173.82	169.72	182.83	175.46	6.71	3.82
As	1.59	1.49	2.84	1.97	0.75	38.14
Se	0.25	0.39	0.62	0.42	0.19	44.51
Mo	0.62	0.62	0.73	0.66	0.06	9.21
Cd	0.15	0.14	0.17	0.15	0.02	11.58
Pb	38.96	31.90	52.86	41.24	10.67	25.87
Hg	0.39	0.31	0.22	0.31	0.09	28.10

C:concentration; M: Mean; STD: Standard deviation; RSD: Relative standard deviation

Elements content measured by ICP-MS analysis (L.d. 36-37.5), 2018

Element (ppm)	C1	C2	C3	M	STD	RSD
Na	3443.47	3317.35	3494.14	3418.32	91.04	2.66
Mg	419.98	425.66	448.68	431.44	15.20	3.52
Al	750.40	555.56	669.05	658.33	97.86	14.87
Si	298.57	251.80	287.87	279.41	24.50	8.77
S	23.09	23.98	23.43	23.50	0.45	1.92
K	1323.65	1288.97	1334.13	1315.58	23.64	1.80
Ca	4359.08	4096.72	4189.00	4214.93	133.09	3.16
Fe	3423.57	3037.57	3375.02	3278.72	210.25	6.41
Ti	16.38	22.18	14.33	17.63	4.07	23.09
V	3.34	4.34	2.52	3.40	0.91	26.73
Cr	7.42	6.45	9.01	7.63	1.29	16.93
Mn	49.16	48.16	47.05	48.13	1.06	2.20
Co	1.99	1.78	1.85	1.88	0.10	5.58
Ni	5.25	3.80	3.32	4.12	1.01	24.50
Cu	17.06	12.07	22.83	17.32	5.39	31.09
Zn	674.76	691.45	543.97	636.73	80.76	12.68
As	0.79	0.78	0.90	0.82	0.07	8.33
Se	0.26	0.49	0.29	0.35	0.13	36.65
Mo	1.49	1.23	1.26	1.32	0.14	10.91
Cd	0.38	0.16	0.18	0.24	0.12	50.34
Pb	40.01	70.94	37.52	49.49	18.62	37.62
Hg	0.17	0.14	0.15	0.15	0.02	11.92

C:concentration; M: Mean ; STD: Standard deviation; RSD: Relative standard deviation

Elements content measured by ICP-MS analysis (L.d. 37.5-39 m), 2018

Element (ppm)	C1	C2	C3	M	STD	RSD
Na	1853.60	2054.55	1905.32	1937.82	104.35	5.38
Mg	1160.10	1126.26	1068.10	1118.15	46.54	4.16
Al	3574.49	2969.64	3125.00	3223.04	314.11	9.75
Si	575.77	657.72	562.03	598.51	51.74	8.64
S	120.08	127.58	112.17	119.95	7.71	6.42
K	1222.17	1247.25	1119.40	1196.28	67.74	5.66
Ca	18000.86	16498.02	15438.43	16645.77	1287.59	7.74
Fe	6635.27	6533.22	6296.64	6488.38	173.71	2.68
Ti	71.28	71.49	65.30	69.36	3.51	5.07
V	9.85	9.30	9.12	9.42	0.38	4.01
Cr	29.32	31.46	23.32	28.03	4.22	15.05
Mn	68.92	64.89	63.43	65.75	2.84	4.32
Co	3.38	3.32	2.89	3.20	0.27	8.36
Ni	10.36	16.98	8.93	12.09	4.30	35.52
Cu	77.48	71.49	54.80	67.93	11.75	17.30
Zn	134.42	121.87	118.24	124.84	8.49	6.80
As	20.51	19.78	13.34	17.87	3.94	22.06
Se	1.39	0.82	0.58	0.93	0.42	44.89
Mo	1.12	1.01	0.97	1.04	0.08	7.52
Cd	0.25	0.17	0.42	0.28	0.12	44.97
Pb	172.95	134.84	135.96	147.92	21.68	14.66
Hg	0.11	0.09	2.21	0.80	1.22	151.41

C:concentration; M: Mean ; STD: Standard deviation; RSD: Relative standard deviation

Elements content measured by ICP-MS analysis (L.d. 40-41.5 m), 2018

Element (ppm)	C1	C2	C3	M	STD	RSD
Na	2439.02	2401.75	2465.70	2435.49	32.12	1.32
Mg	422.37	393.01	387.75	401.04	18.65	4.65
Al	237.95	166.73	140.39	181.69	50.47	27.78
Si	204.24	154.03	127.46	161.91	38.99	24.08
S	53.14	41.48	33.61	42.74	9.83	23.00
K	630.58	601.43	594.55	608.85	19.13	3.14
Ca	5353.96	4049.23	3698.55	4367.24	872.3	19.97
Fe	2002.78	1740.77	1720.02	1821.19	157.60	8.65
Ti	26.17	21.44	15.13	20.91	5.54	26.49
V	0.79	0.53	0.46	0.59	0.17	29.45
Cr	13.70	14.43	20.48	16.20	3.72	22.97
Mn	21.81	18.36	18.33	19.50	2.00	10.26
Co	3.55	3.12	2.88	3.18	0.34	10.62
Ni	24.79	3.26	6.94	11.66	11.52	98.76
Cu	10.89	7.58	6.30	8.26	2.36	28.64
Zn	349.00	452.56	238.62	346.73	106.9	30.86
As	1.28	1.02	0.81	1.04	0.24	22.79
Se	0.13	0.18	0.21	0.17	0.04	24.12
Mo	0.22	0.21	0.27	0.24	0.03	13.47
Cd	0.82	0.24	0.15	0.41	0.37	90.48
Pb	596.87	686.78	526.94	603.53	80.13	13.28
Hg	0.17	0.13	0.10	0.13	0.04	26.92

C:concentration; M: Mean ; STD: Standard deviation; RSD: Relative standard deviation

Elements content measured by ICP-MS analysis (L.d. 41-43 m), 2018

Element (ppm)	C1	C2	C3	M	STD	RSD
Na	2395.21	1963.79	2173.48	2177.49	215.74	9.91
Mg	870.26	602.87	636.24	703.12	145.70	20.72
Al	1137.72	1215.68	634.26	995.89	315.59	31.69
Si	510.98	666.53	381.35	519.62	142.79	27.48
S	72.26	50.14	56.51	59.64	11.38	19.09
K	926.15	861.52	798.26	861.98	63.94	7.42
Ca	23752.50	9669.72	11381.15	14934.45	7684.44	51.45
Fe	3952.10	3859.93	4188.90	4000.31	169.70	4.24
Ti	21.16	20.49	14.94	18.86	3.42	18.11
V	4.47	3.62	3.04	3.71	0.72	19.35
Cr	132.93	214.88	103.73	150.52	57.62	38.28
Mn	45.71	39.99	47.42	44.37	3.89	8.77
Co	2.61	4.52	3.02	3.38	1.00	29.58
Ni	9.44	11.88	10.33	10.55	1.23	11.69
Cu	179.44	191.40	160.84	177.23	15.40	8.69
Zn	151.70	105.05	116.97	124.57	24.23	19.45
As	68.46	118.58	57.70	81.58	32.49	39.83
Se	0.54	0.78	0.63	0.65	0.12	18.51
Mo	0.89	0.91	0.72	0.84	0.10	12.14
Cd	0.21	0.18	0.18	0.19	0.02	8.75
Pb	76.25	64.66	71.72	70.88	5.84	8.24
Hg	1.12	0.69	0.51	0.77	0.31	40.52

C:concentration; M: Mean ; STD: Standard deviation; RSD: Relative standard deviation

Elements content measured by ICP-MS analysis (L.d. 46-48m), 2018

Element (ppm)	C1	C2	C3	M	STD	RSD
Na	1770.17	1426.33	1517.15	1571.22	178.19	11.34
Mg	365.90	292.33	364.83	341.02	42.17	12.37
Al	197.39	110.85	166.27	158.17	43.83	27.71
Si	282.83	196.19	259.17	246.07	44.78	18.20
S	98.30	88.29	101.67	96.09	6.96	7.25
K	866.30	712.18	769.54	782.67	77.89	9.95
Ca	4568.83	3394.15	8652.31	5538.43	2759.92	49.83
Fe	1867.09	979.01	2212.92	1686.34	636.50	37.74
Ti	9.81	4.18	8.77	7.59	3.00	39.50
V	1.25	0.58	1.22	1.01	0.38	37.18
Cr	10.36	4.34	7.76	7.48	3.02	40.39
Mn	37.38	29.23	33.09	33.24	4.08	12.26
Co	0.51	0.45	0.49	0.48	0.03	7.07
Ni	3.70	2.79	14.15	6.88	6.32	91.82
Cu	4.00	2.43	2.75	3.06	0.83	26.98
Zn	83.86	31.78	52.23	55.96	26.24	46.89
As	2.20	1.45	1.76	1.80	0.38	20.89
Se	0.01	0.15	0.07	0.08	0.07	92.06
Mo	0.22	0.19	0.42	0.28	0.13	45.22
Cd	0.09	0.08	0.09	0.09	0.01	9.24
Pb	9.97	4.32	6.62	6.97	2.84	40.79
Hg	0.16	0.11	0.09	0.12	0.04	30.03

C:concentration; M: Mean; STD: Standard deviation; RSD: Relative standard deviation

Elements content measured by ICP-MS analysis (L.d. 48-50.5m), 2018

Element (ppm)	C1	C2	C3	M	STD	RSD
Na	1844.21	1155.51	1824.10	1607.94	391.95	24.38
Mg	501.05	280.78	483.95	421.93	122.54	29.04
Al	4021.05	1403.89	1486.74	2303.89	1487.68	64.57
Si	364.21	209.50	335.04	302.92	82.20	27.14
S	108.84	61.02	100.51	90.12	25.55	28.35
K	993.68	500.00	742.21	745.30	246.86	33.12
Ca	5431.58	2991.36	4932.53	4451.82	1289.18	28.96
Fe	4336.84	2192.22	4374.13	3634.40	1249.10	34.37
Ti	32.00	11.45	21.06	21.50	10.28	47.83
V	3.81	1.95	3.19	2.98	0.94	31.65
Cr	11.37	5.63	9.89	8.96	2.98	33.27
Mn	39.58	22.57	39.32	33.82	9.75	28.82
Co	5.12	1.58	4.00	3.56	1.81	50.76
Ni	40.42	4.63	7.10	17.38	19.99	114.99
Cu	37.47	27.00	51.88	38.79	12.50	32.22
Zn	250.53	154.43	237.32	214.09	52.09	24.33
As	8.00	4.06	6.40	6.15	1.98	32.20
Se	0.47	0.24	0.48	0.40	0.13	33.49
Mo	0.81	0.43	0.63	0.62	0.19	30.06
Cd	0.12	0.07	0.14	0.11	0.04	34.87
Pb	148.63	51.40	83.29	94.44	49.56	52.48
Hg	0.19	0.07	0.11	0.12	0.06	48.42

C:concentration; M: Mean STD: Standard deviation; RSD: Relative standard deviation

Elements content measured by ICP-MS analysis (L.d. 50-51 m), 2018

Element (ppm)	C1	C2	C3	M	STD	RSD
Na	3349.28	3284.89	629.81	2421.33	1551.83	64.09
Mg	370.81	318.53	300.10	329.82	36.68	11.12
Al	324.96	312.56	171.77	269.76	85.09	31.54
Si	275.12	298.63	205.33	259.69	48.52	18.68
S	177.23	164.64	48.57	130.15	70.93	54.50
K	1375.60	1363.73	527.15	1088.82	486.46	44.68
Ca	4944.18	3663.15	5212.24	4606.52	827.91	17.97
Fe	3050.24	2966.35	4225.07	3413.89	703.76	20.61
Ti	24.32	25.08	9.56	19.65	8.75	44.54
V	3.31	3.21	1.34	2.62	1.11	42.36
Cr	22.73	20.90	11.69	18.44	5.92	32.09
Mn	25.12	17.64	49.75	30.84	16.80	54.49
Co	1.90	1.89	1.35	1.71	0.31	18.41
Ni	6.86	6.91	3.93	5.90	1.71	28.92
Cu	25.92	24.09	8.11	19.37	9.79	50.55
Zn	188.20	189.53	72.26	150.00	67.32	44.88
As	13.48	14.99	2.05	10.17	7.07	69.52
Se	0.52	0.23	0.24	0.33	0.16	49.65
Mo	1.12	1.13	0.30	0.85	0.48	55.90
Cd	0.15	0.13	1.06	0.44	0.53	119.37
Pb	73.56	67.49	1081.93	407.66	583.94	143.24
Hg	0.41	0.31	0.24	0.32	0.08	26.42

C:concentration; M: Mean ; STD: Standard deviation; RSD: Relative standard deviation

Elements content measured by ICP-MS analysis (L.d. 53-55m), 2018

Element (ppm)	C1	C2	C3	M	STD	RSD
Na	650.86	3193.65	1064.73	1636.42	1364.39	83.38
Mg	299.32	343.78	407.34	350.14	54.29	15.51
Al	148.05	427.18	352.89	309.37	144.56	46.73
Si	187.22	315.30	237.95	246.82	64.50	26.13
S	64.48	164.97	114.54	114.66	50.24	43.82
K	548.41	1346.62	522.28	805.77	468.57	58.15
Ca	5423.87	3864.93	7824.16	5704.32	1994.46	34.96
Fe	4339.09	3234.34	6372.25	4648.56	1591.68	34.24
Ti	8.64	25.02	17.26	16.97	8.19	48.28
V	1.24	3.25	2.64	2.38	1.04	43.55
Cr	10.85	20.06	13.13	14.68	4.80	32.68
Mn	47.81	21.36	36.90	35.36	13.29	37.60
Co	1.41	1.62	1.77	1.60	0.18	11.11
Ni	3.62	9.78	8.81	7.40	3.32	44.79
Cu	6.81	25.63	11.03	14.49	9.88	68.15
Zn	78.14	272.58	89.53	146.75	109.12	74.36
As	1.84	14.75	5.06	7.22	6.72	93.06
Se	0.15	0.28	0.46	0.30	0.15	51.92
Mo	0.30	1.14	0.52	0.65	0.43	66.19
Cd	0.91	0.13	1.80	0.94	0.84	88.72
Pb	1243.47	54.11	1314.78	870.79	708.16	81.32
Hg	0.21	0.18	0.15	0.18	0.03	15.39

C:concentration; M: Mean ; STD: Standard deviation; RSD: Relative standard deviation

Appendix E Chapter 6

E.1 Models application

E.1.1 The total moles of the elements to be fed to MTDATA for original waste wood samples (streams)

E.1.2 The total moles of the elements to be fed to MTDATA for original waste wood samples (industrial)

E.1.3 The total moles of the elements to be fed to MTDATA for original waste wood samples (landfill)

E.1.4 The total moles of the elements to be fed to MTDATA for artificial waste wood samples (Ni-As)

E.1.5 The total moles of the elements to be fed to MTDATA for blends waste wood samples (blending 60/40: W/W)

E.1.1 The total moles of the elements to be fed to MTDATA for original waste wood samples (streams).

Calculation of the total moles of the elements to be fed to MTDATA for mixed furniture.

Atomic Mass	Unit	Elements	Actual fuel composition	Kg/hr (10000)	g/hr (0.001)	Fuel feed (wt.3.098)	Total input (MTDATA) Fuel +agent Moles/hr
12	Weight (%)	Carbon (C)	51.4544	514544	514.544	1594.057	132.8381
1		Hydrogen (H)	7.3541	163595.1	163.5951	506.8176	506.8176
14		Nitrogen (N)	0.0877	1280	1.28	3.96544	100.105
32		Sulphur(S)	0.0019	19	0.019	0.058862	0.001839
16		Oxygen(O)	41.1019	456046	456.046	1412.831	88.30191
35.5		Chlorine (Cl)	0.03	300	0.3	0.9294	0.02618
26.98	Weight mg/kg	Aluminium (Al)	35.19	35.19	0.03519	0.109019	0.004041
40		Calcium (Ca)	1023.76	1023.76	1.02376	3.171608	0.07929
39.0983		Potassium (K)	611.18	611.18	0.61118	1.893436	0.048428
55.84		Iron (Fe)	198.35	198.35	0.19835	0.614488	0.011004
23		Sodium (Na)	92.18	92.18	0.09218	0.285574	0.012416
28.0855		Silicon (Si)	62.25	62.25	0.06225	0.192851	0.006867
47.86		Titanium (Ti)	155.23	155.23	0.15523	0.480903	0.010048
74.92		Arsenic (As)	0.04	0.04	0.00004	0.000124	1.65E-06
112.41		Cadmium (Cd)	0.16	0.16	0.00016	0.000496	4.41E-06
58.93		Cobalt (Co)	1.16	1.16	0.00116	0.003594	6.1E-05
51.996		Chromium (Cr)	14.14	14.14	0.01414	0.043806	0.000842
63.54		Copper (Cu)	10.1	10.1	0.0101	0.03129	0.000492
54.938		Manganese (Mn)	44.99	44.99	0.04499	0.139379	0.002537
58.69		Nickel (Ni)	11.12	11.12	0.01112	0.03445	0.000587
207.2		Lead (Pb)	0.97	0.97	0.00097	0.003005	1.45E-05
50.94		Vanadium (V)	0.12	0.12	0.00012	0.000372	7.3E-06
65.38		Zinc (Zn)	64.85	64.85	0.06485	0.200905	0.003073
200.59		Mercury (Hg)	0.38	0.38	0.00038	0.001177	5.87E-06
95.94		Molybdenum (Mo)	0.38	0.38	0.00038	0.001177	1.23E-05
78.96		Selenium (Se)	0.09	0.09	0.00009	0.000279	3.53E-06

*Total Hydrogen (from fuel + from moisture)

** Total Oxygen (from fuel + from moisture)

& Total Nitrogen (from fuel + from agent)

Moisture content -wt. %(ar) = 8.935

O from Moisture = 4.502

H from Moisture = 9.00

N₂ feeding input

Nitrogen (N ₂)	40 L/min	2400 L/hr	99.822 Moles/hr
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Calculation of the total moles of the elements to be fed to MTDATA for new furniture.

Atomic Mass	Unit	Elements	Actual fuel composition	Kg/hr (10000)	g/hr (0.001)	Fuel feed (wt. 4.2418 g)	Total input (MTDATA) Fuel +agent Mols/hr
12	Weight (%)	Carbon (C)	49.0599	490599	490.599	2081.02283	173.418569
1		Hydrogen (H)	7.0265	169601.652	169.601652	719.416290	719.416290
14		Nitrogen (N)	0.128	1280	1.28	5.429504	99.98562
32		Sulphur(S)	0.0009	9	0.009	0.0381762	0.00119301
16		Oxygen(O)	43.7847	487515.326	487.51533	2067.94251	129.246407
35.5		Chlorine (Cl)	0.03	300	0.3	1.27254	0.035846197
26.98		Aluminium (Al)	41.36	41.36	0.04136	0.175440848	0.006502626
40	Weight mg/kg	Calcium (Ca)	1011.56	1011.56	1.01156	4.290835208	0.10727088
39.0983		Potassium (K)	1125.87	1125.87	1.12587	4.775715366	0.122146369
55.84		Iron (Fe)	333.01	333.01	0.33301	1.412561818	0.025296594
23		Sodium (Na)	87.48	87.48	0.08748	0.371072664	0.016133594
28.0855		Silicon (Si)	95.94	95.94	0.09594	0.406958292	0.014489979
47.86		Titanium (Ti)	0.83	0.83	0.00083	0.003520694	7.35623E-05
74.92		Arsenic (As)	0.08	0.08	0.00008	0.000339344	4.52942E-06
112.41		Cadmium (Cd)	0.13	0.13	0.00013	0.000551434	4.90556E-06
58.93		Cobalt (Co)	0.66	0.66	0.00066	0.002799588	4.7507E-05
51.996		Chromium (Cr)	19.46	19.46	0.01946	0.082545428	0.001587534
63.54		Copper (Cu)	3.27	3.27	0.00327	0.013870686	0.000218298
54.938		Manganese (Mn)	61.25	61.25	0.06125	0.25981025	0.004729154
58.69		Nickel (Ni)	21.87	21.87	0.02187	0.092768166	0.001580647
207.2		Lead (Pb)	0.58	0.58	0.00058	0.002460244	1.18738E-05
50.94		Vanadium (V)	0.14	0.14	0.00014	0.000593852	1.16579E-05
65.38		Zinc (Zn)	12.69	12.69	0.01269	0.053828442	0.000823317
200.59		Mercury (Hg)	0.11	0.11	0.00011	0.000466598	2.32613E-06
95.94		Molybdenum (Mo)	0.66	0.66	0.00066	0.002799588	2.91806E-05
78.96		Selenium (Se)	0.04	0.04	0.00004	0.000169672	2.14883E-06

*Total Hydrogen (from fuel + from moisture)

** Total Oxygen (from fuel + from moisture)

& Total Nitrogen (from fuel + from agent)

Moisture content -wt. %(ar) = 9.856

O from Moisture = 0.50394 4.96683264

H from Moisture = 1.00788 9.93366528

N₂ feeding input

Nitrogen (N₂) 40 L/min 2400 L/hr 99.822 Mols/hr

Calculation of the total moles of the elements to be fed to MTDATA for demolition.

Atomic Mass	Unit	Elements	Actual fuel composition	Kg/hr (10000)	g/hr (0.001)	Fuel feed (wt.3.021g)	Total input (MTDATA) Fuel +agent Mols/hr
12	Weight (%)	Carbon (C)	50.2414	502414	502.414	1517.793	126.4827
1		Hydrogen (H)	7.1362	170698.7	170.69865	515.6806	515.6806
14		Nitrogen (N)	0.0602	602	0.602	1.818642	99.9519
32		Sulphur(S)	0.0018	18	0.018	0.054378	0.001699
16		Oxygen(O)	42.5604	475272.3	475.27233	1435.798	89.73736
35.5		Chlorine (Cl)	0.03	300	0.3	0.9063	0.02553
26.98		Aluminium (Al)	218.04	218.04	0.21804	0.658699	0.024414
40	Weight mg/kg	Calcium (Ca)	1365.78	1365.78	1.36578	4.126021	0.103151
39.0983		Potassium (K)	252.42	252.42	0.25242	0.762561	0.019504
55.84		Iron (Fe)	2277.91	2277.91	2.27791	6.881566	0.123237
23		Sodium (Na)	188.64	188.64	0.18864	0.569881	0.024777
28.0855		Silicon (Si)	102.77	102.77	0.10277	0.310468	0.011054
47.86		Titanium (Ti)	171.65	171.65	0.17165	0.518555	0.010835
74.92		Arsenic (As)	0.19	0.19	0.00019	0.000574	7.66E-06
112.41		Cadmium (Cd)	0.13	0.13	0.00013	0.000393	3.49E-06
58.93		Cobalt (Co)	1.18	1.18	0.00118	0.003565	6.05E-05
51.996		Chromium (Cr)	53.61	53.61	0.05361	0.161956	0.003115
63.54		Copper (Cu)	6.83	6.83	0.00683	0.020633	0.000325
54.938		Manganese (Mn)	111.14	111.14	0.11114	0.335754	0.006112
58.69		Nickel (Ni)	28.1	28.1	0.0281	0.08489	0.001446
207.2		Lead (Pb)	4.62	4.62	0.00462	0.013957	6.74E-05
50.94		Vanadium (V)	0.37	0.37	0.00037	0.001118	2.19E-05
65.38		Zinc (Zn)	28.3	28.3	0.0283	0.085494	0.001308
200.59		Mercury (Hg)	0.22	0.22	0.00022	0.000665	3.31E-06
95.94		Molybdenum (Mo)	1.21	1.21	0.00121	0.003655	3.81E-05
78.96		Selenium (Se)	0.04	0.04	0.00004	0.000121	1.53E-06

*Total Hydrogen (from fuel + from moisture)

** Total Oxygen (from fuel + from moisture)

& Total Nitrogen (from fuel + from agent)

Moisture content -wt. %(ar) = 9.856

O from Moisture = 0.50394 4.96

H from Moisture = 1.00788 9.93366528

N₂ feeding input

Nitrogen (N₂) 40 L/min 2400 L/hr 99.822 Mols/hr

E.1.2 The total moles of the elements to be fed to MTDATA for original waste wood samples (industrial).

Calculation of the total moles of the elements to be fed to MTDATA for wood chips.

Atomic Mass	Unit	Elements	Actual fuel composition	Kg/hr (10000)	g/hr (0.001)	Fuel feed (wt.2.1538g)	Total input (MTDATA) Fuel +agent Mols/hr
12	Weight (%)	Carbon (C)	6.91	157087.92	157.0879	338.33597	338.33597
1		Hydrogen (H)	1.97	19700	19.7	42.42986	102.852704
14		Nitrogen (N)	0.0022	22	0.022	0.0473836	0.00148078
32		Sulphur(S)	42.83	472293.96	472.29396	1017.22674	63.576671
16		Oxygen(O)	0.04	400	0.4	0.86152	0.02426817
35.5		Chlorine (Cl)	247.75	247.75	0.24775	0.53360395	0.01977776
26.98		Aluminium (Al)	3161.37	3161.37	3.16137	6.8089587	0.17022396
40	Weight mg/kg	Calcium (Ca)	580	580	0.58	1.249204	0.03195034
39.0983		Potassium (K)	8074.19	8074.19	8.07419	17.3901904	0.31142891
55.84		Iron (Fe)	623.15	623.15	0.62315	1.34214047	0.05835393
23		Sodium (Na)	168.38	168.38	0.16838	0.36265684	0.01291260
28.085		Silicon (Si)	16.54	16.54	0.01654	0.03562385	0.00074434
47.86		Titanium (Ti)	16.77	16.77	0.01677	0.03611923	0.00048211
74.92		Arsenic (As)	0.29	0.29	0.00029	0.00062460	5.55646E-06
112.41		Cadmium (Cd)	1.83	1.83	0.00183	0.00394145	6.68837E-05
58.93		Cobalt (Co)	42.65	42.65	0.04265	0.09185957	0.00176666
51.996		Chromium (Cr)	23.79	23.79	0.02379	0.05123890	0.00080640
63.54		Copper (Cu)	118.39	118.39	0.11839	0.25498838	0.00464138
54.938		Manganese (Mn)	5.91	5.91	0.00591	0.01272895	0.00021688
58.69		Nickel (Ni)	151.32	151.32	0.15132	0.32591302	0.00157294
207.2		Lead (Pb)	0.73	0.73	0.00073	0.00157228	3.08652E-05
50.94		Vanadium (V)	66.98	66.98	0.06698	0.14426153	0.002206508
65.38		Zinc (Zn)	0.71	0.71	0.00071	0.00152919	7.6235E-06
200.59		Mercury (Hg)	0.52	0.52	0.00052	0.00111997	1.16737E-05
95.94		Molybdenum (Mo)	0.08	0.08	0.00008	0.00017230	2.18217E-06
78.96		Selenium (Se)	6.91	157087.92	157.08792	338.3359707	338.3359707

*Total Hydrogen (from fuel + from moisture)

** Total Oxygen (from fuel + from moisture)

& Total Nitrogen (from fuel + from agent)

Moisture content -wt. %(ar) = 8.73

O from Moisture = 0.50394 4.3993962

H from Moisture = 1.00788 8.7987924

N₂ feeding input

Nitrogen (N₂) 40 L/min 2400 L/hr 99.822 Mols/hr

E.1.3 The total moles of the elements to be fed to MTDATA for original waste wood samples (landfill).

Calculation of the total moles of the elements to be fed to MTDATA for L.d. 50-51 m.

Atomic Mass	Unit	Elements	Actual fuel composition	Kg/hr (10000)	g/hr (0.001)	Fuel feed (wt. 1.1204g)	Total input (MTDATA) Fuel +agent Mols/hr
12	Weight (%)	Carbon (C)	45.5557	455557	455.557	510.40606	42.533838
1		Hydrogen (H)	6.9677	4540050.4	4540.0504	5086.6724	5086.6725
14		Nitrogen (N)	0.2913	2913	2.913	3.2637252	100.05512
32		Sulphur(S)	0.013	130	0.13	0.145652	0.004551625
16		Oxygen(O)	47.1723	52.15525872	0.052155259	0.058434752	0.003652172
35.5		Chlorine (Cl)	0.12	1200	1.2	1.34448	0.037872676
26.98	Weight mg/kg	Aluminium (Al)	269.76	269.76	0.26976	0.302239104	0.011202339
40		Calcium (Ca)	4606.52	4606.52	4.60652	5.16114500	0.12902862
39.0983		Potassium (K)	527.15	527.15	0.52715	0.59061886	0.01510599
55.84		Iron (Fe)	3413.89	3413.89	3.41389	3.82492235	0.06849789
23		Sodium (Na)	2421.33	2421.33	2.42133	2.71285813	0.11795035
28.0855		Silicon (Si)	259.69	259.69	0.25969	0.29095667	0.01035967
47.86		Titanium (Ti)	19.65	19.65	0.01965	0.02201586	0.00046000
74.92		Arsenic (As)	10.17	10.17	0.01017	0.01139446	0.00015208
112.41		Cadmium (Cd)	0.44	0.44	0.00044	0.000492976	4.38552E-06
58.93		Cobalt (Co)	1.71	1.71	0.00171	0.00191588	3.25112E-05
51.996		Chromium (Cr)	18.44	18.44	0.01844	0.02066017	0.00039734
63.54		Copper (Cu)	19.37	19.37	0.01937	0.02170214	0.00034155
54.938		Manganese (Mn)	30.84	30.84	0.03084	0.03455313	0.00062894
58.69		Nickel (Ni)	5.9	5.9	0.0059	0.00661036	0.00011263
207.2		Lead (Pb)	407.66	407.66	0.40766	0.45674226	0.00220435
50.94		Vanadium (V)	2.62	2.62	0.00262	0.00293544	5.76256E-05
65.38		Zinc (Zn)	150	150	0.15	0.16806	0.00257051
200.59		Mercury (Hg)	0.32	0.32	0.00032	0.00035852	1.78737E-06
95.94		Molybdenum (Mo)	0.85	0.85	0.00085	0.00095234	9.92641E-06
78.96		Selenium (Se)	0.33	0.33	0.00033	0.00036973	4.68252E-06

*Total Hydrogen (from fuel + from moisture)

** Total Oxygen (from fuel + from moisture)

& Total Nitrogen (from fuel + from agent)

Moisture content -wt. %(ar) = 9.888

O from Moisture = 0.50394 5.64615

H from Moisture = 1.00788 11.293

N₂ feeding input

Nitrogen (N₂) 40 L/min 2400 L/hr 99.822 Mols/hr

Calculation of the total moles of the elements to be fed to MTDATA for L.d. 41-43 m.

Atomic Mass	Unit	Elements	Actual fuel composition	Kg/hr (10000)	g/hr (0.001)	Fuel feed (wt.3.0756g)	Total input (MTDATA) Fuel +agent Mols/hr
12	Weight (%)	Carbon (C)	42.2419	422419	422.419	1299.191876	108.2659897
1		Hydrogen (H)	6.1725	520817.3636	520.8173636	1601.825884	1601.825884
14		Nitrogen (N)	0.6819	6819	6.819	20.9725164	101.3200369
32		Sulphur(S)	0.006	60	0.06	0.184536	0.00576675
16		Oxygen(O)	50.8977	738523.1818	738.5231818	2271.401898	141.9626186
35.5		Chlorine (Cl)	0.13	1300	1.3	3.99828	0.112627606
26.98	Weight mg/kg	Aluminium (Al)	995.89	995.89	0.99589	3.062959284	0.113527031
40		Calcium (Ca)	14934.45	14934.45	14.93445	45.93239442	1.148309861
39.0983		Potassium (K)	861.98	861.98	0.86198	2.651105688	0.067806163
55.84		Iron (Fe)	4000.31	4000.31	4.00031	12.30335344	0.220332261
23		Sodium (Na)	2177.49	2177.49	2.17749	6.697088244	0.29117775
28.0855		Silicon (Si)	519.62	519.62	0.51962	1.598143272	0.056902789
47.86		Titanium (Ti)	18.86	18.86	0.01886	0.058005816	0.001211989
74.92		Arsenic (As)	81.58	81.58	0.08158	0.250907448	0.003349005
112.41		Cadmium (Cd)	0.19	0.19	0.00019	0.000584364	5.19851E-06
58.93		Cobalt (Co)	3.38	3.38	0.00338	0.010395528	0.000176405
51.996		Chromium (Cr)	150.52	150.52	0.15052	0.462939312	0.008903364
63.54		Copper (Cu)	177.23	177.23	0.17723	0.545088588	0.008578668
54.938		Manganese (Mn)	44.37	44.37	0.04437	0.136464372	0.002483971
58.69		Nickel (Ni)	10.55	10.55	0.01055	0.03244758	0.000552864
207.2		Lead (Pb)	70.88	70.88	0.07088	0.217998528	0.001052116
50.94		Vanadium (V)	3.71	3.71	0.00371	0.011410476	0.000223998
65.38		Zinc (Zn)	124.57	124.57	0.12457	0.383127492	0.005860011
200.59		Mercury (Hg)	0.77	0.77	0.00077	0.002368212	1.18062E-05
95.94		Molybdenum (Mo)	0.84	0.84	0.00084	0.002583504	2.69283E-05
78.96		Selenium (Se)	0.65	0.65	0.00065	0.00199914	2.53184E-05

*Total Hydrogen (from fuel + from moisture)

** Total Oxygen (from fuel + from moisture)

& Total Nitrogen (from fuel + from agent)

Moisture content -wt. %(ar) = 45.5503

O from Moisture = 0.50394 22.95461818

H from Moisture = 1.00788 145.90923636

N₂ feeding input

Nitrogen (N₂) 40 L/min 2400 L/hr 99.822 Mols/hr

Calculation of the total moles of the elements to be fed to MTDATA for L.d.37.5-39 m.

Atomic Mass	Unit	Elements	Actual fuel composition	Kg/hr (10000)	g/hr (0.001)	Fuel feed (wt. 3.3379g)	Total input (MTDATA) Fuel +agent Mols/hr
12	Weight (%)	Carbon (C)	46.0319	460319	460.319	1536.49879	128.0415658
1		Hydrogen (H)	38.76974612	387697.4612	387.6974612	1294.095356	1294.095356
14		Nitrogen (N)	0.4792	4792	4.792	15.9952168	100.9645155
32		Sulphur(S)	0.012	120	0.12	0.400548	0.012517125
16		Oxygen(O)	64.86227306	648622.7306	648.6227306	2165.037812	135.3148633
35.5		Chlorine (Cl)	0.11	1100	1.1	3.67169	0.103427887
26.98	Weight mg/kg	Aluminium (Al)	3223.04	3223.04	3.22304	10.75818522	0.398746672
40		Calcium (Ca)	16645.77	16645.77	16.64577	55.56191568	1.389047892
39.0983		Potassium (K)	1196.28	1196.28	1.19628	3.993063012	0.102128814
55.84		Iron (Fe)	6488.38	6488.38	6.48838	21.6575636	0.387850351
23		Sodium (Na)	1937.82	1937.82	1.93782	6.468249378	0.281228234
28.0855		Silicon (Si)	598.51	598.51	0.59851	1.997766529	0.071131599
47.86		Titanium (Ti)	69.36	69.36	0.06936	0.231516744	0.004837375
74.92		Arsenic (As)	17.87	17.87	0.01787	0.059648273	FALSE
112.41		Cadmium (Cd)	0.28	0.28	0.00028	0.000934612	8.31431E-06
58.93		Cobalt (Co)	3.2	3.2	0.0032	0.01068128	0.000181254
51.996		Chromium (Cr)	28.03	28.03	0.02803	0.093561337	0.001799395
63.54		Copper (Cu)	67.93	67.93	0.06793	0.226743547	0.003568517
54.938		Manganese (Mn)	65.75	65.75	0.06575	0.219466925	0.003994811
58.69		Nickel (Ni)	12.09	12.09	0.01209	0.040355211	0.000687599
207.2		Lead (Pb)	147.92	147.92	0.14792	0.493742168	0.002382926
50.94		Vanadium (V)	9.42	9.42	0.00942	0.031443018	0.000617256
65.38		Zinc (Zn)	124.84	124.84	0.12484	0.416703436	0.006373561
200.59		Mercury (Hg)	0.8	0.8	0.0008	0.00267032	1.33123E-05
95.94		Molybdenum (Mo)	1.04	1.04	0.00104	0.003471416	3.61832E-05
78.96		Selenium (Se)	0.93	0.93	0.00093	0.003104247	3.93142E-05

*Total Hydrogen (from fuel + from moisture)

** Total Oxygen (from fuel + from moisture)

& Total Nitrogen (from fuel + from agent)

Moisture content -wt. %(ar) = 32.049

O from Moisture = 0.50394 16.15077306

H from Moisture = 1.00788 32.30154612

N₂ feeding input

Nitrogen (N₂) 40 L/min 2400 L/hr 99.822 Mols/hr

Calculation of the total moles of the elements to be fed to MTDATA for L.d. 3-7 m.

Atomic Mass	Unit	Elements	Actual fuel composition	Kg/hr (10000)	g/hr (0.001)	Fuel feed (wt. 1.4931g)	Total input (MTDATA) Fuel +agent Mols/hr
12	Weight (%)	Carbon (C)	49.3626	493626	493.626	737.0329806	61.41941505
1		Hydrogen (H)	7.4835	414746.5615	414.7465615	619.258091	619.258091
14		Nitrogen (N)	0.1905	1905	1.905	2.8443555	100.0251683
32		Sulphur(S)	0.0036	36	0.036	0.0537516	0.001679738
16		Oxygen(O)	42.9598	599553.7808	599.5537808	895.1937501	55.94960938
35.5		Chlorine (Cl)	0.06	600	0.6	0.89586	0.025235493
26.98	Weight mg/kg	Aluminium (Al)	112.22	112.22	0.11222	0.167555682	0.006210366
40		Calcium (Ca)	3274.69	3274.69	3.27469	4.889439639	0.122235991
39.0983		Potassium (K)	801.01	801.01	0.80101	1.195988031	0.030589259
55.84		Iron (Fe)	577.03	577.03	0.57703	0.861563493	0.015429146
23		Sodium (Na)	761.24	761.24	0.76124	1.136607444	0.049417715
28.0855		Silicon (Si)	144.16	144.16	0.14416	0.215245296	0.00766393
47.86		Titanium (Ti)	2	2	0.002	0.0029862	6.23945E-05
74.92		Arsenic (As)	160.97	160.97	0.16097	0.240344307	0.003208013
112.41		Cadmium (Cd)	0.07	0.07	0.00007	0.000104517	9.29784E-07
58.93		Cobalt (Co)	1.01	1.01	0.00101	0.001508031	2.55902E-05
51.996		Chromium (Cr)	238.88	238.88	0.23888	0.356671728	0.006859599
63.54		Copper (Cu)	136.2	136.2	0.1362	0.20336022	0.003200507
54.938		Manganese (Mn)	34.53	34.53	0.03453	0.051556743	0.000938453
58.69		Nickel (Ni)	3.37	3.37	0.00337	0.005031747	8.57343E-05
207.2		Lead (Pb)	3.3	3.3	0.0033	0.00492723	2.37801E-05
50.94		Vanadium (V)	0.38	0.38	0.00038	0.000567378	1.11382E-05
65.38		Zinc (Zn)	19.56	19.56	0.01956	0.029205036	0.000446697
200.59		Mercury (Hg)	0.27	0.27	0.00027	0.000403137	2.00976E-06
95.94		Molybdenum (Mo)	0.34	0.34	0.00034	0.000507654	5.29137E-06
78.96		Selenium (Se)	0.12	0.12	0.00012	0.000179172	2.26915E-06

*Total Hydrogen (from fuel + from moisture)

** Total Oxygen (from fuel + from moisture)

& Total Nitrogen (from fuel + from agent)

Moisture content -wt. %(ar) = 33.7254

O from Moisture = 0.50394 16.99557808

H from Moisture = 1.00788 33.99115615

N₂ feeding input

Nitrogen (N₂) 40 L/min 2400 L/hr 99.822 Mols/hr

E.1.4 The total moles of the elements to be fed to MTDATA for artificial waste wood samples

Calculation of the total moles of the elements to be fed to MTDATA for artificial waste wood sample (AS₁).

Atomic Mass	Unit	Elements	Actual fuel composition	Kg/hr (10000)	g/hr (0.001)	Fuel feed (wt. 1.3174g)	Total input (MTDATA) Fuel +agent Mols/hr
12	Weight (%)	Carbon (C)	50.69	506900	506.9	667.7901	55.64917
1		Hydrogen (H)	7.17	71700	71.7	94.45758	125.4463
14		Nitrogen (N)	0.09	900	0.9	1.18566	99.90669
32		Sulphur(S)	0.0025	25	0.025	0.032935	0.001029
16		Oxygen(O)	42.06	420600	420.6	554.0984	34.67265
35.5		Chlorine (Cl)	83.39	83.39	0.08339	0.109858	0.004072
26.98		Aluminium (Al)	1512.81	1512.81	1.51281	1.992976	0.049824
40	Weight mg/kg	Calcium (Ca)	506.49	506.49	0.50649	0.66725	0.017066
39.0983		Potassium (K)	200.33	200.33	0.20033	0.263915	0.004726
55.84		Iron (Fe)	106.56	106.56	0.10656	0.140382	0.006104
23		Sodium (Na)	107.82	107.82	0.10782	0.142042	0.005057
28.0855		Silicon (Si)	197.34	197.34	0.19734	0.259976	0.010694
47.86		Titanium (Ti)	1.92	1.92	0.00192	0.002529	5.29E-05
74.92		Arsenic (As)	16.64975	16.64975	0.01665	0.021934	0.000293
112.41		Cadmium (Cd)	0.17	0.17	0.00017	0.000224	1.99E-06
58.93		Cobalt (Co)	0.1	0.1	0.0001	0.000132	2.24E-06
51.996		Chromium (Cr)	11.27	11.27	0.01127	0.014847	0.000286
63.54		Copper (Cu)	7.34	7.34	0.00734	0.00967	0.000152
54.938		Manganese (Mn)	62.43	62.43	0.06243	0.082245	0.001497
58.69		Nickel (Ni)	40.60914	40.60914	0.040609	0.053498	0.000912
207.2		Lead (Pb)	0.34	0.34	0.00034	0.000448	2.16E-06
50.94		Vanadium (V)	0.19	0.19	0.00019	0.00025	4.91E-06
65.38		Zinc (Zn)	14.24	14.24	0.01424	0.01876	0.000287
200.59		Mercury (Hg)	1	1	0.001	0.001317	6.57E-06
95.94		Molybdenum (Mo)	0.17	0.17	0.00017	0.000224	2.33E-06
78.96		Selenium (Se)	0.07	0.07	0.00007	9.22E-05	1.17E-06

*Total Hydrogen (from fuel + from moisture)

** Total Oxygen (from fuel + from moisture)

& Total Nitrogen (from fuel + from agent)

Moisture content -wt. %(ar) = 9.08

O from Moisture = 0.50394 4.575

H from Moisture = 1.00788 9.151

N₂ feeding input

Nitrogen (N₂) 40 L/min 2400 L/hr 99.822 Mols/hr

Calculation of the total moles of the elements to be fed to MTDATA for artificial waste wood sample (AS₂).

Atomic Mass	Unit	Elements	Actual fuel composition	Kg/hr (10000)	g/hr (0.001)	Fuel feed (wt. 1.1774g)	Total input (MTDATA) Fuel +agent Mols/hr
12	Weight (%)	Carbon (C)	50.69	506900	506.9	596.8241	49.73534
1		Hydrogen (H)	7.17	163215.5	163.2155	192.1699	192.1699
14		Nitrogen (N)	0.09	900	0.9	1.05966	99.89769
32		Sulphur(S)	0.0025	25	0.025	0.029435	0.00092
16		Oxygen(O)	42.06	466357.8	466.3578	549.0896	34.3181
35.5		Chlorine (Cl)	0.09	900	0.9	1.05966	0.02985
26.98	Weight mg/kg	Aluminium (Al)	83.39	83.39	0.08339	0.098183	0.003639
40		Calcium (Ca)	1512.81	1512.81	1.51281	1.781182	0.04453
39.0983		Potassium (K)	506.49	506.49	0.50649	0.596341	0.015252
55.84		Iron (Fe)	200.33	200.33	0.20033	0.235869	0.004224
23		Sodium (Na)	106.56	106.56	0.10656	0.125464	0.005455
28.0855		Silicon (Si)	107.82	107.82	0.10782	0.126947	0.00452
47.86		Titanium (Ti)	1.92	1.92	0.00192	0.002261	4.72E-05
74.92		Arsenic (As)	28.91184	28.91184	0.028912	0.034041	0.000454
112.41		Cadmium (Cd)	0.17	0.17	0.00017	0.0002	1.78E-06
58.93		Cobalt (Co)	0.1	0.1	0.0001	0.000118	2E-06
51.996		Chromium (Cr)	11.27	11.27	0.01127	0.013269	0.000255
63.54		Copper (Cu)	7.34	7.34	0.00734	0.008642	0.000136
54.938		Manganese (Mn)	62.43	62.43	0.06243	0.073505	0.001338
58.69		Nickel (Ni)	103.5648	103.5648	0.103565	0.121937	0.002078
207.2		Lead (Pb)	0.34	0.34	0.00034	0.0004	1.93E-06
50.94		Vanadium (V)	0.19	0.19	0.00019	0.000224	4.39E-06
65.38		Zinc (Zn)	14.24	14.24	0.01424	0.016766	0.000256
200.59		Mercury (Hg)	1	1	0.001	0.001177	5.87E-06
95.94		Molybdenum (Mo)	0.17	0.17	0.00017	0.0002	2.09E-06
78.96		Selenium (Se)	0.07	0.07	0.00007	8.24E-05	1.04E-06

*Total Hydrogen (from fuel + from moisture)

** Total Oxygen (from fuel + from moisture)

& Total Nitrogen (from fuel + from agent)

Moisture content -wt. %(ar) = 9.08

O from Moisture = 0.50394 4.5757752

H from Moisture = 1.00788 9.1515504

N₂ feeding input

Nitrogen (N₂) 40 L/min 2400 L/hr 99.822 Mols/hr

Calculation of the total moles of the elements to be fed to MTDATA for artificial waste wood sample (AS₃).

Atomic Mass	Unit	Elements	Actual fuel composition	Kg/hr (10000)	g/hr (0.001)	Fuel feed (wt. 1.6139g)	Total input (MTDATA) Fuel +agent Mols/hr
12	Weight (%)	Carbon (C)	50.69	506900	506.9	818.0859	68.17383
1		Hydrogen (H)	7.17	163215.5	163.2155	263.4135	263.4135
14		Nitrogen (N)	0.09	900	0.9	1.45251	99.92575071
32		Sulphur(S)	0.0025	25	0.025	0.040348	0.001261
16		Oxygen(O)	42.06	466357.8	466.3578	752.6548	47.04092
35.5		Chlorine (Cl)	0.09	900	0.9	1.45251	0.040916
26.98		Aluminium (Al)	83.39	83.39	0.08339	0.134583	0.004988
40	Weight mg/kg	Calcium (Ca)	1512.81	1512.81	1.51281	2.441524	0.061038
39.0983		Potassium (K)	506.49	506.49	0.50649	0.817424	0.020907
55.84		Iron (Fe)	200.33	200.33	0.20033	0.323313	0.00579
23		Sodium (Na)	106.56	106.56	0.10656	0.171977	0.007477
28.0855		Silicon (Si)	107.82	107.82	0.10782	0.174011	0.006196
47.86		Titanium (Ti)	1.92	1.92	0.00192	0.003099	6.47E-05
74.92		Arsenic (As)	41.69869	41.69869	0.041699	0.067298	0.000898
112.41		Cadmium (Cd)	0.17	0.17	0.00017	0.000274	2.44E-06
58.93		Cobalt (Co)	0.1	0.1	0.0001	0.000161	2.74E-06
51.996		Chromium (Cr)	11.27	11.27	0.01127	0.018189	0.00035
63.54		Copper (Cu)	7.34	7.34	0.00734	0.011846	0.000186
54.938		Manganese (Mn)	62.43	62.43	0.06243	0.100756	0.001834
58.69		Nickel (Ni)	84.55035	84.55035	0.08455	0.136456	0.002325
207.2		Lead (Pb)	0.34	0.34	0.00034	0.000549	2.65E-06
50.94		Vanadium (V)	0.19	0.19	0.00019	0.000307	6.02E-06
65.38		Zinc (Zn)	14.24	14.24	0.01424	0.022982	0.000352
200.59		Mercury (Hg)	1	1	0.001	0.001614	8.05E-06
95.94		Molybdenum (Mo)	0.17	0.17	0.00017	0.000274	2.86E-06
78.96		Selenium (Se)	0.07	0.07	0.00007	0.000113	1.43E-06

*Total Hydrogen (from fuel + from moisture)

** Total Oxygen (from fuel + from moisture)

& Total Nitrogen (from fuel + from agent)

Moisture content -wt. %(ar) = 9.08

O from Moisture = 0.50394 4.5757752

H from Moisture = 1.00788 9.1515504

N₂ feeding input

Nitrogen (N₂) 40 L/min 2400 L/hr 99.822 Mols/hr

E.1.5 The total moles of the elements to be fed to MTDATA for blends waste wood samples (blending 60/40: W/W)

Calculation of the total moles of the elements to be fed to MTDATA for artificial waste wood sample (BS).

Atomic Mass	Unit	Elements	Actual fuel composition	Kg/hr (10000)	g/hr (0.001)	Fuel feed (wt. 3.098g)	Total input (MTDATA) Fuel +agent Mols/hr
12	Weight (%)	Carbon (C)	50.1398	501398	501.398	1553.331	129.4443
1		Hydrogen (H)	7.1386	158970.8	158.9708	492.4915	492.4915
14		Nitrogen (N)	0.4454	4454	4.454	13.79849	100.807
32		Sulphur(S)	0.0007	7	0.007	0.021686	0.000678
16		Oxygen(O)	42.2754	466546.4	466.5464	1445.361	90.33504
35.5		Chlorine (Cl)	0.03	300	0.3	0.9294	0.02618
26.98	Weight mg/kg	Aluminium (Al)	263.55	263.55	0.26355	0.816478	0.030262
40		Calcium (Ca)	3802.48	3802.48	3.80248	11.78008	0.294502
39.0983		Potassium (K)	1587.87	1587.87	1.58787	4.919221	0.125817
55.84		Iron (Fe)	1375.58	1375.58	1.37558	4.261547	0.076317
23		Sodium (Na)	521.33	521.33	0.52133	1.61508	0.070221
28.0855		Silicon (Si)	271.87	271.87	0.27187	0.842253	0.029989
47.86		Titanium (Ti)	18.68	18.68	0.01868	0.057871	0.001209
74.92		Arsenic (As)	5.94	5.94	0.00594	0.018402	0.000246
112.41		Cadmium (Cd)	0.41	0.41	0.00041	0.00127	1.13E-05
58.93		Cobalt (Co)	2.11	2.11	0.00211	0.006537	0.000111
51.996		Chromium (Cr)	66.97	66.97	0.06697	0.207473	0.00399
63.54		Copper (Cu)	20.61	20.61	0.02061	0.06385	0.001005
54.938		Manganese (Mn)	182.21	182.21	0.18221	0.564487	0.010275
58.69		Nickel (Ni)	6.64	6.64	0.0664	0.144491	0.002462
207.2		Lead (Pb)	60.02	60.02	0.06002	0.185942	0.000897
50.94		Vanadium (V)	0.66	0.66	0.00066	0.002045	4.01E-05
65.38		Zinc (Zn)	111.17	111.17	0.11117	0.344405	0.005268
200.59		Mercury (Hg)	0.43	0.43	0.00043	0.001332	6.64E-06
95.94		Molybdenum (Mo)	1.3	1.3	0.0013	0.004027	4.2E-05
78.96		Selenium (Se)	0.1	0.1	0.0001	0.00031	3.92E-06

*Total Hydrogen (from fuel + from moisture)

** Total Oxygen (from fuel + from moisture)

& Total Nitrogen (from fuel + from agent)

Moisture content -wt. %(ar) = 8.69

O from Moisture = 0.50394 4.3792386

H from Moisture = 1.00788 8.7584772

N₂ feeding input

Nitrogen (N₂) 40 L/min 2400 L/hr 99.822 Mols/hr