Recovery of Arsenic from CCA-treated Timber

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Abstract

To extend the service life of softwood timber, such timbers are commonly treated with chromated copper arsenate (CCA) – a preservative that inhibits the natural decaying process of timber. However, due to the toxic nature of the preservative contained within the wood, its disposal after service-life has proven to be problematic. Not only the preservative entering the disposal sector, but also the limited opportunities for alternative use and growing quantities of this waste, are further complicating the problem. The linear product pathway of cradle-to-grave promotes the need for continued use of virgin CCA preservative, resulting in ever larger quantities entering the immediate environment. Currently, CCA-treated timber waste is disposed of in Class II landfills in New Zealand. In order to mitigate the environmental concerns and to achieve a circular economy, an alternative and more sustainable waste management strategy is required, shifting away from landfill disposal of CCA timber wastes.

The objectives of this thesis are to explore suitable processing technologies for CCA-treated timber wastes for recovery, reuse and recycling; furthermore, to develop a corresponding waste management strategy applicable to the New Zealand circumstance. From literature review, pyrolysis has been identified as the key recovery technology for a waste management strategy that enables the recovery of the treatment metal(oid)s in the CCA-treated timber waste. Thus, this thesis sets out to test the hypothesis that pyrolysis can provide a feasible solution, not only allowing for the decomposition of the woody biomass (including the recovery of its energy value) but also recovering the arsenic in a suitable form for future application.

Proof of this hypothesis will open up the opportunity for the development of a circular economy in regard to the recovery and reuse of the preservative chemicals, thereby reducing environmental harm by limiting the quantities of CCA-treated timber waste entering landfills. In addition, the preservative product route could be adapted to that of a cradle-to-cradle pathway, thereby reducing the requirement for virgin preservative use.

The emphasis in this thesis was placed on arsenic recovery. As arsenic is a highly toxic and volatile chemical, a thorough understanding of its release processes from wood structures during pyrolysis is essential for its effective and safe recovery. Experimental and thermodynamic modelling was undertaken to identify the optimal conditions for arsenic recovery into the pyrolysis bio-oil product. To this end, experimental and thermodynamic investigations were carried out, in regard to arsenic interactions, oxidation states and chemical reactions that occur during pyrolysis. Furthermore, pyrolysis product yields and metal(oid) concentrations were determined. The findings were visualised and integrated into a conceptual process design suitable for industry application.

Experiments were conducted in a batch pyrolysis system at operating temperatures from 280°C to 580°C with a residence time of 30 minutes. In the experiments, 25 g of freshly treated H4-CCA-treated *Pinus radiata* wood were pyrolysed in an inert nitrogen environment. Liquid (bio-oil), solid (char) and non-condensable gas yields were measured, and their compositions were analysed. For comparison purposes, untreated *Pinus radiata* wood was also pyrolysed as a control.

The experimental results indicate that batch pyrolysis of CCA-treated wood - in comparison to that of untreated wood - results in lower liquid yields but higher yields of char and non-condensable gas products. This is attributed to the presence of CCA compounds in the wood, which promote charring and secondary cracking reactions. The onset of arsenic release from the solid state (arsenic pentoxide or As(V), As_2O_5) was observed to occur at 300°C, with a maximum total recovery at 475°C. The arsenic release at temperatures within the pyrolysis regime is attributed to the breakdown of As_2O_5, which has remained in the wood in its unfixated form. The other form of arsenic compound contained within the wood, $CrAsO_4$, is stable during pyrolysis. This form of arsenic is fixated through the chromium compound to the wood structures.

As stated above, the highest bio-oil yield is achieved at a pyrolysis temperature of 475°C. Under this condition, the resulting liquid yield was 29 wt% with an arsenic concentration of 606 ppm – equating to 6.7 wt% of the original arsenic content. The arsenic present in the bio-oil was found to be As(III) (As_2O_3), indicating that the reduction of As(V) to As(III) took place during the pyrolysis process at temperatures lower than those that would have occurred in an inert environment. The catalytic effect of lower a reaction temperature is attributed to the reducing environment, created during pyrolysis. At temperatures higher than 475°C the volatilisation of arsenic is promoted, driving it into the gaseous non-condensable pyrolysis product.

To clarify the pyrolysis reactions involved, when using CCA-treated wood as a feedstock, a pyrolysis model was proposed, based on studies reported in literature. Additionally, a thermodynamic equilibrium model was developed to investigate the decomposition process of arsenic compounds.

Experimental results and thermodynamic equilibrium modelling showed that chromium and copper are essentially retained in the char. Temperature was found to be the key parameter in determining the onset of arsenic release. In addition, comparison of this study's findings and those reported in literature indicate that both heating rate and residence time play important roles in regard to the extent of arsenic release and its recovery in liquid or gaseous products.

In order to achieve the maximum bio-oil yield and arsenic recoveries within the pyrolysis liquid product, a fast heating rate and short residence time are deemed to be favourable. Consequently, continuous fast pyrolysis is the preferred technology for pyrolysis decomposition of the biomass. In this thesis, to meet the above parameters of maximum oil yield and arsenic recovery, results from continuous fast pyrolysis experiments, as reported in the literature review, were used. On the basis of these data, a simplified process model to simulate industrial performance was developed and, in addition, the feasibility for recovery of the treatment preservatives for further use in timber treatment was examined. The results were then applied to establish a conceptual waste management scheme and engineering design for a possible commercial plant. The proposed plant with a capacity of processing 1 tonne h^{-1} of dry CCA-treated timber wastes produces 211 kg of CCA-free char, alongside 237 kg of a CCA-free LOSP analogue liquid and 331 kg of CCA-free gas. A heavy oil fraction (151 kg) containing 0.61 kg of As(III) and 69 kg of CCA-contaminated char can also be recovered, together with 0.35 kg of As_4O_6, which needs to be removed from the gas product.

The applicability of the bio-oil as a wood preservative still requires experimental proof. However, literature shows a potential suitability in its crude form. Furthermore, a light organic solvent preservative (LOSP) analogue liquid can be recovered that has similar properties to LOSP and which could be augmented with LOSP for wood treatment.

This thesis provides an initial proof-of-concept for pyrolysis as a waste management technology for CCA-treated timber waste and validates that further scientific investigation into this process is warranted. Importantly, the outcome of the research and engineering appraisals undertaken in this thesis offers a novel end-of-life solution for CCA-treated timber waste that moves beyond current disposal methods towards a circular economy approach.

Table of Contents

Nomenclature

List of Abbreviations

CCA	Chromated Copper Arsenate
EDTA	Ethylenediaminetetracetic Acid
EPA	Environmental Protection Authority
EPR	Extended Producer Responsibility
EPS	Electrostatic Recipitator
GC-MS	Gas Chromatography–Mass Spectrometry
HG	Hydrige Generation
HPLC	High Performance Liquid Chromotrography
HSNO	Hazardous Substances and New Organisms Act 1996
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
LFG	Landfill Gas
LIBS	Laser-Induced Breakdown Spectrometry
LOSP	Light Organic Solvent Preservatives
MDF	Medium Density Fibreboard
NC	Non-Condensable
NMR	Nuclear Magnetic Resonance Spectrometry
NTP	Normal Temperature and Pressure
NZ	New Zealand
NZD	New Zealand Dollar
ODE	Ordinary Differential Equation
RMA	Resource Management Act
SP	Setpoint
STP	Standard Temperature and Pressure
TGA	Thermogravimetric Analysis
UV-Vis	Ultraviolet–visible Spectrometry
WMA	Waste Management Act
wt%	Weight percent
XRF	X-Ray Fluorescence Spectrometry

List of Symbols

A	Atomic Mass
A	Pre-exponential Arrhenius Factor (s^{-1})
a_{ik}	Number of Atoms of element k per species i (dimensionless)
Cp	Heat Capacity ($J \cdot K^{-1} kg^{-1}$)
C_p	Specific heat capacity ($J \cdot mol^{-1}\ K^{-1}$)
E_A	Activation Energy ($J \cdot mol^{-1}$)
ΔG_f	Gibbs Free Energy of Formation ($J \cdot mol^{-1}$)
ΔH	Enthalpy Change ($J \cdot mol^{-1}$)
K	Rate Constant (s^{-1})
$\dot{m}$	Mass Flowrate ($kg \cdot s^{-1}$)
M	Mass (kg)
N	Number of Moles (mol)
P	Pressure (Pa)
Q	Duty Enthalpy flowrate ($J \cdot s^{-1}$)
Q_{rev}	Reversible work ($J \cdot mol^{-1}$)
R	Universal Gas Constant ($J \cdot mol^{-1} K^{-1}$)
ΔS	Entropy Change ($J \cdot mol^{-1} K^{-1}$)
T	Temperature (K)
T	Time (s)
V	Volume (m^3)
$\dot{V}$	Volumetric Flowrate ($m^3 \cdot s^{-1}$)
Greek	
Λ	Lagrangian Multiplier (dimensionless)
T	Residence Time (s^{-1})
Φ	Fugacity Coefficient (dimensionless)
Subscript	
I	Species
K	Element
W	Wood
C	Char
G	Gas
T	Tar
Superscript	
T	Total Value
Other	
⌀	Diameter

1 Introduction

1.1 CCA-treated Timber

Chromated copper arsenate (CCA) is a preservative used for the treatment of wood which would otherwise naturally decompose. Through this treatment, wood is made resistant to fungi and bacterial decay, as well as insect and water damage. This thereby extends the wood's service life, making it a practical and feasible option for timber that is exposed to weathering and other forms of degradation [1, 2]. CCA is a type of waterborne wood preservative that, once applied, is resistant to leaching leaving a dry, paintable surface; consequently, CCA-treated timber is commonly used for construction wood which will come in contact with the ground and in residential applications such as decks and fences [3]. Significant quantities of this preservative have been used for wood treatment since its invention in the 1930s [4]. Through treatment with CCA, the service life of wood can be extended by up to approximately 60 years [5].

Once wood has reached the end of its service life it is usually landfilled in New Zealand, Australia and the U.S. [6, 7]. Although landfilling is an inexpensive way to dispose of wood waste, environmental concerns are associated with this practice. Research has shown that over time CCA preservative leaches out of the treated wood, allowing potential exposure to humans, animals, plants and the contamination of surrounding ground [8]. Once a specific exposure time is exceeded, the preservative is toxic to humans, animals and plants [9]. All three CCA compounds are known to irritate the respiratory system and the gastrointestinal tract [10]. Additionally, chromium and arsenic are carcinogenic to animals and humans [11]. Studies have shown that all three elements leach out of CCA-treated timber and CCA wood waste, at times in concentrations exceeding regulatory thresholds by two to three orders of magnitude. In such a case, plants and soil organisms exposed to these compounds could absorb them and thereby potentially risk contaminating the food chain [12]. When CCA-treated wood waste is disposed of in a landfill, the design, underlying soil type, weather and rainfall, as well as the rate of new CCA wood waste entering the landfill are all factors influencing the extent to which the ground soil and surrounding groundwater will be contaminated [13].

Incineration is used to dispose of CCA wood waste within the European Union [2]. The primary concerns with this method of disposal are the emissions of heavy metal(oid)s into the atmosphere and the contamination of the bottom- and fly-ash with heavy metal(oid)s [14]. During the incineration process up to 77% of the original arsenic preservative in the treated timber may vaporise [15], leading to the requirement of extensive gas cleaning in order to meet air pollution regulations [2, 16].

Therefore, incineration is not deemed a practical and economically justifiable waste management method in New Zealand.

In addition to the previously mentioned environmental and health concerns, from an economic standpoint, the disposal of treated timber as currently practised via landfill is a loss of resources, both in respect to energy and the preservative metal(oid)s. Considering that the quantity of CCA-treated timber waste entering the disposal sector is expected to grow [17], a new waste management strategy needs to be proposed for an end-of-life solution that reduces the potential environmental harm of CCA wood waste. Based on waste hierarchies used in addressing similar issues with other waste materials, the waste hierarchy, as shown in Figure 1.1, has been adopted for this thesis [18]:

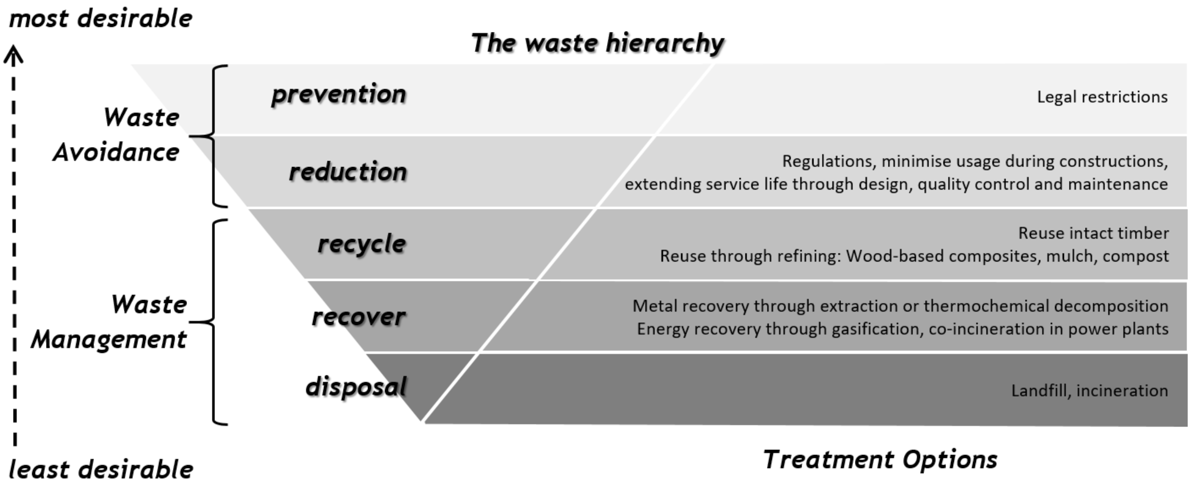

Figure 1.1: The waste hierarchy as a framework for potential treatment options for the end-of-life management of CCA-treated timber waste based on a similar concept for other waste materials [18].

Figure 1.1 suggests that waste avoidance is the most desirable strategy, focusing on "*prevention* and *reduction"*. Since the early 2000s, "*prevention and reduction*" has been adopted as the strategy in Europe and the U.S., introducing restrictions and limitations on the sales and application of CCA-treated timber [4, 19]. In 2012, Australia adopted a "*reduction*" strategy with regulations limiting the application of treated wood [20]. New Zealand has currently no restrictions on sales and applications of CCA-treated timber.

However, neither prevention nor reduction deal with the issue of waste generation and waste entering the disposal sector. Due to the wide use of CCA-treated timber in the past and its continued use in the present in some countries, "*recycle*, *recovery* and *disposal"* needs to be adopted as the waste management strategy for CCA wood waste. The recycling into a wood-based composite is tantamount to a deferral of the problem, and the ongoing risk of leaching remains a concern. Its reuse as mulch, compost or animal bedding allows CCA compounds to be distributed over an increasingly large area and allows the metal(oid)s to disperse unrestricted into the environment. Therefore, strict policies are in place to prohibit CCA wood waste to be used in this way and to limit its end-use to the disposal sector [2].

The development of a more sustainable process needs to address the recovery and recycling of the timber and treatment chemicals. By recovering metal(oid)s from CCA-treated timber waste, the negative impact that this waste stream has on the environment could be reduced and potentially eliminated. Furthermore, adopting recovery as the preferred waste management strategy may create the possibility of a full and closed recycle.

Research has explored different waste management strategies in the past two decades, including thermochemical conversion processes (gasification and pyrolysis) and methods to extract the CCA preservative from treated timber structures with leaching procedures. As will become evident through the literature review in the following chapter, pyrolysis shows promise for the recovery of the used preservative whilst also allowing the inherent energy of the wood to be recovered. Pyrolysis is a thermochemical conversion process in which a carbonaceous material is converted into char, condensable vapours, and non-condensable gas at elevated temperatures in the absence of oxygen or its limited supply. The condensable vapours may be condensed to a liquid product. As pyrolysis takes place without oxygen and thereby lacking the heat produced from the partial oxidation of the material, it differs from other thermochemical conversion processes by relying on an external heat supply.

1.2 Problem Statement

CCA is beneficial in preserving timber and protecting it from natural decay and thereby extending the treated timber's service life. However, CCA has caused concerns due to its potentially negative impacts on humans, animals and plants when exposed to treated wood for sufficient time. Although a fraction of the CCA chemicals will have leached out during the service, most of these chemicals remain in the wood after the service life. Therefore, waste management is tied to stringent regulations overseas and in New Zealand.

Management of CCA wood waste has attracted significant interest from a research perspective and in particular in regard to finding practical solutions for its disposal. In addition to concerns surrounding the hazardous nature of this waste product, there is also apprehension in regard to the growing quantity of CCA-treated timber reaching its end of service life and entering the disposal sector.

Depending on the country, the current practice for CCA wood waste is disposal to landfill or through incineration. In a worst case scenario the materials are simply stored at the application sites. None of the above mentioned methods allow for the recovery of the treatment chemicals, although the heating value of the wood waste may be recovered through incineration. However, incineration processes release hazardous fumes into the environment, particularly volatile arsenic compounds that require treatment to mitigate hazardous gas emissions. Additionally, the ash from incineration may require treatment before disposal. In New Zealand, incineration is deemed an impractical technology for the near future, due to the high environmental standards imposed upon the technology which then leads to high capital and operational costs. In New Zealand presently landfilling of CCA-treated wood waste is regarded as a low-cost disposal method; however, leaching of CCA compounds poses the risk of contaminating surrounding soil and underground water. Therefore, landfill leachate must fulfil regulations in regard to its collection and appropriate treatment. Furthermore, landfills occupy an increasingly large land area, and the leaching process may take many years before it is completed. Landfilling sites in some regions of New Zealand are reaching their capacity limit, and new areas are becoming increasingly difficult to establish. Therefore, landfilling of CCA-treated timber wastes as a long-term solution is a deferral of the problem and unless an alternative solution is found, is likely to result in cumulative issues for generations to come.

The above issues highlight the need for a new waste management strategy for CCA wood waste, focusing on recovery and recycling. Factors to be considered in the development of a new and effective waste management strategy should include that:

- Products and emissions from the waste conversion process(es) must be safe to humans, animals and plants;
- The process is sustainable;
- The process ideally allows for the full recovery of the metal(oid)s;
- Any products recovered are suitable for application;
- The process allows for the recovery of either the wood or its heating value.

1.3 Technical Solution and Hypothesis

Previous research indicates that pyrolysis is potentially the most promising treatment technology for CCA wood waste. In comparison to incineration and gasification, the implementation of pyrolysis technology allows for the recovery of the CCA preservative from both the liquid and char products, whilst gaseous emissions could be reduced, and finally the gas stream could be treated at reduced costs.

- However, in any thermochemical treatment process, the release of CCA chemicals, particularly arsenic, is of major concern and must be managed. Pyrolysis uses much lower operating temperatures than incineration and gasification, and thus the extent of CCA release is likely to be reduced.
- Previous studies have tried to establish an operating regime that retains all metal(oid)s in the solid char product. Unfortunately, this is neither practical nor economically feasible, because arsenic volatilisation cannot be eliminated at the operating temperatures of pyrolysis.
- Pyrolysis also produces a liquid oil product containing arsenic, chromium and copper, which has been reported to be an undesirable attribute in past studies. However, investigation of this product stream may open up opportunities for the reuse of the liquid that have, as yet, not been explored.

It is thus hypothesised that pyrolysis can provide a suitable operating regime that allows for the decomposition of the woody biomass (recovery of its energy value) as well as the recovery of the arsenic compounds in the oil fractions, thereby offering a new means in which to recover arsenic for reuse. Of interest is its application in the wood treatment industry similar to that of oil or light organic solvent preservatives (LOSP), which is already an established wood treatment process. If all arsenic can be driven into the liquid fraction and a suitable application can be found, the potential for a circular economy for arsenic use arises. To determine the optimum operating conditions for a pyrolysis process requires experimental investigation and a fundamental understanding of the CCA wood waste and its behaviour under pyrolysis conditions. Combining these two approaches can validate the chemical reaction processes occurring during pyrolysis and the likely yields and recoveries achievable. If desirable recovery levels can be achieved, pyrolysis could potentially be implemented as a promising solution for diverting CCA-treated wood wastes away from disposal. The factors listed in the above section need to be considered to ensure a circular economy approach and the following aspects need to be investigated to provide proof-of-concept:

- The behaviour of CCA preservative chemicals during pyrolysis;
- The release mechanisms of CCA preservative chemicals under pyrolysis conditions;
- The physio-chemical characteristic of the pyrolysis products;
- The species and oxidation states of CCA preservative chemicals in the pyrolysis products;

- The recovery of CCA preservative chemicals from the solid and the liquid products or the potential application of these products;
- Feasible gas cleaning technologies;
- Conceptual plant design and process schemes for industrial application;
- Overall likely environmental performance of the developed waste management strategy and comparison against current disposal practice from a circular economy perspective.

1.4 Objectives and Scope

This research project focuses on the solution of CCA wood waste disposal via pyrolysis, allowing for the heating value of the wood and CCA compounds to be recovered. Under the desired pyrolysis conditions, most arsenic compounds are released into the liquid product, while the chromium and copper compounds are retained mostly within the solid char product. Although a complete waste management scheme needs to take into account the recovery of the heating value and retrieval of the three metal(oid)s, this PhD project focuses on the recovery and reuse of arsenic, considering the complexity of the issue, involving its high toxicity, low volatilisation temperature and its high leachability. To this end, the research gives particular attention to the dissociation of arsenic oxides under pyrolysis conditions so as to maximise the arsenic content in the liquid product. Furthermore, the liquid product is to be characterised regarding its thermochemical properties to determine its suitability as a preservative. The companion gas and char product characteristics are researched and analysed, as well as the chromium and copper recoveries.

This project sets out to explore:

- Experimentally, the pyrolysis product yields and CCA recoveries under differing pyrolysis conditions;
- The arsenic release reactions occurring during pyrolysis;
- The arsenic states in the final products;
- A theoretical modelling approach to better understand the arsenic release mechanisms;
- A conceptual process scheme for recovery and recycle.

Combined with future work exploring gas cleaning and metal(oid) recovery from the char – or contaminated char application – this approach could establish the viability of recovery of the CCA compounds to allow economic retrieval in an industrial process.

1.5 Thesis Structure

This thesis is divided into seven chapters, beginning with this introduction. The following six chapters are briefly outlined below.

In the literature review, Chapter 2, the CCA preservative chemicals and the CCA-treatment process of timber are initially described in detail. Subsequently, the effect of CCA in regard to health and environmental concerns as well as the arising issues surrounding the chemical leaching both during the service and after service life are discussed. Potential new waste management strategies using thermochemical conversion processes and leaching procedures are compared. As pyrolysis is found to be the most promising technology, the effect of pyrolysis temperature, particle size, heating and residence time is assessed in relation to future industrial-sized waste management processes. Finally, as the focus is on the recovery and reuse of arsenic compounds, previous studies will be evaluated, and the knowledge gaps identified.

Chapter 3 will present the experimental rig used and analysis methods for testing the CCA-treated timber feedstock and pyrolysis products. All methodologies and approaches for the experimental work are laid out and described.

Chapter 4 discusses the experimental pyrolysis results and the findings from the analysis of the char and liquid products. These results are compared with those found in the literature review presented in Chapter 2. The analysis and comparison of the experimental results have demonstrated the need to develop a mathematical model for a better understanding of the pyrolysis process.

In Chapter 5, a mathematical model is developed to describe the pyrolysis reactions occurring and the thermodynamic equilibrium between the different chemical species under pyrolysis conditions; so as to better understand the decomposition of arsenic and its associated chemical formation. Determining the oxidation state of the arsenic as recovered in the bio-oil is critical to its recovery and reuse.

Based on the arsenic decomposition model and experimental pyrolysis results, Chapter 6 presents a conceptual process scheme and a design basis for a hypothetical commercial plant. A process model of the proposed scheme has been developed to allow a first assessment of the suggested waste management scheme. Analysis of the bio-oil's chemical composition was undertaken to evaluate the oil's suitability for industrial application. Finally, a concept plan for adopting a circular economy for the use of arsenic within the wood treatment industry is suggested, with the scientific evidence arising from this research presented to support its validity and fitness for purpose.

The last chapter of this thesis summarises the significant findings of this work as conclusions and provides an outlook to future work and recommendations.

Finally, additional material can be found in the Appendices, such as engineering drawings of the experimental reactor and condenser, micro-GC and UV-vis calibration charts and raw experimental data.

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2 Literature Review

This chapter offers a review of the relevant literature that has been used as a basis for this thesis. Initially the chapter discusses the CCA-treatment process, treated timber applications, wood waste generation after service life and waste management strategies; making a distinction between approaches commercially implemented and those still at the research and development stage. Section 2.1 covers background information on CCA preservative, the wood treatment process and its chemistry, as well as the final application and usage of the chemically treated wood products. The current practice of CCA-treated wood waste management from a New Zealand perspective is presented and evaluated in Section 2.2. The second part of the chapter addresses conversion technologies for CCA-treated wood wastes, focusing on pyrolysis (Section 2.3). This is followed by a discussion of the need for a new waste management strategy (Section 2.4).

2.1 CCA-Treatment of Timber and the Timber Product Applications

2.1.1 CCA-Preservative

When exposed to natural conditions, most softwood timber begins to decay within 2 - 3 years due to attack by fungi and bacteria, water damage and, in some countries, through termites or other deteriorating factors [1]. Softwood timber is therefore commonly chemically treated with preservatives to mitigate decay and extend service life. One widely used preservative for softwoods is chromated copper arsenate (CCA). Timber treated with this preservative is known as CCA-treated, tanalised or green-treated timber [2, 3]. Since its invention in 1934 by Indian scientist Sonti Kamesam, CCA has been commonly used worldwide for a large variety of exterior wood applications [4, 5]. CCA is a water-based wood preservative that utilises chromium(VI), copper(II) and arsenic(V) for timber treatment. Cu(II) is used as an antifungal agent and protects from marine borers; soluble As(V) protects from insect attack and gives protection to some copper-resistant fungi. Soluble Cr(VI) is used to fixate the copper and arsenic to the lignin and cellulose structures of the wood [1, 2, 6].

2.1.2 Wood Chemistry and Treatment Process

In the wood treatment process, the aqueous solution containing chromium, copper and arsenic is supplied to a treatment vessel containing the wood. These chemicals are present in one or more of the following forms [2, 6, 7]:

- Chromium – CrO_3, H_2CrO_4, $K_2Cr_2O_7$ or $Na_2Cr_2O_7$
- Copper – CuO, $CuSO_4 \cdot 5H_2O$, $Cu(OH)_2$ or $CuCO_3 \cdot Cu(OH)_2$
- Arsenic – As_2O_5, H_3AsO_4, Na_3AsO_4 or $Na_4As_2O_7$

In a typical industrial treatment process, the wood is first debarked, then cut to dimension if required, and finally dried to the desired extent [2]. The treatment process may take place under either pressure or vacuum. Other treatment methods do exist, such as surface application, cold-soaking and steeping; however, these processes are generally used for oil-based preservatives.

During pressure treatment, timber is immersed in a vessel filled with the preservative solution. In the next stage, pressure is applied, driving the waterborne salts into the timber. Pressure is maintained until the desired amount of preservative has been absorbed, and penetration has occurred to the desired depth. Alternatively, a vacuum process can be used, known as VAC-VAC. In this case timber is initially exposed to a vacuum environment so that the air can be evacuated from within the timber, the vacuum is then lifted, and the preservative solution is released into the vessel. Lifting the vacuum subsequently forces the preservative to be absorbed into the timber due to its lower internal pressure.

In both pressure and vacuum treatment operations, a vacuum is employed to remove any excess preservative from the timber surface after the initial penetration process is completed [3, 8]. The treated wood is then allowed to dry whilst active chemicals react with the wood components. Fixation of chromium oxides within the wood structures is achieved through the adsorption of Cr(VI) onto cellulose and reduction to Cr(III). The reduced chromium reacts with H_3AsO_4 to form $CrAsO_4$ and binds to the lignin structures or precipitates onto the wood constituents. Mixed Cr(III), Cr(V) and its hydroxides/oxides precipitate onto cellulose. Unreduced Cr(VI) forms $CuCrO_4$, again bound within the lignin structures. Other chemical species identified in the fixation process include Cu(II) bound to cellulose and lignin structures as well as Cr(VI) oxide complexes with the lignin itself [2].

The fixation mechanisms of the various CCA compounds within the wood structure depend on reaction time, operation temperature, wood species, pH, and the subsequent drying conditions. Preservation is more effective in softwood than in hardwood due to the high lignin content and the relatively high permeability of the softwood. Fixation usually takes up to 14 days for completion, which is indicated by all hexavalent chromium having been reduced to trivalent chromium [1]. CCA-treated timber is expected to have a service life of between 30 to 60 years, depending on the preservative loading and the treatment process's operation conditions [9].

In New Zealand, treated timber is grouped into six hazard classes reflecting the treatment methods and preservatives used and, thereby, the expected durability of the treated wood. Each class gives the service conditions at which the treated wood is suitable for use and the biological hazards that the wood is resistant to. Table 2.1 summarises these hazard classes and also includes the amount of preservative used to treat timber with - as relevant to each class.

Table 2.1: Hazard Classes according to references of [1] and [10] (SW: Softwood; HW: Hardwood; El. As.: Elemental As)

Class	*Exposure*	*Service Conditions*	*Biological Hazard*	*%CCA/mass oven-dried*
H1	Indoors, above ground	Protected from weather, dry, exposed to ground atmosphere where well ventilated.	Anobiid lyctid	El.As 0.035
H2	Indoors, above ground	Protected from weather, dry, exposed to ground atmosphere where well ventilated but not in contact with ground.	Anobiid lyctid	0.32
H3	Outside, above ground	Periodic wetting, not in contact with the ground.	Decay fungi, insects	0.38
H4	Outside, in-ground	Severe or continuous wetting, continuous ground contact.	Decay fungi, insects	SW 0.63 HW 0.7
H5	Outside, in-ground, contact with or in fresh water	Severe or continuous wetting, continuous ground contact where uses are critical and a high level of protection is expected.	Decay fungi, insects	SW 1.00 HW 1.20
H6	Marine Waters	Immersion in seawater or estuarine ground.	Decay fungi, marine wood borers	SW 2.00 HW 1.20

The requirements for timber use in buildings in NZ are also defined by *NZS 3602:2003 Timber and wood-based products for use in building*. This standard specifies the minimum preservative treatment levels for given end uses and quality control requirements [11]. Compliance with these preservation standards is considered an *acceptable solution* under New Zealand building regulations and thus code compliant with the New Zealand Building Code [12].

2.1.3 Applications and Exposure through Leaching

CCA-treated wood can provide effective resistance to natural decay and can therefore be used for a wide variety of exterior applications such as, but not limited to, structural foundations, framing timber, exterior cladding, retaining walls, boat bulkheads, decking, dock pilings, external seating, fencing, garden furniture, gazebos, handrails, playground equipment, picnic tables, posts, trellises in vineyards and telephone poles [5].

It is estimated that New Zealand produces up to 650,000 m^3 of freshly treated wood annually [1, 13], of which 69% is CCA-treated timber, with the remainder being boron-, LOSP, ACQ- and Copper Azoletreated wood [14]. CCA-treated timber is widely used in New Zealand for home construction, building, farming and horticulture.

In the U.S., CCA-treated timber production grew from 1 million m^3 in the 1970s to 13 million m^3 in 1996 [15]. Unfortunately, since then, public domain production data has been scarce [16]. Studies estimate that the production volume of treated timber in the U.S. in 2002 was 19.5 million m^3. However, production was drastically reduced in 2003 with the introduction of a ban on CCA-treated timber for residential use. As a result, the production of the CCA-treated timber dropped to 7.5 million m^3 in 2004 and to less than 2 million m^3 in 2015 [17]. In the European Union, the annual production of CCA-treated timber was estimated to be 18 million m^3 before a change in legislation restricted the use of CCA-treated timber in 2003 [18].

Worldwide concerns as to the toxicity of the CCA preservative have been raised, focusing particularly on arsenic. These concerns will be discussed in depth in the following section. A drastic reduction in the use of CCA-treated timber in several countries including the U.S., the European Union and Australia has resulted in response to these concerns.

- Since 2003, the U.S. timber industry and the U.S. environmental protection agency have agreed to phase out CCA-treated timber for residential applications to reduce the use of arsenic in living areas and to improve environmental safety [4].
- In the European Union, amendments to *Council Directive 76/769/EEC* through the *Commission Directive 2003/2/EC* have restricted arsenic use and its marketing, thereby also curbing the usage of CCA-treated timber. Consequently, the employment of CCA-treated timber has been limited to professional and industrial applications, where the structural integrity of the wood is required for human or livestock safety, and skin contact by the general public is unlikely [19]. These regulations are still in effect through regulation (EC) No 1907/2006 in 2021 [20].
- In Australia, the use of CCA preservatives has been excluded from usage in high contact timber structures such as playground equipment, garden furniture, and handrails, to name a few [21].

New Zealand currently has no restrictions in regard to the production and application of CCA-treated timber. However its application is prohibited for the fabrication of food utensils [22]. Nevertheless, CCA-treated timber is considered to be a hazardous substance according to the New Zealand Hazardous Substances and New Organisms Act 1996 [23] and thus must be manufactured and used in an appropriate manner.

Studies have shown non-negligible leaching of CCA from freshly treated and in-service timber based on the concentrations of the preservative-related chemicals in the surrounding ground [24-26]. The leaching process takes place in three stages; beginning with initial surface wash-off, followed by diffusion leaching and lastly, the release of preservatives due to weather. In the wash-off and the diffusion leaching stage, exposure of the treated wood to water is the key parameter with moisture absorption and diffusion resulting in movement of the preservative through the wood and out of the wood structure. If timber is exposed to water, water attaches to the wood surface and then diffuses through the wood structures (cell lumens, bordered pits and checks) effectively redissolving the treatment chemicals and allowing their movement within the wood due to its capillary structure. Supported by experimental findings, this results in a chemical redistribution of the preservatives to the peripheral zones around checks [27, 28].

Preservative leaching due to weathering is further caused by free radical-induced depolymerisation through UV-vis radiation making the wood constituents degrade. As the lignin structures begin to break down, preservative fixated to lignin is released, dissolved and washed off when in contact with water. The loss of preservatives due to weathering can therefore be associated with the breakdown of wood fibres caused by UV-induced surface erosion as well as an increase in surface area due to warping, cracking and splitting of the wood [28, 29].

Previous studies have shown that the extent of leaching of arsenic, chromium and copper from CCA-treated timber in service (not mulched or chipped) is dependent on weather conditions [24-26]. Lebow et al. [29] reported that leaching is highest at the beginning of exposure and decreases with exposure time. The extent of leaching increases through exposure to rain and UV-vis, rather than just rain or UV exposure. In their study, 5 CCA-treated Southern Pine samples of 38 mm (thick) × 140 mm (wide) × 254 mm (long) wood pieces were exposed to rain for different durations. The CCA preservative retention in the treated wood was 6.4 $kg \cdot m^{-3}$ (retention of arsenic 2.3 kg m^{-3}), equivalent to 43.24 g preservatives (15.54 g arsenic) in the test samples. After 5 days of exposure to rain, the results showed that 5.03 mg arsenic, 2.80 mg chromium, and 3.49 mg copper had leached out. After 25-days of rain, a further 5-day rain exposure resulted in reduced leaching of 1.44 mg arsenic, 0.14 mg chromium and 0.31 mg copper, respectively. Wood exposed to rain and UV-vis showed leaching of 8.71 mg arsenic, 2.04 mg chromium, and 4.00 mg copper after a total of 30 days of rain exposure. CCA-treated timber exposed to only rain showed significant losses in preservative, whilst total losses increased two-fold when exposed to both UV-Vis and water [29]. As might be expected, a clear trend can be observed of less preservative loss over time.

Direct measurement of preservative leaching from the treated wood throughout its entire service life is impractical. However, research and modelling of arsenic release from H4-treated posts in the Marlborough region of New Zealand show arsenic losses of 4 – 6 mg per month per post over 20 years, which accounts for about 10% of the arsenic in the freshly treated wood. Over a 20-year life span of a post, the surrounding soil may record 100 to 200 mg of arsenic per 1 kg of soil. The soil chemistry determines the spatial flux of arsenic and soil adsorption, alongside weather. Modelling water movements and aquifers shows that if water movement is slow, arsenic can accumulate in the groundwater as insufficient dilution is available – values of 13 ppb for arsenic are predicted [30].

Mercer and Frostick [31] investigated the leaching of treatment chemicals from weathered CCA-treated timber that had been in service for 15 years by using a laboratory-based synthetic precipitation leaching procedure. Retention levels of preservative chemicals as measured in the weathered timber suggests that the preservatives remained largely fixed throughout their service life. However, noticeable quantities of arsenic, chromium and copper were lost from the timber at 0.28 wt%, 0.08 wt% and 1.14 wt% based on the initial concentration of chemicals, respectively, which exceeds the maximum *Environmental Quality Standard* of the European *Water Framework Directive*. Speciation analysis of the leachate shows that arsenic is predominantly present as As(V) and chromium as Cr(III); however, the presence of As(III) could not be eliminated [31].

The studies presented above confirm that CCA compounds leach from freshly treated as well as weathered wood. Release of the compounds is highest from freshly treated wood, and the extent of the release decreases with exposure time. Sunlight and rainfall contribute to the release of CCA compounds, of which the release of arsenic is recorded to be the highest. Through the release into the environment, the metal(oid)s can contaminate the ground soil and groundwater, leading to the exposure of these substances to plants, animals and humans.

It is for these reasons that regulators world-wide continue to place an emphasis on the possibility of environmental harm from the ongoing use of CCA-treated timbers.

2.1.4 Release of CCA into the Environment: Toxicity and Environmental Harm

As stated in the introduction, CCA compounds are toxic to humans, animals and many plants. This section will discuss the toxicity and effect of CCA chemicals and thereafter discuss the adverse effects of arsenic in more detail.

CCA compounds are toxic to humans, animals and many plants. Of primary concern for humans is the contact with arsenic and chromium, whereas copper salts are also toxic, however to a much lesser extent. Exposure may occur through swallowing, inhalation of contaminated dust or aerosol mists, or direct contact with the skin [23, 32]. Additionally, exposure may come from contact with contaminated ground or water, as described in the previous section.

The effect of the combined CCA chemicals in treated wood has not been thoroughly investigated, as most research focuses on the CCA compounds separately. Potential health effects for humans include, but are not limited to, an irritant or corrosive effect with all three components having irritant effects on the respiratory system and gastrointestinal tracts; further, arsenic and chromium are skin irritants. In addition, all three compounds affect the haematological system, the liver and kidneys. Both arsenic and chromium are known carcinogens. Arsenic causes skin and bladder cancer when ingested, lung cancer when ingested or inhaled. Chromium causes lung cancer when inhaled [33, 34].

Studies have been carried out to analyse the lethal doses of the CCA compounds for animals. Arsenic acid has a lethal dose that would kill 50% of subjects when ingested (LD50) of 1750 $mg \cdot kg^{-1}$ for a rabbit (dermal) and 48 $mg \cdot kg^{-1}$ for a rat (oral). Chromium trioxide has a LD50 of 57 $mg \cdot kg^{-1}$ for a rabbit (dermal) and 52 $mg \cdot kg^{-1}$ for a rat (oral). Copper(II) oxide has an LD50 of 52 $mg \cdot kg^{-1}$ for a rat (oral) [32].

The CCA chemicals in treated timber may be recognised on the wood surface. Over time, the CCA-treated wood may develop a green deposit on the surface, a form of toxic copper arsenate. Therefore, the dust of such wood should not be inhaled, and it is advised to wear respirators if exposure may exceed the Workplace Exposure Standard (WES) [23], as shown in Table 2.2. Additionally, the Temporary Emergency Exposure Limits (TEELs) for the general population are shown in the table.

Table 2.2: TEELs for compounds commonly found in CCA-treated timber [32, 35]

	WES-TWA[1] *[mg·m^{-3}]*	*TEEL-1[2]* *[mg·m^{-3}]*	*TEEL-2[3]* *[mg·m^{-3}]*	*TEEL-3[4]* *[mg·m^{-3}]*
Arsenic acid	0.05	2.9	32	190
Chromium trioxide	0.05	0.29	5	30
Copper (II) oxide	0.2	0.75	11	93

[1] *TWA is the time-weighted average concentration and refers to the maximum average airborne concentration of a substance when calculated over an eight-hour working day.*
[2] *TEEL-1 is the airborne concentration at which the general population after 1-hour exposure could experience notable discomfort.*
[3] *TEEL-2 the population could experience irreversible or other serious, long-lasting, adverse health effects or an impaired ability to escape.*
[4] *TEEL-3 the population could experience life-threatening adverse health effects or death.*

As this thesis focuses in particular on arsenic, a more in-depth analysis of its toxicity is presented here. Organic arsenic compounds are much less toxic than inorganic arsenic compounds, differing in this case from many other heavy metals [36]. According to Adriano [37], the order of toxicity of common arsenic compounds is given as follows – where arsine gas is the most toxic and elemental arsenic the least:

Arsines > Inorganic Arsenites > Organic Trivalent Compounds (Arsenoxides) > Inorganic Arsenates > Organic Trivalent Compounds (Arsenoxides) > Inorganic Arsenates > Organic Pentavalent Compounds > Arsonium Compounds > Elemental Arsenic [37].

Arsine gas is the most toxic form of arsenic, functioning as a haemolytic agent. Inhalation over 10 ppm is lethal, concentrations higher than 25 ppm are lethal within 1 hour of exposure, and 250 ppm is instantaneously lethal [38]. The toxicity is strongly related to the water solubility of the compounds. Elemental arsenic is virtually insoluble in water and body fluids; hence does not have a major impact on human health. As(III) is considered more toxic as it is more easily absorbed by cells than As(V), attributed to its higher water solubility. Furthermore, As(III) has a slower excretion rate than As(V) within the human body [39].

If exposed to water-soluble As(V) compounds, body cells accumulate arsenic by utilising an active transport system design for phosphate transport. As arsenic’s position on the periodic table is directly above phosphorus, their chemical similarities (similar atomic radii, the same number of valence electrons, and nearly identical electronegativity and orbital configurations) allow bodies to absorb arsenic via the phosphate absorption system. Arsenic replaces phosphate in cells but is much less stable than phosphate, disrupting and inhibiting the production of ATP molecules within cells [40, 41].

Acute symptoms of arsenic poisoning may include vomiting, abdominal pain, watery diarrhoea; chronic symptoms include thickened and darker skin, as well as cancer [40].

Alternatively, As(III), monomethylarsonic acid and dimethylarsinic acid is adsorbed via aquaglyceroporins channels – a subgroup of aquaporins (an integral membrane protein that facilitates water transfer [42]). There arsenic forms a strong, nearly covalent, bond with the thiolates of closely spaced cysteine residues (small, relatively hydrophobic amino acids that are often buried in the protein core [43]), thereby inhibiting the function of many proteins [44].

Furthermore, As(III) can be absorbed through the silicic acid transporters into plants. Rice is of particular concern as its cultivation method uses the flooding of fields, leading to reducing conditions in the soil and thereby the predominance of As(III) over As(V) [45].

The above information is useful for any impact assessment of the effects of arsenic compounds present in CCA-treated wood on the environment and humans. Water-soluble compounds leach out relatively easily and thus can have a more significant impact on the environment during service and after service life in a landfill. Furthermore, the persistence of arsenic in the environment is an issue of particular concern [46, 47].

Due to the toxicity of CCA chemicals and their persistence, it is of significant interest to look at means for recovery of these compounds once treated timber has reached the end of its life cycle. The ability to do so would mitigate pollution, reduce the likely impact of human and animal exposure and, as well, enables the possibility for the metal(oid)s to be recycled.

Acceptable levels of arsenic in soil are difficult to pinpoint, as arsenic is a naturally occurring element in the earth’s crust; appearing in the form of arsenides and arsenates, arsenopyrite (iron arsenic sulphide), arsenite and volcanic gases from geothermal springs [48]. The mean concentration of arsenic in soil is 2 mg per kg of soil, with upper levels of 10 to 15 mg per kg of soil depending on the ground's mineralisation, pH, and contamination [36]. The current standard limit for arsenic in drinking water is 10 ppb in New Zealand [49], Europe [50] and the U.S. [51]. This is consistent with the standard set by the World Health Organization [52].

2.2 CCA-treated Timber Waste – The Problem

The disposal of CCA-treated timber waste has proven to be problematic, primarily as a result of three issues:

- the quantity of waste entering the disposal sector,
- the toxicity of the waste and persistence in the environment, and
- the subsequent limitations of its end-of-life use being restrained to disposal in either landfill or incineration.

However, in New Zealand there is a further dominant issue: the importance of softwoods to the New Zealand economy. Forestry contributes some 3.55 billion NZD to New Zealand's GDP, and is the country's third-largest export earner after dairy and meat products. The sector employs around 35,000 people [53] with approximately 1.7 million hectares of sustainably managed planted forests [54]. Of the timber species planted, 89% is *Pinus radiata*, with the remainder a mix of Douglas fir, eucalyptus and other soft- and hardwood- species. [55].

Pinus radiata is a fast-growing, medium-density softwood [56] which is well adapted to New Zealand's climate and harvestable after 25-30 years [57, 58]. The major disadvantage of *Pinus radiata* wood is its lower density and its susceptibility to both insect attack and decay. If in contact with the ground, untreated *Pinus radiata* timber will start to decompose within 2 – 3 years, and whilst above ground the average life-span varies, but it is typically much less than desired [1].

Whilst there are uses for the timber without chemical treatment, its application in New Zealand is significantly dependent on preservative treatment. The requirement for preservation is amplified by *Pinus radiata* being the most common economic timber species in this country. Consequently, CCA preservatives are widely deployed in New Zealand. Unless a solution to the disposal of CCA-treated timber waste is found and sustainably addressed, the continued use of *Pinus radiata* in New Zealand is in question. Any diversion strategy, however, would need to span for over 30 years; the economic rotation period of a *Pinus radiata* forest.

This section of the literature review looks at the overall waste management system for CCA timber waste, quantities entering the disposal sector, methods and technologies to differentiate treated from untreated timber and, thereafter, a discussion of the current disposal methods of landfilling and incineration is presented. This, in turn, leads to a discussion of methods that are still at their research and development stage. The section concludes with a comparison of the different treatment methods and assessment of their potential for development of a new waste management strategy within the New Zealand context.

2.2.1 Quantities of CCA-treated Wood Waste

Jones et al. [16] have researched the disposal of CCA-treated wood wastes in the U.S. and predicted that the quantities of CCA-treated timber waste entering the disposal sector will increase in the future. Their research developed a model based on production statistics, leaching rates and the typical service lifetime of wood products. The developed model was then deployed to predict the quantities of CCA-treated timber waste and its associated treatment chemicals and when they are destined to be disposed of. From the model predictions, 12 million m^3 of CCA-treated timber waste are expected to enter the disposal sector annually by 2030 in the U.S. The disposal of such quantities of wood wastes would contain up to 15,000 metric tonnes of arsenic, 12,000 tonnes of copper and 18,000 tonnes of chromium [16]. Most of this waste goes to landfills or incineration [59, 60].

In New Zealand, the Ministry for the Environment estimates the proportion of timber in landfills to be 13% of the national total of waste entering landfills annually (12.59 million tonnes). Therefore, it can be assumed that 1.57 million tonne of timber wastes enter New Zealand's landfills each year [61, 62]. Unfortunately, there is no national data available for landfilled CCA-treated wood wastes. However, a report prepared by True North Consultancy for Environment Canterbury estimated 13,500 tonnes per annum of total treated timber waste is disposed of for the Canterbury region alone [62].

As stated earlier in the chapter, New Zealand produces approximately 448,500 m^3 of CCA-treated timber per year, equating to roughly 258,000 tonnes. The main application of the CCA-treated timber in New Zealand lies in the construction sector, followed by its use as fence post- and vineyard post-material. Although the exact volume of CCA-treated wood wastes entering New Zealand landfills is unknown, it can be expected that some wood will be left on-site or burnt before reaching landfill, both of which are undesirable. Of particular concern is the burning of CCA-treated wood wastes, this being the primary source of arsenic contamination in urban air. Air quality monitoring in residential areas of Auckland shows that arsenic concentration peaks during the wintertime and is associated with residential wood burning to heat homes [63, 64]. Nelson District Council came to the same conclusion with annual data showing a clear spike in airborne arsenic throughout the winter months [65].

With the accumulation of CCA-treated timber in use, it can be predicted that the quantities of treated timber entering the disposal streams will increase in the future, emphasising the need for a safe and sustainable waste management practice.

2.2.2 Identifying and Sorting Methods for CCA-treated Timber

An effective waste strategy for the recovery, reuse and recycling of CCA-treated wood wastes requires CCA-treated timber to be identified and sorted from other wood wastes in the municipal waste stream. An essential element for the management of mixed timber waste streams is that these are separated, in particular, since recycling and disposal of the untreated timber is by far less problematic than that of CCA-treated wood. In general, it is easier to separate CCA-treated wood wastes derived from industrial applications in comparison to timber wastes from residential building applications. This has unfortunately been proven to be far more challenging. The quantities of residentially-sourced CCA-treated timber waste have been increasing over time from an ever broader range of applications. Therefore, it is essential that a successful identification and sorting process be established to address this problem. In future, mandatory collection, transportation and processing schemes may be required, but currently, such measures are not in place [14, 59]. As aged treated timber has a typical green colour, visual sorting can be initiated as a first step in the separation process. This technique however is not considered to be effective and in the end may only lead to a reduction of approximately 15 – 20% of the amount of CCA-treated timber entering the waste stream [59].

Chemical stains such as PAN indicators ($C_{15}H_{11}N_3O$) can be used to identify CCA-treated timber from untreated timber for relatively small quantities. [66]. Other options for larger-scale sorting include laser-induced breakdown spectroscopy (LIBS) and X-ray fluorescence spectroscopy (XRF). Gundupalli et al. [67] compared LIBS and XRF methods in their detailed review paper of automated municipal solid waste sorting and showed recovery rates ranging from 80 to 97% using LIBS and from 90 to 97% by XRF [67]. Further research by Jacobi et al. [68] into visual sorting, using PAN indicators and/or hand-held XRF units concluded that visual sorting was not accurate for source-separated timber waste, and sorting should additionally be augmented by PAN indicator stains where practical. For timber waste with excess surface dirt (e.g. commingled construction and demolition waste), handheld XRF proved effective [68].

After sorting, the untreated wood wastes may be recycled and used for the manufacture of medium-density fibreboard (MDF), mulch or be safely disposed of in a landfill or by incineration.

From a downstream processing perspective, the ability to have a pure CCA-treated wood waste stream would do much to improve the effectiveness and efficiency of any recovery, reuse and recycling scheme.

2.2.3 Present Disposal Options of Landfilling and Incineration

The world's disposal of CCA-treated timber waste is currently largely limited to landfilling and incineration [59, 60]. In the U.S., CCA-treated timber waste is typically disposed of in landfills [5, 69]. In circumstances, when incineration is used, arsenic emissions must be captured as per U.S. regulations [59]. In the European Union, CCA-treated timber waste is classified as hazardous and subject to strict requirements, limiting options for recycling and disposal. Consequently this leads to the majority of CCA-treated timber waste being incinerated [59, 62]. In Australia and New Zealand, CCA-treated timber waste is predominantly landfilled [62], although a substantial quantity of vineyard posts and fence posts are burnt or left on-site. As significant environmental concerns have been observed in both the landfilling and incineration of CCA-treated timber waste, improved methods of disposal are required.

Landfilling

In 2018, 70% of all worldwide generated solid waste was disposed of in landfills. Thereby consuming ever larger areas of ground space, and increasing energy costs for the transport, sorting, treating, and recycling of this refuse [70-72].

Landfills in industrialised nations accepting hazardous wastes are typically lined with complex layers of rock, sand, and geotextile membranes and/or liners. Additionally, where required, landfill leachate collection systems are in place [73]. Focussing on the New Zealand situation, CCA-treated timber is considered to be construction and demolition waste destined for a Class 2 landfill. Class 2 landfills are situated in appropriate geology, hydrogeology and surface hydrology areas, and fitted with an engineered liner, a leachate collection system and groundwater and surface water qualities are monitored. Leachate treatment may also be required [74].

Jambeck [75], Jambeck et al. [76], and Khan et al. [77] studied the leaching characteristics of CCA-treated timber in a simulated landfill environment and concluded that arsenic is preferentially more mobile than copper and chromium [75-77]. The leachate concentration of arsenic was 42 $mg{\cdot}L^{-1}$ and those of chromium and copper were 9.4 $mg{\cdot}L^{-1}$ and 2.4 $mg{\cdot}L^{-1}$, respectively. Measurements were obtained using DI water in a ratio of 0.63:1 to solid [76].

Laboratory studies simulating CCA-leaching from construction and demolition wood waste found significant preservatives leaching, resulting in concentrations above regulatory levels [78, 79]. Studies of Hasan et al. [80] reached a similar conclusion and further found that leaching is influenced by rainfall and weathering. These findings agree with earlier statements in Section 2.1.3 of UV-Vis and water affecting CCA release from wood.

Factors likely to influence the extent of contamination of the ground soil and surrounding groundwater are the underlying soil type, weather and rainfall as well as the rate of new CCA-treated timber waste entering the landfill [78]. Unless retained on-site, leaching potentially allows CCA compounds to contaminate the surrounding soil and ground water [31].

Data from two Waikato Regional Council Class 2 landfills [74] show that the collected leachate concentrations were 18 – 200 $mg{\cdot}L^{-1}$ for arsenic, 0.027 – 0.64 $mg{\cdot}L^{-1}$ for chromium and 0.001 – 0.102 $mg{\cdot}L^{-1}$ for copper. In New Zealand (2018), the dominant method of disposal of leachate is its discharge to a wastewater treatment plant or its discharge to land by spraying or subsurface irrigation. A cause of grave concern is the practice of discharging or spraying untreated leachate into the environment with the potential for significant pollution [74].

Incineration

Incineration is a thermal oxidation process in which waste materials are combusted at high temperatures to generate heat. In the process by-product ash is generated, and combustion gases (flue gas) are emitted to the atmosphere. In conjunction with extensive gas cleaning, incineration can be an acceptable technique for managing CCA-treated timber waste [59, 81]. In addition, suitable chemical processes can stabilise or extract the metal(oid)s from the resultant ash [5]. It has been shown that by using appropriate sorbents which have the ability to react with the vaporised metals air contamination is reduced. The selection of sorbents, capable of forming insoluble products with the ash, minimises the leaching of metal(oid)s from the ash into the environment [82].

Disadvantageous to incineration is the associated risk of air pollution from incomplete capture of metal(oid)s and release of hazardous arsenic species in the flue gas into the atmosphere when not properly treated. The heat generated from the incineration process requires an available thermal load or conversion facilities to generate steam and, subsequently, electricity, which essentially requires steady-state operation and constant feed. Co-incineration with other solid fuels may provide a more viable solution to meet these requirements.

In this respect co-incineration at an existing power station offers an economically feasible solution for commercial-scale processing of the CCA-treated timber waste. However, adding CCA-treated waste to an existing power station’s fuel produces bottom ash with a higher concentration of water-soluble arsenic and contaminated flue gas, containing other arsenic species [59]. Therefore, incineration and co-incineration do not meet the desired waste management target for this thesis of "*recovery and recycling".* These technologies may however provide an economic pathway for safe disposal and effective energy recovery.

During incineration of CCA-treated wood waste, heavy metal(oid)s are released into the atmosphere and become present in the produced fly ash [82]. Incineration can vaporise 22% to 77% of the original arsenic in the treated wood [83]. To meet stringent pollution regulations extensive gas cleaning in the downstream flue gas treatments are required [59]. The concentration in the remaining ash has been reported to range from 9.0 to 45 $g \cdot kg^{-1}$, 1.8 to 22.5 $g \cdot kg^{-1}$ and 2.7 to 31.5 $g \cdot kg^{-1}$ for arsenic, chromium and copper, respectively [15]. Furthermore, chromium can oxidise to its more toxic and mobile form Cr(VI) [84]. The potential to leach hazardous chemicals from the ash poses a serious environmental concern [82]. For this very reason, the use of CCA-treated timber in household fireplaces is prohibited.

Nevertheless, elemental arsenic concentrations as high as 80 $ng \cdot m^{-3}$ have been recorded in Nelson [65] and 10 $ng \cdot m^{-3}$ in Auckland [63, 64] during winter months. The New Zealand air emission standard for arsenic is 5.5 $ng \cdot m^{-3}$ [85].

2.2.4 Recovery of CCA Compounds through Extraction and Leaching Procedures

One of the proposed methods of extracting the various CCA compounds from CCA-treated timber wastes is leaching. Extraction relies on reducing the piece size of the CCA-treated wood waste to a desired particle size, followed by immersion of the particles in a selected solvent for a specific time at desired temperatures and pressures.

Commonly used in the minerals industry for the value recovery of precious metals, chelates are molecules that bind ions and transitional ions in extremely strong and complex ways. These compounds are also often used to remediate heavy metal contaminated soil [86, 87]. Ethylenediaminetetracetic acid (EDTA) is another frequently used solvent to remove CCA compounds by the formation of water-soluble complexes, thereby releasing the metal(oid)s from their prior complex structure. Removal efficiencies have been reported to be up to 93%, 36% and 38% for copper, chromium and arsenic, respectively, over a 24 h period. Copper is more mobile, whereas the chelating ability of EDTA on chromium and arsenic is weak [87].

Although EDTA is widely used, it has a low biodegradability and is persistent in the environment, causing an ongoing risk of metal leaching into the environment. Readily biodegradable SS-EDDS and

NTA have been researched by Ko et al. [88] as substitutes for EDTA and analysed their application with regards to establishing the optimal solvent pH levels and EDDS-CCA stoichiometric ratios. Using EDDS, removal efficiencies of 66%, 93% and 62% for chromium, copper and arsenic, respectively, were achieved over a pH range of 2.0 to 4.0 [88].

Choi et al. [89] investigated the use of pyroligneous acid (wood vinegar) for the removal of CCA compounds from treated timber. Wood vinegar is a promising alternative to synthetic chemicals for food flavouring and is the condensed liquid obtained from the smoke produced by charcoal. The results show that with a higher wood vinegar concentration, the leaching efficiency increases with operating temperatures and time. The best leaching results were realised using undiluted wood vinegar at 60°C for 48 hours, achieving 95.7% removal of copper, 86.3% removal of chromium and 92.7% of arsenic [89].

Ribeiro et al. [90] examined the use of a low-level direct current treatment as a "cleaning agent, combining the electrokinetic movement of ions in the matrix with the principle of electrodialysis". In this research, sawdust was saturated with water or oxalic acid at various concentrations. The optimum removal efficiencies of 93%, 95% and 99% for copper, chromium and arsenic, respectively, were achieved using 2.5 wt% oxalic acid as an assisting agent. In their study, a current density of $0.2\ \text{mA}\cdot\text{cm}^{-2}$ was used for a duration of 30 days. The authors suggest that the treated sawdust could be reused for cardboard, fibreboards or particle boards [90]. Although this method achieves a high removal efficiency for all three compounds, long operating times are likely to form a barrier to commercialisation. Further studies showed that optimising the operating procedures could reduce operating time to 14 days, but removal efficiencies were reduced to 84%, 87% and 95% for copper, chromium and arsenic, respectively [91].

The above reports do not address the recovery of the CCA compounds from the solvent liquids, although methods and technologies for this exist. Alka et al. [92] conducted an extensive review on arsenic removal technologies, including adsorption and ion exchange methods, electrokinetic processes, electrocoagulation, chemical precipitation, phytoremediation, nano phytoremediation, membrane technology, and phytobial remediation. The advantages and disadvantages of each technology are assessed in this review paper. Their work concludes that adsorption methods are of particular interest for future investigation and application due to the simplicity of design, low cost, and ease of operational procedure. Highlighted are novel functional materials, e.g. graphite oxides, metal-organic frameworks and carbon nanotubes. Recovery rates of up to 95% for arsenic have been achieved using iron oxide-covered sand and magnetic nanoparticles from tea waste being used as an adsorbent. However, the lasting adsorption efficiency and material reusability are unknown, and costs are not reported.

Research by Helsen and Van Bulck [59] assessed the advantages and disadvantages of the extraction of CCA from treated timbers comparing a range of different recovery methods. Their results suggest that barriers to leaching processes lie in the fact that the process is slow and costly and thus has a poor price-performance ratio. Their prognosis was that whilst there may be a potential application for small quantities of timber, for larger quantities the commercial viability of this technology had yet to be proven [59].

2.2.5 Gasification

Gasification is another thermochemical conversion process involving the cracking of carbonaceous materials into a gaseous product (termed as producer gas or product gas) via a controlled gasification agent, which can be air, oxygen or steam. The operating temperature for gasification is generally between 800 and 1200°C [93, 94], with a key advantage being its higher energy efficiency compared to other thermal conversion processes [59]. Due to the high reaction temperatures of gasification and the presence of CCA, the metal(oid)s present may lead to the producer gas becoming contaminated. Therefore, gas cleaning is required before the producer gas is used for liquid fuel synthesis or for heat and power. However, the intensity of gas cleaning required for gasification will be less than that for incineration, as a consequence of less arsenic being volatilised during the gasification process, particularly at lower gasification temperatures [95]. In addition, high-temperature gasification of the CCA-treated timber waste is likely to completely convert the arsenic to metallic arsenic, which is much easier to remove from the producer gas, than the otherwise released arsenic trioxides. This being due to the fact that metallic arsenic does not enter the liquid phase upon condensation [59].

Whilst gasification is an attractive option for recovering energy and metal(oid)s from the CCA-treated timber waste, incineration is the technology that is usually commercially implemented. Gasification requires more expert engineering for an industrial application. In both gasification and incineration, the recovery of arsenic compounds from the gas cleaning solvents is complex and costly. Helsen and Van den Bulck [59] proposed co-incineration as the preferred thermochemical conversion process for the disposal of CCA-treated timber waste within the short term. However, in the long-term low-temperature pyrolysis or high-temperature gasification were proposed as promising alternative technologies [59].

2.2.6 Pyrolysis

Pyrolysis is a thermochemical decomposition process of any carbonaceous material in the absence of oxygen or its limited supply. The feedstock material is converted into char, liquid and gaseous products. As pyrolysis is overall an endothermic process, it requires heat, which can be supplied either by an external heating source or via partial oxidation of the raw feed material in the presence of limited oxygen. This route differs considerably from the more conventional gasification and combustion processes in that the target products can be liquid or solid (char) [96]. Pyrolysis is considered to be a realistic disposal method for CCA-treated timber waste in that arsenic losses can be controlled to concentrate preferentially in the solid [59].

Previous research shows that during pyrolysis of CCA-treated timber, the preservative metal(oid)s compounds form agglomerates in the charcoal [97, 98], which can be recuperated [97, 99]. Arsenic losses have been observed at temperatures as low as 200°C [100] if any unreacted preservative is present in the timber, indicating that lower pyrolysis temperatures are required to ensure that the maximum arsenic content is retained in the solid product. However, such low-temperature pyrolysis requires longer reaction times (slow pyrolysis) which is deemed not viable in industrial applications. Therefore, zero arsenic volatilisation is considered impractical and economically infeasible. This, in turn, suggests the adoption of higher temperature pyrolysis regimes in combination with gas cleaning [59].

Fast pyrolysis operates typically at temperatures of about 400°C and produces more liquid product (oil) than the slow pyrolysis route. Significant amounts of arsenic may be contained in the oil and volatile arsenic can be found in the produced non-condensable gas (off-gas) [101]. However, gas volumes produced from pyrolysis and the quantity of arsenic volatilised are much lower than with gasification and incineration [59]. Therefore, the gas requires less gas handling and cleaning, reducing the size of gas cleaning equipment and, thereby, the capital and the operating cost.

2.2.7 Comparison of Technologies in New Zealand Context

Based on the New Zealand situation, the potential environmental impacts of CCA-treated timber during service and landfill disposal have been assessed, taking into account the leaching of the preservative. These results are presented in Table 2.4 showing that over 450 tonnes of CCA-preservative chemicals accumulate in New Zealand landfills each year form current disposal methods.

Table 2.3: Analysis of CCA-treated timber during its service life and its accumulation in landfill at end-of-life with attention to CCA entering the environment

Estimated annual production of CCA-treated wood in NZ	650,000 m^3, or approximately 258,000 tonnes As: 568 tonnes Cr: 593 tonnes Cu: 697 tonnes } assuming H4-treatment class
In service leaching of CCA / loss to environment. Depending on treatment class and exposure to weather	As: 1935 kg p.a. (based on 7.5 mg·(kg·yr)$^{-1}$) [30] [a] As: 9804 kg p.a. (based on 38 mg·(kg·yr)$^{-1}$) [31] [b] Cr: 5418 kg p.a. (based on 21 mg·(kg·yr)$^{-1}$) [31] Cu: 21,156 kg p.a. (based on 82 mg·(kg·yr)$^{-1}$) [31]
Estimated service time	30 – 60 years Assume 20 years for this case (based on vineyard posts)
In circulation Constant production over 20 years assumed	5.16 mil tonne in circulation in total
CCA loss to environment due to leaching in service	As: 194 tonnes [b] Cr: 109 tonnes Cu: 425 tonnes [31]
CCA-treated timber entering disposal sector	33,000 to 109,000 tonnes·yr^{-1} [c]
Accumulation	up to 225,000 tonnes·yr^{-1} → CCA can last up to 60 years → still in service → Illegally landfilled / stored on sight → Illegally incinerated

[a] *assume size: 75 mm x 75 mm x 2.4 m [102], assumed density: 475 kg m^{-3} [103] → One post: 6.4 kg*

[b] *from [30] loss per year for As estimated to be 48 mg per post: 7.5 mg·kg^{-1}*
Assuming 5.16 mil tonne of CCA in circulation, annual loss 38,700 kg of arsenic to the environment
Alternatively, [31] used weathered wood and reported data for CCA: losses of 0.28%, 0.08% and 1.14% for As, Cr and Cu based on initial loadings for a 21 week period.

[c] *NZ's estimated total waste going to landfills annually: 12.59 mil ton [104]*
Of that 12.6% is wood [62]: 1.57 mil ton
3 – 10% is estimated to be treated wood, of which 69% is CCA [14].
→ 32,837 - 109,457 tonnes of CCA-treated timber going into landfill
Losses of 38, 21 and 82 mg of As, Cr and Cu, respectively, per 1 kg of wood per year can be expected based on [31]
→ 194, 109 and 423 tonnes of As, Cr and Cu, respectively, would be expected.
However, [31] initial loading is very high, assuming the same percentage losses but using initial loadings of Table 3.5 gives losses of 79, 24 and 393 tonnes per year for As, Cr and Cu, respectively.

Futher, Table 2.4 summarises the advantages and disadvantages of different disposal technologies for CCA-treated wood wastes based on the assessments presented in this chapter.

Table 2.4: Advantages and disadvantages of different disposal technologies for CCA-treated timber

	Technology	*Advantages*	*Disadvantages*
Current Methods	Landfilling	Immediate and available technology	Waste of resources Leaching of heavy metals
	Incineration	Proven technology Low operating cost Can be coupled with metal recycling process	High capital cost Gas cleaning equipment required High CCA in ash Ash treatment and disposal required
	Co-Incineration	Lower investment cost, flexible fuel choice, lower emissions due to dilution	Gas cleaning equipment required High CCA in ash Ash treatment and disposal required
R&D Methods	Solvent Extraction	Removal of up to 93%, 95% and 99% of Cu, Cr and As	Long operating hours Cost of solvents Not feasible on a large scale Removal from solution still required
	Gasification	High energetic efficiencies	Gas cleaning equipment required High temperature required
	Pyrolysis	Less arsenic volatilisation than other thermochemical methods	Arsenic volatilisation Arsenic in oil Smaller processing volumes

In comparison to other countries, landfilling is an easy and inexpensive method of managing waste products in New Zealand [105]. However, there is a growing trend to move away from waste landfilling towards recovery and recycling. Recycling CCA-treated wood through reusage requires first and foremost the transportation of bulky timber waste, which is likely to be contaminated with nails, fasteners and other previously used construction objects. This process of wood reuse is deemed to be altogether inefficient. Alternatively, the timber waste could be recycled and components reused, for example, in wood-based composites, mulch, compost or animal bedding. However, the reuse as mulch, compost or animal bedding poses a considerable risk, as leaching of CCA chemicals may occur over an increased land area, allowing the metal(oid)s to disperse into an ever wider environment. Consequently, policies have been introduced to ban the use of CCA-treated waste in such a way [59]; [74]. Using CCA-treated timber waste for wood-based composites is merely a deferral of the problem, with the potential for environmental harm from subsequent disposal options remaining unaddressed.

Overseas, incineration is successfully used, however, it is deemed a technology unlikely to be deployed in New Zealand in the near future, due to the high initial expenditure and extensive gas cleaning to mitigate hazardous air emissions [62]. An additional obstacle lies in the costs for the transport of these hazardous wastes to an incinerating facility.

Wood waste incineration takes place at Golden Bay Cement in Whangarei, where 32% of the energy input is supplied through wood waste. However, only approximately 1% (320 kg·h^{-1}) of the wood waste input is that of CCA-treated timber waste. Trials in 2009 showed that treated wood waste could be utilised to this degree without alterations to the plant or existing resource consent. Further increasing the wood input can cause a bottleneck in the firing process due to the increased gas output associated with using wood as fuel [62].

Although successful, the Golden Bay cement plant processes less than 3,000 tonnes of CCA-treated timber waste per year, this amount is however only a small fraction of New Zealand's estimated annual CCA-treated timber waste. Canterbury alone produces an estimated 13,500 tonnes annually. As this is New Zealand's only cement kiln and being one of the few incineration facilities in the country this process can be regarded as an impractical solution for the scale of the issue.

In other existing facilities, co-incineration as boiler fuel has been considered. However, air discharge is likely to be above their resource consent requirements, leading to the necessity of costly wet scrubbers; the disposal of the contaminated ash would add further to the costs. Additionally, the CCA compounds cause boiler and flue corrosion [62].

In regard to technologies in the research and development stage, solvent extraction utilising leaching procedures to recover the CCA compounds shows high recovery efficiency; however, hindering the commercialisation are high costs of solvents and treatment procedures as well as slow operating times (in comparison to thermochemical processes). For the thermochemical conversion process, pyrolysis is of particular interest. Pyrolysis offers lower arsenic volatilisation in comparison to gasification, thereby reducing gas cleaning requirements. However, pyrolysis has the potential drawback of producing an arsenic-rich liquid product and CCA-contaminated char. As will be discussed further in this thesis, recovery of this arsenic-containing oil opens up further opportunities to reuse the arsenic that have not yet been fully explored.

Although the pyrolysis technology is well established, the operating temperature for CCA-treated wood waste needs further research to better understand and optimise the process. In addition, recovery and reuse of the contaminated char and oil products need to be explored. A conventional batch-operated pyrolysis unit operates in Timaru, producing charcoal from untreated timber waste. If pyrolysis technology achieves the desired outcome, this already existing plant may offer an opportunity to perform test trials on an industrial scale which would aid in providing evidence for future resource applications. The question arises, if conventional pyrolysis, as it is used in Timaru, can be utilised and optimised to suit the needs of CCA-treated waste pyrolysis. Pyrolysis then needs to be compared to New Zealand's current baseline activity.

For this research, pyrolysis as a waste management scheme will be compared against the counterfactual of landfilling of CCA-treated waste. To be an improvement, pyrolysis needs to be shown to be more cost-effective, and also allow for the economic recovery of the metal(oid)s and heat whilst minimising any adverse environmental effects when compared against other options.

As previously stated, this thesis research proposes to investigate the pyrolysis of CCA-treated wood in more detail and to address the issue of arsenic volatilisation during this process. The kinetics and reaction mechanisms of arsenic volatilisation are complex. Based on the literature review findings presented in the following section, different reaction pathways can be proposed.

2.3 Pyrolysis Process and Release of Arsenic Compounds from CCA-treated Wood

Based on the literature review, it can be concluded that pyrolysis is a promising technology for the recovery of arsenic from CCA-treated wood waste. This section, therefore, begins with introducing pyrolysis of woody biomass, followed by an examination of the pyrolysis process from the perspective of how operating conditions influence product yields and also the distribution of the CCA compounds within the products. Different operating conditions are discussed; e.g. operating temperature, residence time, heating rate and particle size. Finally, the chemical reaction mechanism of the release of arsenic compounds under pyrolysis conditions will be explored, and the removal of arsenic from the product gas discussed.

2.3.1 Pyrolysis of Woody Biomass

During pyrolysis of woody biomass, solid char, vapours, and non-condensable gas are produced. The vapours condense to a liquid when cooled, this product is typically termed bio-oil or pyrolysis liquid. The non-condensable gas is generally termed producer gas or pyrolysis gas. Pyrolysis of woody biomass is usually carried out at temperatures of between 300 and 650°C, depending on the target product (solid char, liquid or gas). The distribution of the various products arising from the pyrolysis reactions depends primarily on the pyrolysis temperature, heating rate, and residence time. The pyrolysis process itself can be described through the following generic reaction [96]:

$$C_nH_mO_p(biomass) \xrightarrow{heat} \sum\nolimits_{liquid} C_xH_yO_z + \sum\nolimits_{gas} C_aH_bO_c + H_2O + C\ (char) \qquad (R2.1)$$

During pyrolysis, a wide array of processes and reaction mechanisms occur consecutively and/or simultaneously. Prediction of pyrolysis characteristics based on the thermal behaviour of the individual biomass constituents (cellulose, hemicellulose and lignin) is difficult [106]. During pyrolysis, dehydration, depolymerisation, isomerisation, aromatisation, decarboxylation, and charring reactions all take place [107-109]. Generally, biomass pyrolysis can be divided into three primary stages:

1) initial evaporation of free moisture,
2) primary decomposition and
3) secondary reactions such as cracking and repolymerisation.

Investigation of the pyrolysis of individual biomass components shows that at around 200°C, any remaining water in the feedstock is evaporated and driven off. Thermal degradation of biomass (cellulose and hemicelluloses) begins at temperatures above 200°C. Between 200 and 260°C, hemicellulose breaks down, followed by cellulose at 240 and 350°C. Last to break down is the lignin which occurs at temperatures above 280°C while any volatiles present are completely released at up to 500°C [110-112]. The bulk conversion of biomass into its product fragments is observed to occur at temperatures between 300 – 400°C, accounting for 80 to 90% conversion [113].

In the pyrolysis operation, target products can be achieved by varying residence time, heating rate and temperature. Details are given in Table 2.5. Conventional carbonisation is a slow pyrolysis process in which biomass is converted into a highly carbonaceous, charcoal-like material. Carbonisation is very similar to the slow pyrolysis process; however, the residence time is longer and the temperature may be lower [114]. Higher vapour yields and, consequently, higher liquid yields can be achieved by increasing the temperature and heating rate and decreasing the residence time. Vacuum pyrolysis differs from other processes in that the biomass reaction is in a vacuum environment. This environment reduces the residence time of pyrolysis vapours, leading to an increase in liquid yield [96, 107, 115].

Table 2.5: Typical biomass pyrolysis technologies defined by their operating conditions and major products [96, 107]

Technology	*Residence Time*	*Heating Rate*	*Temperature /°C*	*Major Products*
Conventional Carbonisation	Days	Very low	300-500	Char
Conventional/Slow Pyrolysis	Hours	Medium	400 – 600	Char
Conventional Pyrolysis	>30 min	Medium	700 – 900	Char, bio-oil, gases
Flash/ Fast Pyrolysis	< 2 s	High	400 – 650	bio-oil
Flash Pyrolysis	< 1 s	High	650 – 900	Bio-oil, gases, chemicals
Flash/ Ultrarapid Pyrolysis	< 1 s	Very high	> 1000	Chemicals, gases
Vacuum	< 30 s	Medium – High	350 – 450	Bio-oil

The definitions of pyrolysis classes vary depending on the literature source; for example, Bridgwater and Demirbas et al. use slightly different residence times and final temperatures for their definitions in comparison to the majority of other authors; however, these differences are marginal [96, 107, 111, 116].

2.3.2 Conventional and Fast Pyrolysis in Comparison

Fast pyrolysis is characterised by a high heating rate and short vapour residence time using small particles and higher pyrolysis temperatures. Conversely, conventional pyrolysis utilises larger particle sizes, slower heating rates and longer residence time at lower pyrolysis temperatures. These operation conditions affect the pyrolysis kinetics and, thereby, the product yield and composition.

Information on the biomass characteristics and performance at elevated temperatures is beneficial to the understanding of the pyrolysis process. Biomass has a low thermal conductivity; thus, when heated, a significant temperature gradient within the particle exists, causing a delay for the biomass particle core to reach the target temperature. The biomass particles' size, shape, and physical structure will thus affect product distribution [117]. Smaller particles have a larger surface area to volume ratio, allowing them to be heated faster and more uniformly.

In fast pyrolysis systems, gases and vapours escape more easily and faster from smaller particles at a given temperature, resulting in a higher gas and vapour yield [96, 118], in comparison to larger particles which require more time to heat uniformly and thereby have a higher resistance to releasing the condensable gases, thus resulting in a higher solid yield [96, 118, 119].

The pyrolysis temperature in itself has a significant effect on the product yield and composition [107, 112], where lower temperatures enhance the yield of solid char. Maximum oil yields can be achieved at pyrolysis temperatures of between 400 and 550°C along with a short resident time and a quick quenching of vapours. A further increase of the pyrolysis temperature leads to a decrease in oil yield and an increase in the production of non-condensable gases.

Proximate and ultimate analysis show that char from lower pyrolysis temperatures has a relative lower fixed carbon content and a higher volatile content; and accordingly, relative lower carbon content and higher hydrogen and oxygen contents are to be observed [96, 120]. Less volatile hydrogen and oxygen compounds are released from the solid at lower temperatures, resulting in a higher char yield; however, the solid char product has a lower heating value [96].

At temperatures above 600°C, secondary cracking reactions occur between the vapours and char; increasing gas yield, whilst decreasing char and oil yields [96, 112]. The mechanisms of secondary cracking reactions confirm that additional gas is formed through vapour product cracking rather than char cracking. Precursors for gas formation can be found in the vapours, indicating that char-to-gas reactions are less significant than the vapour-to-gas reactions [121].

To minimise cracking reactions, shorter residence times are used. However, a very short residence time may lead to incomplete decomposition of biomass, due to the temperature gradient required for heat transfer [122]. A slow heating rate and a long gas residence time are required to maximise char production, whereas to maximise liquid yield, high heating rates and short gas residence time are recommended. On the other hand, to maximise gas production, a moderate to slow heating rate with long gas residence time together with a high pyrolysis temperature is recommended [97].

In biomass pyrolysis, a high heating rate, such as occurs in fast pyrolysis, promotes the rapid decomposition of the biomass into its fragments, leading to an increased volatile yield. The high heating rate limits the time for secondary cracking reactions and repolymerisation to take place [123, 124] and, therefore, increases the oil yield. To further inhibit the secondary decomposition of the vapours, rapid quenching of the product stream is suggested [100, 109] as well as sweeping away the vapours using an inert gas [113, 125].

In addition to the product yields, the operating conditions also impact the chemical composition of the pyrolysis products, particularly in regard to the oil. The organic compounds in pyrolysis oil are derived from functional groups present in the biomass phenols. Longer residence time tends to enhance the production of an oxygenate-free bio-oil [113]. The higher operating temperature used in fast pyrolysis increases the water content in the liquid product, this being generated from both moisture in the feedstock and reactions among the primary products [113, 116]. The contents of acetaldehyde, methanol, propanol and acetone are decreased when these compounds have undergone secondary cracking reactions at higher temperatures. After the secondary cracking, the final compounds present in the oil are of a more stable species such as benzene, naphthalene, cresols, and phenols [113, 120, 126, 127]. Additionally, the gas composition shows higher CO, CO_2, CH_4, C_2H_6, and C_2H_4 content when the secondary cracking reactions are promoted at high temperatures [120].

As New Zealand has only one timber pyrolysis plant – and this uses a conventional pyrolysis process – the initial investigation of this work focuses on utilising this method of pyrolysis. If conventional pyrolysis can achieve desirable solid and liquid recoveries this could encourage the realisation of using pyrolysis as a means to divert waste from landfills.

Based on the above understandings of the effect that pyrolysis conditions have on product yields and distribution, the following sections examine arsenic release and metal distribution within the different pyrolysis products. The focus here is on arsenic, as it has the lowest retention of the CCA compounds, and its volatilisation during pyrolysis is guaranteed – see Section 2.2.6. The behaviour of copper and chromium is further discussed in the following section on metal distribution – Section 2.3.4.

2.3.3 Arsenic Release during Pyrolysis

To date, the exact pathways, mechanics, and kinetics of arsenic release during the pyrolysis of CCA-treated timber are not fully understood. However, initial models reported in the literature go some way towards describing the likely release mechanisms and their reaction pathways.

Kakitani et al. [128] proposed two possible pathways for the release of arsenic during pyrolysis. The first pathway is via release from unreacted arsenate, in the form of arsenic pentoxide (As_2O_5), that remains absorbed in the timber from the original treatment process. Arsenic pentoxide is released via a reduction reaction which breaks the arsenic pentoxide down into arsenic trioxide (As_2O_3) and oxygen; subsequently, arsenic trioxide is gasified to the form of arsenic oxide (As_4O_6) [128]:

$$2\,As_2O_5(s) \rightleftharpoons 2\,As_2O_3(l) + 2\,O_2(g) \qquad (R2.2)$$

$$2\,As_2O_3(l) \rightleftharpoons As_4O_6(g) \qquad (R2.3)$$

Kercher and Nagle [100] conducted thermogravimetric analysis (TGA) of pure As_2O_5 and A_2O_3 and found that As_2O_5 begins to volatilise at 600°C with complete volatilisation occurring at 815°C. Helsen et al. [129] performed TGA and DTG and observed that As_2O_5 begins to be released at 600°C with peak release (from DTG analysis) at 797°C. Both Helsen et al. [129] and Kercher and Nagle [100] reported that the arsenic release from As_2O_3 begins at temperatures below 200°C, with Kercher and Nagle adding that complete volatilisation has occurred at 350°C. Temperature is the key parameter driving this reaction towards product formation.

Kakitani et al. [128] showed that the weathered CCA-treated timber waste contained little unreacted arsenic, which was most likely to have been washed out or had leached out over time during its service life [128]. They further proposed a second possible pathway for arsenic release from reacted and fixated arsenic in the form of chromium arsenate ($CrAsO_4$). Chromium arsenate first decomposes to arsenic pentoxide, which, similar to the unreacted arsenic, reduces to arsenic trioxide via pyrolysis [128, 130]:

$$4\,CrAsO_4(s) \rightleftharpoons 2\,Cr_2O_3(s) + 2\,As_2O_5(s) \tag{R2.4}$$

$$2\,As_2O_5(s) \rightleftharpoons 2\,As_2O_3(l) + 2\,O_2(g) \tag{$R2.5$}$$

$$2\,As_2O_3(l) \rightleftharpoons As_4O_6(g) \tag{$R2.6$}$$

Hata et al. [98], Helsen et al. [131] and Kakitani et al. [128] have all conducted pyrolysis experiments, of CCA-treated timbers with the results showing that the arsenic release occurs in the temperature range of 300 to 350°C. However, in TGA experiments using solid or aqueous arsenic pentoxide (As_2O_5), the release temperatures vary significantly with an onset temperature at around 600°C and a release completion temperature as high as 815°C [100]. The TGA results also show that the arsenic release from arsenic trioxide occurs at much lower temperatures i.e. from 200 to 350°C [100]. The details of these results are shown in Table 2.6:

Table 2.6: Release temperatures of arsenic from CCA-treated timber during pyrolysis experiments and the release of gaseous arsenic species using TGA analysis

Source	*As Release Temperature*	*Experimental Method*	*Reference*
Hata et al.	Onset below 300°C	Pyrolysis of CCA-treated timber	[98]
Helsen et al.	between 300 and 320°C	Pyrolysis of CCA-treated timber	[131]
Kakitani et al.	300 to 350°C	Pyrolysis of CCA-treated timber	[128]
Kercher and Nagle	Onset 600°C, complete volatilisation at 815°C	TGA of pure As_2O_5	[100]
	Onset 200°C, complete volatilisation at 350°C	TGA of pure As_2O_3	
Helsen et al.	Small losses above 500°C, primarily above 600°C	TGA of pure As_2O_5(aq)	[129]
	Below 200°C	TGA of pure As_2O_3	

The hypothesis that arsenic is released as volatile arsenic trioxide is supported by the separate studies of Helsen and Van den Bulck [132], Kakitani et al. [128], Hirate et al. [133] and McMahon et al. [83]. McMahon et al. [83] also identified the release of negligible amounts of arsine and observed various arsenites (AsO_3^{3-}) present in the released gas of arsenic trioxide [83].

However, differences in the arsenic release temperature between the TGA and the pyrolysis experiments are observed. Both Helsen et al. [129] and Kercher and Nagle [100] found that As_2O_5 does not decompose, reduce or volatilise at temperatures lower than 500. However, all three studies involving pyrolysis of CCA-treated timber confirm that the release temperature is lower than 350°C, as shown in Table 2.6.

Helsen et al. [129] proposed that the reduction of As_2O_5 to As_2O_3 (reaction R2.2 and R2.5) within wood structures occurs at temperatures below 400°C. Furthermore, trivalent arsenic (As_2O_3) was found in pyrolysis residues from the decomposition at 350°C, although initially, arsenic is only present in the timber in its pentavalent form $CrAsO_4$ or As_2O_5 [134].

In a separate study, Helsen and Van den Bulck [132] investigated the mass reduction and arsenic loss for CCA-treated timber and CCA-treated wood components (cellulose, lignin and combined cellulose and lignin) using TGA methods. Their study established a relationship between the mass reduction of wood and the release of arsenic for different reaction temperatures and residence times. A positive correlation was found between arsenic release and the observed mass reduction of wood or wood components by plotting the experimental data. However, they reported that the relationship between the *"variables seems to be not unambiguous"* [132].

Further investigation was conducted by Helsen et al. [129] on the thermal behaviour of As_2O_5 in the presence of glucose and activated carbon, and the results show that both glucose and activated carbon have a reducing effect on the arsenic compound. Further TGA shows that the interactions between the glucose and the activated carbon with As_2O_5 result in a faster decomposition of the arsenic species at temperatures above 300°C. This is attributed to the reducing action of glucose and activated carbon; therefore, the reduction of pentavalent arsenic to trivalent arsenic is favoured in a reducing environment [129]. As a similar reducing environment is created during the pyrolysis of wood, the results from Helsen et al. [129] support the theory that reaction R2.2 occurs at a temperature above 300°C, but at a much lower temperature than that for pure As_2O_5, as shown in Table 2.6.

Kakitani et al. [128] examined the release of $CrAsO_4$ from d-glucose and proposed a simple pathway model. They suggested that some of the volatilised arsenic may be absorbed by the wood structures at temperatures below the boiling point of the arsenic pentoxide (at atmospheric pressure, 465°C). Hence, a hypothesis was proposed that the actual arsenic release is greater than expected, due to the arsenic being volatilised explosively in quantities that the wood structure cannot adsorb at pyrolysis temperatures over 465°C.

Table 2.7 below provides information on the available thermodynamic data for different species involved in the decomposition reactions during pyrolysis. These data are required to evaluate the arsenic speciation at varying temperatures. This concept will be introduced in Chapter 5 and used in developing a thermodynamic model of the arsenic release process.

Table 2.7: Gibbs free enthalpy ($G°_{fi}$) and heat capacity (C_p) at standard temperature and pressure for chromium and arsenic species present during the decomposition of $CrAsO_4$ and As_2O_5

Species	*$G°_{fi}$ at STP /$J·mol^{-1}$*		*C_p at STP /$J·mol^{-1}·K^{-1}$*	
$CrAsO_4$	-968,360	[135]	119.10	[135]
Cr_2O_3	-1,058,100	[136]	118.7	[136]
As_2O_3	-576,340	[135]	96.88	[135]
As_2O_5	-774,960	[135]	115.9	[135]
As_4O_6	-1,092,200	[135]	173.60	[135]
O_2	0	[136]	29.4	[136]

In a separate study, Helsen and Van den Bulck [132] examined the release of arsenic during pyrolysis consistent with the aforementioned reaction scheme. Their focus was on the impact that the presence of arsenic might have on wood decomposition reactions, which occur during pyrolysis. Arsenic volatilisation was regarded to take place independently of the wood decomposition. It was further assumed that arsenic is released according to a single reaction of order *n*.

Therefore, the heterogeneous arsenic release reaction is modelled using pseudo-homogeneous kinetics and assuming a rate constant dependent on the Arrhenius equation [132]:

$$-\frac{dw}{dt} = k(T)w^{n} \tag{2.1}$$

with

$$k(T) = A\,exp\left(-\frac{E}{RT}\right) \tag{2.2}$$

where *w* represents the decomposable fraction, which in this context is the releasable amount of arsenate. Furthermore, *k* in the above equations is the rate constant, *T* is the absolute temperature, and *n* is the reaction order. The Arrhenius equation includes the pre-exponential factor, *A*, and the activation energy, *E*. *R* in Equation (2.2) is the universal gas constant. It can be assumed that the releasable amount of arsenic remains constant over time at isothermal conditions; hence integration over time t_0 to t results in $w_0 = w_{t=t0} = 1$. Using the integrated equations and results from lab-scale and TGA experiments, the authors were able to show with high certainty that the arsenic release can be described using a single reaction of order *n*. However, the reaction order *n* could not be identified through these experiments and was determined based on reaction assumptions: for reaction orders higher than 1, the reaction must be initiated through molecules colliding with one another. However, as the reaction is considered to be heterogeneous, the reaction order was set to 1:

$$-\,ln(w) = k(T)(t - t_0) \tag{2.3}$$

This allowed the pre-exponential factor *A* and the activation energy *E* to be determined as 0.39 min^{-1}= 6.5 $\times 10^{-3}$ s^{-1} and 20.4 kJ mol^{-1}, respectively [132].

Helsen and Van den Bulck [132] then went on to evaluate the kinetic scheme and proposed that the release of arsenic may be more accurately modelled using two reactions: firstly, the reduction of arsenic pentoxide to trioxide arsenic; and secondly, the volatilisation of trioxide arsenic. The following rate equations describe this:

$$\frac{d[As(III)]_s}{dt} = k_{red}[As(V)]_s \tag{2.4}$$

$$\frac{d[As(III)]_s}{dt} = k_{vol}[As(III)]_s \tag{2.5}$$

where k_{red} and k_{vol} represent the reduction and volatilisation reaction rate constants, respectively. However, in their work, the values for k_{red} and k_{vol} were not determined, although the above two equations were combined to model the reduction and volatilisation together

$$[As\ (III)]_g = [CrAsO_4]_0\left(1 - \frac{1}{k_{vol} - k_{red}}\left(k_{vol}e^{-tk_{red}} - k_{red}e^{-tk_{vol}}\right)\right) \tag{2.6}$$

As the volatilisation occurs much faster than the reduction reaction, it can be expected that $k_{red} << k_{vol}$ which simplifies the consecutive reactions of reduction and volatilisation described in Equations 2.3, 2.4 and 2.5 to Equation 2.6 [132].

These considerations are further expanded upon in Chapter 5, where the alternative reaction pathways are examined in more depth and a model is developed based on minimisation of Gibbs Free Energy.

2.3.4 Pyrolysis Products and CCA Metal(oid) Distribution

This section discusses the two products of char and oil. The non-condensable gas fraction will be discussed in section 2.4.3.

Kim et al. [137] conducted research on fast pyrolysis of CCA-treated timber at 500°C in a nitrogen environment and arrived at a char yield of 23 wt%, an oil yield of 43.3 wt% and a yield of non-condensable gases of 33.7 wt%. In comparison, at the same pyrolysis conditions, char, oil and non-condensable gas yields from pyrolysis of untreated pitch pine were 21.9 wt%, 61.6 wt% and 16.5 wt%, respectively. Therefore, considerably less oil and more non-condensable gas were produced from the pyrolysis of CCA-treated timber than from non-treated timber [137]. This is believed to be attributed to the catalytic effect of the metal(oid)s in the timber. During the fixation process, chromium (VI) trioxide, an insoluble complex salt, is formed by binding to free hydroxyl groups within the carbohydrates and lignin structures of the wood. As these hydroxyls are bound to the chromium compounds within the CCA-treated timber, they become unavailable to form hydrogen bonds with water. Hence the timber has greater water repellence and dimensional stability. Due to this change in wood chemistry, cellulose and lignin do not degrade into smaller molecules during the pyrolysis process and thus, the tar yield decreases [138].

Helsen et al. [97] researched the pyrolysis of freshly CCA-treated timber using a fixed bed pyrolysis reactor at an operating temperature of 350°C for 20 min and under nitrogen environment at a flow rate of 5 $Nm^3 \cdot h^{-1}$. It was found that the mass reduction was 61 % based on the wood mass '*as received'*, while 82.3% of the arsenic was contained in the solid char, 2.9% was transferred into the liquid with 0.12% in the filter, and the remaining 14.7% was in the gas. The retention of chromium and copper in the solid char was 98% and 97.9%, respectively [97].

Kim et al. [99] also performed fast pyrolysis experiments of freshly treated timber at 500°C. The results of this study showed that 36.4% of arsenic, 74.0% of copper and 75.4% of chromium were retained in the char.

Attention needs to be drawn to the fact that almost all of the reported studies used freshly treated timber as feedstock for pyrolysis. Therefore, the effects of unreacted and non-fixated treatment chemicals, when used in pyrolysis, remain uncertain. This includes chemicals such as As_2O_5, which remains in the timber after treatment. Furthermore, their effect on the metal(oid)s distribution and concentrations in the pyrolysis products is unknown. Although leaching studies have been carried out on weathered CCA-treated wood, studies on thermochemical conversion of weathered wood are not available in literature.

The following section discusses research describing the characteristics of the char and the oil produced through pyrolysis of CCA-treated timber. It is worth noting that only limited publications could be found in literature on the characterisation of the pyrolysis products; thus, the application of these results need to be treated with care.

2.4 Waste Management Strategy Development

As the focus of this thesis is on directing current disposal practices for CCA-treated wood waste away from landfill and incineration towards waste management schemes that enable recycling and recovery, pyrolysis has been chosen as the most promising technology. During pyrolysis, some of the arsenic in the original timbers is recovered into the pyrolysis bio-oil product; thus, application and recovery of the arsenic compounds from this fraction needs to be established. The application of this oil as a wood preservative has been reported in literature (see Section 2.4.1) with the results suggesting, it may be possible to use such a bio-oil product derived from CCA-treated timbers in a way, similar to that of traditional oil and tar for wood treatments. Alternatively, as will be discussed in Chapter 6, the derived oil could be processed to an LOSP analogue.

The scope of the research, described in this thesis, aims to address the proposition as to whether pyrolysis can be used to recover significant quantities of arsenic-rich oil suitable for further reuse. If feasible recovery rates can be achieved, the extent, to which the CCA-chemicals enhance the oil's preservative capabilities needs to be established, with particular emphasis on the arsenic component. To implement a full recovery scheme for CCA-treated wood wastes, the gas and char products from the pyrolysis are also required to be suitably utilised without imposing any additional risks of environmental harm. To this end, chromium and copper also need to be investigated for their potential recovery and recycling.

2.4.1 Bio-Oil's Preservative Ability

Previous studies have shown that bio-oil from pyrolysis of non-treated wood and wood bark has a significant antifungal effect. From SEM analysis of wood samples treated with bio-oil, it was found that some chemical components in the bio-oil were adsorbed into the wood structure, forming agglomerations and clusters during the subsequent drying process. It is these clusters, which are mainly derived from lignin polymers, that are believed to enhance the antifungal performance of the treated wood [139]. This finding is supported by Mohan et al. [140], who found that lignin-rich fractions produced a greater fungal inhibition [140]. It was further observed that the pyrolysis bio-oil absorbed into the wood blocked the capillary microstructure of the wood, thus hindering liquid uptake and flow; consequently, the bio-oil acts as a water repellent [141].

Research by Temiz et al. [142] showed that wood treated with 20% bio-oil from pyrolysis of fresh wood biomass diluted with ethanol effectively resisted white and brown rot fungi, this being attributed to the presence of phenol compounds in the bio-oil. The leachability of bio-oil is a major drawback to the treatment of wood with this product. However, the bio-oil leaching had been effectively reduced through "*proprietary polymerisation of its compound and/or co-impregnation for synergistically enhanced activity*" [127]. Their study further tested preservability by combining the original bio-oil with epoxidised linseed oil and found that this method reduced water adsorption and enhanced wood durability [142]. In comparison to this work, research conducted by Cooper et al. [143] found that wood treated with pyrolysis oil showed only a limited effect against brown-rot fungi. In contrast, when enriched with tebuconazole, the antifungal effects were significantly augmented [143].

Arsenic is used in conventional CCA treatment processes to prevent decay caused by fungi and insects. Hence, wood treated with bio-oil derived from pyrolysis of CCA-treated timber waste can be expected to show preservative effects against these types of decay. The dominant form of arsenic present in the oil will need to be determined to confirm this enhanced effect. Both As(III) and As(V) have preservative abilities. Nevertheless As(V) is conventionally used in CCA-treated timber – as it reacts with chromium and thereby is able to bind to wood structures. The retention of arsenic within the bio-oil will also need to be established. If suitable retention levels can be achieved, then adding a fixation agent – e.g. chromium - may not be required. Otherwise, a treatment to alter the oxidation state of the arsenic can be anticipated.

Another approach to determine the bio-oils antifungal effect is to compare the arsenic-rich bio-oil to Light Organic Solvent Preservative (LOSP). LOSP is a class of timber treatment preservatives that use white spirit, or light oils such as kerosene, as a solvent carrier to transport preservative chemicals into the timber. White spirit, also known as mineral turpentine, is a petroleum-derived clear liquid consisting of a mixture of aliphatic, open-chain or alicyclic C_7 to C_{12} hydrocarbons. The material is commonly used as an extraction solvent, cleaning or degreasing solvent, and as an organic solvent in paints, aerosols, wood preservatives, lacquers, and vanishes [144].

Kerosene is a distillate obtained from petroleum with a boiling point ranging from 150 to 275°C. It is a clear liquid with low viscosity and a density of around 800 $g \cdot L^{-1}$. It is typically composed of carbon chains between 9 and 16 carbon atoms per molecule [145]. Kerosene is widely used as a fuel in aviation, for cooking and as a lighting fuel, also for fire toys such as poi [146].

Hydrodesulphurised heavy naphtha (petroleum; CAS: 64742-82-1) is used extensively in wood treatment application within New Zealand. This is predominantly made up of hydrocarbons in the range of C7 through C12 and has a boiling point between 90°C for light components and a final boiling point of 230°C for the heavy fractions [147]. It has a density of 763 kg·m^{-3}, a viscosity of 0.74 – 1.65 mPa·s and solubility of less than 0.1 wt% in water [144].

In New Zealand and Australia other preservative chemicals are added to the heavy naphtha, such as tributyl oxide (TBTO), copper napthenate (CuN), iodopropynyl butylcarbamate (IPBC), propiconazole and tebuconazole as well as permethrin. Their properties can be found in the following table (Table 2.8) [148].

Table 2.8: Physical properties of LOSP and its commonly used additive preservative chemicals

	Chemical Formula	*Boiling Point /°C*	*Solubility in water /mg·L^{-1}*	*Density /kg·m^{-3}*	
*LOSP**		130 -220	> 100	763	[144]
*TBTO**	$[(C_4H_9)_3Sn]_2O$	180	20	1170	[149]
*CuN**	$C_{22}H_{14}CuO_4$	154 - 202		1055	[150]
*IPBC**	$C_8H_{12}INO_2$	321 ± 25	156	1575	[151]
Propiconazole and tebuconazole	$C_{15}H_{17}Cl_2N_3O_2$ $C_{16}H_{22}ClN_3O$	180 476	100 36	1400- 1249	[152], [153, 154], [155]
Permethrin	$C_{21}Cl_2H_{20}O_3$	290	0.006	1.19-1.27	[156]

* *LOSP: Light organic solvent oil, TBTO:* tributyl oxide, *CuN:* copper napthenate, *IPBC:* iodopropynyl butylcarbamate

It can be concluded from the above literature review – and with a perspective on future implementation - that if the pyrolysis process can be optimised so as to retain much of the arsenic in the bio-oil then, in addition, a viable application for the reuse of this oil as a wood treatment may well be able to be established. This leads to the proposition that a suitably configured pyrolysis regime, which takes into account temperature and residence time, and designed to optimise the arsenic recovery within the oil fraction is desired. This arsenic will need to be stable and not prone to leaching or precipitation, otherwise similar leaching issues as with virgin CCA-preservative are to be anticipated. If achievable, pyrolysis may then offer a viable end-of-life waste management solution.

2.4.2 Char Applications

A variety of options discussed in literature for the use of solid char generated from the pyrolysis of CCA-treated wood waste are worthy of more consideration. Whilst not explored in detail, a brief summary of these findings is presented here.

One application identified for produced char containing CCA compounds is as activated carbon for CO_2 capture. Somy et al. [157] found that heavy metals such as chromium and copper present in the activated carbon increase the ability of the carbon to adsorb CO_2. Further, Caglayan and Aksoylu [158] suggested that advanced CO_2 adsorption can arise through chemical and physical interactions of the loaded metal ion group in the carbon. Similarly, Botomé et al. [159] supported the findings that chromium and copper may positively affect CO_2 adsorption.

In another application, Lucchni et al. [160] investigated the use of char from CCA-treated wood waste as a soil amendment for increasing the bioavailability of metals in the soil. The observed temporary increase in soil pH was considered to be advantageous, however, this did not outweigh the adverse effects of the free metal released into the soil [160]. Another study investigated plant growth as well as soil quality. After adding metal-contaminated char to soil, negative effects on plant growth and soil quality were noted at high levels of char contamination; albeit at low levels minimal environmental risk is posed [161].

Due to its porous and polyaromatic structure, pyrolysis char from untreated wood can be used as an adsorbent for heavy metals, reducing the ecotoxicity of soil and water. To remove any adsorbed heavy metals, the char is then regenerated (adsorbate desorption and adsorbate decomposition). A similar process may be applicable for the removal of CCA from contaminated pyrolysis char [162]. The ecotoxicity of char with respect to chromium can be reduced using noble metal nanoparticles as catalysts, thereby reducing Cr(VI) to Cr(III) with HCOOH [163]. Methylation can be applied to convert inorganic arsenic to the detoxified form. Arsenic could be removed efficiently through oxidation of As(III) to As(IV) with zero-valent iron or an electrocoagulation process [164-167]. Membranes, coagulation, anion exchange and disposable iron media, which have been used to remove arsenic from water, may also be applied [168].

Research carried out by Helsen et al. [97] used physical separation techniques to remove the metal(oid)s from the char. Char was processed in a bead grinder, releasing the metal particles from the char. The powder produced in this way was pneumatically sieved and then centrifuged, at which point the density differences allowed for the metals and the char to be separated. The recovered a char fraction that was free of CCA compounds and a metal(oid)-rich fraction that contained 78% char, the remainder being minerals, i.e., heavy metals and alkali metals [97].

More experimental recovery methods for the CCA compounds present in pyrolysis char are discussed in Kim et al.'s review paper [99].

Research has shown that the chromium recovered in the char after arsenic release is in the form of Cr(III), which is less toxic than the Cr(VI) used as a treatment chemical. This indicates that if the metals recovered from the char can be processed to the right oxidation state, the possibility of recycling these compounds as a preservative treatment chemical could allow for their full recycle within the wood treatment industry.

In addition, recovery of the copper and chromium species from within the solid char could follow common practice as found in the mineral processing and refining industry. These methods are briefly summarised in the following paragraphs.

During mineral processing of chromium, Cr_2O_3 and carbon are subjected to temperatures above 2,000°C, forming pure chromium and carbon monoxide. However, in practice, a high-carbon ferrochromium is produced due to impurities in the feedstock. This can subsequently be refined into a low carbon product. Through the thermal reduction of Cr_2O_3 with aluminium, a high purity metal (above 97%) can be recovered. Alternatively, the high carbon ferrochromium could be milled, mixed into an electrolyte solution and processed through electrochemical methods to 99.9% purity [169, 170].

Arsenic is present in many copper mines and addressed as part of the ore processing and metal refining methods. If suitable, the copper- and chromium-rich char could supplement coke to be used in furnaces to produce copper from coke, ores and flux (limestone). Volatile impurities are removed at lower temperatures, and a copper-iron sulphide is recoverable with further increases in temperatures (1,230 – 1,300°C). This mixture can be further refined to above 98.5% purity using pyro- or hydro-metallurgical processing [171].

Alternatively, the produced char blended with other solid fuels could be used for industrial boiler fuel, with gas cleaning to mitigate arsenic emissions. To better understand the relevance of CCA content in fuel for industrial boilers, the arsenic, chromium and copper contents of New Zealand coal, H4-CCA-treated timber and the char produced by pyrolysing H4 CCA-treated timber at 475°C are shown in Table 2.9. As heating value significantly impacts boiler performance, the table considers the metal(oid) content relative to the heating value of coal, timber and pyrolysis char.

Table 2.9: CCA content in treated timber, char and coal

		NZ Coal (sub-bitumen)	*H4 CCA-timber*	*H4 CCA-timber pyrolysis char*
Lower Heating value	Dry basis, $MJ \cdot kg^{-1}$	24	18	28
Arsenic	Dry basis, ppm	~2	2,300	5,500
Chromium	Dry basis, ppm	~8	1,300	9,100
Copper	Dry basis, ppm	~6	1,600	7,300
Arsenic	$ppm \cdot MJ^{-1}$	0.07	230	196
Chromium	$ppm \cdot MJ^{-1}$	0.3	130	325
Copper	$ppm \cdot MJ^{-1}$	0.2	160	260

If CCA-derived char is used in industrial boilers, arsenic emissions in flue gas will require further treatment before being discharged into the environment. It can be anticipated that chromium and copper will remain in the combustion ash. In practice, co-firing of solid fuel (coal or non-treated wood) with the char reduces NOx and CO emissions compared to combustion of pure coal. Particulate emissions are also reduced. The solid char has a much higher heating value and lower moisture content than raw wood, therefore it improves the boilers' combustion performance and energy efficiency.

Boiler performance with blended fuels is likely to be significantly enhanced but will require individual site assessments to determine the maximum allowable quantities of solid char that might be blended, whilst remaining inside any discharge limits. As per the National Environmental Standard for Air Quality, NO_2 in the flue gas cannot exceed 200 $\mu g \cdot m^{-3}$ (averaged over 1 hour), and CO should be less than 10 $mg \cdot m^{-3}$ (averaged over 8 hours) [20]. As previously stated corrosion of the boiler and flue is likely with the presence of CCA compounds [62].

When the char from pyrolysis of H4 CCA-treated timber is burnt in a boiler, the ash is heavily contaminated with the treatment metal(oid)s. Chromium and copper compounds are stable in the ash, becoming even more so in ash produced at the high temperatures. At combustion temperatures of over 1000°C, arsenic tends to leach out of the ash more easily (>80%) in comparison to chromium and copper (<10%) [172]. Due to the high metal content and arsenic instability, the ash requires further treatment, before it can be disposed of or used in cement or concrete [59]. Further information on recycling options can be found in literature [173]; whilst this is an interesting development, these are as yet not commercially practical.

The ash fusion temperature of CCA char is ~1500°C, which is higher than that of typical New Zealand coal (~1100°C). Therefore, blends of coal and CCA char show increasing fusion temperature, which is approximately proportional to the blend ratio of pyrolysis char to coal [174]. This is an advantage for grate-fired boilers, allowing higher operating temperatures than that with pure coal. Thus, any concerns about ash fusion of CCA-treated timber or its pyrolysis char are superfluous.

To use CCA-treated timber char in boilers, modification of the boiler system and operating procedures will be required (as mentioned in Section 2.2.7). Other options discussed focus on the produced char's ability to adsorb CO_2. Together with solvent extraction of the metal(oid)s, these options may be viable, but further research is required to establish this.

From the above discussion, it can be concluded that there are options for the reuse of char produced from the pyrolysis of CCA-treated timber waste, although these are still at the research stage. Nonetheless, from the perspective of eliminating any potential harm to the environment, a more desired approach is to separate and recover metal(oid)s separately from the char. This mitigates the potential for contaminated char posing the same dilemma as the waste management of CCA-treated wood waste.

2.4.3 Gas Cleaning

As discussed above, some of the arsenic within the CCA-treated waste is lost to the non-condensable gas product during pyrolysis.

It can be expected that using pyrolysis will produce less gas with a lower arsenic concentration in comparison to other processes, i.e. gasification or incineration. Research has however reported that arsenic emission from combustion of the non-condensable gas can be as high as 6.2 $g \cdot m^{-3}$ of flue gas without gas cleaning and removal [137]. Thus the removal of arsenic species from the gas product would be necessary, or a high dilution factor would be required to meet the New Zealand air emission standard of less than 5.5 $ng \cdot m^{-3}$ [85]. It is worth noting that the dilution of gas emissions is not a desirable approach in mitigating environmental concerns, even though it may be seen to be a practical solution. Some of the emitted arsenic might be in the form of vaporous pentavalent arsenic (As_2O_5) and therefore condensable, consequently accumulating in any liquids resulting from the quenching process. Gas cleaning may in any case still be required to ensure the emissions of the non-condensable gas stream meet local limits.

Under the reported operating conditions - as reviewed in the literature - it is evident that during the pyrolysis of CCA-treated wood, copper does not volatilise to any large degree. Instead, most of the copper remains in the pyrolysis char product and is relatively stable over an extended time span. Although the volatility of chromium is very low, this element is still more volatile than copper. If chromium retention is the prevailing consideration, a reactor environment with an oxygen content of between 10% and that of air (21%) can achieve the highest chromium stability. Of all three CCA compounds, arsenic has the highest volatility. Unlike chromium, oxygen content appears to have an insignificant effect on arsenic volatility. However, arsenic volatility is significantly affected by the pyrolysis temperature [175].

Helsen and Van den Bulck [132]] found that measuring and capturing arsenic trioxide from the non-condensable gas product is challenging. On the other hand, arsenic pentoxide compounds are released in the particulate or aerosol phase (as condensed arsenates), which can then be effectively captured by scrubbing and filtering [132].

Sorbent Addition

To reduce arsenic volatilisation, one method is to use the addition of a sorbent to the reactor, which will subsequently react with arsenic oxide to form a thermally stable species. Sorbent injection has been shown to reduce arsenic emissions during coal combustion. The sorbent can be in the form of fly ash, activated carbon or mineral material [59]. Similarly to their employment in coal combustion, sorbents may be applicable during the pyrolysis process of CCA-treated timber.

Wu et al. [176] tested various metal-based arsenic sorbents and proposed a thermodynamic equilibrium model. Based on their study, the order of effectiveness for arsenic capture of these sorbents is Li > K > Na > Al > Ca > Mg. With the absence of chlorine and sulphur, the sorbents show 100% efficiency. Under these conditions Al-based sorbents showed the most effective performance (100%)[176].

Hydrated lime and limestone are very effective in adsorption of arsenic during combustion of arsenic-contaminated solid fuels. With the addition of the limestone, tricalcium orthoarsenate ($Ca_3As_2O_8$) is formed at temperatures below 600°C, capturing 6 mg of arsenic per 1 g of sorbent within a 10 minute reaction time [177]. The availability of the active surface on the calcium sorbent is an important factor for the rate of reaction in the arsenic capture [178].

Haynes et al. [175] used calcium-based sorbent with CCA-treated wood chips and found that the sorbent on the one hand was effective for the arsenic capture but on the other hand had the negative side effect of increased leachability of the ash in diluted acetic acids. At 600°C, arsenic retention of up to 85% could be achieved in the solid. Magnesium-based sorbents were slightly less effective (60%), and potassium and aluminium sorbents promote arsenic capture at low loadings. However, over-loading of these sorbents may *"upset the natural sorbent behaviour of the ash inherently present in the wood".* Research findings show that even with the use of sorbents, arsenic volatilisation cannot be inhibited completely, and further post-combustion treatments would still be required. Consequently, the practical application of solid sorbents is questionable, since flue-gas treatment will nevertheless be required [175].

Although helpful in reducing arsenic emissions, sorbents can allow the conversion of Cr(III) to the much more toxic Cr(VI) [59]. Additionally, for the purposes of this research, the recovery of arsenic from solid sorbents will not offer the desired recovery of arsenic for its future use as a wood preservative, and thus would be simply a false trail for future investigation.

Flue Gas Treatment

Arsenic removal from flue gas in the combustion of the solid char from pyrolysis of CCA-treated wood can adopt technologies already available from the chemical industry and their related environmental treatments. The target is to remove arsenic gases from the flue gas mixture into a suitable liquid for recovery and/or disposal. These technologies would also be suitable for removing arsenic species in the flue gas from combustion of the non-condensable gases or directly from the non-condensable gas, when the concentration of arsenic species is higher than the regulated requirement.

Arsenic species can be absorbed using a gas-solid sorbent such as lime, similar to that of sorbent addition to the combustion reactor to capture arsenic oxide by forming calcium arsenate [179]. Again, the product from the sorbent adsorption depends on the temperature (as described in the previous section), either forming tricalcium orthoarsenate (< 600°C) or dicalcium pyroarsenate (700 to 900°C) [177]. Several studies have found that the CaO's ability to adsorb arsenic increases with operation temperature [178-180]. However, Jadhav et al. [177] found an upper limit of 600°C for the increase in the CaO's ability to adsorb arsenic species. They reported that further increasing the temperature from 600 to 1000°C resulted in a reduced ability for the sorbent to adsorb arsenic species [177].

The reactions involving arsenic trioxide and calcium oxide are described by Li et al. as follows [180]:

$$3\ CaO(s) + As_2O_3(g) + O_2\ (g) \longrightarrow Ca_3(AsO_4)_2\ (s) \qquad (R2.7)$$

The possible adsorption mechanism can be described by the following two reactions [180]:

$$CaCO_3\ (s) \rightleftharpoons CaO(s) + CO_2\ (g) \qquad (R2.8)$$

$$3\ CaO(s) + As_2O_3\ (g) + O_2\ (g) \longrightarrow Ca_3(AsO_4)_2\ (s) \qquad (R2.7)$$

Chen et al. [181] further investigated the effect of temperature on arsenic capture by calcium oxide. Again, it was shown that the efficiency of arsenic capture increases with reaction temperature of up to 900°C (1173 K). At reaction temperatures above 900°C, the occurrence of CaO sintering suppresses the arsenic capture. If SO_2 is present in the gas stream, it will compete with arsenic for CaO adsorption and inhibit arsenic capture. Regardless of this the formation of $CaSO_4$ is still capable of adsorbing arsenic vapours at high temperatures. Ideally, the temperature should be around 600°C to achieve the maximum arsenic capture [181].

Studies show that arsenic has an affinity towards iron-modified activated carbon. Oxyanionic arsenic species are adsorbed at the iron oxyhydroxide surface by forming complexes with the surface sites. The arsenic removal is accredited to the ion exchange and the specific adsorption to surface hydroxyl groups or co-precipitation [182]. Kudaravalli [183] compared the adsorption efficiency of CAG, FeOx and GAC/ZVI. The results show that GAC has the highest efficiency in removing arsenic from wastewater with a removal efficiency of 85% [183].

Industrial applications typically use baghouses, electrostatic precipitators (ESPs), wet scrubbers and multi-cyclones to reduce arsenic release to the atmosphere. Arsenic compounds can condense onto particulate materials inside the baghouse, and ESPs can capture the condensate effectively at a removal efficiency of up to 94% [175, 184]. Research into further reducing arsenic levels has been reported using Nuclepore and Millipore filters [185], water and sodium hydroxide impingers [185], and wet scrubbers via calcium-based sorbents [186].

Accordingly, it can be concluded that the required gas cleaning for the non-condensable gases from pyrolysis and flue gas from combustion can be achieved using typical industrial treatment methods.

2.4.4 Extended Producer Responsibility

The OECD defines the concept of Extended Producer Responsibility (EPR) as “a policy approach under which producers are given a significant responsibility (financial and/or physical) for the treatment or disposal of post-consumer products” [187]. According to the EPR scheme, increasing awareness and the recovery and recycling of post-consumer resources aim to significantly reduce the amount of waste timber being discarded or stored. Although this concept has been proposed for some time, the EPR scheme for treated timber waste has only found acceptance in Finland [188], where a fee is charged at the time of timber purchase to fund any remediation project. When large quantities of timber are required, a further disposal fee is charged, these funds going towards the EPR scheme run by a company, in this case Demolite Oy, established in 2000. It is a non-profit organisation, and the charged fees are used only to cover the costs of recycling [188].

New Zealand has not adopted the EPR scheme for treated timber [14]. The greatest hinderance is the cost factor for the implementation of an EPR scheme here; although the outlay could be covered through a levy integrated into the price of the timber at the time of purchase. New Zealand has a “regulated product stewardships” program to increase the circular resource use of products and to place the responsibilities of a product’s end-of-life management into the hands of producers, importers and retailers – rather than communities and councils. This concept extends the responsibilities as stated in the EPR policy to everyone involved in the product’s life cycle [189]. In 2020, the New Zealand government declared a range of products, including tyres, batteries, farm and packaging plastics to be prioritised for the establishment of a regulated scheme under the Waste Management Act (WMA) 2008 [190]. It has been proposed that treated timber be adopted into this scheme [191].

Whilst not a major consideration for this thesis, the above initiatives reinforce the need for an improved approach to CCA-treated timber waste management. Should such a scheme be adopted in NZ, the approaches described here may potentially offer a channel for future planning and response.

2.4.5 Options Assessment

The above discussion leads to the conclusion that a number of processing steps are required to enable recycling and recovery of the metal(oid)s present in CCA-treated wood waste. Many landfills have established sorting facilities to identify CCA-treated timber from other timber wastes; however, technologies and methods for timber sorting vary in efficiency and practicality. Although landfills with leachate collection facilities are common, the disposal of the CCA-treated timber wastes here, is not considered to be a sustainable solution. Landfills occupy space, and the leachate requires storage and treatment before the leachate can be discharged into the environment. In addition, there is always a potential risk of overflow in heavy rains and flooding.

Diverting CCA-treated timber waste from landfills is of benefit to the environment, provided effective end-of-life solutions are available. Options to recover the CCA treatment chemicals include solvent extraction and thermochemical conversion of the waste to release the metals. Table 2.10 sets out the advantages and disadvantages of the different disposal technologies assessed here.

Table 2.10: Advantages and disadvantages of different disposal technologies

Disposal Technology	*Advantages*	*Disadvantages*
Landfilling	Immediate and available technology	Waste of resources Leaching of heavy metals and contamination of ground
Solvent Extraction	Removal of up to 93%, 95% and 99% of Cu, Cr and As	Not feasible on a large scale Removal from solution still required
Pyrolysis	Less arsenic volatilisation than other thermochemical methods	Arsenic volatilisation, arsenic in oil (potentially available for reuse)
Incineration	Can be coupled with metal recycling process	Gas cleaning equipment required High As in ash
Co-Incineration	Low investment cost, flexible fuel choice, lower emissions due to dilution	Gas cleaning equipment required High As in ash
Gasification	High energetic efficiencies	Gas cleaning equipment required High temperature required

Although solvent extraction can achieve high removal efficiencies, its drawbacks are slow operating times and costly solvents. It is thus reasonable to assume that these methods are unlikely to be commercially viable in the near future. Thermochemical conversion and pyrolysis in particular, therefore become the preferred approach. Through pyrolysis, the quantities of timber waste for disposal are significantly reduced, and the majority of arsenic compounds can be retained in the bio-oil and char. Pyrolysis offers a process route that allows for the recovery of the metal(oid)s from the char and the possibility of using the arsenic enriched oil as a timber preservative or as a supplement to the existing CCA preservative process. It is worth noting that this opens up opportunities that are still to be investigated.

These recovery and reuse possibilities are described diagrammatically in Figure 2.1:

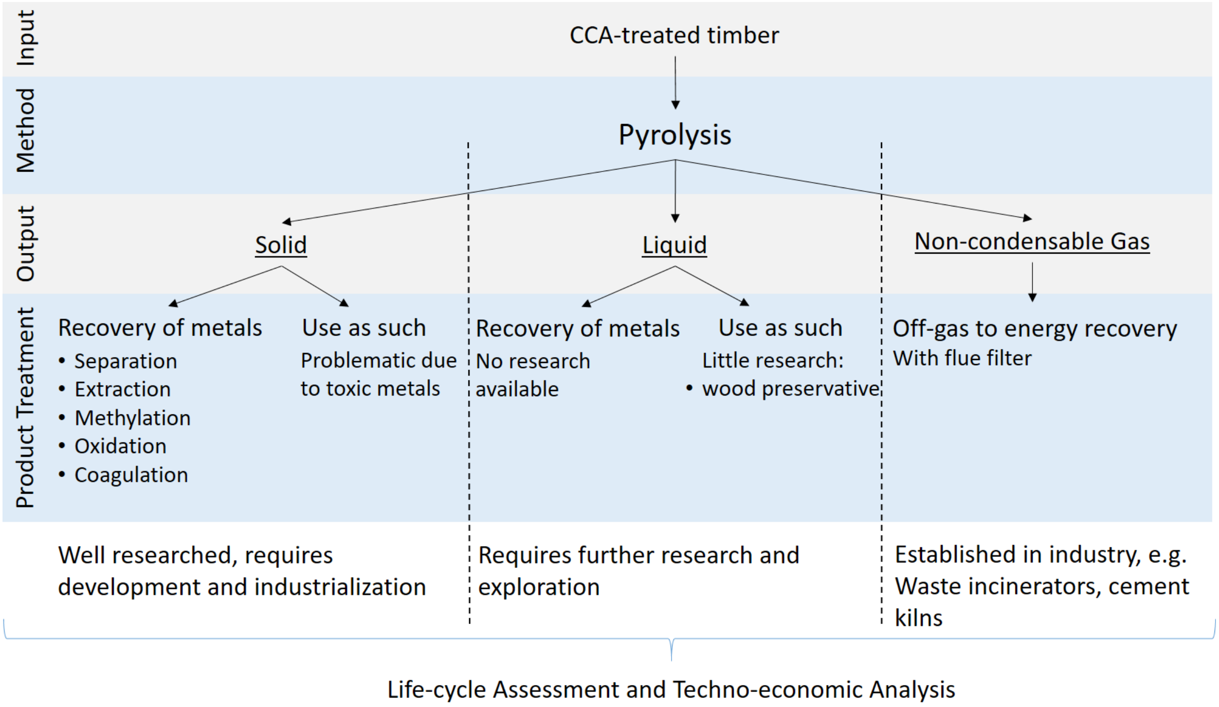

Figure 2.1: Readiness of technologies for the treatment of pyrolysis products of CCA-treated timber waste

To maximise retention of arsenic in the liquid oil product, the pyrolysis temperature should be between 400 to 550°C. Whereas, if solid char is required to retain metals, low-temperature pyrolysis will be necessary. The removal of metals in the char can be achieved via physical and chemical extraction, methylation, oxidation and coagulation techniques. When the arsenic content is maximised in the oil product, the oil may be used accordingly for wood preservation; creating a potentially valuable recovery and reuse scheme for the liquid. Whilst results are encouraging, further investigation and development are required. Recovering the metals is an important value-add component and will aid the recovery and total utilisation of the waste.

2.5 Conclusions

The disposal of CCA-treated timber waste presents significant challenges to the timber treatment industry. The current practice of landfilling causes serious concern in regards to the potentially negative environmental impacts of continued use. Economic recovery and recycling of the CCA treatment chemicals are urgently required, but the pathway forward towards commercial implementation remains unclear.

The environmental footprint of CCA-treated timber can be reduced through end-of-life recycling and the recovery of treatment chemicals. In comparison to other technologies pyrolysis is the preferred course as it promises a range of value-add opportunities whilst having the lowest environmental impact. Generally pyrolysis appears to be capable of addressing the growing quantities of CCA-treated timber waste; firstly by diverting waste materials from entering landfills and then through the conversion of this resource into oil and char products. The metal(oid)s in the char can be recovered using known techniques such as solvent extraction and physical separation. However, the development and commercialisation of such processes is yet to be fully demonstrated. Research into the recovery of the metal(oid)s from the derived bio-oil is still required; similarly, the application of the arsenic-rich bio-oil as a potential alternative wood treatment option requires further investigation.

The literature review indicates that pyrolysis operating conditions significantly affect the pyrolysis yield and the distribution of the preservative metals within the solid char, liquid oil and gaseous products. The review undertaken here demonstrates the need to further investigate the effect of temperature, particle size, heating rate, and residence time in order to determine the optimum operating regime suitable for industrial-scale application.

The dissociation reaction kinetics of arsenic under pyrolysis conditions requires further examination with the intention of improving the current understanding of arsenic transformation during the pyrolysis process and, thereby, maximising arsenic recovery into the oil. The bio-oil composition should be established, as well as its preservation efficacy.

The experimental and theoretical work as described in the subsequent chapters of this thesis is intended to address these issues. A mathematical model of the pyrolysis reactions is used to aid in directing the experimental trial and for the validation of the results. These findings are then combined to enable an evaluation of the industrial applicability of the adopted process scheme.

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3 Methodology, Materials and Experimental System

This chapter describes the experimental system employed, materials, sample preparation, experimental methods utilised, and all analytical techniques used in this study. The experimental work performed focused on the effects of different operating conditions on the pyrolysis of CCA-treated timber, with attention given to establishing the optimum operating conditions that maximise arsenic recovery in the pyrolysis liquid product (bio-oil). The pyrolysis char and oil were subsequently analysed to determine their chemical composition and physical properties.

The literature review shows that operation temperature is the main parameter affecting CCA distribution in the pyrolysis products. Consequently, the objective of the experimental study was to investigate the effect of temperature on pyrolysis product yields and the extent of arsenic volatilisation. Based on previous studies reviewed in Chapter 2, the temperature range of 300 to 600°C was explored at 50°C intervals.

This chapter will cover the following topics:

- The pyrolysis equipment and experimental setup;
- Operating procedures and sampling;
- Feedstock analysis;
- Analysis of the pyrolysis products, i.e. char, gas and bio-oil;
- Mass balance for experimental validation.

3.1 Pyrolysis

3.1.1 Overview of the Pyrolysis System

In this study, design and modification of the experimental system was based on that previously used by Feng Gao[1], a former PhD student and member of this research group lead by Professor Shusheng Pang at the University of Canterbury.

The design criteria for the experimental setup to be met were:

- Easy assembly and disassembly for repetitive use, ease of operation and maintenance;
- Precise temperature control;
- Inert environment;

- No liquid hold-up; and
- Complete mass balance.

The experimental pyrolysis rig was located in the Special Purpose lab of the Chemical Engineering Department at the University of Canterbury. A schematic diagram of the system setup and a photo of is shown in Figure 3.1 and Figure 3.2, respectively,which consists of a vertical reactor positioned within a *Labec vertical* furnace. Approximately 25 grams of oven-dried H4-CCA-treated wood particles were inserted into the reactor for each experimental run. The sample was positioned on a metal tripod, 15 cm above the bottom of the furnace, to ensure it was well within the heating zones of the furnace – a more detailed account of the design is discussed in the sections following hereafter. Heated nitrogen gas was injected at the bottom of the reactor to provide an inert environment. This was used as a sweep gas to carry any pyrolysis vapours and gases through the system. Nitrogen flowrate was supplied from a gas bottle and was controlled at 3 $L \cdot min^{-1}$ at normal conditions of 20°C and 1 atm using a rotameter located immediately after the gas bottle’s pressure valves. The nitrogen gas was preheated to 200°C before being injected into the reactor using a custom preheating system.

During pyrolysis, the pyrolysis vapours and non-condensable gases exited from the top of the reactor and then passed through the centre pipe of an annular tube condenser. The condenser was installed at a 45-degree angle, with cooling water circulating in counter-current flow around the centre pipe, allowing condensed liquid to flow downwards by gravity and accumulate in a Büchner flask. Nitrogen and non-condensable gases left the Büchner flask from the top. For analysis, the gas volume and flowrate were determined using a positive displacement flowmeter installed after the condenser; where pressure and temperature were known. Gas composition was determined using an online gas chromatographer (GC) (Agilent micro-GC 490). Finally, the non-condensable gases were vented into the university’s gas cleaning system through the extraction system.

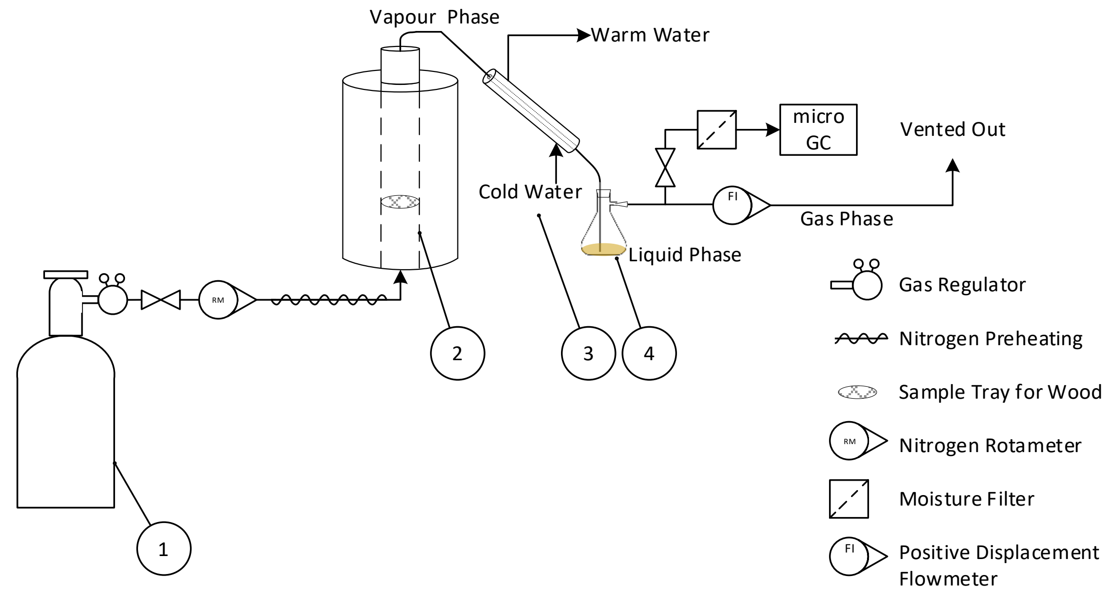

Figure 3.1: Schematic diagram of the experimental setup for the pyrolysis of CCA-treated wood. In the chart, 1. N_2 bottle with pressure regulator, 2. Vertical tube reactor inside a Labec electric furnace with sample tray for wood/char within the heating zone, 3. Annular tube condenser, and 4. Büchner flask for liquid accumulation and collection.

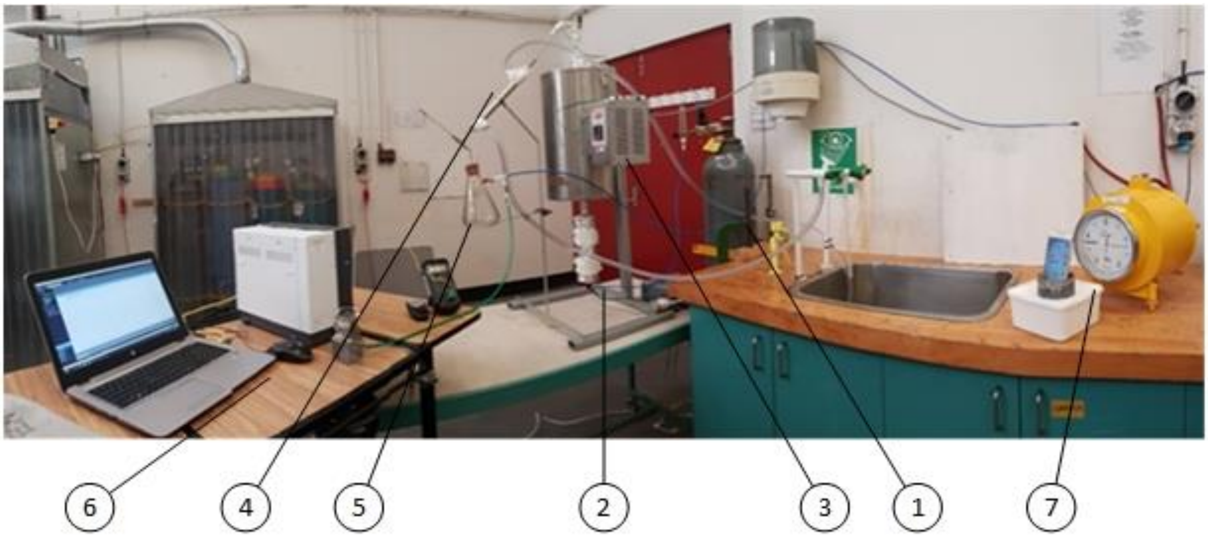

Figure 3.2: Experimental rig for the pyrolysis of CCA-treated wood. In the diagram, 1. Nitrogen bottle with gas regulator and rotameter (to its top left), 2. Nitrogen preheating with insulation around it at the bottom of the reactor, 3. Labec furnace with tube reactor inside, 4. Annular tube condenser with water supply from the bench water tap, 5. Büchner flask for liquid accumulation, 6. On-line GC connect to gas stream (after Büchner flask), and 7. Positive displacement flowmeter with phone positioned in front to record dial.

The wood samples used were oven-dried particles of H4-CCA-treated GS8-grade *Pinus radiata* timber, further details of which can be found in Section 3.3 of this chapter. The wood decomposed into char, pyrolysis vapours, and non-condensable gases through the pyrolysis process. Char and ash accumulated at the bottom of the reactor and were collected for analysis at the end of each run.

3.1.2 Control of Nitrogen Flow and Preheating

The nitrogen flowrate through the experimental system was controlled using a *Cigweld* flow controller. During the commissioning stage, it was found that supplying nitrogen from the bottom of the reactor cooled the wood samples during pyrolysis to such an extent that decomposition of these samples did not occur. Consequently, a custom-made trace heating system was installed on the reactor inlet pipe to heat the nitrogen stream to 200°C before entering the reactor, as shown in Figure 3.3. The heat tracing used *Hotwatt Glasrope* as the heating element, with the heating load controlled by a *Shimaden SR91 Digital Controller*. The system's components were safety rated for 200°C, and trials showed this provided sufficient preheating capacity to allow pyrolysis reactions to occur in the reactor as desired.

(a) (b)

Figure 3.3: Nitrogen feed into the bottom of the reactor. Set up for (a) initial design without preheating installed, and (b) final design with preheating (to 200°C) installed and insulated.

Nitrogen flow and preheating were switched on during each experimental run once the reactor was loaded with biomass and fully connected to the system. This allowed the reactor and system to be purged of any air and filled with an inert environment for the pyrolysis step. Once the micro-GC recorded only the presence of nitrogen in the gas stream, the furnace was switched to the desired temperature setpoint.

3.1.3 Furnace and Reactor Setup

The final experimental setup used a fixed bed batch reactor constructed of stainless steel with a diameter of 40 mm and a length of 500 mm. The reactor sat within the Labec vertical tube furnace (model VTF 40/12), which has a single heating zone of 450 mm. The furnace's 1500 W heating capacity was achieved using embedded electric elements for heating. The outer surfaces of the elements were covered with ceramic fibres for insulation [2]. The top of the reactor comprised of a flange used to suspend the reactor on the support frame of the furnace. The lid was fixed to the reactor tube by a simple screw fix, a copper disk inside the lid ensured a good seal between the reactor and the lid. A stainless steel tripod and a stainless steel mesh tray were used to elevate the wood sample, thereby ensuring that it sat within the heating zone of the furnace. The tripod allowed the sample to sit on the mesh tray 150 mm from the bottom of the reactor, as shown in Figure 3.4 and Figure 3.5. The mesh was of sieve size No. 35 with a 500 µm nominal size opening. Detailed engineering drawings are shown in Appendix A.

Figure 3.4: Stainless steel reactor tube (ø 40 mm, L = 500 mm) with nitrogen port at the bottom (right). On the right, screw-on lid with gas outlet port and thermocouple port. Also, 150 mm long sample stand (tripod) with mesh tray (No. 35 sieve size).

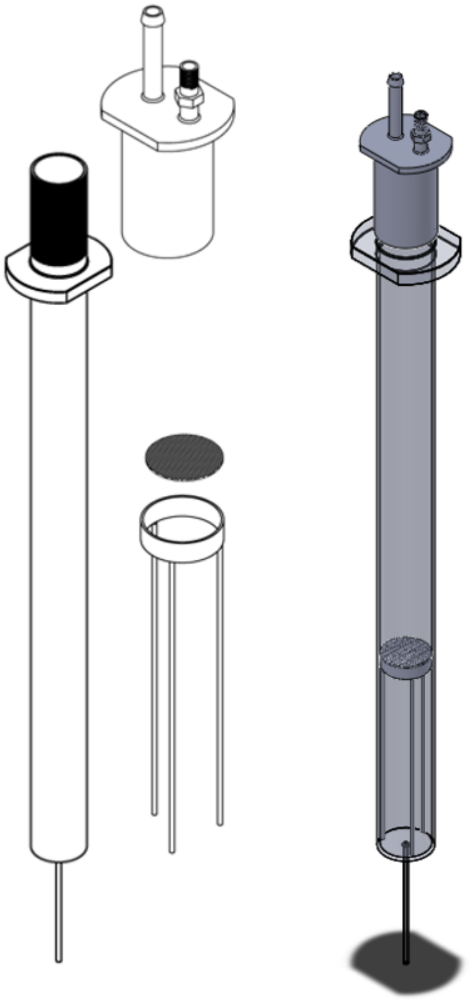

Figure 3.5: Drawing of the reactor parts: Left showing the drawing of the reactor, tripod mesh and lid; and right is the assembly of these parts in position when used during experiments. Details and dimensions of the parts of the experimental system are presented in Appendix A.

Temperature Profile

In the course of the commissioning process, it became evident that there was a temperature gradient along the vertical direction within the reactor, as shown in temperature Figure 3.6. This data was taken without nitrogen gas or any wood sample within the reactor. Doing so mitigated any possible influence from the gas stream and / or the pyrolysis reactions allowing proper determination of the heating zone as well as establishment of the reactor’s temperature profile within the furnace. During the temperature measurements, the furnace was set to a target temperature of 500°C and was allowed to reach steady-state (> 0.5°C variation) before measurement. A K-type temperature probe was suspended within the reactor tube at various heights. When the temperature probe showed constant temperature readings, temperatures were recorded.

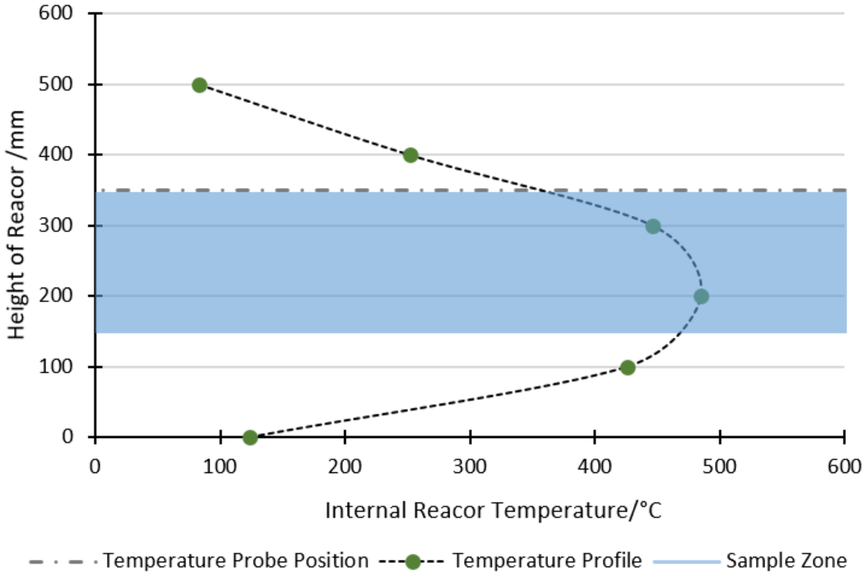

Figure 3.6: Temperature profile inside the reactor along its vertical height, positioned inside the Labec furnace set to 500°C – no N_2 flow or wood particles were present.

Figure 3.6 shows the variation in the temperature profile that one can expect within the reactor; with either ends of the reactor tube recording temperatures below 150°C at a furnace setpoint of 500°C. This profile explains, why the wood samples were not pyrolysed when placed at the bottom of the reactor during the commissioning process, where temperatures merely reached 120°C. It was for this reason that the wood samples were elevated by placing them on a tripod 150 mm from the reactor bottom. The sample occupied the reactor space from a height of 150 mm to approximately 350 mm, as shown in blue in Figure 3.6. The dashed/dotted line in the figure indicates the position of the temperature probe in the reactor during the experiment.

Temperatures in the reactor were also measured at the beforementioned position with preheated nitrogen fed into the reactor from the bottom. For safety reasons, the temperature profile within the reactor with a heated nitrogen flowrate stream was not analysed due to the likely exposure of the operator to a hot gas stream. The final temperature recorded was 475°C (versus 349°C without nitrogen) at a furnace setpoint of 500°C, indicating that the presence of heated nitrogen has a significant effect on achieving the desired temperature within the reactor.

The temperature profile shows that the position of the thermocouple actually measures the lowest temperature within the sample zone of the reactor (approximately 350°C), and thus records the minimum temperature within the reactor. However, heat transfer calculations show that the sample should reach a uniform temperature well within its residence time in the reactor. It can therefore be assumed that the final, steady-state temperature reported by the probe is that of the sample. Calculations can be found in the Appendix B.

Heating Rate

As previously stated in the literature review Cuypers and Helsen [3] investigated the effect of heating rate on pyrolysis products of CCA-treated timber and concluded that heavy metal(oid) volatilisation is only weakly affected by this [3]. A range of heating rates have been explored in literature for the conventional slow pyrolysis of CCA-treated wood by Fu et al. (3°C·min^{-1}) [4], Helsen and Van den Bulck (10°C·min^{-1}) [5] and Cuypers and Helsen (5 – 20°C·min^{-1}) [3].

In the experimental work reported here, the heating rate of the *Labec* furnace could not be controlled, although it is known that this will change with temperature setpoint. Heating rate, however, can be determined from the temperature-time profile as illustrated in Figure 3.7 (recorded using the temperature probe positioned at 350 mm from the bottom of the reactor as displayed in Figure 3.6). The temperature setpoints across the different experimental runs were between 300 to 600°C in 50°C increments. For these trials, the heated nitrogen gas flowrate was 3 L·min^{-1} at standard conditions (Section 3.1.1 and 2.1.2).

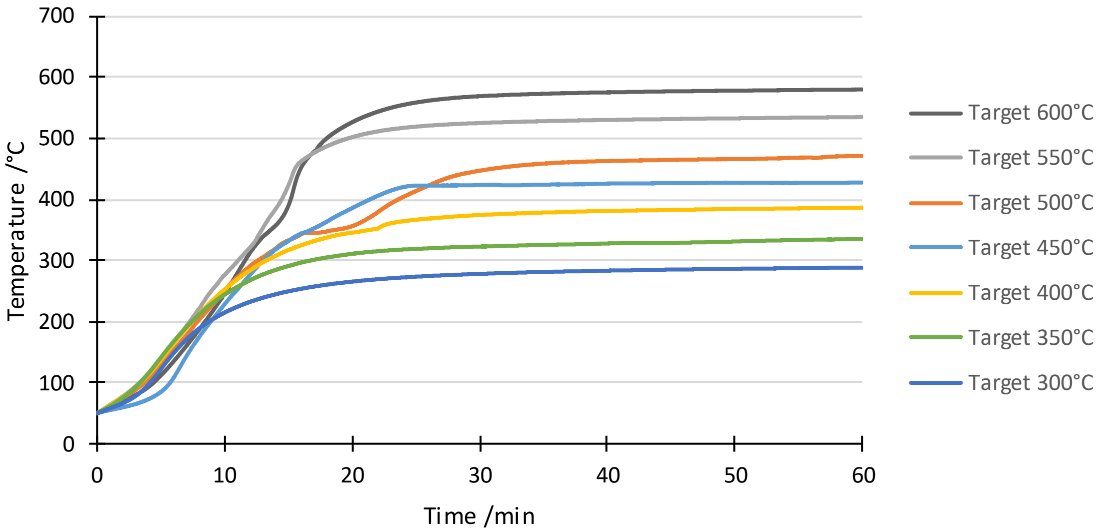

Figure 3.7: Temperature profile of the reactor in the furnace with nitrogen flow (preheated to 200°C at 3 L·min^{-1} at standard conditions) – using a temperature probe positioned 350 mm from the bottom of the reactor (note – to standardise the profile the time was to zero once 50°C was observed)

From the results shown in Figure 3.7, the heating rate (°C·min^{-1}) was determined from 50°C to steady-state target temperature, where steady-state is assumed to be when temperature changes were measured at less than 0.5°C over 2 minutes. Table 3.1 shows that the derived overall heating rate ranged between 5 and 15°C·min-1 depending on the furnace setpoint, which is within the typical heating rate range for batch-wise conventional pyrolysis as previously stated.

Table 3.1 Furnace heating rate as the mean slope of the ramp section across the first 20 minutes while using nitrogen as the sweep gas (heated to 200°C at 3 L·min^{-1} at standard conditions)

Setpoint Temperature	300	350	400	450	500	550	600
Overall Heating Rate /°C·min^{-1}	10.7	13.0	14.7	16.5	15.2	22.5	23.6

The furnace remained operational during the experimental runs until no further liquid and gas production was recorded, indicating that pyrolysis had ended. This batch-wise operation meant that the residence time was not a variable, but, in turn, the heat-up rate of the sample would be different at different temperature setpoints. The effect of this variability on liquid yield has not been evaluated but is expected to be minor based on literature [6, 7] where it was shown that raising the heating rate from to 10 to 50°C·min^{-1} resulted in no significant change, in response to the already low heating rate.

3.1.4 Safety

For the pyrolysis experiments, measures were taken to reduce the health and safety risk within the laboratory and in the handling of the pyrolysis products. Firstly, to be able to operate the equipment, it is standard procedure in the department to work through a Hazard and Safety Checklist, which requires the operators to fully understand the toxicity and potential hazardous impacts of all materials involved in the experiments. At the beginning of each trial run, the equipment was checked for possible leaks, and detectors for toxic and combustible gases were switched on. All electrical equipment was plugged into a residual-current device (RCD) to minimise the risk of the heat tracing and the furnace short-circuiting. There were no valves installed after the reactor to inhibit pressure build-up and prevent any associated dangers. The gas exhaust was vented through the extraction system. The quantity of the exhausted gases had been assessed to be extremely low considering the low feedstock input (25 g).

Wood, char and liquid were handled by the operator wearing appropriate gloves. Char and liquid products were stored for analysis in appropriate containers and kept in secondary containment.

A *ToxiRae II* personal CO-monitor was worn at all times by the operator while running pyrolysis experiments. The CO-meter was calibrated every six months by *apc techsafe*. Further, the operator wore either or both dust and gas masks as necessary.

3.1.5 The Design for Vapour Condensation, Liquid Collection and Gas Exhaustion

The vapour condenser used to cool the gas stream and to condense pyrolysis vapours was a stainless-steel annular tube heat exchanger, as shown in Figure 3.8. The vapour-gas stream from the pyrolysis reactor is fed through the centre pipe of the condenser, whilst coolant water is circulated through the cavity space between the outer and centre pipes. The coolant water used was sourced directly from the laboratory water supply, this at approximately 14°C, and subsequently flowed through the condenser in a counter-current configuration. Details of the condenser and its dimensions can be found in Appendix A.

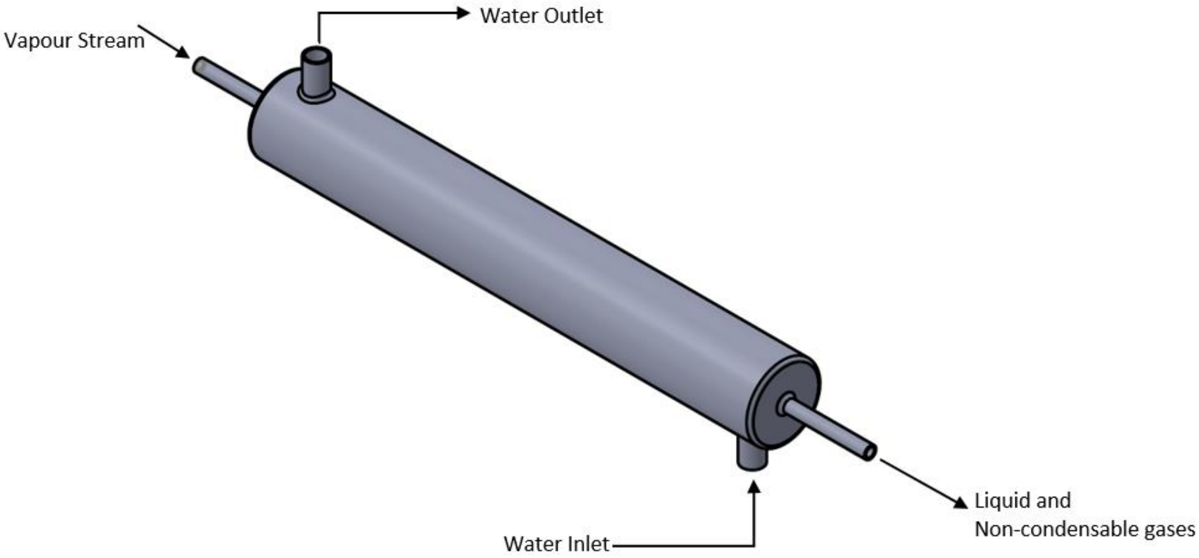

Figure 3.8: Drawing of the annular tube condenser used to cool pyrolysis vapour. Water (14°C) circulated in counter-current flow direction around the centre gas pipe, allowing vapours to condense. Details and dimensions are presented in Appendix A.

The condenser was installed at a 45° angle allowing any liquids to flow into the Büchner flask. The condensed liquid accumulated at the bottom of the flask, while non-condensable gas passed through the flask and out its top outlet. The flask was sealed using a rubber stopper. The condenser gas outlet temperature was 20°C.

After exiting the Büchner flask, the non-condensable gas stream composition was analysed via an online GC. As the experimental setup uses a batch system rather than a steady-state system, the gas composition varies as a function of time. A continuous GC analysis was carried out to determine the gas composition over time using the Agilent micro-GC 490. The GC was connected to the gas line using a T-intersection allowing a fraction of the gas to be re-directed to the measuring instrument.

Before the gas entered the GC, it had passed through a moisture filter. Gas sample analysis took approximately 3.5 minutes, allowing a new gas sample to be analysed every 4 minutes. The GC software was set up to continue until it was manually interrupted by the user. Gas volume was measured using a positive displacement flowmeter, and the time recorded. Together, this allowed for the volumetric gas flowrate to be calculated.

A mobile phone camera was often used to video-record the flowmeter dial for later analysis. The time-stamped video allowed any experiment to be continued without in-person supervision. Within the 4-minute interval it took for each gas sample analysis, the gas composition was assumed to be constant to that determined using the GC analysis. The corresponding gas volume during the 4-minute interval was then determined using the volumetric displacement meter data. The gas mass could be calculated from composition and gas volume. Data on the Micro-GC column and operating conditions can be found in Section 3.3.2, while calibration data of the instrument is described in Appendix C.

3.1.6 Temperature Measurements

The final design of the experimental system included two K-type temperature probes, one positioned inside the pyrolysis reactor at the height of 350 mm from the reactor bottom and the second one placed immediately after the condenser. The reactor temperature probe data was recorded using *Lascar Data Logger* and retrieved using the *EasyLog* software. Whilst the data was not recorded for the second temperature probe, the condenser temperature was monitored to ensure sufficient cooling was achieved so that the gas temperature at the condenser exit reached a room temperature of 20°C. This temperature was measured using a *CIE 306 Digital Handheld* thermometer.

3.2 Commissioning of the Pyrolysis Test Rig

As standard practice before actual investigation and experimentation took place, the pyrolysis test rig was commissioned. This involved three pyrolysis trials using non treated wood at a pyrolysis temperature of 300°C. After these trials were successfully completed, the commissioning process was deemed to be concluded. The trials took place using approximately 25 g of non-treated, oven-dried *Pinus radiata* wood particles which were transferred into the reactor during each test. The exact weight of the wood sample, the reactor and the Büchner flask were recorded. Nitrogen preheating elements were turned on (200°C) with a nitrogen flowrate of 3 L·min^{-1}. Once the GC recorded only the presence of nitrogen gas, the furnace was switched on and set to 300°C. After each pyrolysis trial, the weight of the reactor with char and the Büchner flask with liquid were measured. The recorded weights allowed for the char and liquid yield to be determined. The gas weight was calculated using the recorded volumetric flowrate and gas composition from the micro-GC data analysis.

Three trials were carried out using the same pyrolysis operating conditions as shown in Table 3.2; however, the degree of water-cooling through the condenser was varied. In the first trial, the water flowrate through the condenser was set to the maximum (12 L·min^{-1}), whilst for the second trial no water-cooling was used, and for trial three approximately 6 L·min^{-1} of water was used. Varying water flowrate resulted in different degrees of liquid recovery; ultimately, it was chosen to always use the maximum water flowrate for cooling to achieve the highest possible liquid yield. A complete mass balance was established for each trial, as shown in Table 3.2.

Table 3.2: Pyrolysis commissioning trials of non-treated wood at 300°C, using 3 L·min^{-1} of nitrogen at 200°C as sweep gas and 3 different water flowrates in the condenser for pyrolysis vapour cooling

Trial	*1*		*2*		*3*	
Water Flowrate	12 L·min^{-1}		0		6 L·min^{-1}	
Wood	100%	16.1 g	100%	21.8 g	100%	16.4 g
Char	77.9%	12.6 g	81.4%	17.7 g	81.5%	13.4 g
Gas	11.2%	1.81 g	15.6%	3.39 g	14.7%	2.40 g
Liquid	9.43%	1.52 g	0.09%	0.02 g	1.89%	0.31 g
Recovery	98.6%	15.9 g	97.1%	21.1 g	98.1%	16.0 g

With the completion of the three consecutive mass balance trials, the commissioning of the rig was completed and deemed ready for experimental use.

The following section discusses the methods used for analysis of the feedstock and the pyrolysis products.

3.2.1 Equipment Cleaning Procedure

Before each experimental run, the weight of the reactor and the piping between the reactor and Büchner flask was recorded. After pyrolysis and once the equipment had cooled to a safe handling temperature, the weight of these parts was re-recorded to allow for the char and liquid yield to be calculated, thereby accounting for any sample that had adhered to the equipment and could not be recovered.

Between runs, any liquid deposits were removed by submerging the piping in hot soapy water, followed by rinsing with water, then with acetone and finally with water again. Next, the inside of the reactor was cleaned using hot soapy water and a pipe cleaner brush. Again, this was followed by a rinse with acetone and water.

The gas pipeline (after the Büchner flask) was regularly cleaned using compressed air. For this, the volumetric gas flowmeter was detached from the system, and compressed air was directed through the gas pipeline.

3.3 Feedstock and Product Analyses

3.3.1 Feedstock

In devising a waste management scheme, weathered CCA-treated wood waste is of particular interest. However, to ensure repeatability and availability of sufficient feed stock of the same quality and treatment grade, freshly CCA-treated timber was chosen as feedstock for the laboratory pyrolysis trials. Oven-dried particles of H4-CCA-treated GS8-grade *Pinus radiata* were used, as shown in Figure 3.9. A 4-meter-long plank of 75 x 40 mm timber was purchased at a local hardware store (Mitre10 Hornby, Christchurch, New Zealand). The timber was reduced to a useable particle size in the Wood Product Lab of the Forestry School at the University of Canterbury. This was first processed into thin shavings using a surface levelling machine, then ground to particles using a *Wiley Laboratory Mill (Model 4)*.

Figure 3.9: Wood structure of H4-CCA-treated GS8-grade Pinus radiata as purchased (left), shavings of the same timber beam (middle), wood particles (average particle size 780 µm) both for wood analysis and for pyrolysis experiments (right).

Before being used for analysis and the pyrolysis experiments, the wood particles were thoroughly mixed to guarantee an even particle size and CCA chemical distribution, which is essential to ensure a uniform feedstock for each run of experiments. During the CCA treatment of timber, the chemicals penetrate the wood and are absorbed into it from the outer surface towards the centre of the timber board. Consequently, a preservative concentration gradient exists through the timber, with the surface concentration being higher than in the interior. If needed, a subsample of the particles (~ 500 g) was taken to ensure consistency of the feedstock and CCA content.

Ultimate and Proximate Analyses

The ultimate and proximate analyses of the wood samples were conducted by Verum Group, an external laboratory located in Christchurch, New Zealand. The wood was ground as per the previously laid out method. The air-dried particles were sealed in a plastic container and delivered to Verum. The analyses results are presented in Table 3.3.

Table 3.3: Ultimate and proximate analysis of pre-dried H4-CCA-treated GS8-grade Pinus radiata as purchased determined by Verum Group

	Method	*As Received (wt%)*	*Dry Basis (wt%)*
Proximate Analysis			
Moisture	(LAD @105degC)	0.5	
Ash	(ISO 1171)	1.3	1.3
Volatile Matter	(ISO 562)	81.7	82.1
Fixed Carbon	(by difference)	16.5	16.6
Ultimate Analysis			
Carbon	(ASTM D5373)	48.4	48.6
Hydrogen	(ASTM D5373)	5.98	6.01
Nitrogen	(ASTM D5373)	<0.01	<0.01
Oxygen	(by difference)	43.9	44.1

The low moisture content of the wood 'as received' is likely due to the presence of CCA compounds within the wood and their water repellent effect.

Furthermore, the ultimate and proximate analysis results show differences in the hydrogen to carbon molar ratios and oxygen to carbon molar ratios for CCA-treated timber versus untreated *Pinus radiata*.

Molar ratios of H:C and O:C are 1.48 and 0.68 for treated wood, respectively, and 1.37 and 0.61 for untreated *Pinus radiata* analysed by the same research group [8]. Further literature investigation compared these values with other research groups and found a natural variability within the measured results, as shown in Table 3.4. Differences in ratios of oxygen and hydrogen to carbon are likely to be due to the wood's location of growth, tree age, forest habitat and the sample's location within the tree [9, 10]. Table 3.4 shows that the values measured in this study fall within the typical range for Pinus radiata.

Table 3.4: Molar ratios of hydrogen and oxygen content to carbon content for Pinus radiata and other pine species – values obtain through ultimate analysis of the feedstock wood

Wood Species	*H/C*	*O/C*	*Reference*
Pinus radiata	1.48	0.68	*This study*
Pinus radiata	1.37	0.61	[8]
Pinus radiata	1.56	0.65	[11]
Pinus radiata	1.63	0.60	[12]
Pinus radiata	1.35	0.61	[13]
Pine (NA)	1.44	0.66	[14]
Pinus pinaster	1.56	0.72	[15]

Particle Size Distribution

The particle size distribution was determined using a vibratory sieve shaker and woven analytical sieves of different sizes. The *Frisch "analysette 3"* PRO shaker was used in combination with *Endecotts Ltd.* Laboratory test sieves with stainless steel meshes available at the University of Canterbury of sizes 150, 250, 355, 500, 600, 710, 1000, 1400, 2000 µm.

The particle size distribution was determined by sieving the ground wood and recording the weight retained by the individual sieves. The results are shown in Figure 3.10. The mass-weighted average particle size was 780 µm.

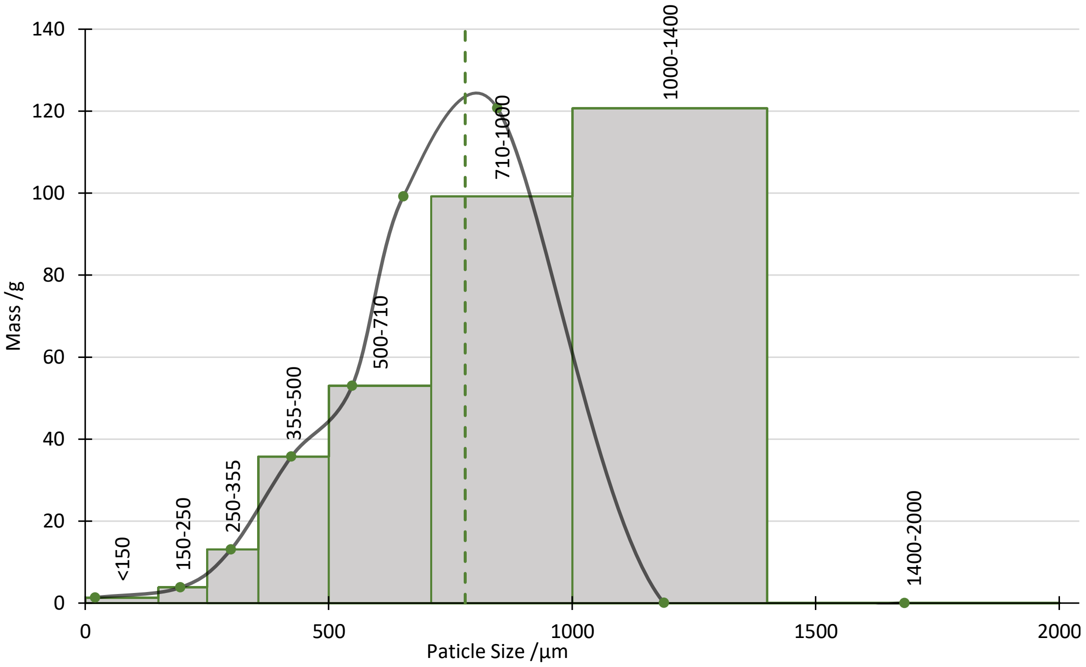

Figure 3.10: Particle size distribution of ground particles of CCA-treated wood used as feedstock for pyrolysis experiments determined using a vibratory sieve shaker. Mean particle size of 680 µm and particle frequency distribution using the log mean of the adjacent sieve sizes.

CCA-Content

Two types of analysis were employed to determine the contents of chromium, copper and arsenic in the CCA-treated timber. The first analysis was conducted by the *Verum Group* using XRF analysis to determine the metal(oid) content in the ash of CCA-treated wood, which was produced by the same method as used for the proximate analysis (ISO 1171).

The second analysis was based on acid digestion and ICP-MS analysis to determine the metal(oid) content in the CCA-treated timber. Details of the ICP-MS analysis are outlaid in Section 3.3.2 (ICP-MS analysis). As only a very small sample (0.1 g) is acid-digested for the ICP-MS analysis, five samples were taken in total to determine the overall CCA content.

The CCA content in timber varies with sample location within the treated wood. Particles from the surface show higher CCA concentrations than particles from the centre. For pyrolysis trials, where products were subsequently analysed, a sub-sample of the wood (~ 500g) was taken to ensure consistency within the feedstock. This sub-sample was thoroughly mixed prior to each pyrolysis run. Three acid digestion and ICP-MS analyses were carried out on the sub-sample, as shown in Table 3.5.

Table 3.5: CCA content in H4-CCA-treated wood particles analysed using XRF by Verum Group and by ICP-MS analysis

	XRF analysis		ICP-MS analysis	
	Ash sample	Wood sample*, dry basis	Average in wood, dry basis	Wood Sub-sample used for pyrolysis, dry basis
Chromium	18.1 wt%	0.23 wt%	0.22 wt%	0.27 wt%
Copper	10.7 wt%	0.13 wt%	0.23 wt%	0.26 wt%
Arsenic	13.0 wt%	0.16 wt%	0.27wt%	0.23 wt%

*Calculated based on results from proximate analysis results Table 3.3

Table 3.5 clearly shows a difference in total CCA content based on the analysis method. This is discussed in-depth in Section 4.3.

Thermogravimetric Analysis

Thermogravimetric analysis (TGA) was carried out on untreated and CCA-treated wood particles using the *Netzsch* thermal analyser *STA 449 F3 Jupiter*. For each trial, approximately 10 mg of sample were transferred to a pre-fired (1200°C) alumina crucible and placed on the instrument's scale alongside a 'correction' crucible. Three vacuum/purge cycles were used before beginning the TG analysis in a nitrogen environment. During the TGA trial, the nitrogen flowrate was set to 50 mL·min^{-1} with a protective gas flowrate of 20 mL·min^{-1}. The samples were heated in five steps, as shown in Table 3.6. A heating rate of 10°C·min^{-1} was chosen as this is comparable to the heating rates achieved by the *Labec* furnace (see Table 3.1).

Table 3.6: TGA procedure for untreated and CCA-treated wood particles, at each step a gas flowrate of 50 mL·min^{-1} and a protective gas flowrate of 20 mL·min^{-1}

Step	*Atmosphere*	*Temperature /°C*	*Heating rate in /°C·min^{-1}*	*Hold time for Isotherm /min*
1	N_2	20°C to 105°C	10	
2	N_2	105°C	Isothermal	60
3	N_2	105°C to 800°C	10	
4	N_2	800°C	Isothermal	60
5	N_2	25°C	20	120

Initially, samples were heated from room temperature (20°C) to 105°C at the heating rate of 10°C·min^{-1} and then held at 105°C for 1 hour to drive off any moisture. After this, the samples were heated at 10°C·min^{-1} to 800°C and held at this temperature for one hour. The weight after 1 hour at

105°C was set to 100% to allow different samples to be compared without variation due to different moisture contents. TGA results are presented in the following chapter, Chapter 4.

3.3.2 Analysis of Pyrolysis Products

Micro-GC Gas Analysis

The non-condensable gas stream from pyrolysis was analysed using an Agilent micro-GC 490. The column material and detector operating parameters are listed in Table 3.7:

Table 3.7: Agilent micro-GC 490 column and operating parameters used for the analysis of non-condensable gases

Channel Parameters	*Channel 1*	*Channel 2*
Column Name	Molecular Sieve 5Å	Porous Polymer Q
Column Material	Zeolites	Polystyrene-divinylbenzene
Column Temperature /°C	90	60
Initial Pressure/kPa	100	70
Column Length /m	10	10
Detector	μTCD	μTCD

The micro-GC measured the volumetric content of N_2, O_2, CO_2, CO, CH_4, and C_2H_6 and C_2H_4.

Using the measured volumetric flow rates and gas composition for each experimental run, the mass flowrate of the gas product can be calculated based on the densities of each component at STP.

Water Content

The water content in the produced bio-oil was determined using a Karl-Fischer Titrator. A Mettler Toledo V10S was used with Hydranal Medium K as the solvent and Hydranal Composite 5 as the titrant. 0.1% water standards were used to calibrate the titrator. The method was set to accept a maximum drift of 25 $\mu g \cdot min^{-1}$, with a mixing time of 180 s at a stirring speed of 35%. An approximate 0.1 g bio-oil sample was used per titration, and triplicate analyses were carried out to minimise errors.

Viscosity

The viscosity of the bio-oil was measured using an *Anton Paar (MCR 302)* modular compact rheometer, which was equipped with a 50 mm, 1° cone and plate. Approximately 0.1 mL of bio-oil sample was pipetted onto the plate in each analysis. The rheometer measured viscosity at 20°C over increasing shear stress from 0.8 Pa to 67 Pa over time.

Density

Due to the small quantity of oil recovered, a 1 mL pipette was chosen as the most accurate volume-measuring device with a density accuracy of 0.006 mL. The bio-oil sample was drawn up into a 1 mL glass pipette, and the weight of the pipette was recorded before and after liquid draw-up. This procedure was repeated three times for each sample, and the density was calculated by dividing the weight difference by the volume.

Total Arsenic Content by ICP-MS Analysis

The total arsenic content of the wood samples, the solid pyrolysis char and the recovered liquid were determined using Van den Broeck and Helsen's reflux method and ICP-MS analysis [16]. In the ICP-MS analysis, 0.1 gram of dried wood sample, pyrolysis char sample or liquid bio-oil sample was transferred into a round bottom flask equipped with a reflux condenser to prevent loss by volatilisation during the dissolution process. Next, 10 mL of concentrated nitric acid was added to the flask and heated using a heating mantle (~60°C) until the sample was dissolved completely (approximately 2 hours for the liquid sample and 4 hours for the solid sample). Once fully dissolved, the acid was passed through a fibreglass filter and diluted twice to 0.1 M (nitric acid).

These samples were then sent to Robert Stainthrope in the Chemistry Department, University of Canterbury, to determine the total arsenic content via inductively coupled plasma mass spectrometry (ICP-MS).

The complete description of this method's procedure can be found in Appendix D.

Arsenic Speciation: UV-Vis Analysis

Literature to date provides no information as to the forms of arsenic that are present in the bio-oil produced from the pyrolysis of CCA-treated wood. However, it is reported that most arsenic contained in the char is As(V). The oxidation state of arsenic may influence the preservative efficacy and leachability of any subsequent wood sample treated with the bio-oil/LOSP analogue derived from the CCA-treated wood. The literature review undertaken found that As(V) is the preferred active species, due to its lower leachability and its ability to react with chromium and thereby binding it to the wood. As(III), although having better preservative abilities, is more water-soluble, and therefore prone to leach. Hence, it is necessary to determine both the quantity and the oxidation state of arsenic in the bio-oil.

As stated in literature, coupled techniques have been recommended for arsenic analysis, such as hydride generation (HG) coupled with ICP-MS or high-performance liquid chromatography (HPLC) coupled with ICP-MS. Both methods have been reported to be reliable and precise. However, these coupled analysing techniques are unavailable locally and therefore could not be used for this study. Advice from the Department of Chemistry of the University of Canterbury and further literature inquiry suggested the method described by Van den Bulck and Helsen [16] to be the most practical approach in regard to arsenic analysis for this research: arsenic in the bio-oil is first dissolved into a solution followed by ultraviolet-visible spectroscopy (UV-Vis) using the method of Dhar et al. [17] to determine the arsenic species.

Following these procedural methods, samples were acid digested in 50 mL of 2.5 M H_2SO_4 and 10 mL H_2O_2 for one hour at 75°C. The digested samples were filtered and diluted to 250 mL using deionised water.

With the application of this method, As(V) forms a complex with reduced molybdate that strongly absorbs infrared while As(III) does not. Unfortunately, phosphate interference can cause a false reading of As(V). Deployed are oxidising and reducing agents manipulating the oxidation states of arsenic as shown in Table 3.8, allowing the true As(V) and As(III) content to be calculated by differences. The first aliquot did not have the oxidation state of arsenic manipulated, allowing for the As(V) and phosphate content to be determined. As(III) was oxidised to As(V) by adding an oxidising agent to the second aliquot. Through the difference of absorbance between aliquot one and two, the As(III) content could be calculated. In the third aliquot, adding a reducing agent leads to all arsenic being present as As(III). Consequently, the measured absorbance was produced solely by phosphate. The difference in absorbance between aliquot one and three shows the As(V) content [17]. The complete procedures and calibration data can be found in Appendix E.

Table 3.8: UV-vis detectable compounds to determine arsenic-oxidation state

Sample	*Sample Preparation*	*UV-vis absorbance by*
1	Only further HCl	As(V) and P
2	Oxidizing Agent (oxidizing As(III) to As(V))	As(V), oxidized As(III) and P
3	Reducing Agent (reducing As(V) to As(III))	Only P

NMR Analysis

Nuclear magnetic resonance (NMR) was chosen as the analysis method to determine the chemical compounds present in the derived bio-oil product. An approximate 600 µL sample of bio-oil was dissolved in equal quantities of dimethyl sulfoxide-d6 (DSMO-d6) and transferred into NMR tubes. The samples were then processed using a *Joel JNM-ECS400S* spectrometer for H-NMR in the Chemistry Department of the University of Canterbury with the assistance of Dr Amanda Inglis. The resultant spectra were analysed using *Jeol Delta* software. Similar aromatic functional groups were grouped to determine their presence in the liquid; some individual peaks were also identified.

3.4 Industrial Trial – Bio-oil Recovery

During the course of this PhD study, there was an opportunity provided by Koppers NZ Ltd to undertake in-house testing of a bio-oil sample with regards to its applicability as an oil-based preservative. It was hoped that such a test might allow comparison of the bio-oil against other wood treatment products and enable evaluation of its suitability for use in existing industrial applications. Unfortunately, the lab-scale pyrolysis experiments could not produce sufficient bio-oil sample for analysis by Koppers NZ Limited. Therefore, consideration was given to collecting a sample from a commercial-scale pyrolysis system owned by Waste Transformation Limited in Timaru, the only commercially operating pyrolysis plant in New Zealand for wood waste. However, as the pyrolysis unit is not designed for bio-oil production, no suitable sample could be collected. A report outlining efforts to collect a sample from the Timaru plant can be found in Appendix F.

3.5 References

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4 Experimental Results and Discussion on Pyrolysis of CCA-treated Timber

This chapter presents the experimental results from the pyrolysis trials of CCA-treated wood. The first section describes and discusses the experimental findings, which are then compared to those reported in literature, focussing on the applicability of the pyrolysis technology for the processing of CCA-treated timber wastes. Thus, providing the first step towards a proof of concept for using pyrolysis as a waste management strategy for CCA-treated timber waste, which is then further discussed in Chapters 5 and 6.

It should be noted that the reported temperature setpoint (SP) of the furnace is different to that of the pyrolysis temperature within the reactor, as was previously established during the commissioning process. This has been discussed in Section 3.1.3 of this thesis. Unless stated otherwise, all temperatures reported here refer to the pyrolysis temperature within the reactor.

As presented in Chapter 2, temperature is the key operating parameter influencing the arsenic release during pyrolysis. The experimental work examined the effect of temperatures between 280 and 600°C on arsenic yield in pyrolysis products. Furthermore, the effect of particle size below 500 µm, 500 – 1000 µm and above 1000 µm was investigated at the pyrolysis temperature yielding the highest arsenic recovery in the liquid.

4.1 Results from Pyrolysis Experiments

4.1.1 Pyrolysis of Untreated Wood Samples

To set a baseline for the pyrolysis experiments, trials with untreated wood were carried out at three temperatures (280, 377 and 475°C) following the same procedure as that as laid out in Chapter 3 for treated wood. Pinus radiata wood samples with an average particle size of 750 µm were used for these experiments, comparable to the feedstock particle size of CCA-treated wood (780 µm). Raw experimental data are displayed in Appendix G. The product yields from the pyrolysis of the untreated wood samples are as shown in Table 4.1.

Table 4.1: Product yields from pyrolysis of untreated Pinus radiata wood at three temperatures

Reactor Temperature,°C	*Solid Yield,wt%*	*Liquid Yield, wt%*	*Gas Yield, wt%*
280	78	9	11
377	24	38	37
475	22	40	34

The results in Table 4.1 show that with increasing pyrolysis temperature, the solid yield decreased while the liquid and gas yields increased. This is in agreement with the reviewed literature [1, 2].

4.1.2 Pyrolysis of CCA-treated Wood Samples

Ground particles of H4-CCA-treated GS8-grade *Pinus radiata* wood were used as the feedstock for these experiments, following the procedure laid out in Section 3.1. Originally consideration was given to using weathered CCA-treated wood waste; however, CCA concentrations may vary significantly among these waste samples. It was then ultimately chosen to use freshly treated wood samples to maintain consistency within the samples and allow for repeatability. The use of freshly treated wood can be assumed to be the worst-case scenario of CCA entering the disposal sector. The details for the choice of feedstock, its ultimate and proximate analysis, and sample particle size distribution are presented in Section 3.3.1. Raw experimental data and calculations are shown in Appendix G.

Mass Balance and Product Distribution

This part of the investigation established that a near complete mass balance for pyrolysis of CCA-treated wood over the range of furnace temperature setpoints from 300 to 600°C was achieved. The results are shown in Figure 4.1, which confirm that over 90 wt% of feedstock was accounted for in the pyrolysis products. The unaccounted weight of less than 10 wt% is likely due to the solid and oil products depositing on the inner walls of the reactor and the pipeline of the system. The procedure of removing these deposits is discussed in Chapter 3. In addition, small gas leaks from fittings may have also occurred. A minor fraction of the product was lost to the micro-GC sampling and analysis, as this sample stream was drawn away from the system, before being accounted for by the volumetric flowmeter. The micro-GC took less than 1 mL samples every 4 minutes.

Initially, thought was given to placing the micro-GC sampling port behind the volumetric gas meter. The volumetric meter uses water to determine the positive displacement of the gas and thereby the gas volume. This option was not implemented, as the possibility of moisture contamination in the sample became likely.

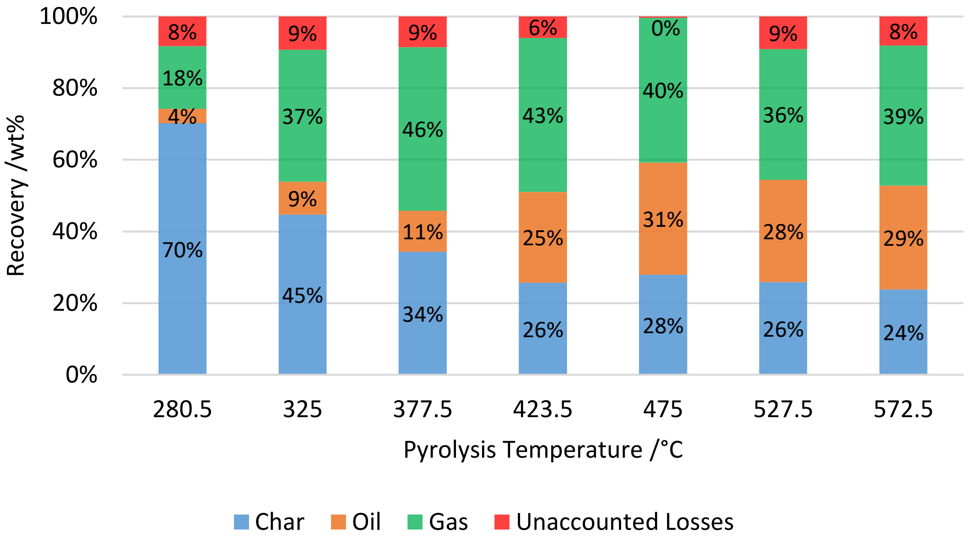

Figure 4.1: Mass balance of the pyrolysis products of H4-CCA-treated wood particles at reactor setpoint temperatures between 300 and 600°C.

A trend in product yield can be established from the mass balance results. The char yield generally decreased, while the oil yield increased with increasing setpoint temperature up until 500°C. However, with a further increase in the reactor setpoint temperature, both char and the oil yields decreased slightly.

At least two pyrolysis trials were carried out at each temperature setpoint to confirm the initially established trend in Figure 4.1. As a significant change in char yield was recorded at 300°C and 350°C (SP), one additional pyrolysis trial was carried out at a furnace setpoint temperature of 325°C (temperature in the reactor: 303°C). Based on the experimental data, the yield of liquid oil and solid char as a function of pyrolysis temperature was determined as displayed in Figure 4.2. A decrease in char yield with increasing pyrolysis temperature up to 480°C is observed, while the liquid yield increases – consistent with the trend established in Figure 4.1.

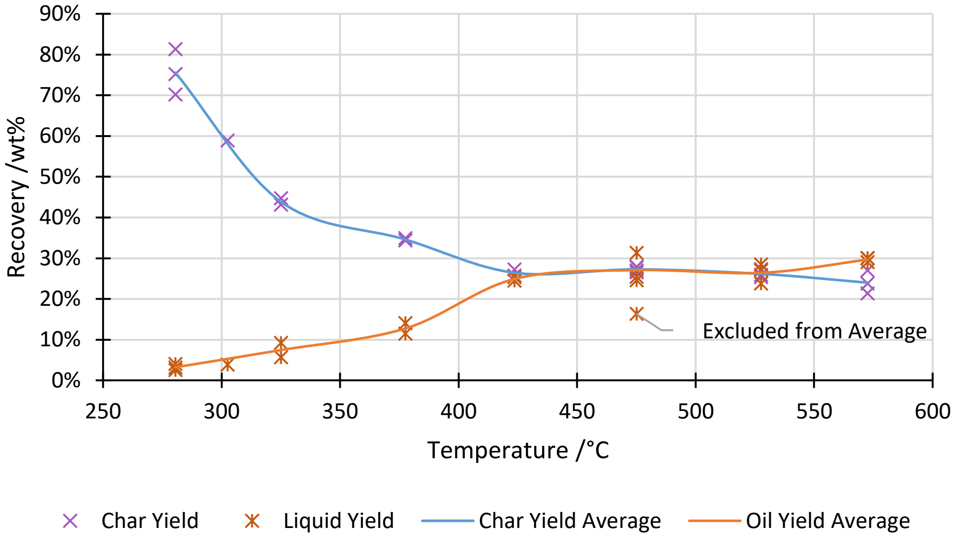

Figure 4.2: Char and liquid oil yields from the pyrolysis of CCA-treated wood particles (average size of 780 µm) at temperatures from 280 to 577°C (oil data point at 480°C excluded from the average, as the condenser was not operating fully)

The bulk conversion of biomass into its fragments via pyrolysis occurs between 300 and 400°C [3]. The trend shown by the data gathered in this study - Figure 4.2 – agrees with literature, wherein gas and oil production are favoured at higher temperatures. Above 400°C, the char yield remains reasonably constant between 23 and 28 wt%.

By comparing the pyrolysis results of untreated (Table 4.1) and CCA-treated wood (Figure 4.2) differences in product yields become apparent, as shown in Figure 4.3. At temperatures below 340°C, the solid char yield of untreated wood was higher than that of treated wood. However, this trend is reversed at temperatures above 340°C. Similar trends were reported by Fu et al. [4], noting a reverse in trend at pyrolysis temperatures of 300°C. Figure 4.3 further shows that the liquid product yield from pyrolysis of the CCA-treated wood was lower, and the gas product yield was higher than that from pyrolysis of untreated wood samples.

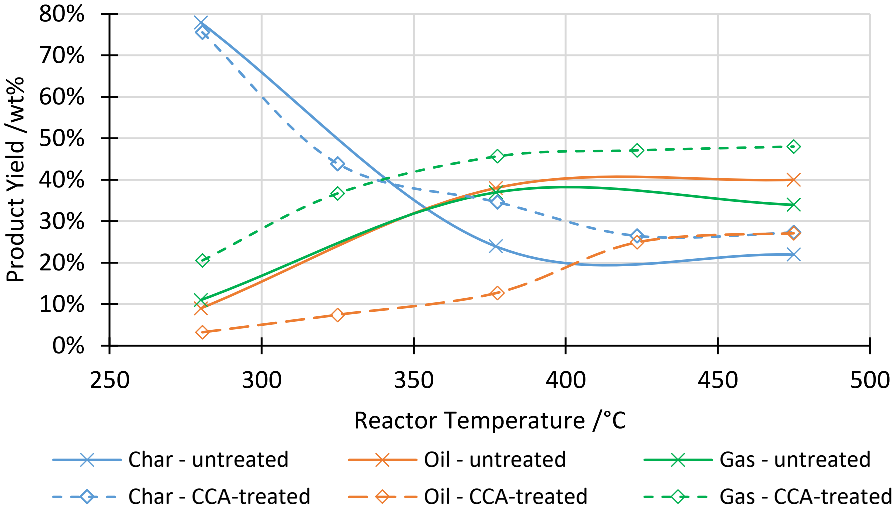

Figure 4.3: Comparison of average pyrolysis product yields between untreated and H4-CCA-treated Pinus radiata wood particles.

To further investigate the decomposition process of both untreated and CCA-treated wood, thermogravimetric analysis (TGA) was carried out as per the methods laid out in Chapter 3. The TGA results, displayed in Figure 4.4 below, show that the mass reduction onset of treated wood was at a lower temperature than that of untreated wood. However, at temperatures above 400°C, the weight reduction of untreated wood exceeded that of treated wood. The solid char yield of treated wood was thus higher than that of untreated wood. The TGA findings agree with Fu et al. [4], who conducted TGA studies on treated and untreated Southern Pine wood.

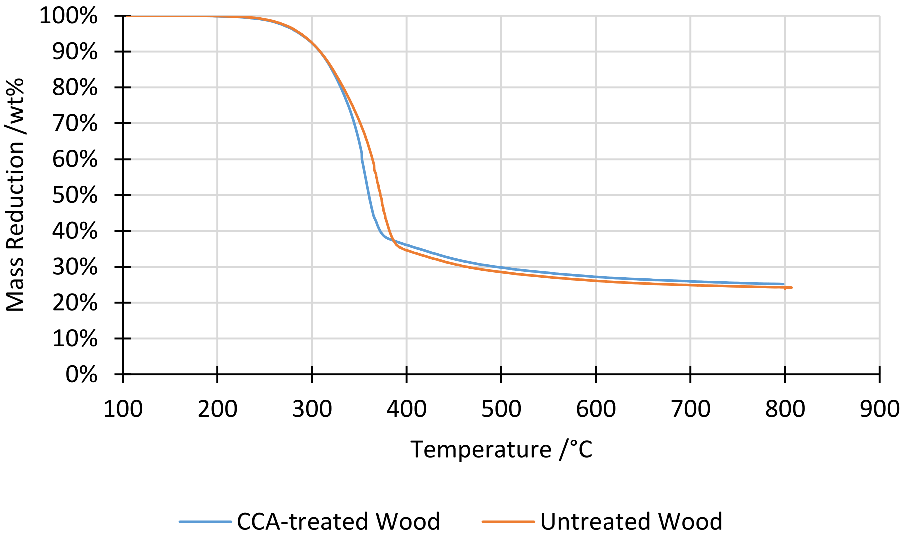

Figure 4.4: TG curves of untreated Pinus radiata and H4-CCA-treated Pinus radiate wood samples in which the moisture-fee weight at 105°C was set to be 1.

The accelerated decomposition of the CCA-treated wood sample can be attributed to the catalytic effect of chromium and copper. Furthermore, the lesser mass reduction observed can be attributed to the presence of CCA compounds. It is equivalent to the elevated ash yield found in CCA-treated pine versus untreated pine. Fu et al. [5] investigated the effect of the preservative chemicals in CCA-treated timber during the TGA tests and found that CrO_3 had the most significant effect on wood decomposition at lower temperatures. A similar catalytic effect was found using $K_2Cr_2O_7$-treated wood, although to a lesser extent. Studies by Helsen and Van den Bulck [6] and Kinata et al. [7] supported the findings of the present study on CCA having a catalytic effect on wood decomposition.

The use of CCA during the treatment processes changes the wood's original chemistry. Chromium (VI) oxide binds with free hydroxyls in the carbohydrate and lignin structures during the fixation process, forming an insoluble complex salt. During pyrolysis, the lignin and cellulose structures cannot degrade into smaller molecules, increasing char yield from CCA-treated wood in comparison to untreated wood [5].

Further TGA data from Kercher and Nagle [8] give insight into the decomposition process of treated and untreated wood. In their study, CCA compounds were analysed in their pure state, as well as those mixed with yellow pine particles of less than 1 mm particle size at different blending ratios. Heating rates of 5 and 50°C·min^{-1} in an inert nitrogen environment were analysed over a temperature range up to 1000°C. Kercher and Nagle [8] found that the reducing environment, created by the decomposition of wood, enhances the decomposition of As_2O_5 to As_2O_3 (*R2.2*) and thereby allows for arsenic volatilisation to take place at temperatures lower than that of pure As_2O_5. Further, Kercher and Nagle [8] showed that CuO had little effect on the extent of mass reduction. These findings are consistent with those reported by Helsen et al. [9].

The liquid product yield, as presented in Figure 4.2, shows that the maximum liquid production of 28 wt% was achieved at pyrolysis temperatures at around 470°C and above. Previous studies, as reported below, show similar findings of a maximum liquid production at approximately 500°C, followed by a drop in liquid production rate at temperatures higher than 600°C due to cracking of lighter tars into non-condensable gases. Depending on the (untreated) biomass, particle size, heating and residence time, and other operational parameters, the temperature to achieve maximum liquid yield can be expected to range between 500 – 550°C [3]. Research by Şensöz and Mukaddes [10] reported a comparable liquid yield of 32 wt% from pyrolysis of untreated pine (*Pinus brutia*) chips (particle size less than 10 mm) at 500°C and heating rate of 40°C·min^{-1} in nitrogen sweep gas.

Fu et al. [4] achieved bio-oil recoveries of 14.6% at 275°C using conventional slow pyrolysis, with increasing temperatures reaching up to 57.7% at 350°C from pyrolysis of CCA-treated wood, where results using untreated wood were also included for comparison. These values of liquid product yields are much higher than those achieved in the present study, which can be ascribed to a much faster heating rate being used in their pyrolysis experiments. The heating rate is not explicitly stated in their work; however, they used a Kugelrohr short-path distillation apparatus that effectively enables fast heating rates.

Kim et al. [11] analysed the product distribution from fast pyrolysis of CCA-treated wood and reported a liquid recovery of 43.3% using pyrolysis with a residence time of 2 s at a pyrolysis temperature of 500°C.

Comparison of the findings indicates that higher liquid yields are likely to be achieved with a higher heating rate and lower residence time. Although capable of achieving higher liquid rates, the effect of these on the arsenic recovery have been said to be of lesser importance. This will be explored further and discussed in Section 4.2.2.

From the above discussion, it can be seen that although there are some similarities between the experimental results of the present study and those reported in the literature, it is difficult to find a common denominator. The results from the pyrolysis of CCA-treated wood, when compared against those of untreated wood, (as shown in Table 4.1 and Figure 4.3) confirm the finding that generally lower liquid recoveries will result from the pyrolysis of CCA-treated wood than that from the pyrolysis of untreated wood. This can be attributed to the fixation of chromium to carbohydrates and lignin structures as laid out in the above discussion of solid yield [5], resulting in a liquid yield decrease and an increase in the solid char yield.

Figure 4.5 shows gas yield as a function of pyrolysis temperature as obtained experimentally. Similar to the char yield results, the gas yield from pyrolysis of the CCA-treated wood was higher than that of untreated wood (Figure 4.3). The elevated gas yield is attributed to the presence of inorganic CCA metal(oid)s which can act as a catalyst to support secondary reactions, reducing the oil yield and increasing gas production [3].

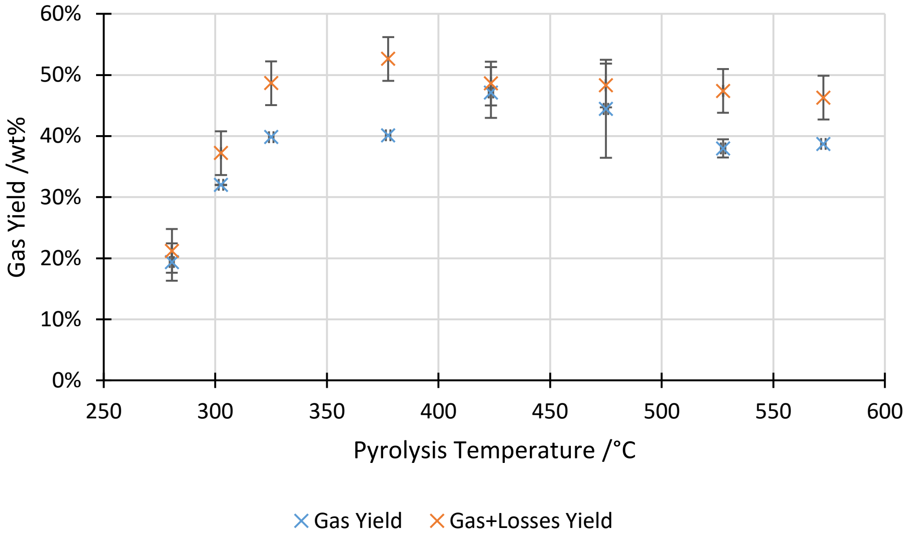

Figure 4.5: Averaged gas product yield and the combined value of the gas product and unaccounted losses from pyrolysis of H4-CCA treated Pinus radiata particles as a function of pyrolysis temperature.

By subtracting the carrier gas nitrogen from the gas composition, the primary component of the non-condensable gas product is CO_2. Low ethane, ethylene, methane, hydrogen, and CO concentrations are recorded in some gas product samples. The gas product composition is shown in Table 4.2 below, where, if applicable, the standard deviation σ is given.

Table 4.2: Composition of non-condensable gas product from pyrolysis of H4-CCA-treated Pinus radiata particles at increasing pyrolysis temperature. Not detected compounds were set to zero, and raw data is given in G.

Temp. /°C	CO_2 / wt%	C_2H_6 / wt%	C_2H_4 / wt%	CH_4 / wt%	H_2 / wt%	CO / wt%
280.5	100	0	0	0	0	0
280.5	99.8	0	0.212	0	0	0
302.5	99.9	0	0.094	0	0	0
325	100	0	0	0	0	0
377.5	100	0	0	0	0	0
423.5	99.87	0.019	0	0	0.116	0.844
423.5	99.39	0	0	0.609	0	0
475	99.25	0	0	0.329	0.423	1.34
475	96.69	0	0	0.992	0	2.32
527.5	68.51	0	0	0	0.421	0
527.5	98.29	0.673	0	1.04	0	0
572.5	98.27	0	0	1.73	0	0
572.5	100	0	0	0	0	0

Surprisingly, the primary component of the produced gas is CO_2, with over 97 wt% at every analysed temperature setting. From previously reported studies a more diverse gas composition was to be expected. Anca-Couce [12] shows that slow pyrolysis, higher ash content, and catalysts (such as CCA) that promote charring reactions all yield higher char, water and CO_2 content. These are all operating factors that apply to this study, and the results align with this statement. Furthermore, the previously introduced hypothesis by Fu et al. [4] (using slow pyrolysis), regarding the absence or limited supply of free hydroxyls, could also inhibit the formation of hydrocarbonaceous gas compounds. The further promotion of secondary cracking reactions by CCA compounds – as proposed by Akhtar and Amin [3] – justifies the observed lack of more complex gas components.

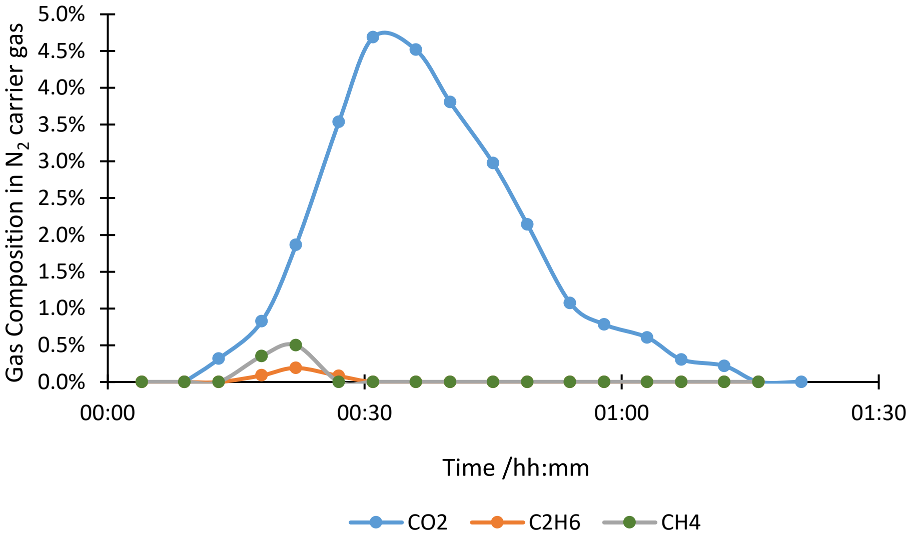

Figure 4.6: Change in gas composition during pyrolysis (480°C) of H4 CCA-treated timber.

Furthermore, the concentration time data during pyrolysis is shown in Figure 4.6. As per the discussion of secondary cracking reactions in the previous paragraph, Figure 4.6 shows the peak in concentration of C_2H_6 and CH_4 earlier than that of CO_2 indicating that these compounds break-down and from part of the CO_2 product.

In the present study, additional pyrolysis experiments were carried out to investigate the effect of particle size on product yield. These tests were conducted at a pyrolysis temperature of 477°C, using particle size ranges from 0 – 500 µm, 500 to 1000 µm, and above 1 mm. However, no significant change in product yields was observed. This was likely due to the already small particle size and only slight variation between the three ranges of particle size. The variations between yields from different particle sizes are within the previously determined standard deviation at 475°C. The experimental system used within this study did not allow for the heating rate or residence time to be varied;

however, particle size may affect the product disposition when higher heating rates and slower residence times are deployed.

Table 4.3: Pyrolysis product yields (wt%) from CCA-treated wood particles at 475°C using three different particle size ranges

Particle Size	*Char*	*Oil*	*Gas and Unaccounted Losses*
0 – 500 µm	27.4%	28.6%	44.0%
500 - 1000 µm	27.7%	27.7%	44.7%
1000 µm and larger	27.6%	28.0%	44.3%

With the central aim of this thesis on maximising the arsenic content in the liquid and the liquid yield itself, pyrolysis temperatures of between 450 and 600°C were of the greatest interest for further experimentation. This temperature range was therefore the focus of subsequent experimental testing of arsenic recoveries. For future research, the application of fast pyrolysis appears to be more promising in achieving higher liquid yields. This is discussed in more detail later in this chapter and in Chapter 6.

4.2 Pyrolysis Product Analysis

4.2.1 CCA Contents in the Pyrolysis Products

Through targeting the examination on the metal(oid) content in the pyrolysis products, a better understanding of the arsenic release mechanisms and pathways to volatilisation can be expected. It is intended that these findings can then be used to support and enable better definition of a proof-of-concept process scheme using pyrolysis for the waste management of CCA-treated timbers.

To determine the chromium, copper and arsenic contents in the oil and char products, the samples obtained from the pyrolysis experiments were analysed using the methods laid out in Chapter 3.

The ICP-MS results for the CCA concentrations in the biomass feedstock, as reported in Table 3.3, are used in this study. XFR analysis (undertaken by Verum Group, Middleton, Christchurch) was carried out on the ash of CCA-treated timber, allowing volatile CCA compounds to be released during the combustion process. As the wood analysed was freshly treated timber, some volatile arsenic and copper oxides would likely be released. The difference in CCA concentrations in the biomass feedstock between the ICP-MS and XRF results and the associated systematic errors are discussed in Section 4.3.

To further increase the consistency of analysis, sub-samples of wood particles were used to carry out seven pyrolysis experiments at temperature setpoints between 300 and 600, in 50°C increments. The ICP-MS results for these sub-samples are shown in Table 3.5 in Chapter 3. To determine the CCA contents in the char and oil products, the fundamental assumption is that all chromium, copper and arsenic were brought into solution during the acid digestion of the sample and that sample analysis is representative of the entire yield.

From the literature review presented in Chapter 2, it is evident that determining the complete mass balance for chromium, copper, and arsenic is difficult due to the different volatilisation behaviours of the individual constituents. All chromium is expected to be present in its fixated form, which is not expected to volatilise at the temperatures explored here. Thus, no chromium is expected to enter the gas or liquid products. This assumption has been verified and will be further discussed in this chapter. On the contrary, arsenic is expected to start volatilising at temperatures as low as 300°C [13-15], and some of the copper that remains in the wood as an unreacted copper oxide may also volatilise. Consequently, the initial focus of this work was on measuring chromium contents in the pyrolysis products and establishing a chromium mass balance. The total elemental chromium contents - shown in Figure 4.7 - were calculated using the evaluated chromium concentrations in the pyrolysis products and the product yields. The raw data of these results and sample calculations are displayed in Appendix G.

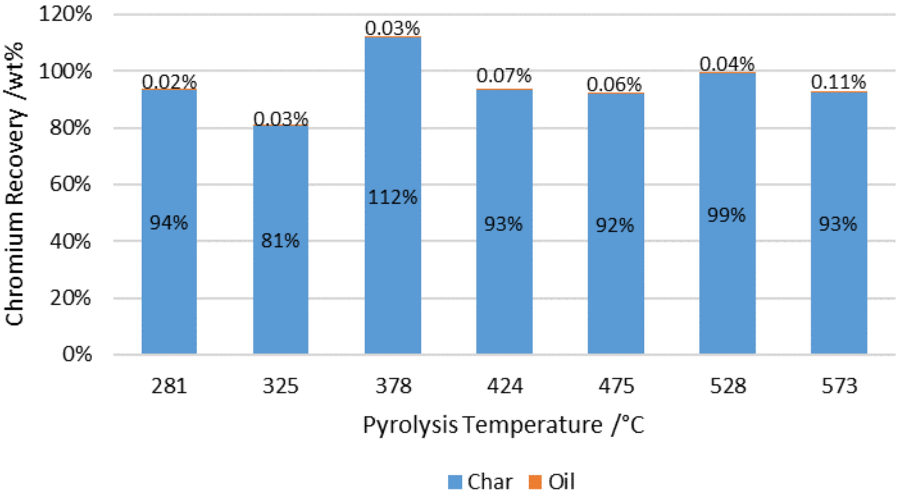

Figure 4.7: Elemental Chromium mass balance for the pyrolysis of H4-CCA-treated wood.

The chromium recovery is consistently above 80% over all experiments, ranging as high as 112% at a pyrolysis temperature of 378°C. The most likely source of the error for values below 100 wt% is that not all chromium dissolved into solution during the acid digestion of the sample. At the pyrolysis temperature of 378°C, a total recovery of chromium above 100% has been calculated. Error sources are discussed in further detail in Section 4.3.

The results of the metal(oid) concentrations in the solid char and the char yield as a function of pyrolysis temperature are shown in Figure 4.8.

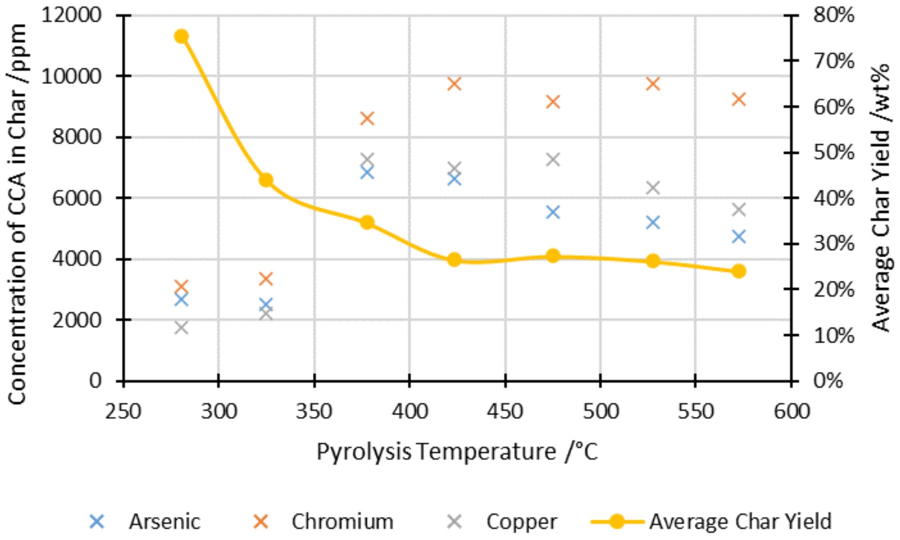

Figure 4.8: CCA concentrations in the char and the char yield from pyrolysis of CCA-treated wood at various temperatures.

As discussed previously, the solid char yield decreased with increasing pyrolysis temperature, as higher temperatures tend to drive more volatiles out of the solid. However, the CCA compounds for the most part remain in the solid and consequently, the concentrations of CCA compounds increased as less char was recovered, as shown in yellow in Figure 4.8.

The variability of the CCA compound distribution can be considered as being negligible due to the fact that the wood particles were thoroughly mixed for all pyrolysis experiments. Therefore, it can be assumed that the chromium concentration in the feedstock was consistent throughout the pyrolysis trials. In this way, chromium can be used as a baseline to analyse the change in the ratios of copper and arsenic to chromium in the feedstock at different pyrolysis conditions. This technique reduces the error caused by any undissolved metal(oid)s, assuming each compound is equally susceptible to any losses during dissolution of the sample. This is particularly effective for the temperatures of 325°C and 378°C, where the chromium mass balance has shown a discrepancy. The results of copper and arsenic retention in the solid char product represented by these ratios are shown in Figure 4.9.

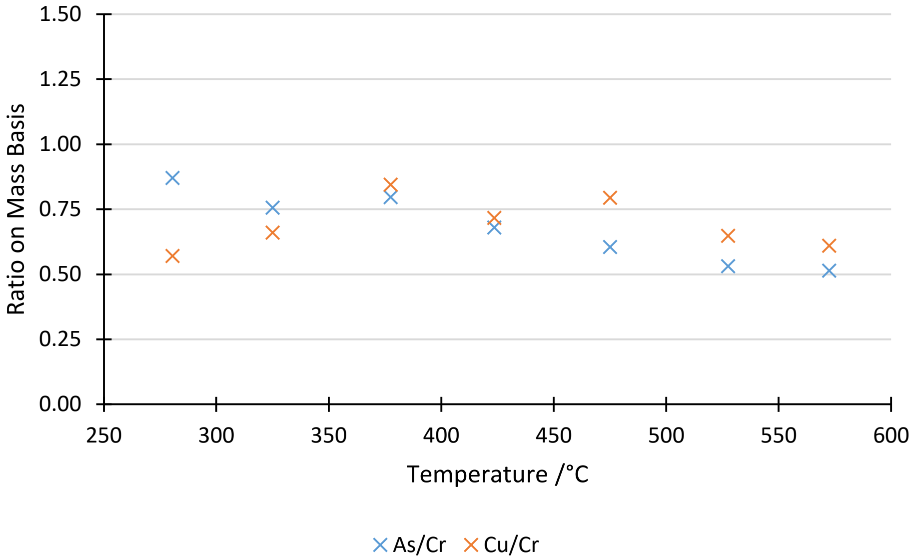

Figure 4.9: Arsenic and copper retention in the pyrolysis char of CCA-treated wood relative to chromium, the most stable compound of the three (elemental analysis).

From Figure 4.9, it can be concluded that the copper to chromium ratio increased with pyrolysis temperatures from 281 to 378°C but then generally decreased with further increments in the pyrolysis temperature. This variation may be caused by copper oxides (remaining in the wood from the treatment process) being released into the liquid or gas. The arsenic content relative to chromium is seen to be decreasing with increasing temperature over the entire temperature range from 281 to 573°C, an indication of arsenic being released as volatiles.

The metal(oid) concentrations in the measured in the bio-oil fraction as a function of pyrolysis temperature are shown in Figure 4.10 alongside the oil product yield on the secondary axis (right).

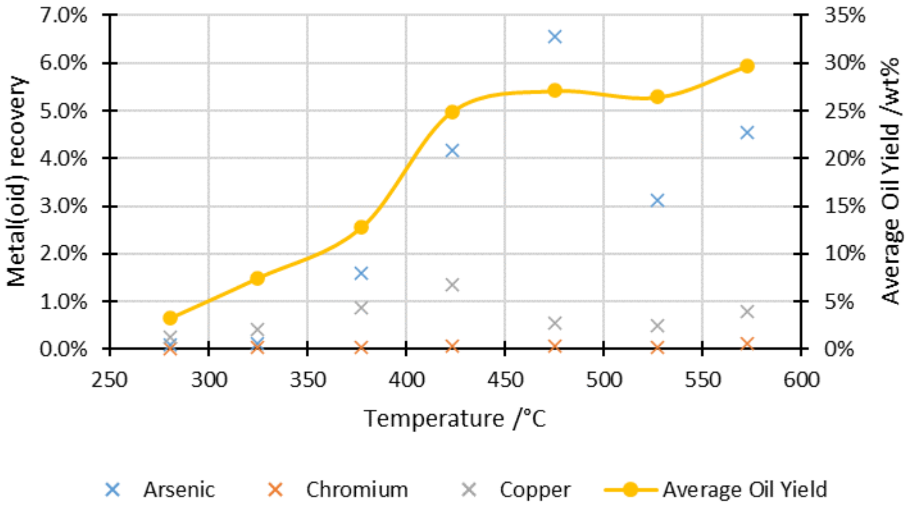

Figure 4.10: CCA recovery in the oil products from pyrolysis of H4-CCA-treated wood alongside the bio-oil yield (right axis). Standard deviations were omitted for clarity.

From Figure 4.10, it is observed that the chromium concentration in the oil was constant and consistently below 20 ppm over the full range of pyrolysis temperatures examined. This agrees with literature reports stating that chromium is mainly retained in the char, and its content in the liquid is negligible. As discussed previously, its stability in the char supports its use as a baseline for copper and arsenic ratios. Copper has been found to primarily remain within the char product, with only small quantities of copper present in the oil (see Figure 4.10). Copper's presence in the bio-oil can be attributed to copper preservative – either copper oxide or copper sulphate – in the feedstock. Copper sulphate has a melting point of 200°C and a boiling point of 650°C, at which it decomposes to cupric oxide in its pure form [16]. Although copper oxide has a melting point of 1,325°C, TGA data does show that copper oxide can begin to break down in a reducing environment – such as pyrolysis creates. Both can result in the presence of copper in the produced bio-oil [8].

Figure 4.9 and Figure 4.10 show that the arsenic concentration in the char decreased with increasing pyrolysis temperature while its content in the liquid increased from 80 ppm at 281°C up to 600 ppm at a pyrolysis temperature of 475°C. However, the arsenic concentration in the liquid decreased with further increases in the pyrolysis temperature to 297 ppm at 528°C, followed by a slight increase (by 43 ppm) at 573°C. The reduction of arsenic concentration in the bio-oil at temperatures above 475°C corresponds with the boiling point of arsenic pentoxide (at atmospheric pressure, 465°C) [14]. At temperatures above the boiling point, the concentration of arsenic in oil begins to decrease, likely due to its volatilisation. Overall, the above results confirm that arsenic is more volatile than copper and chromium during the pyrolysis of the CCA-treated wood.

To determine the optimum operating condition that enables the highest net recovery of arsenic in the pyrolysis liquid, the recovery of arsenic has been calculated based on 100 g of CCA-wood feedstock. The absolute value of arsenic is calculated using liquid yields and arsenic concentrations. Figure 4.11 shows the highest recovery of arsenic within the liquid at a pyrolysis temperature of 475°C. To confirm the measured arsenic content, the acid digestion and ICP-MS analysis were carried out two-fold for each of the liquid samples from pyrolysis at 377, 475 and 572°C. In addition, ICP-MS analysis was carried out in duplicate for the acid-digested sample at 572°C. The standard deviations of the measurements were 0.19, 1.3 and 0.72 at 377, 475 and 572°C, respectively.

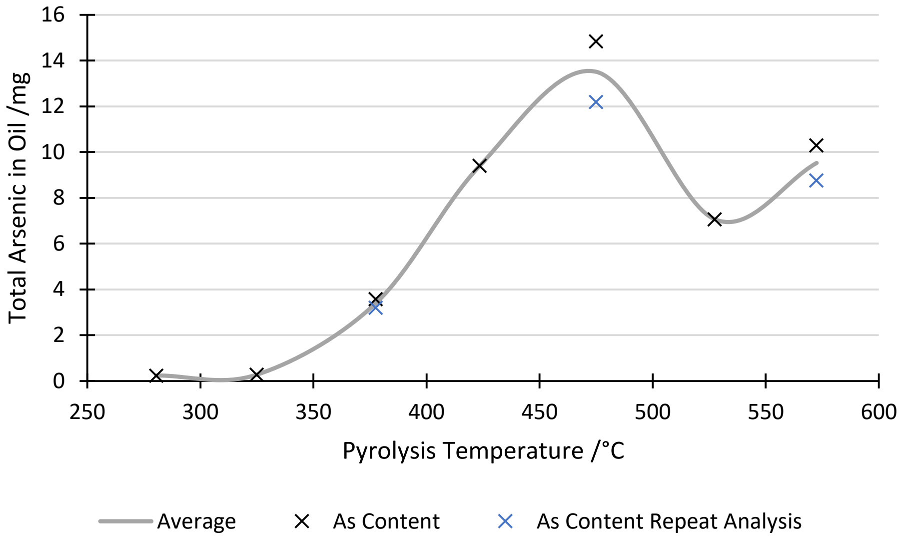

Figure 4.11: Total arsenic recoveries in bio-oil product from pyrolysis of H4-CCA-treated wood particles, on the basis of 100 g of wood feedstock.

The results of pyrolysis yields and arsenic concentrations show that in this work 27 wt% of the feedstock was recovered as a liquid, containing 6 wt% of the feedstock's original arsenic content. This low arsenic recovery suggests that conventional pyrolysis is likely unsuitable for the desired application; but fast pyrolysis is expected to be more favourable in accordance with the previously reported literature data by Kim et al. [11]. Unfortunately, other available literature focuses on the char recovery and does not report liquid yields.

The experimental results as presented above are the average values from at least two trials, and the trends of these results are consistent with those reported in literature. Therefore, the effect of any data anomaly is deemed insignificant, as illustrated by error bars in the figures and standard deviation in the data tables. These can be found in detail in Appendix G.

In order to gain an in-depth understanding of arsenic decomposition and recovery, further investigation into the arsenic species in the pyrolysis products is needed, and details of this will be presented in the next section.

For completion, the arsenic distribution in each pyrolysis product is given in Table 4.4. Arsenic, not accounted for in the char and oil, is attributed to the gas and unaccounted losses.

Table 4.4: Pyrolysis product yields and arsenic distribution

Pyrolysis Temperature /°C	*Char (wt%)*		*Oil (wt%)*		*Gas + Losses (wt%)*	
	Yield	As recovery	Yield	As recovery	Yield	As recovery*
280	73.0	96.9	3.3	0.10	20.6	2.9
325	43.8	72.7	7.4	0.12	42.0	27.2
377	34.3	106.1	11.4	1.6	45.7	-7.7
423	25.7	75.4	25.3	4.2	43.0	20.4
475	28.2	66.2	28.9	6.6	40.0	27.2
527	25.6	62.8	27.7	3.1	43.0	34.1
572	23.8	56.7	29.0	4.6	43.0	38.7

4.2.2 Arsenic Oxidation States in Treated Wood Feedstock and Pyrolysis Products

Previous studies have shown that the release of arsenic happens as per the Reactions (*R2.2*) to (*R2.6*) described in the literature review (Chapter 2). The oxidation state, in which arsenic is present in the bio-oil and the char, offers insight into reaction mechanisms and the potential applications for the pyrolysis products. The arsenic oxidation state in the bio-oil fraction with the highest arsenic recovery (475°C) is of particular interest.

The arsenic species within freshly treated H4-CCA timber particles and weathered CCA timber particles were analysed using UV-Vis, and the results are given in Table 4.5. Whilst not essential to this discussion, the phosphate levels are recorded for completion.

The weathered wood sample was obtained from a landfill waste stream, and therefore treatment class, service age and service conditions are unknown. These factors are all known to influence the chemical composition of the wood. However, the sample's appearance suggests it may have been a fence post (possibly from a vineyard) which are typically H4 class [17].

For the pyrolysis product analysis, the focus is on the oil with the highest arsenic content. Hence, the char and oil products from the pyrolysis of freshly treated H4-CCA timber at 475°C were analysed, and the results are presented in Table 4.5.

Table 4.5: Arsenic species present in freshly treated and weather H4-CCA-treated timber, as well as the char and oil products from pyrolysis of freshly treated H4-CCA-treated timber at 475°C. The results are obtained by UV-Vis analysis and normalised with respect to their sample weight.

Samples or products	*Concentration /ppm*		
	As(V)	As(III)	P
Freshly treated Wood	2,250	65.0	131
Weathered Wood	1,830	6.36	110
Pyrolysis Oil	28.5	595	78.0
Pyrolysis Char	8,730	17.4	398

By comparing the results in Table 4.5 with those presented in Table 4.4, it can be concluded that overall, the UV-Vis method gives a lower measured arsenic content in the wood samples than those determined by the ICP-MS method. This is likely due to weaker acids used to digest the samples and to dissolve the arsenic compounds into solution. This is confirmed by Van den Broeck et al. [18], who compared CCA-extraction methods from wood and pyrolysis residue samples. Using sulphuric acid and hydrogen peroxide to digest the sample and dissolve the CCA compounds into solution does not work as effectively as using nitric acid. The latter was used in the ICP-MS method. However, the presence of nitric acid leads to colour instability and inhibits complex formation in the oxidised sample, whilst enhancing it in the reduced sample [19]. Therefore, nitric acid could not be deployed for arsenic speciation, and sulphuric acid and hydrogen peroxide were used instead.

From Table 4.5, it can be concluded that the concentrations of As(V) and As(III) for the freshly treated wood samples were higher than those for the weathered wood samples, indicating leaching of the arsenic compounds from the treated wood over time in service. As(III) has a higher water-solubility than As(V) and, when present in wood, will not fixated in this form. Therefore, the As(III) concentration in the weathered wood is very low (6.3 ppm), less than 10% of that contained within the freshly treated wood (66 ppm), this being likely caused by arsenic leaching out of the wood structures over time. Furthermore, the weathered wood shows a lower As(V) concentration than freshly treated timber, which can also be attributed to the leaching behaviour of arsenic from wood, detailed in Section 2.1.3 of the literature review. Further, necessary steps to convert As (III) to As(V) are highlighted in Section 2.4.2 of the literature review.

Whilst these results are unsurprising, they are a useful reminder as to the purpose and rationale for this thesis. Landfilling of CCA-treated wastes presents a long-term environmental hazard that, unless properly managed, carries a potentially significant risk for environmental harm.

The concentration of arsenic in the char is higher than in wood due to the mass reduction during pyrolysis. Although some arsenic was transferred into the oil and gas products, the majority remained in the solid product. As the mass of char and ash is much less than the original wood sample (28.2 wt%), the arsenic concentration measured here was higher than that of the original wood sample. Nevertheless, the recovery of arsenic in the char is higher than the ICP-MS results reported in Figure 4.8. This may be attributed to the different methods deployed, or the location of the sample during pyrolysis – which was not noted or analysed during these studies.

The ratio of As(III) to As(V) concentrations - as shown in Table 4.5 - is lower in the char (0.002) than in the feedstock wood (0.029). This indicated that As(III) has left the solid product during pyrolysis and has probably volatilised. Any existing As(III) present in feedstock should have volatilised at temperatures as low as 200°C, with complete volatilisation having occurred by 350°C [8]. Therefore, it can be assumed that any As(III) present in the char does not originate from the feedstock As(III) but rather from the reduction reaction of As(V) to As(III) that takes place during pyrolysis as per reaction *(R2.2)*.

The assumption that As(V) reduces to As(III) during pyrolysis is further supported by the higher net value of Arsenic (III) present in the oil after pyrolysis in comparison to the original amount in the feedstock. Further, less than 30 ppm of As(V) was recorded from the bio-oil product. Such a low concentration of arsenic can be attributed to char particles in the oil.

By considering the findings both from the present study and from the literature data, the following conclusions can be drawn:

- The optimum pyrolysis temperature of 475°C found from the present study is close to the boiling point of arsenic pentoxide at atmospheric pressure. This agrees with the proposal made by Kakitani et al. [14]. The release of arsenic into volatiles increases with further rise in the pyrolysis temperature.
- TGA data of pure As_2O_5 shows its release at temperatures above 500°C, and that of As_2O_3 at around 300°C [8, 9]. As(III) quantities larger than that originally in the feedstock were recovered in the oil, indicating that the reduction reaction – as follows – takes place at temperatures below 400°C in a reducing environment.

$$2\,As_2O_5(s) \rightleftharpoons 2\,As_2O_3(l) + 2\,O_2(g) \tag{R2.2}$$

- Therefore, temperature and the reducing reaction environment are the key parameters determining the onset of arsenic release. However, it is acknowledged, that compared to literature results using fast pyrolysis [11], a low yield of arsenic content in the bio-oil is achieved in this study. It can also be concluded that heating rate and residence time are key parameters determining the extent of arsenic release.
- It is hypothesised that fast heating rate, short residence time and fast quenching of the vapour stream hinder the volatilisation reaction *(R2.3)* – as follows - of As_2O_3 and thereby allowing for its recovery in the liquid product.

$$2\,As_2O_3(l) \rightleftharpoons As_4O_6(g) \tag{R2.3}$$

Kim et al. [11] achieved an arsenic recovery in the liquid six times higher (34.5 wt% of the original feedstock weight) than that achieved in the this study. Using fast pyrolysis with a residence time of 2s allows only a limited time for the volatilisation reaction (*R2.3*) to take place. In the study by Kim et al. [11], the vapour stream was quenched rapidly at 0°C in ethanol which would halt any further heat supply to the reaction, aiding the high arsenic recovery.

4.2.3 Other Properties of the Bio-oil Product

At lower pyrolysis temperatures, the oil yield was very low (less than 2 g), of which not all could be recovered due to the viscous nature of the pyrolysis oil product. The focus was directed toward analysing the properties of the oil produced at the pyrolysis conditions that maximise arsenic recovery in liquid (475°C). The oil was characterised with regards to its water content, density, viscosity and composition. The methods for these analyses are set out in Section 3.3.2 in Chapter 3, and the results are discussed here in the following sections.

Water Content

The water content of the bio-oil product from pyrolysis of the CCA-treated wood was determined to be 27.3%. This is lower than that reported by Xin et al. [20] for pyrolysis of the raw *Pinus radiata* wood at 450°C (36.7 wt%). This will be due in part to the moisture content of the wood particles in the present study being just 0.5%, whereas Xin et al. [20] used wood samples with a moisture content of 10%, nonetheless the water contents in the bio-oil products in both studies are similar. Albeit, in a review by Oasmaa and Czernik [21]on bio-oil properties from pyrolysis of various woody biomass species, the water content of pyrolysis oil was reported to be in the range of 15 to 30% [21]. Interestingly, although overall, a lower liquid yield was achieved from the pyrolysis of CCA-treated wood, the water content is comparable to that of untreated wood. The water content in oil is derived from reactions among volatiles involving oxygen and hydrogen and further increases with the initial moisture content of the feedstock. As the wood samples used in this study were oven-dried containing no excess moisture, the water content of the produced bio-oil in this study can be attributed to these reactions.

Research shows that when charring is promoted – i.e., through slow pyrolysis, the elevated ash content in the feedstock or the presence of a catalyst (such as CCA) – the production of char, water and CO_2 yield is enhanced [12].

Density and Viscosity

The density of the oil product from pyrolysis of the CCA-treated wood was measured to be 1.4 g·mL^{-1} or 1,400 kg·m^{-3}. This is slightly higher than that of pyrolysis oil derived from other biomass sources, which is reported to be approximately 1,240 kg·m^{-3} [21, 22].

Bio-oil viscosity is affected by its composition [22], and it is likely that the presence of the CCA compounds had an influence on the measured viscosity. The oil's viscosity is shown in Figure 4.12 below.

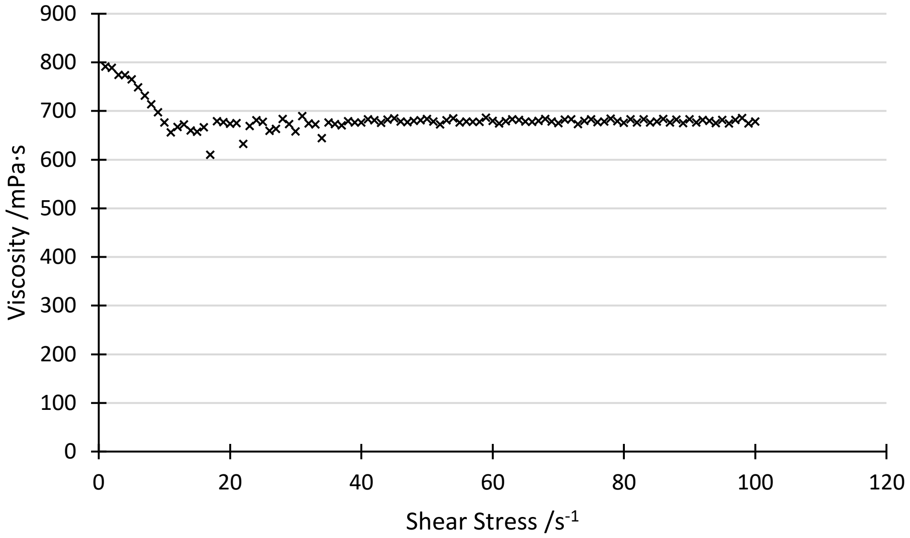

Figure 4.12: Viscosity of the oil sample from pyrolysis of H4-CCA-treated wood at 475°C, measured against shear stress using an Anton Paar rheometer.

From Figure 4.12, it is observed that the viscosity of the oil produced from the present study was stable at about 680 mPa·s (680 cP) at shear stress above 20 s^{-1}. This is significantly higher than values reported in literature, which range from 1 to 100 mPa·s [23, 24]. Elevated viscosity values were expected due to the CCA compounds in the bio-oil. However, such high viscosity values as reported here may be attributed to the aging of the oil. Viscosity analysis was carried out four months after pyrolysis due to the Covid-19 lockdown in 2020. In this case, the aging effect of the oil sample and moisture loss could be significant. The oil sample was mixed using a test tube shaker for viscosity measurement. The aging effect and moisture loss are also believed to contribute to the higher density of the oil product.

In addition, the CCA compounds in the bio-oil also contributed to the high oil density. The fixation of chromium to free hydroxyls within the lignin and carbohydrates structures may promote the content of water-insoluble compounds and thereby explain the increase of density and viscosity in the oil.

Compound Analysis of the Liquid Product

Multiple analysing techniques such as GC-MS and NMR are available to determine oil composition. However, past studies have found significant inconsistencies in bio-oil composition determined using GC-MS from different laboratories [25]. GC-MS is reported to be only able to determine 25 – 40% of the oil compounds which need to be volatile. The remaining species, which are non-volatile compounds, thus cannot be detected. Additionally, there are difficulties with overlapping signals [26]. Consequently, NMR was chosen as the method employed in this study.

Proton NMR (H-NMR) was used for the analysis as per the methods laid out in Chapter 3. Whilst the major peaks could be identified, some compounds with similar functional groups were grouped, and thus there are some errors in discrimination. The results are shown in Table 4.6.

Table 4.6: Chemical shift (resonant frequency of a nucleus relative to hydrogen) range for H-NMR of oil [26-28]

Shift	*Functional groups present*
0.5 – 1.6	Alkane
1.6 – 2.2	Organic Acids, alkane, carbnyl
2.2 – 3.0	Ketone, methyl groups attached to benzene ring
3.0 – 4.2	Alcohols, methoxy, ether
4.2 – 6.0	Ethers (lignin derived methoxyphenols), carbohydrates, phenols
6.0 – 8.5	Aromatics, phenols, olefins
9.5 – 10.1	Aldehydes

Individual compounds commonly present in pyrolysis oil have been extensively reported in previous studies [29-32] and summarised in the PhD thesis of Wigley [28]. According to the reported H-NMR shift data, individual peaks in the H-NMR spectrum can be matched to specific compounds, as shown in Figure 4.13.

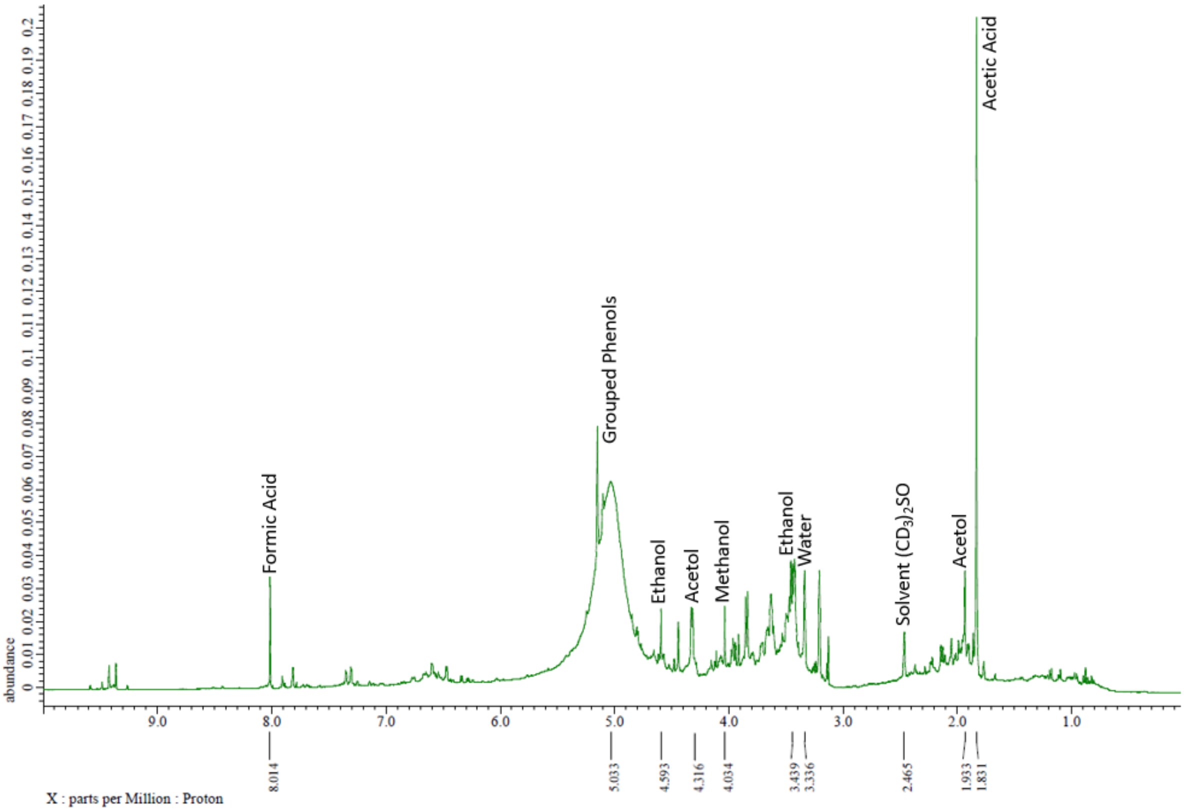

Figure 4.13: H-NMR spectrum of oil sample from pyrolysis of H4-CCA-treated wood particles.

More details of the spectrum obtained in the present study can be found in Appendix G.

From Figure 4.13, acetic acid (1.83 ppm), acetol (1.99 and 4.02 ppm), water (3.34 ppm), ethanol (1.00 ppm and 3.44 ppm), methanol (4.03 ppm) and formic acid (8.01 ppm) can be identified. Peaks for aromatic phenols, carbohydrates and ethers from lignin-derived methoxyphenols overlapped and were thus grouped to cover the shift between 4.2 and 6 ppm. Some compounds could not be detected as they are either present in too small a quantity or their peak could not be reliably identified above the baseline noise.

The compounds present in the oil give insight into the decomposition reactions, as discussed in detail in the subsequent section 4.3.1. Furthermore, the oil composition may aid future work in understanding the liquid’s performance as a preservative or preservative additive.

4.3 Implications of the Experimental Findings

To summarise the experimental results, a maximum bio-oil yield of 28 wt% was obtained from pyrolysis of the CCA-treated wood at a temperature of 480°C using slow pyrolysis. The oil product obtained at this condition contains 605 ppm of arsenic compounds, which is only 6.6 wt% of the original arsenic content in the wood feedstock. The arsenic is present primarily in the form of arsenite – As(III). The bio-oil has a water content of 27%, a density of 1.4 $g{\cdot}mL^{-1}$ and a viscosity of 680 mPa·s. The presence of water, acetic acid, formic acid, acetol, ethanol and methanol have been determined using H-NMR analysis.

To put the experimental work into perspective, it is valuable to analyse the sources of errors within the experimental work. These include the discrepancies in the mass balances, the inaccuracies in the pyrolysis temperature control and the analysis methods.

The mass balance shows minor discrepancies, attributed mainly to losses during the pyrolysis product collection, in the form of tar deposits on the inner walls of the reactor and piping, as well as minor gas leaks.

As discussed in the beginning of this section and in Chapter 3, differences between the temperature setpoints and the actual temperatures in the pyrolysis reactor were observed, hence the temperature recordings within the reactor were used for analysis. The wood sample used for each experimental run weighed approximately 25 g. As the mass of each wood sample was small, the samples were expected to reach a uniform temperature well within their residence time. This assumption was further supported by the slow heating rate, allowing the heat to transfer uniformly through the wood sample. Although the sample bed did not sit within one heating zone, as shown in Figure 3.6, the space temperature profile of the reactor zone in which the sample bed is situated was relatively uniform. Furthermore, the close proximity of the temperature probe to the sample bed, also shown in Figure 3.6, allows for the actual pyrolysis temperature to be recorded.

To determine the arsenic content in the wood feedstock, the results of the ICP-MS analysis were used rather than those of the XRF analysis, shown in Figure 3.5. The XRF analysis method provides data in regard to the CCA content present in the ash and thereby the CCA concentration in the original wood sample can be determined. However, in the process of ash production, some volatile arsenic and copper compounds within the freshly treated timber are gasified and therefore not accounted for in the XRF results. The ICP-MS method used acid digestion to bring non-volatile and volatile CCA compounds into solution, ensuring volatile compounds were recovered using a reflux condenser – as described in Section 3.3.2. However, the samples were diluted twice to sit within the ICP-MS detection range, which may have caused minor uncertainties. To ensure consistency of the results, ICP-MS was preferred, as it was the method used to determine CCA content in char and bio-oil. Using the same method for the wood feedstock and the pyrolysis products ensured that any error in the analysis would be systematic rather than random. Any inaccuracy caused by using this method was reduced as much as possible through the previously mentioned steps of using acid digestion with a reflux condenser.

4.3.1 The Effect of Operating Conditions

This study has experimentally investigated the effects of pyrolysis temperature and particle size. The experimental results show that the effect of particle size is negligible, likely due to the already significantly reduced particle sizes within the range examined. Temperature however does have a significant effect on the arsenic recovery as shown by the product yields and the arsenic concentrations in the products. This is consistent with the findings from previous studies as discussed in the literature review in Chapter 2. It has been observed that the arsenic recovery from the present study was much less than that achieved in previous studies by Kim et al. [11], and as a result, it is suggested that fast pyrolysis with a high heating rate and short residence time needs to be considered for process optimisation. Fu et al. [5] show that the presence of CCA compounds, particularly chromium, hinders the breakdown of the wood feedstock into smaller molecules which consequently vaporise. The experimental results in the present study are consistent with that finding, where the solid yield is consistently higher from pyrolysis of CCA-treated timber than that from pyrolysis of non-treated timber, as seen in Figure 4.3.

Previous studies [14, 15, 33, 34] have examined the effect of temperature, heating rate, residence time and particle size on arsenic release during pyrolysis and its recovery in the char product. Temperature was determined to be the key parameter affecting the arsenic release; however, comparing this study’s findings with those reported in literature found that the heating rate and the residence time had a significant effect on the extent of arsenic release. From the findings of this study combined with knowledge from literature, it can be deduced that whilst temperature determines the onset of the release, the extent of release is determined by residence time and heating rate. This is important for future industrial application. Fast heating rates and shorter residence time promote pyrolysis reactions to occur faster than the conversion of As(V) to As(III), allowing for arsenic recovery in the liquid. Unfortunately, neither of these parameters could be varied with the experimental set-up (fixed bed batch reactor) as used in the present study.

Given the conclusion that residence times and heating rates are significant influencing factors, it is suggested that a continuous pyrolysis reactor be used in future studies in this area. Chapter six examines the proof-of-concept of a commercial plant. Fast pyrolysis is adopted for this purpose, as the fast heating rates and short residence time allow for a higher arsenic recovery in the pyrolysis oil. No conclusions can be drawn regarding the reaction environment with different carrier gases.

Of particular interest is the presence of CCA compounds and how theses affect the decomposition of wood constituents. Reflecting back on the literature review (Section 2.1.2), it is known that $CrAsO_4$ and $CrCuO_4$ are bound to lignin structures, alongside some Cu(II) and Cr(VI) compounds. Cr(III), Cr(V) and its hydroxides or oxides precipitate onto cellulose, whilst Cu(II) can also be bound to cellulose [35]. When the wood decomposes during the pyrolysis process, the cellulose, hemicellulose and lignin break down into lighter compounds, some of which were detected in liquid and gas products. In the following discussion, the possible effect of CCA on each wood constituent is discussed separately.

The oil product derived through the pyrolysis of lignin is referred to as pyroligneous acid [36]. Typical products from lignin pyrolysis are guaiacols, syringols, and other substituted phenols and smaller quantities of aromatic hydrocarbons, methanol, organic acids, and aromatic acids. Some of these compounds were detected in the liquid; however, other compounds such as guaiacols and syringols were unable to be measured using the deployed NMR technique. It could be concluded that the breakdown of lignin may be inhibited. Fahmi et al. [37] found that feedstock's with lower lignin content produce a lower liquid yield. The results from the present study show a significantly lower yield in the pyrolysis of CCA-treated timber compared to that of untreated timber. This result could support the premise that the lignin breakdown is hindered.

Cellulose breaks down into acetic acid, water, sugar derivatives, such as levoglucosan, and possibly furans and phenols [28]. Cracking reactions of cellulose generate intermediate products, which may also produce light oxygenates such as organic acids, hydroxyacetaldehyde, and 1-hydroxy-2-propanone [38, 39]. The NMR analysis shows the presence of acetic acid, water and phenols in the liquid product. Additionally, Yang et al. [40] examined the effect of cellulose impregnated metal salts and found that the presence of the metal salts reduced the cellulose degradation temperature and enhanced dehydration reactions. This is consistent with the previously discussed catalytic effect of CCA reducing the onset temperature of mass reduction. These results need further consideration before any conclusion can be drawn about the effect that CCA preservatives might have on product yields and distribution, but the presence of preservatives may well hinder the further breakdown of cellulose into its decomposition products.

Hemicellulose main products during pyrolysis are acetic acid and other organic acids, sugars and furans [28]. Xylan, often used as a substitute for hemicellulose in research, breaks down into CO, CO_2, formic acid, acetic acid, hydroxyacetaldehyde, and 1 -hydroxy-2-propanone [41]. The GC and NMR analysis results show that acetic acid, CO and CO_2 and other compounds are present in the pyrolysis products, indicating that it is likely that the presence of CCA compounds does not strongly influence the breakdown of hemicellulose during pyrolysis.

4.4 Conclusions and Implications for Industrial Uptake

The experimental results from the present study show that a conventional fixed bed batch pyrolysis reactor cannot achieve the desired goal of a high oil yield and high arsenic recovery. The presence of the CCA compounds, particularly copper, appears to inhibit liquid production during pyrolysis and increase char yield. Additionally, the long reaction time and slow heating rate in the experimental set-up were limiting factors, which allowed some of the arsenic in the wood to volatilise rather than remain in the oil fraction.

New Zealand's only commercial timber pyrolysis unit operates using a conventional batch-wise pyrolysis process. The findings from the present study imply that this plant is not ideal for the processing of CCA-treated timber wastes for arsenic recovery. Conventional batch pyrolysis does not allow for arsenic recovery to a degree that enables this process to be industrially viable. Less arsenic is recovered in the liquid through this form of pyrolysis process and more arsenic is driven off with the gas or remains in the solid char. The arsenic contained in the liquid is in its trivalent form, which is known to show favourable antifungal effects; consequently, it is potentially suitable for wood preservation. However, trivalent arsenic has higher water solubility and carries a higher risk of causing harm if it is exposed to the environment. Retentiveness and stability of the arsenic in the oil are yet to be determined.

More needs to be known about arsenic transformation during pyrolysis and the thermodynamic equilibrium for the decomposition of $CrAsO_4$ and As_2O_5 under typical pyrolysis conditions. Therefore, the following chapter presents the modelling of wood decomposition during pyrolysis and the arsenic release mechanisms. These will be discussed in the next chapter of this thesis.

The literature review indicates that high recovery of arsenic is achievable from fast pyrolysis processes such as those reported by Kim et al. [11]. They achieved 43 wt% bio-oil yield at a pyrolysis temperature of 500°C, which contained 34.5 wt% of the original arsenic content. This will be addressed further in Chapter 6, which focuses on an industrial solution to the CCA waste management problem.

4.5 References

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5 Modelling of Arsenic Release during Pyrolysis of CCA-Treated Timber

This chapter is divided into two sections, describing both a pyrolysis model for woody biomass and an equilibrium model for the decomposition of arsenic compounds typically present in CCA-treated wood.

Firstly, the pyrolysis model has been developed based on prior literature [1-10], describing the reaction mechanisms for the conversion of woody biomass under pyrolysis conditions. The aim of the model is to enable the prediction of pyrolysis kinetics and the distribution of the pyrolysis products; specifically, solid char, bio-oil and non-condensable gas. In addition, the pyrolysis model can be used to examine the effects of operating conditions on the pyrolysis process itself. A comparison of model predictions and experimental results assist in validating the experimental work undertaken and the influence of the operation conditions in the experiments.

Secondly, a Gibbs free energy minimisation model is developed to establish the thermodynamic equilibrium expected for the decomposition of $CrAsO_4$ and As_2O_5 under typical pyrolysis conditions. The model allows the product composition at a set temperature to be determined independently from the previously introduced reaction pathways (*R2.2 – 2.6*). The thermodynamic equilibrium model provides insight into the nature of the arsenic species released into the liquid and gaseous state and their oxidation states.

5.1 Pyrolysis Model: Wood Decomposition into Char, Oil and Gas

The thermal decomposition of biomass during pyrolysis into products via primary and secondary reactions are modelled following the reaction scheme based on work by Shafizadeh and Chin [1]. In the past the complex decomposition process has been modelled using different approaches. In these model applications, researchers have considered the decomposition of wood as a whole [1, 2]; the breakdown of its various constituents of hemicellulose [3], cellulose [4] and lignin [5] as well as the effects of particle size [6, 7], or type of reactor (packed or fluidised beds) [8]. Modelling approaches have been reviewed in detail by Vikram et al. [9].

As the focus of this work is on the pyrolysis of CCA-treated wood, a simple heat and mass transfer model of wood degradation is adapted, based on the works of Fantozzi et al. [7], Ratte et al. [10] and Di Blasi [11]. Firstly, the thermal process is described by three parallel, competitive reactions producing gas, tars and char *(R5.1 to R5.3)*. This is followed by the consecutive reactions describing the secondary cracking of tar into gas and char, based on the kinetic modelling approach adopted by Shafizadeh and Chin [1]:

$$Wood \xrightarrow{k_1} Gas \tag{R5.1}$$

$$Wood \xrightarrow{k_2} Tar \tag{R5.2}$$

$$Wood \xrightarrow{k_3} Char \tag{R5.3}$$

$$Tar \xrightarrow{k_4} Gas \tag{R5.4}$$

$$Tar \xrightarrow{k_5} Char \tag{R5.5}$$

Where k_i represents the reaction rate coefficient for reaction *i* and is assumed to follow Arrhenius expression in the following form

$$k_i = A_i e^{-\frac{E_{Ai}}{RT}} \tag{5.1}$$

In Equation (5.1), A_i is the pre-exponential Arrhenius factor (s^{-1}), E_{Ai}, is the activation energy ($kJ\cdot mol^{-1}$), R is the universal gas constant, and T is the temperature (K) ,at which the reaction takes place. Values of activation energies and the pre-exponential factors for k_1 to k_5 are provided in literature as given in Table 5.1.

Table 5.1: Kinetic parameters and heat of reactions for primary and secondary reactions of wood decomposition during pyrolysis

Reactions	*Pre-exponential Arrhenius Factor, A_i, s^{-1}*	*Activation Energy, E_{Ai}, $kJ\cdot mol^{-1}$*	*Heat of reaction, $kJ\cdot kg^{-1}$*	*References*
R5.1	1.435×10^4	88.6	420	[12]
R5.2	4.125×10^6	112.7	420	[12]
R5.3	7.377×10^5	106.5	420	[12]
R5.4	4.28×10^6	107.5	-40	[2]
R5.5	1.0×10^6	107.5	-40	[11]

Using the above model pathways and the kinetic rate coefficients given in Table 5.1, the feedstock consumption and product generation can be predicted. Furthermore, for a given reactor, the mass flows into and out of the reactor can be included in the model. As the experimental system design in this study is batch-wise, the solid was modelled to remain in the reactor for a set residence time of 1 hour. A residence time for gas and vapour (tar) stream was calculated using the gas flow values from the experimental design and operation. The calculated vapour evolution rate of the experimental work (of Chapter 4) is 0.13 L min^{-1}, which is low in comparison to the nitrogen sweep gas flowrate of 3 L min^{-1}. For the purpose of this model, the gas and vapour products are assumed to leave the system at the same flowrate as the sweep gas, and hence, the superficial gas velocity v through the sample bed can be determined. This, in turn, allows for the residence time τ to be estimated:

$$\tau = \frac{Bed\ height}{v} \tag{5.2}$$

The first order reactions (*R5.1*) to (*R5.5*) follow the differential rate law and are combined with Equation (5.2) to give the following set of mass conservation equations:

$$\frac{dm_W}{dt} = -(k_1 + k_2 + k_3)m_W \tag{5.3}$$

$$\frac{dm_C}{dt} = k_3 m_W + k_5 \tau \frac{dm_T}{dt} \tag{5.4}$$

$$\frac{dm_G}{dt} = k_1 m_W + k_4 \tau \frac{dm_T}{dt} - \frac{m_G}{\tau} \tag{5.5}$$

$$\frac{dm_T}{dt} = \frac{k_2 m_W - \frac{m_T}{\tau}}{1 + \tau(k_4 + k_5)} \tag{5.6}$$

where m is the mass of the corresponding compound at given time t, and k_1 to k_4 represent the rate coefficients for the corresponding reactions. Subscripts W, C, G and T denote wood, char, gas and tar, respectively. The gas and tar flowrates from the system are calculated as follows:

$$\frac{dm_{G\ out}}{dt} = \frac{m_G}{\tau} \tag{5.7}$$

$$\frac{dm_{T\ out}}{dt} = \frac{m_T}{\tau} \tag{5.8}$$

A simple approach was taken to modelling the energy transfer, following the studies of Fantozzi et al. [7] and described in the subsequent pages. The energy balance, as described in Equation (5.9), includes the energy supplied by the furnace, the energy used for the production of pyrolysis products, and the energy absorbed by the reaction and reaction compounds. The terms for water vapour have been excluded, as the wood is assumed to be oven-dried.

$$E_S = E_G + E_T + E_C + Q_G + Q_T + Q_B \tag{5.9}$$

where

E_S = External energy supplied from the electric furnace, assumed 100% efficient, J
E_G= Energy used for gas production, J
E_T = Energy used for tar production, J
E_C= Energy used for char production, J
Q_G = Energy absorbed to heat up the produced gas, J
Q_T = Energy absorbed to heat up the produced tar, J
Q_C = Energy absorbed to heat up the produced char, J
Q_B = Energy absorbed to heat up the residual dry biomass, J.

The energies required for the production of gas, tar and char can be expressed as the product of mass produced and heat of reaction, and hence can be calculated through four equations in the form of:

$$E_i = H_i \times m_i \tag{5.10}$$

Where index *i* refers to the *i*th reaction, *E* and *m* are the energy required or released by the *i*th reaction and the corresponding product mass. The heat of reaction *H* is positive for reactions (*R5.*1) to (*R5.*3) (endothermic) and negative for reactions (*R5.4*) and (*R5.5*) (exothermic).

The heat required to heat up the products to the set pyrolysis temperature is expressed as:

$$Q_j = \int\int dm_j C_j dT \qquad j = G, T, C \tag{5.11}$$

where dm_j is the infinitesimal mass changes of gas, tar and char that experience a temperature change dT, and C_j is the corresponding heat capacity. dm_j can be determined from the kinetic rates of each component:

$$dm_G = dm_1 + dm_4 = (k_1 m_W - \tfrac{m_G}{tau})\, dt + k_4 \tau\, dm_T \tag{5.12}$$

$$dm_T = \frac{k_2 m_W - \frac{m_T}{\tau}}{1 + \tau(k_4 + k_5)} dt \tag{5.13}$$

$$dm_C = dm_3 = k_3 m_W\, dt + k_5 \tau\, dm_T \tag{5.14}$$

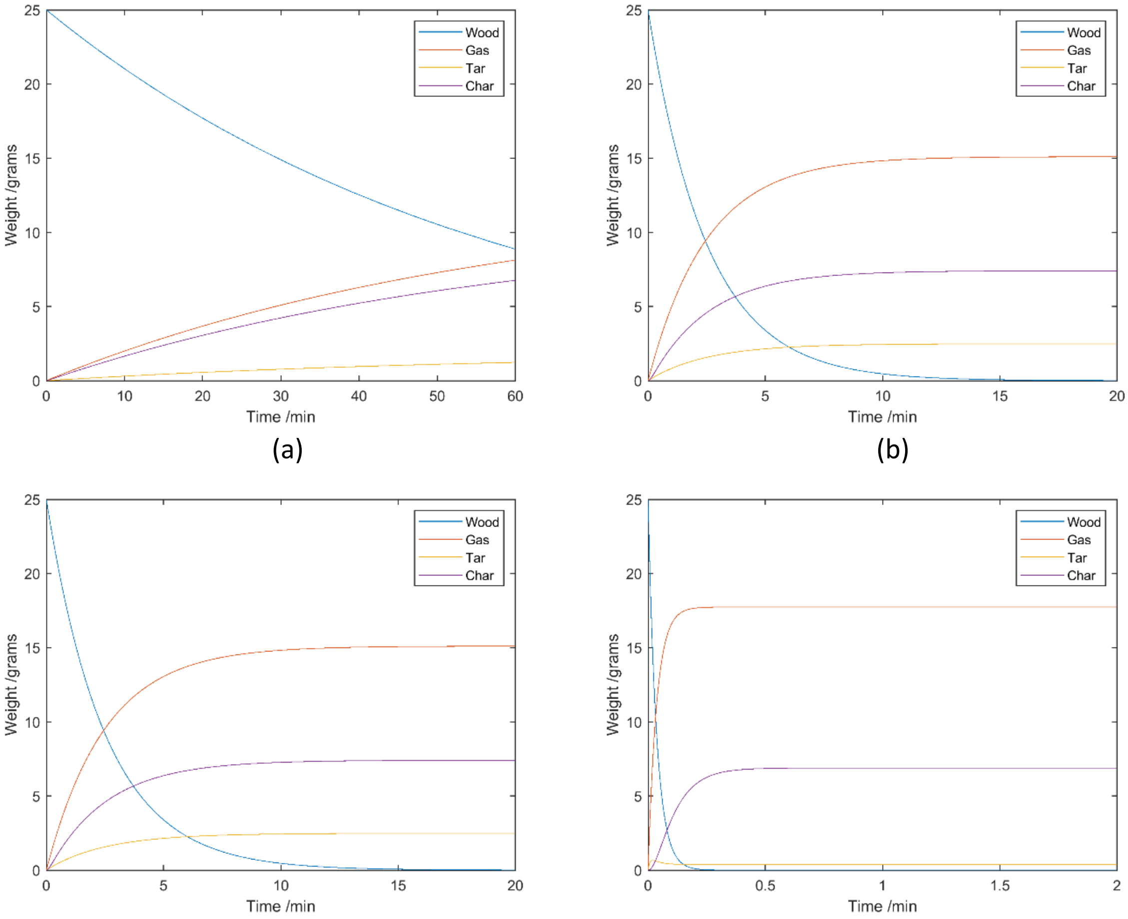
Additionally, the heat absorbed to heat up any residual biomass from room temperature, is determined as:

$$Q_B = m_0 C_W (T - 298.15\ K) - \int\int (k_1 + k_2 + k_3) m_W C_W dt dT \tag{5.15}$$

Values for the heat capacity for wood, gas, tar and char follow temperature-dependent equations introduced by Grønli and Melaaen [13].

The heat and mass transfer equations were established as a set of ordinary differential equations (ODE) and solved using MATLAB's integrated ODE solver. *Ode45* was initially tried as a solver; however, the set of equations was stiff, and solver *ode23s* was used instead with success. *Ode23s* is based on the modified Rosenbrock formula of order two and uses the Jacobian matrix to evaluate the set of ODEs [14]. The problem was evaluated with reaction duration from 0 to 3600 seconds (1 hour) with the initial conditions of 25 g of wood as m_w. The relative tolerance for the solver was set to 1×10^{-6}.

The model was validated through a mass balance, which produces an error of no greater than 5.26×10^{-7} at the evaluated temperature. Using this method, the reactions were evaluated at reaction temperatures of 300, 400, 500 and 600°C, respectively. The change of mass over time is displayed in Figure 5.1:



(a) (b)

(c) (d)

Figure 5.1: Model predicted weight change of wood and product yields over time at reaction temperatures of (a) 300°C, (b) 400°C, (c) 500°C and (d) 600°C.

Figure 5.1 shows that as reaction temperature increases, the reaction time required for complete pyrolysis reduces. The reaction is considered completed when no further changes in product yields are observed. As a simple approach was taken to modelling heat transfer, the reaction time is likely to be longer for practical pyrolysis operation. The time required, to heat up the wood particles within a packed bed, will also be likely to extend the observed reaction time. Furthermore, the temperature gradient through a packed bed may cause delayed onset of reactions in inner parts of the bed along the gas flow direction. This, in turn, may lead to reduced tar (liquid) yield, as more time is available for secondary reactions to occur. Whilst not the focus of this work, understanding and modelling of secondary reactions are important in establishing a generalised pyrolysis reactions scheme and thus, the overall heat of pyrolysis for reaction design purposes. This has been explored in detail by Jones et al. [15]; however, in this study focus is directed at the product yield distribution at different temperatures and the modelling of arsenic release. For the purposes of this work, the simplified pyrolysis approach adopted was deemed sufficient.

The wood composition after one hour of pyrolysis was modelled over a temperature range of 150°C to 800°C as shown in the following figure, Figure 5.2:

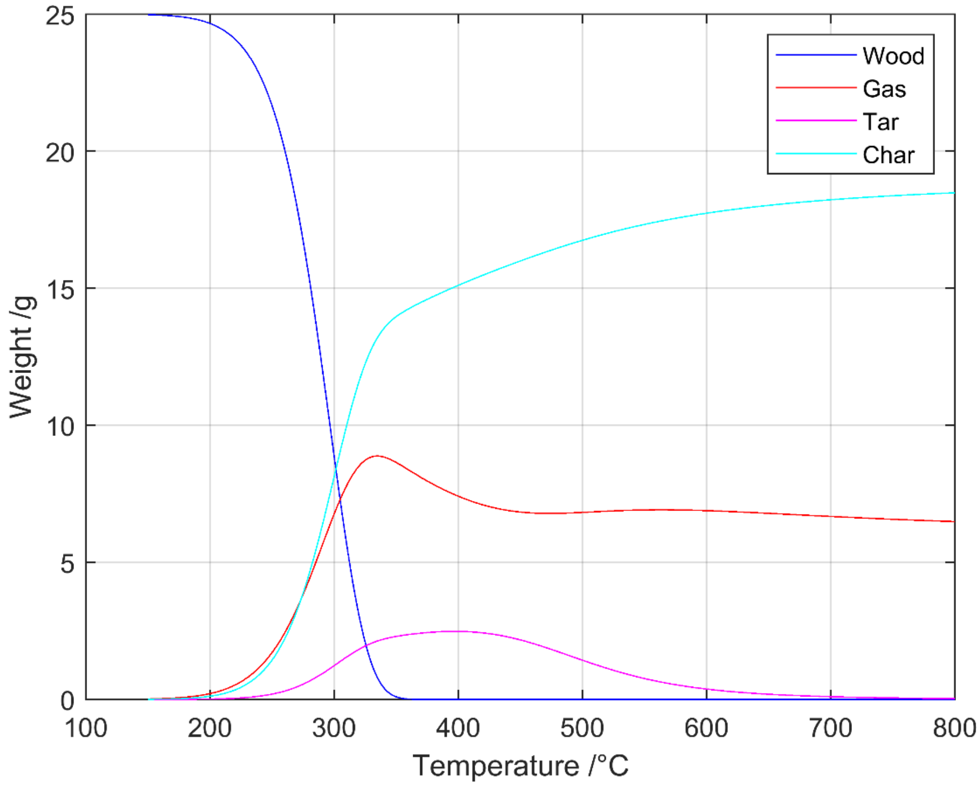


Figure 5.2: Weight Change of wood and product yields after one hour of pyrolysis at different temperatures from 150 to 800°C.

From Figure 5.2, the onset of the decomposition of biomass can be seen to be at a temperature of 160°C. With increasing temperature, gas and char products begin to form at a lower temperature than oil does. The highest oil yield is achieved at a pyrolysis temperature of 397°C. With further temperature increases, secondary cracking reactions become more dominant, resulting in a decrease in oil yield, whilst promoting char and gas production. This trend is consistent with that reported in literature, where it is stated that the thermal degradation of biomass begins at a temperature of 200°C, with the bulk conversion of 80 – 90% by 400°C [16-19].

The model supports the conclusions drawn from the above referred to literature, which describes the experimentally explored operating regime and product yields between 300 and 600°C. The pyrolysis model, in turn, validates the experimental results obtained in the present study. The following figure shows a comparison between model-predicted and experimentally measured solid weight change (the sum of wood and char) and liquid (oil) yield after 30 minutes operation (at the pyrolysis temperature) at different pyrolysis temperatures.

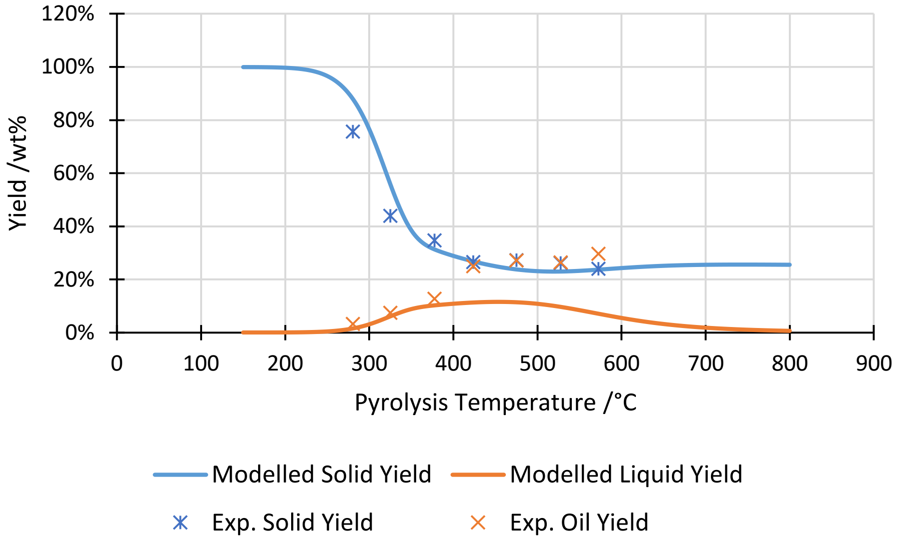


Figure 5.3: Comparison product yields determined experimentally through pyrolysis of CCA-treated timber (30 minutes operation) and model predicted values of product yield after 30 minutes.

Figure 5.3 shows that the experimental results follow the same trend as predicted by the pyrolysis model, although the pyrolysis model used in this study, is a simplified simulation of the practical pyrolysis process. These simplifications will lead to inaccurate heat and temperature assumptions within the wood particles and packed bed. This is likely to be the direct cause of errors seen in the predicted oil and gas yields. However, although stark simplifications were made to model wood decomposition during pyrolysis, the same trend is observed within the model, as well as within the experimental results obtained and data reported in literature for the primary reaction pathway of wood to char. Thus, the experimental work can be said to have operated within a true pyrolysis regime.

Although Figure 5.3 shows that experimental liquid yields are twice the model predictions at temperatures above 380°C, yet the model allows for the effect of residence time on product yields to be explored – a variable that remained constant throughout the experimental trials described in Chapter 4. The gas and liquid residence time was varied between 1 second and 10 minutes at a pyrolysis temperature of 397°C – the temperature that achieved the highest liquid yield. The results are shown in Figure 5.4, and clearly indicate that with decreasing residence time liquid yield is maximised. This supports the conclusions drawn earlier (Section 4.2.2) that future experimental work should focus on fast pyrolysis with short residence times and fast heating rates.

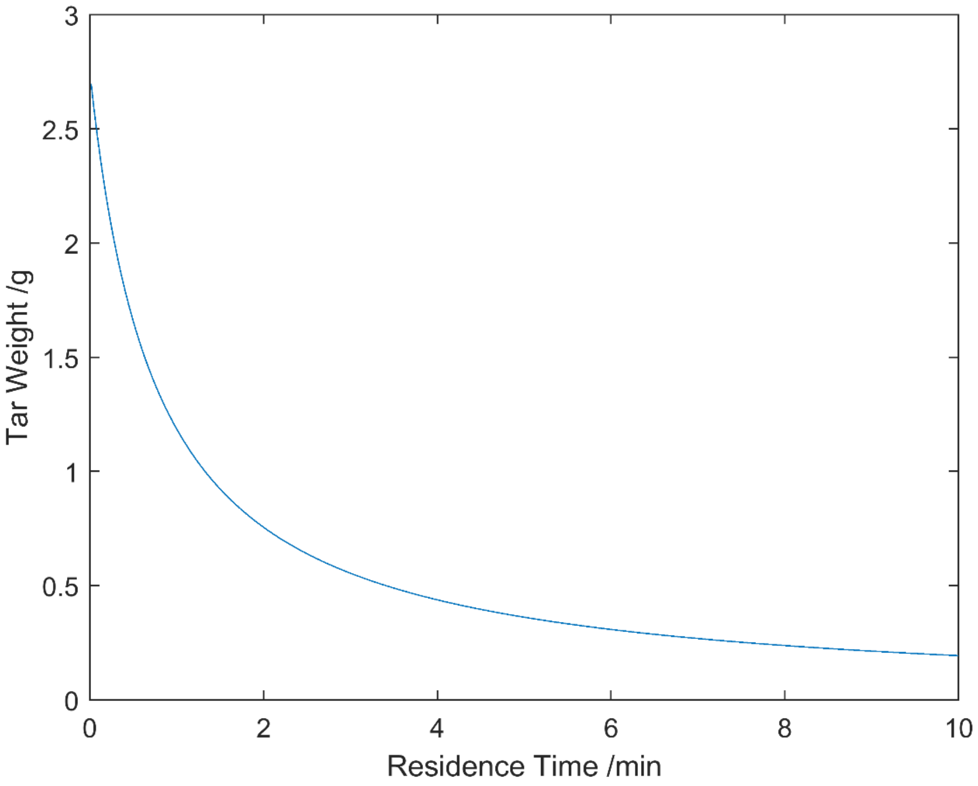


Figure 5.4: Model predicted effect of increasing the liquid (and gas) residence time on the liquid yield during pyrolysis of wood at a reaction temperature of 397°C.

5.2 Arsenic Release Model

The forms of arsenic present in CCA-treated timber have been reported in literature as $CrAsO_4$ and As_2O_5 [20], and release pathways during pyrolysis have been suggested by several authors[21-23]. However, due to the complexity of the release process, these release pathways have as of yet not been confirmed; neither theoretically nor experimentally. The final form, in which arsenic is present in the bio-oil and how this relates to the pyrolysis temperature, is of great importance, as this property determines the oil's applicability as a wood preservative. The final arsenic species needs further exploration at a set temperature as well as the associated arsenic oxidation state. By establishing a thermodynamic model, based on Gibbs free energy, the equilibrium species of arsenic compounds can be established independently of reaction pathways.

In this present study, to enable this, a mathematical model has been developed, that uses a *Gibb's free energy minimisation* approach, to determine the thermodynamic equilibrium for the decomposition of $CrAsO_4$ and As_2O_5. The equilibrium species and thereby the arsenic oxidation states occurring during pyrolysis, can be predicted at different pyrolysis temperatures. Using the approach of minimising the Gibb's free energy of the system allows for arsenic products to be established independent of reaction pathways and pyrolysis kinetics. Furthermore, the model can predict the maximum recovery of the arsenic in the pyrolysis oil component, depending on the optimum pyrolysis temperature. This is critical for the recovery and reuse of the active arsenic species as a further preservative chemical. With optimisation of the pyrolysis conditions, it may then be possible to retain the metal(oid)s in the liquid and /or solid state, thus providing the means for recovery and recycling of the preservative chemicals.

5.2.1 Arsenic Release Background

In Chapter 2 (Section 2.1.2) of this thesis, the treatment process of CCA-treated timber is described. Regarding the arsenic species, the presence of reacted and fixated $CrAsO_4$ and unreacted, unfixed As_2O_5 have been established as being present within the wood. Under pyrolysis conditions, various redox reactions surrounding the decomposition of these compounds may occur, which has been described in the literature review (Chapter 2) as Reactions (*R2.2 – R2.6*), where the product compounds are determined as being Cr_2O_3, As_2O_5, As_2O_3, O_2, As_4O_6.

Using a *Gibbs free energy minimisation* approach, the system equilibrium composition can be determined independently of the kinetic reaction scheme. This allows a broader range of chemicals to be included in the system and be explored. Therefore, chromium species Cr, CrO_2, CrO_3, Cr_2O_3 and arsenic species AsO are also included in the equilibrium model.

5.2.2 Model Development of Arsenic Release during Pyrolysis Conditions

When the total Gibbs free energy of a system at a given temperature and pressure is at its minimum, the system has reached equilibrium composition for the set conditions. To determine the minimum of the total Gibbs free energy – $(G^t)_{T,P}$ – the method of Lagrange multipliers is used. In mathematical optimisation, the Lagrangian multiplier method is a strategy to determine the extremes of a function subject to an equality constraint [24]. Here, the function – denoted as *f*(n) – is the total Gibbs free energy and the constraining equality – denoted as *h*(n) – is the material balance of the system, shown as Equations (5.16) and (5.17), respectively.

$$f(n) = (G^t)_{T,P} \tag{5.16}$$

where *n* is the moles of each chemical species *i*, which minimises the total Gibbs free energy, subject to specific temperature *T* and pressure *P*. The function *f*(n) is subject to the constraining equation *h*(n) below:

$$h(n) = \sum_i n_i a_{ik} - A_k \quad (k = 1,2, \ldots . w) \tag{5.17}$$

where A_k is the total atomic masses of the k^{th} element in the system, as set by the initial constitution of the system. Furthermore, a_{ik} in the above equation is the number of atoms of the k^{th} element present in each molecule of chemical species *i*, and *w* is the total number of distinct elements comprising the system.

To solve the problem of *f(n)* subject to the constraints defined by *h(n),* the Lagrange multiplier λ is introduced. The Lagrangian function $\mathcal{L}$ (Equation 5.18) brings together the function *f(n)* (Equation 5.16), the constraining equation *h(n)* (Equation 5.17) and the multiplier λ:

$$\mathcal{L}(n, \lambda) = f(n) + \lambda h(n) \tag{5.18}$$

Introducing the Lagrangian multipliers λ_k to the mass balance equation (Equation 5.17) and summing over each element *k* results in:

$$\lambda_k h(n) = \sum_k \lambda_k \left(\sum_i n_i a_{ik} - A_k \right) = 0 \tag{5.19}$$

Substituting the objective equation *f(n)* (Equation 5.16) and the constraining Equation (5.19) into the Lagrangian Equation (5.20) leads to the new function $\mathcal{L}$:

$$\mathcal{L}(n, \lambda_k) = G^t + \sum_k \lambda_k \left(\sum_i n_i a_{ik} - A_k \right) \tag{5.20}$$

This new function (Equation 5.20) is identical to G^t as the summation term is zero (see Equation 5.19). However, the partial derivatives of $\mathcal{L}$ and G^t with respect to n_i are different, as Lagrangian function $\mathcal{L}$ incorporates the material balance constraints.

The minimum value of $\mathcal{L}$ and G^t occurs, when the partial derivatives are equivalent to zero. Using the differentiated Equation (5.20) and setting the resulting derivative to zero, finally leads to Equation (5.21) as follows:

$$\left(\frac{\partial \mathcal{L}}{\partial n_i} \right)_{T,P,n_j} = \left(\frac{\partial G^t}{\partial n_i} \right)_{T,P,n_j} + \sum_k \lambda_k a_{ik} = 0 \quad (i = 1,2,\dots,N) \tag{5.21}$$

where the subscript n_j indicates that all mole numbers, except the i^{th}, are held constant. The first term on the right-hand side of the equation is synonymous with the definition of chemical potential μ_i

$$\mu_i = \left(\frac{\partial G^t}{\partial n_i} \right)_{T,P,n_j} \tag{5.22}$$

Therefore, Equation (5.21) can be rewritten as Equation (5.23):

$$\mu_i + \sum_k \lambda_k a_{ik} = 0 \ (i = 1,2,\dots,N) \tag{5.23}$$

The chemical potential for mixtures is defined in terms of activities a_i as shown in the following equation:

$$\mu_i = G°_i + RT\, ln(\mathrm{a_i}) \tag{5.24}$$

where $G°_i$ is set to zero for all elements in their standard states, so for compounds $G°_i = \Delta G°_{fi}$, the standard Gibbs energy change of formation. Furthermore, *R* is the universal gas constant and *T* is the temperature. The activity for gas phases is calculated using fugacity $\widehat{f_\iota}$ relative to standard or reference pressure P° (Equation 5.25):

$$a_i = \frac{\widehat{f_\iota}}{P°} \qquad (5.25)$$

The fugacity is eliminated in favour of the fugacity coefficient, $\widehat{f_\iota} = y_i \hat{\phi} P / P°$; and assuming ϕ_i is unity, and atmospheric pressure for *P* reduces the activity to a mole fraction $y_i = {}^{n_i}/_{\sum_i n_i}$.

For condensed phases – liquids and solids – the activity is set to 1 (present) or 0 (not present), following the conventions by Ramshaw [25].

Overall, the final form of the minimum Gibbs free energy with constraining equation and Lagrangian multiplier is:

$$\frac{\Delta G°_{f_i}}{RT} + ln(a_i) + \frac{\sum_k \lambda_k a_{ik}}{RT} = 0 \quad (i = 1,2,\dots,N) \qquad (5.26)$$

To evaluate Equation (5.26), the standard Gibbs free energies of formations need to be adjusted to the set temperature. The change in energy from standard state to set temperature can be calculated using Equation (5.27):

$$\Delta G°_{f_i} = G°^{STP}_{f_i} + \Delta G \qquad (5.27)$$

Values for $G°^{STP}_{f_i}$ can be found in literature and are as displayed in Table 2.7, and repeated in Table 5.2. The change in energy from standard state to set temperature can be calculated by Equation (5.28) using the enthalpy of the system Δ*H* and the entropy Δ*S*:

$$\Delta G = \Delta H - T\Delta S \qquad (5.28)$$

The system's enthalpy can be established from the molar heat capacity C_p and temperature, assuming an isobaric process and - for this study – a constant heat capacity with temperature. Similarly, the change in entropy for a substance heated from standard temperature to a set temperature within a constant pressure system can be calculated using temperature and the molar heat capacity.

$$\Delta G = C_p \Delta T - T\, C_p\, ln\left(\frac{T}{T_{STP}}\right) \tag{5.29}$$

The specific heat C_p was assumed constant over the temperature range for all species involved, as C_p is said to be constant over a wide temperature range for metallic vapours. Further, diatomic gases, such as O_2, are said to be constant at ordinary temperatures and increase only slowly at higher temperatures [26].

Table 5.2: Gibbs free enthalpy and heat capacity at standard temperature and pressure for species modelled in the decomposition of $CrAsO_4$ and As_2O_5, and A_{ik} - the number of atoms present in each element.

*Species and their state at STP**	*$G°_{fi}$ at STP /$J{\cdot}mol^{-1}$*		*C_p at STP /$J{\cdot}mol^{-1}{\cdot}K^{-1}$*		*A_{ik}*		
					Cr	As	O
$Cr_{(s)}$	0	[27]**	23.4	[27]	1	0	0
$Cr_{(g)}$	351,800	[27]	20.8	[27]	1	0	0
$CrAsO_{4(s)}$	-968,360	[28]	119.10	[28]	1	1	4
$Cr_2O_{3(s)}$	-1,058,100	[27]	118.7	[27]	2	0	3
$CrO_{2(s)}$	-529,400	[29]	43.4	[30]	1	0	2
$CrO_{3\,(s)}$	-501,300	[29]	56.1	[30]	1	0	3
$AsO_{(g)}$	-84,715	[28]	32.342	[28]	0	1	1
$As_2O_{3(l)}$	-576,340	[28]	96.88	[28]	0	2	3
$As_2O_{5(l)}$	-774,960	[28]	115.9	[28]	0	2	5
$As_4O_{6(g)}$	-1,092,200	[28]	173.60	[28]	0	4	6
$O_{2(g)}$	0	[27]	29.4	[27]	0	0	2

** Standard temperature (0°C) and pressure (100 kPa)*
*** References*

5.2.3 Numerical Procedure

To solve Equation (5.26), as well as the set of atom balance equations involved in the reactions, the MATLAB solver for constrained nonlinear multivariable function *fmincon* with its default algorithm *'interior-point'* was used. The original problem is passed into the solver in the following form:

$\min_{x} f(n)$, subject to $\lambda h(n) = 0$ and $g(n) \leq 0$

Where *f(n)* is described in Equation (5.26) and *h(n)* in Equation (5.19). *g(n)* is used to set the lower boundary of the problem where $g(n) = n > 1\times10^{-12}$. The numeric procedure is displayed in Figure 5.5.

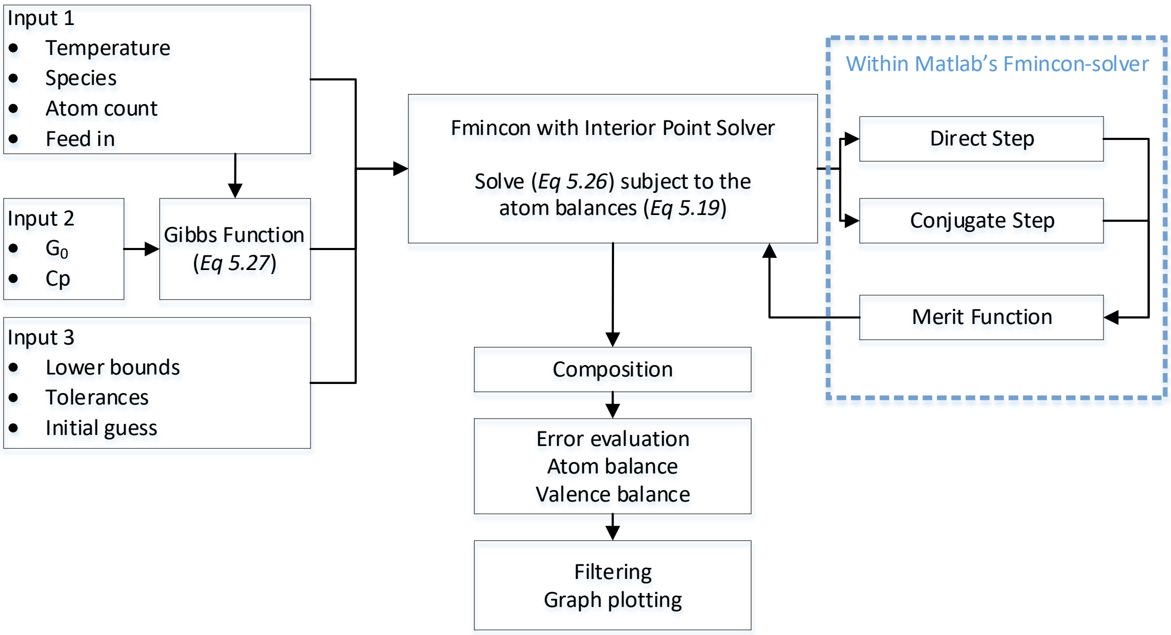


Figure 5.5: Flow diagram of the numerical procedure to evaluate the Gibbs Free energy model determining the equilibrium composition of the decomposition of $CrAsO_4$ and As_2O_5.

A brief explanation of the numerical procedures used by MATLAB's solver *fmincon* is given in Appendix H, whereas a more in-depth explanation can be found elsewhere in MathWorks [31] and in the work of Byrd et al. [32, 33] and Waltz et al. [34].

Filter

Occasionally, the solver converged towards the trivial answer of 0; the graph of composition along the temperature axis then showed oscillations between the actual answer and zero, as shown in Figure 5.6 for the case of As_2O_5 decomposition. In the case of the solver converging to zero, a filter was used that removed the trivial answers of 0 from the solutions matrix to be plotted.

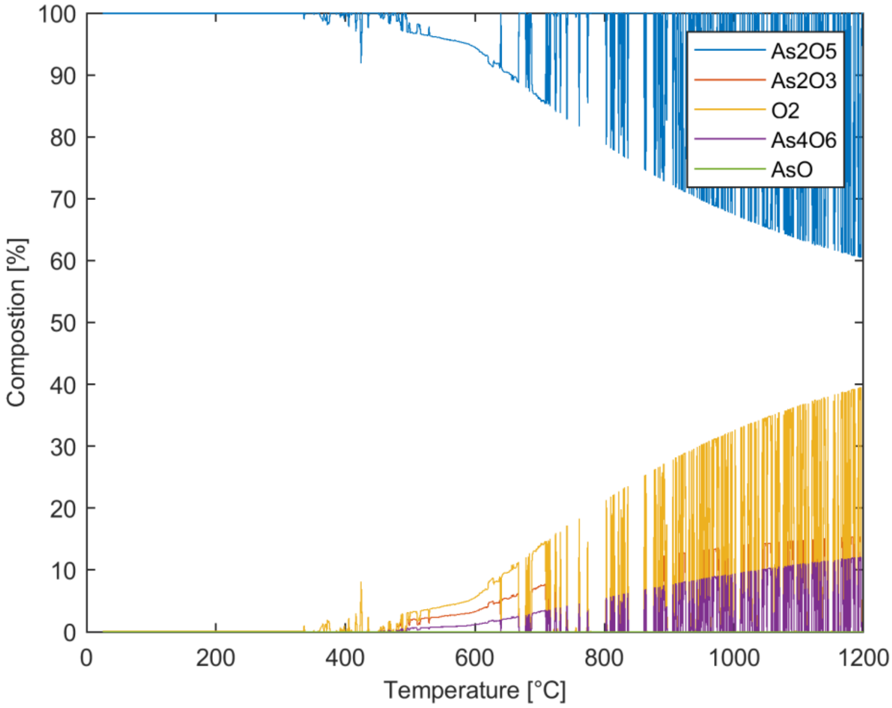


Figure 5.6: Unfiltered model results for the decomposition of As_2O_5 at various temperatures, showing the oscillating solver results towards the trivial answer of 0.

Although the filter removed the trivial answer from the solution matrix, it resulted in small spikes through the plotted figures (Figure 5.7 and Figure 5.8). Therefore, it was decided in the following discussion not to smooth out the curves, but rather to display the minor variations in composition, as they were predicted by the model.

5.2.4 Results and Discussion

The developed thermodynamic model for arsenic release was used to establish the effect of reaction temperature on the arsenic species produced, through the decomposition of $CrAsO_4$ and As_2O_5. Reaction pathways have been introduced in the literature review [35], [21] and are described by reactions (*R2.2 – 2.6*). The thermodynamic equilibrium composition, predicted through this model, enabled the comparison of species composition independent from reaction mechanisms against experimental data obtained from this present study and from previous studies reported in literature.

Verification of the Developed Model

To verify the accuracy of the developed thermodynamic equilibrium model, the law of mass conservation was applied using an atom balance – *the atom itself is neither created nor destroyed but cycles among the chemical compounds* [36]. The atom balance was closed at each evaluated temperature within a discrepancy of 1.2×10^{-11} for atoms entering the system versus those exiting. As the atom balance was used within the constitution equations of the system, a valence balance was also applied to provide a fully independent verification of the simulated solutions. The valence electron of a compound was determined by subtracting the oxidation state of each element from the element's atomic number. These were then multiplied by the determined molar composition and balanced.

It was found that the discrepancy of species atoms, between entering and exiting the system, was within the pre-set limit of 1×10^{-9} as given in Table 5.3.

Table 5.3: Highest discrepancy in atom and valence balance of model results for the decomposition equilibrium of $CrAsO_4$ and As_5O_2

Highest Discrepancy	*$CrAsO_4$*	*As_2O_5*
Atom Balance	1.07×10^{-11}	5.97×10^{-13}
Valence Balance	2.96×10^{-12}	1.19×10^{-11}

From Table 5.3, it is concluded that the discrepancy of the atom and valence balance is negligibly low, and thereby the model predictions are sufficiently accurate.

To increase the model's accuracy for further research, it is recommended to extend the model to include chromium and copper species.

Model Predicted release of $CrAs0_4$ and As_2O_5

Figure 5.7 shows the decomposition of $CrAsO_4$ as established by the thermodynamic equilibrium model. The initial release of $CrAsO_4$ occurs at 418°C; however, negligible amounts (less than 1% $CrAsO_4$) are released at temperatures lower than 760°C. Significant decomposition of $CrAsO_4$ occurs at temperatures above 734°C, with the products at thermodynamic equilibrium being Cr_2O_3, As_2O_5, As_2O_3, O_2 and CrO_2. As_2O_5 is produced as an intermediate and breaks down further to As_2O_3 as per the reaction scheme (*R2.4*); consequently, its equilibrium concentration is zero. Removing As_2O_5 from the solution matrix showed no decomposition of $CrAsO_4$, proving that As_2O_5 is indeed an intermediate. The model also shows that at 1011°C, 25% of the $CrAsO_4$ has been released, with close to 50% volatilisation occurring at 1200°C. It is not possible to accurately model the arsenic decomposition reactions at temperatures beyond 1200°C due to model instability. These conditions are well above the pyrolysis operating regime, which set the model’s scope.

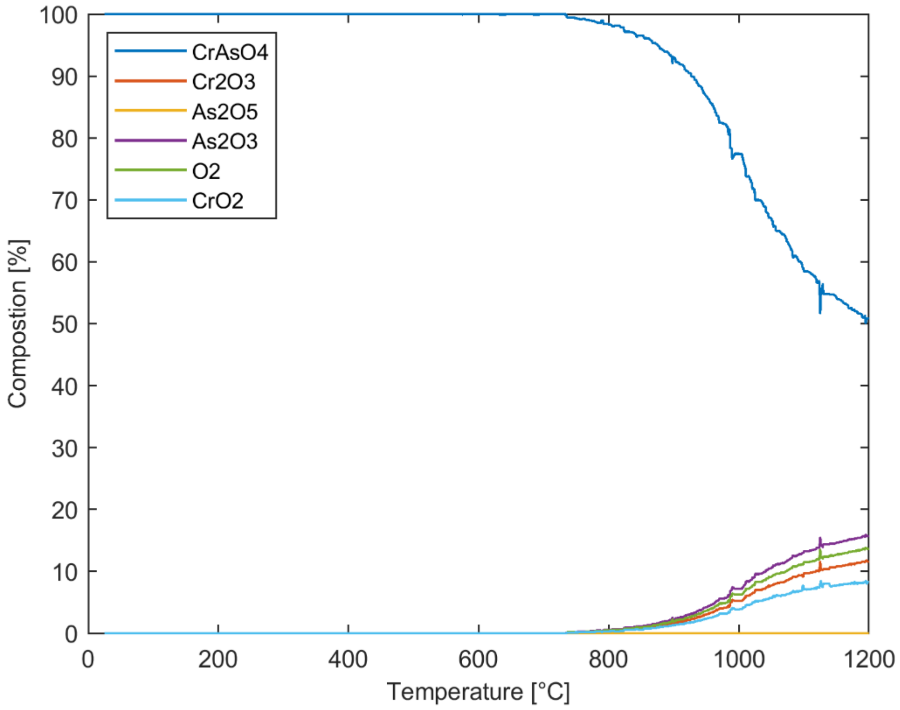


Figure 5.7: Release of $CrAsO_4$ during simulated pyrolysis conditions evaluated at a temperature step of 1°C.

In contrast, the decomposition of As_2O_5 begins to occur at 336°C with the products being As_2O_3 (liquid), O_2 (gas), and As_4O_6 (gas) as shown in Figure 5.8. A negligible amount of AsO is also released at thermodynamic equilibrium. Interestingly, with increase in the reaction temperature, the release product As_2O_3 begins to form and increases in quantity up until 423°C, at which point a sudden decrease of As_2O_5 is noted, whilst As_4O_6 becomes part of the product. Significant releases of As_2O_5 occurs at temperatures above 600°C, whereas less than 8% is released at temperatures lower than 600°C. With temperature increasing to 856°C, 25% As_2O_5 is released as shown in Figure 5.8. Similar to the consideration of $CrAsO_4$ release, arsenic release at higher temperatures was not included in the model, as these temperatures are considered to be outside the scope of the pyrolysis regime.

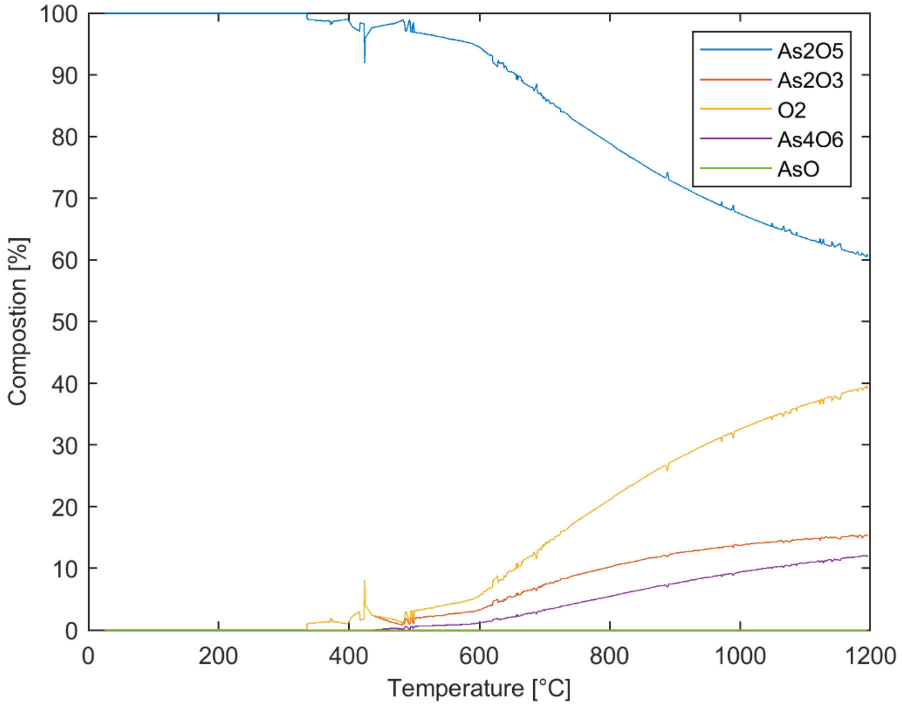


Figure 5.8: Decomposition of As_2O_5, simulated by the thermodynamic equilibrium model evaluated at a temperature step pf 1°C. Results have been filtered to remove the trivial answer of 0.

Many of the studies reported in literature address the arsenic release from CCA-treated timber rather than the isolation of the preservative compounds. Therefore, for the purpose of this study, the model results were compared to TGA results of pure substances as reported by Kercher and Nagle [22] and Helsen et al. [23], as shown in Table 2.6. Helsen et al. found only insignificant losses of arsenic below 600°C and concluded that the primary release occurred above 600°C [23]. Similarly, Kercher and Nagle found that the onset of arsenic release was at 600°C [22]. Based on the thermodynamic equilibrium model proposed in the present study – although the temperature of release onset of arsenic pentoxide was 336°C – the primary release occurs at temperatures above 600°C as shown in Figure 5.8. This primary release temperature of 600°C agrees with the previously mentioned studies.

This confirms that the assumptions made to evaluate the model were reasonable. The proximity of the model and the experimental results from literature are within uncertainty bounds and are thus sufficiently close in agreement with each other to be relied upon. Therefore, it can be concluded that the developed model can be applied to a broader range of conditions with sufficient accuracy to give assurance as to the model outcomes in terms of the release of arsenic.

Oxidation States

The model predicts that the primary dissociation product of the $CrAsO_4$ release is As_2O_3, with the arsenic present in the arsenite form (As(III)). Only small amounts of As_2O_5 are present at equilibrium, as arsenate (As(V)). Further reduction of As_2O_5 will release As_2O_3 and As_4O_6, both being arsenite.

Both As_2O_5 and As_2O_3 have preservative properties; however, arsenate is commonly used in the wood treatment process. As already introduced in the literature review (Section 2.1.4), As_2O_3 has a higher toxicity towards insects but has a higher solubility and is more likely to leach out of the treated wood over time. As_2O_3 is also more challenging to remove from water, which could be problematic if leaching occurred and contaminated surrounding soil and groundwater [20, 37-39]. The modelling also predicts that the primary product is As_2O_3in its liquid form and most likely to be present in tar. Thus, it will be of interest for future research, to investigate as to whether the arsenic is bound within the tar and how easily it leaches out. If As_2O_3 is fixated within the oil – e.g. through the formation of lipophilic arsenic compounds bound to organic complexes (see Section 2.1.4), it could be a promising opportunity to use the tar as a wood preservative, which could be applied similarly to commonly-used wood treatment oils, with the addition of arsenic acting as a further preservative agent.

The model predicts that $CrAsO_4$ breaks down into Cr_2O_3 and As_2O_5 In turn, the As_2O_5 reduces to $As_2O_3$and oxygen (see Figure 5.7). Furthermore, the model shows the presence of CrO_2, which is either produced from a parallel reaction of $CrAsO_4$ decomposition or as part of a secondary reaction of the previously produced Cr_2O_3. The equilibrium species confirm the reaction pathways (*R2.2 – 2.6*) which were determined based on pyrolysis and TGA experiments, as reported in the literature.

The reaction pathways (*R2.4 – 2.6*) proposed by Helsen and Van den Bulck [35] are based on thermogravimetric analysis of CCA-treated wood and the individual preservative compounds. They then related their findings to thermodynamic calculations of pure metal(oid)s in incineration processes. Thus, the influence and behaviour of $CrAsO_4$ could not be determined with certainty. The modelling approach used here overcomes that limitation.

Kakitani et al. [21] proposed two schemes for arsenic release during pyrolysis from As_2O_5 and $CrAsO_4$ as represented by (*R2.2* and *2.3*) and (*R2.4 – 2.6*), respectively. These were based on their pyrolysis work, TGA studies by Kercher and Nagle [22] and the above-introduced work by Helsen and Van den Bulck [35].

The experimental results in the present study, as discussed in Chapter 4, show that through pyrolysis of CCA-treated timber, arsenic is released in the liquid state at temperatures as low as 300°C – see Figure 4.10. Traces of arsenic are found in the liquid product, indicating that As_2O_5 has been reduced to the liquid form of As_2O_3 via reaction (*R2.2*). This is supported by the observed arsenic speciation given in Table 4.5, where the majority of arsenic is present as As(III) in the liquid. Arsenic release was observed to peak at 475°C before it drops, prior to a slow increase in the amount released at temperatures above 525°C.

As shown in Figure 5.9, the developed model predicts that As_2O_3 release increases with temperature and reaches a peak at 423°C. Above 423°C, the release of gaseous As_4O_6 is promoted (*R5.7*), reducing the As_2O_3 present in the liquid. Above 480°C, the release of As_2O_3 and As_4O_6 is predicted to increase in accordance with the model. The experimental results from Chapter 4 are also shown in Figure 5.9 for comparison against the model simulation results. It can be noted that although the model simulation results show similar trends as the experimental results, the model predicted arsenic in the liquid form to be half the amount of that which was actually measured in the experimental work.

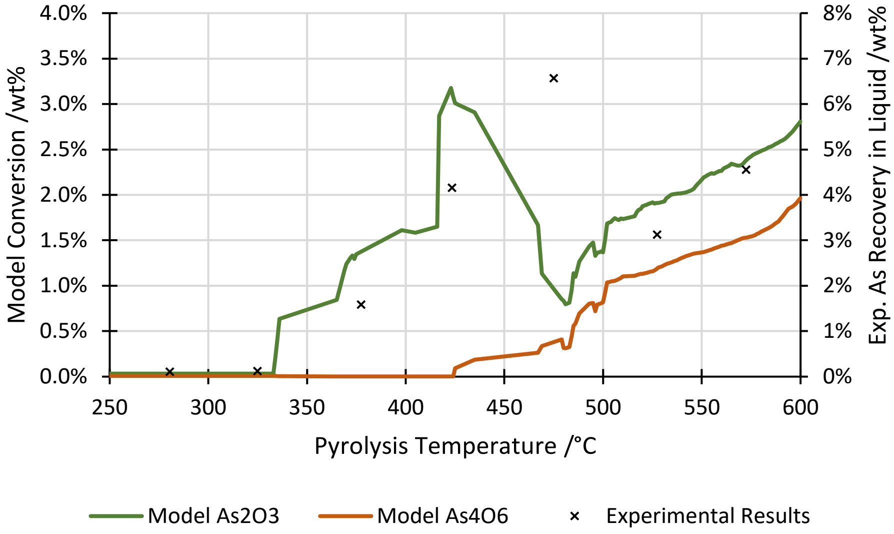


Figure 5.9: Comparison between the model predicted release of As_2O_5 to liquid As_2O_3 and gaseous As_4O_6 versus the experimentally recovered arsenic yield in oil as given in Chapter 4.

Although there are differences in arsenic conversion (wt%) and a 50°C temperature shift for the peak as shown in Figure 5.10, it is interesting to note that the trend and the peak, predicted by the model, were also observed experimentally. Differences between the model outputs and the experimental findings of Chapter 4 may be attributed to the catalytic effect of the reducing pyrolysis environment, which is not included in the model. The mass reduction and volatilisation reactions are likely to play a role in the onset of the arsenic release temperature. The shift of peak values in the experiments are likely due to the driving forces needed for the wood to heat up and gas diffusion from solid particles.

The amalgamation of experimental and modelling findings indicate that the yield of liquid As_2O_3 and gaseous As_4O_6 increases with increasing temperature. The ratio of As_2O_3 to As_4O_6 reduces with increasing temperature, indicating that the consumption of As_2O_3 (to As_4O_6) is faster than its production (from As_2O_5).

Furthermore, the experimental findings indicate that twice as much arsenic is released as compared to the quantities predicted by the model. Then again, the experimental findings of this study show considerably smaller quantities of arsenic recovery in the bio-oil than the experimental findings by Kim et al. [40], in which 34.5 wt% of the original arsenic content is recovered in the liquid. This discrepancy can be attributed in part to the findings described in Chapter 4, which concludes that the experimental results demonstrate that whilst the onset of arsenic release is strongly temperature-dependent, other factors such as residence time and heat-up rate are decisive in determining the extent of the arsenic release.

The equilibrium model is based on the assumption that all species involved reach thermodynamic equilibrium at given conditions of temperature and pressure. However, the state of equilibrium is not instantaneous, and a certain amount of time is required to reach equilibrium. If the time is shortened – e.g. through reduced residence time and fast heating rate with subsequent rapid quenching of the reaction pathways – the products and reactants will not reach a true equilibrium and will thus fail to reach the predicted thermodynamic equilibrium concentrations. Such a process could hinder the reaction of As_2O_5 to As_2O_3, whilst allowing for higher recoveries of As_2O_3. This concept is visualised in the Figure 5.10.

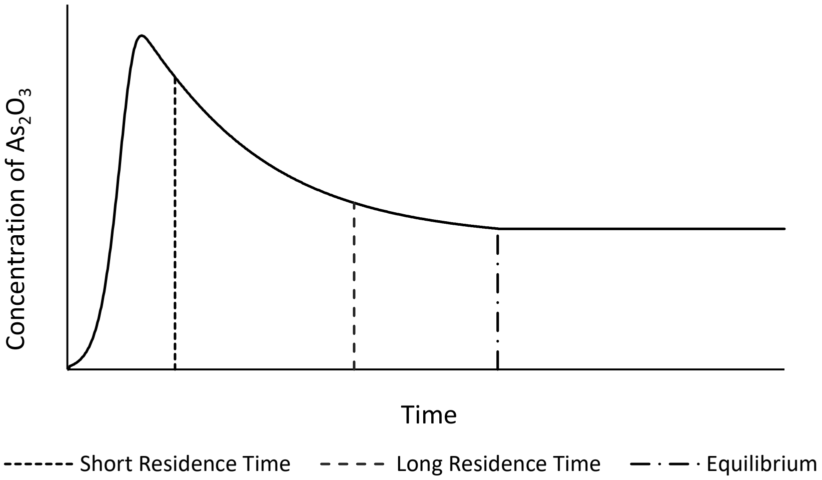


Figure 5.10: Expected effect of residence time on As_2O_3 concentration in the liquid product of pyrolysis of CCA-treated wood.

On this basis and given the broad agreement of the model with experimental findings, it can be reasonably assured that the model, within its uncertainty bounds, is a useful tool to predict the final equilibrium conditions for the arsenic species present in CCA-treated timber, when sufficient reaction time is allowed for. The model is also useful to predict the effect of temperature on arsenic release and product distribution. The model shows that the maximum amount of arsenic is recovered at 423°C in its liquid form.

However, more detailed modelling of the kinetics and diffusion within the wood particle, as well as the catalytic effect of the reducing pyrolysis environment, would be required to more accurately predict the extent of arsenic release in an industrial situation.

5.3 Conclusions

In this chapter, a kinetic model was developed to simulate the pyrolysis of woody biomass and a thermodynamic equilibrium model was developed to better understand the arsenic release during pyrolysis of CCA-treated wood.

The kinetic model has been solved to enable predictions of the pyrolysis product distribution and the effects of pyrolysis temperature.

The thermodynamic equilibrium model has been solved to allow arsenic conversion and speciation to be predicted at different temperatures. The equilibrium model proved itself as a valuable tool in establishing the oxidation states of arsenic species present in the pyrolysis products. The model predictions within the typical pyrolysis temperature range were consistent with trends established in

Chapter 4, as well as with results reported in literature. Based on the developed model and supported by the literature, the maximum arsenic release in its desired chemical form was shown to occur at a pyrolysis temperature range of 423 – 480°C. The results from the modelling and analysis reported here support the possibility of recycling the pyrolysis products, thereby enabling the recycling of the preservative chemicals as part of an end-of-life management plan for CCA-treated timbers.

Arsenic is present in the form of As(III) in the bio-oil; however, there is currently no understanding of arsenic retention within this oil. If the arsenic can be entirely fixated within the oil, it could be used as an oil-based wood preservative. By recycling an arsenic-rich oil back into the wood preservation industry, a circular economy regarding the recovered arsenic may well be achieved.

However, it is noted that much higher arsenic conversion into the liquid and the gaseous products was achieved in the experiments than that predicted by the thermodynamic equilibrium model. Further modelling of the diffusion and transport reactions, and reaction environment, may allow the extent of the release to be predicted more accurately.

Pyrolysis thus offers the prospect of being an industrialised, commercialised method to manage CCA-treated wood waste. The modelling work undertaken here is a first step in understanding the process requirements for a commercial plant. Establishing this model has enabled the decomposition and oxidation state of the CCA compounds to be appropriately described. In the next chapter, the experimental work and modelling findings are combined to address how the potential for environmental harm caused by CCA-treated timber can be reduced through a conceptual new waste management strategy.

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6 Achieving Industrial Implementation – A Circular Economy Approach

The focus of this thesis has been to establish an end-of-life product scheme for CCA-treated timber waste that is suitable for New Zealand and leads to improved environmental outcomes. The work concentrated on arsenic specifically, as it is the most toxic of the preservative chemicals, most prone to leach out of the wood and is the most volatile of the compounds present.

To bring together the findings of Chapter 4 and 5, as well as data reported in literature, a conceptual waste management scheme using fast pyrolysis is devised. The proposed process scheme is modelled using the UniSim software package, allowing for mass and energy balances to be established on an industrial scale. These gathered data are used as part of an environmental impact analysis to compare pyrolysis against the counterfactual of landfilling of CCA-treated timber waste, with the chapter concluding with a view on proof-of-concept and a possible development pathway.

The previous chapters have underlined the importance of CCA-treatment for *Pinus radiata*, and the role these materials play within New Zealand's economy. Currently, CCA-treated timber waste is disposed of in class 2 landfills, which cannot be considered a long-term solution, as the toxic preservatives entrained within the wood can cause environmental harm. Furthermore, the linear cradle-to-grave pathway leads to the requirement for further virgin CCA preservative to be used to treat new timber, ultimately increasing CCA persistence's within the environment. A new waste management strategy for CCA-treated timber waste that suits the New Zealand context is needed. Pyrolysis technology has been deemed the most appropriate and promising solution within New Zealand, due to the low emissions (in comparison to gasification and incineration) and being an already established technology. Waste Transformation Ltd. has commissioned and operated a wood waste pyrolysis plant (for untreated wood) in Timaru, New Zealand, since 2014.

Pyrolysis not only allows for the decomposition of the woody biomass (and recovery of its energy value), but it may also provide the means to recover the arsenic for reuse.

This chapter presents a preliminary conceptual design scheme for a new waste management strategy. If future work proves successful in developing a sustainable and economic deployment pathway of the here described waste management scheme, critical comparison is needed to the disposal of CCA-treated timber waste into landfill. Such work would include critical and quantitative analysis of class 2 landfills and an environmental analysis of current best practices and any proposed practices.

Previous pyrolysis research documented in the literature (Section 2.4.2) has focused on concentrating and recovering the preservative compounds from the char. Consequently, much research is focused on characterising the char and on concentrating the preservative contained therein. However, arsenic volatilisation is a major drawback of all thermochemical conversion processes using CCA-treated wood as feedstock. This requires costly gas cleaning processes and specialised equipment. As pyrolysis uses lower temperatures than incineration and gasification, less arsenic is volatilised, of which some can be condensed and recovered within a liquid oil product. This contaminated bio-oil has previously been considered to be a major shortcoming for the use of pyrolysis for CCA-treated wood waste; however, this work sets out to explore new opportunities for the future use of this product. Significant quantities of the CCA compounds nevertheless remain within the produced char and although not the focus of this work, its recovery plays an integral role in establishing a full recycle scheme. As the objectives of this thesis is the investigation and application of the oil product, the reuse of the char is considered outside of the limitations of this work, yet worthy of further study in the future.

Applications and recovery methods for arsenic from the char have been considered in Section 2.4.2 of Chapter 2. Discussed are the application of char in industrial boilers, removal of arsenic using zero-valent iron and other commonly deployed methods within the chromium and copper refining industry. Technologies and methods to address the CCA compounds in the char are of importance in closing the recycle of the preservatives, as the research reported in this thesis shows that not all CCA can be directed into the liquid fractions derived from pyrolysis. Achievement of a high CCA recovery from the char and oil components combined opens up the opportunity for a circular economy approach as well as helping reduce environmental harm by diverting CCA-treated timber waste away from landfills.

Results and findings outlined in the previous two chapters (Chapters 4 and 5), covering the experimental investigations and modelling, are brought together here in Chapter 6 to develop a conceptual process scheme. The results from reported studies in the literature have also been incorporated. In addition, the engineering requirements for a possible commercial plant are examined. A simplified process model was developed to simulate the likely industrial performance and to test the adequacy of the experimental and modelling results. Subsequently industrial readiness is discussed in terms of the underlying technologies, the use of recovered arsenic-rich oil as a preservative, the efficacy of the process and product, as well as potential regulatory and environmental hurdles. The chapter concludes with a reflection on proof-of-concept and an outlook towards future work and applications.

6.1 Findings of the Studies Presented in Chapters 4 and 5

Pyrolysis was shown to be the preferred means of processing for CCA-treated timber waste. This process route allows the capture of a large percentage of the CCA metal(oid)s present in the treated-timber waste and their eventual recovery from the pyrolysis products. Initially, it was thought that conventional batch-wise pyrolysis could be optimised to produce a high yield liquid product with a high arsenic concentration. This in turn could be reused in the wood treatment industry as an arsenic-rich preservative. The experimental work undertaken in this thesis, using a batch-wise pyrolysis technique, yielded 29 wt% oil, containing 7 wt% of the original arsenic content. However, from literature it is known that oil yields of as much as 43 wt% and arsenic recoveries of 34 wt% are possible using fast pyrolysis [1]. The lower oil yield and arsenic recovery in the present study were partly due to the experimental set-up employed, in which the samples were tested in-situ and thus were subject to an extended heat-up time, resulting in volatilisation of the arsenic into the gas phase and also lower oil yields.

The experimental work has shown that the limitations of conventional pyrolysis, i.e., slow heating rate and long residence time as well as the complicating effects of the CCA compounds on the decomposition process, all lead to a conclusion that conventional pyrolysis is unlikely to produce the required operating conditions to achieve the desired maximum liquid yields and arsenic recovery.

The present research has confirmed the effects of pyrolysis temperature on the onset of arsenic volatilisation and refined the requirements for successful pyrolysis of CCA-treated timber wastes. These findings were also supported by the theoretical modelling undertaken. Key outcomes of the experimental and theoretical work have been:

- Pyrolysis temperature is the key parameter determining the onset of the arsenic volatilisation process; however, the extent of arsenic release and vaporisation is dependent on pyrolysis residence time and heating rate, showing liquid yield increases of 14% and arsenic recoveries in the liquid of 36% when using fast pyrolysis rather than conventional pyrolysis (see Section 4.2.2);
- Experimental and modelling results agree with reported studies in literature that pure As_2O_5 is released in significant quantities above 600°C, whereas its reduction to As_2O_3 is catalysed in a reducing pyrolysis environment (see Section 5.2.4);
- Mass reduction of treated timber is catalysed by the presence of the preservatives, where the onset of biomass decomposition occurred 5 – 10°C lower using CCA-treated timber than untreated timber (see Section 4.1.2);

- Within the produced char, arsenic is primarily present as As(V) and arsenic within the oil is As(III) (see Table 4.5).

Although the pathway forward to industrial application remains uncertain, this assessment supports pyrolysis as a means of processing CCA-treated timber waste. The experimental and modelling work undertaken in this study shows that pyrolysis, particularly fast pyrolysis, has promising applicability as a waste management method and is worthy of further research to establish a detailed proof-of-concept. In support of the concept, an initial process scheme is introduced below for the pyrolysis of CCA-treated timber waste and recovery of the oil as a potential alternative preservative for timber treatment. Apparent limitations and impediments are identified.

6.2 Processing Scheme and Potential Application

Figure 6.1 presents a block flow diagram of a proposed process scheme for a pyrolysis-based waste treatment scheme capable of handling CCA-treated timber waste, including a separation unit to produce an oil-based preservative. The proposed scheme also enables the recovery of the residual metals from char. Introduced in Section 2.4.2, through milling and treatment of the produced char, a fraction free on CCA-contamination (less than 0.01% heavy metals) can be recovered, and contaminated char fraction (75% carbon, 22% minerals of which 14% are heavy metals). Alongside the feedstock, energy is shown as an input, which is required for the endothermic pyrolysis reactions. To create an inert atmosphere for pyrolysis, nitrogen is introduced into the reactor; however, in an industrial plant, the non-condensable gas stream from the pyrolysis operation can be recycled back to replace the nitrogen gas. In such case, the non-condensable gases are used as the sweep gas carrying vapours through the designed system. Any surplus gas would still be required to be vented into a flue gas system or to be burned in an afterburner. This is common practise in industry, and its design would form part of next stage of development. This would avoid the costs for nitrogen and offer potential heat integration benefits.

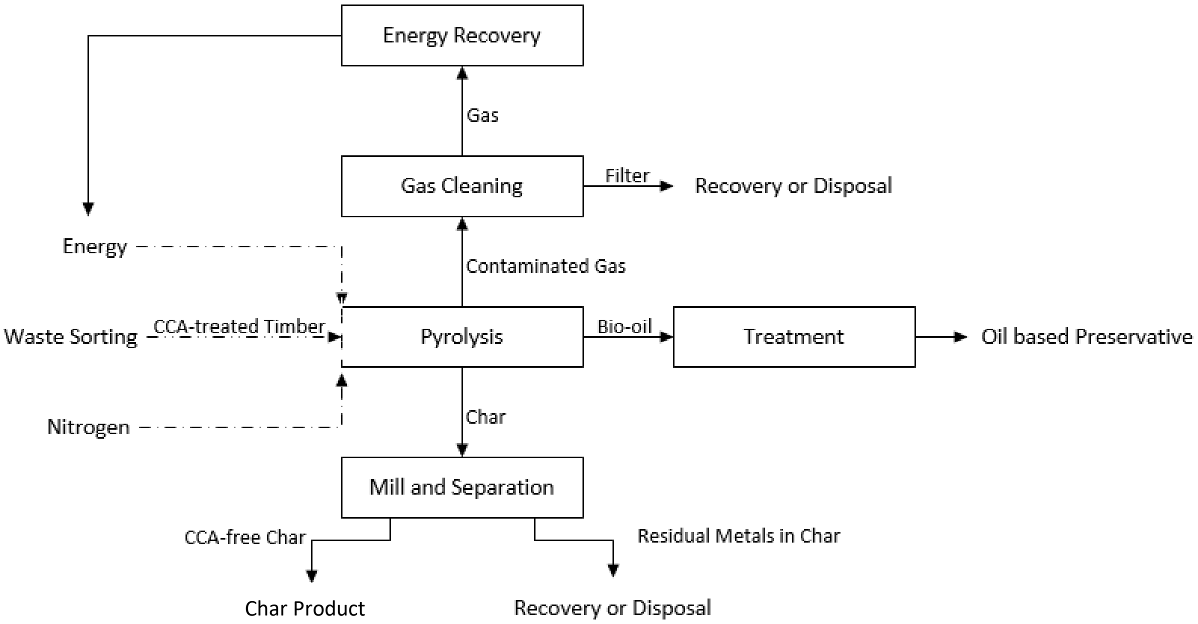

Figure 6.1: Block flow diagram of conceptual process scheme based on pyrolysis of CCA-treated timber waste for the production of an oil-based preservative, with the recovery of the residual metals from the char product.

The non-condensable gas product, resulting from the pyrolysis process, requires clean-up before being discharged into the environment. There is an option to recycle the gases for heat recovery prior to discharge, or alternatively, the non-condensable gas could be used as a carrier gas in the pyrolysis process. However in the latter case, not all of the gas is needed, thus gas treatment is still required. After utilisation and combustion of the non-condensable gases, gas-cleaning will be required as the experimental and modelling work shows that arsenic emissions will be above New Zealand's air emissions standards. Section 2.4.3 discusses the applications of calcium oxide and iron-modified activated carbon to remove arsenic from the flue gas as well as the use of baghouse, electrostatic precipitators (ESPs), wet scrubbers and multi-cyclones.

Char is an inherent product of the pyrolysis of CCA-treated timber waste, and its economic value requires it to be considered as part of the industrial process. From reported studies in the literature, it is apparent that there are a number of options for the reuse of char in ways that allow for any residual contaminants of copper and chromium to be taken into account. However, from the perspective of eliminating any potential harm to the environment, the more desirable approach of separating and recovering the metal(oid)s from the char has been adopted here.

Although this thesis focuses on the bio-oil and the recovery of arsenic within the liquid oil stream, the importance of preservative compound recovery from char and gas cleaning is stressed as an integral part of the industrial implementation.

The arsenic concentration in the liquid product is dependent on the pyrolysis operating conditions. Separating the arsenic from the oil product requires further processing steps and may prove challenging in implementation, as arsenic may be bound to organic compounds within the oil [2]. In the meantime, a short-term solution focusing on the use of the bio-oil, including its metal content, as a means of augmenting existing timber preservative treatments is proposed. Doing so avoids separation issues, but further research is still needed to validate suitability and process requirements for the timber treatment industry.

6.2.1 Pyrolysis Oil Treatment and Utilisation

The experimental and modelling work described in this thesis has shown that arsenic recovered in the bio-oil will be in the form of As(III). The arsenic may have reacted with organic compounds, forming metal-organic complexes through the pyrolysis process, which, if this is the case, could be organic trivalent arsenoxides (See section 2.1.4). Therefore, the behaviour of As(III) within the bio-oil needs to be determined regarding its retention and solubility in water for potential use in wood treatment. If it can be shown that As(III) in the bio-oil does not leach under normal service conditions, then the oil could be used directly as an oil-based wood preservative. Using the arsenic-rich pyrolysis oil as an alternative preservative for the wood treatment opens up the opportunity for a fully circular economy embracing all the CCA compounds.

However it is known from the literature review, that As(III) and As(V) are both water-soluble and likely to leach out, if exposed to water. Solubility data are given as 65.5 g of As_2O_5 per 100 mL water, whereas for As_2O_3, this is considerably lower at 1.3 – 3.7 g per 100 mL (both at 20°C). However, as As_2O_5 reacts with chromium in the treatment process, it becomes fixated to the wood structures and little leaching occurs, as discussed in Section 2.1.3. Therefore the question arises as to level of retention of As(III) within the oil or, alternatively, it may be required to oxidise the arsenic to As(V) and then use a fixating agent to bind the arsenic to the oil; in a similar way in which chromium is deployed in the initial treatment process.

Although As(III) is less water-soluble, it is said to be 60 times more toxic and more mobile than As(V). An essential step in stabilising As(III) in groundwater contamination is its oxidation to As(V) [3, 4]. Thus, it is unlikely that As(III) can be safely and effectively fixated to the bio-oil. Instead, oxidation of As(V) prior to fixation will be required.

In Section 2.4.2, zero-valent iron and electrocoagulation processes were introduced. These have shown high effectiveness in oxidising As(III) and subsequently absorbing it [5-7]. However, both of these processes can also absorb arsenic. Alternatively, oxidation methods that are typically deployed in wastewater treatment could be used. Chlorine, sulphite, permanganate and ozone are successful oxidising agents, achieving above 95% oxidation of As(III) within less than 1 minute [8, 9].

The use of chromium as a fixating agent has already been introduced in the literature review, in Section 2.1.2. It is of interest, whether chromium could have similar fixating abilities within the bio-oil. Other available research focuses on the fixation of arsenic in contaminated soil.

Questions remain however, as to how such an application might be implemented on an industrial scale. Further research is required to fully explore the efficacy of this oil as a timber preservative, although as described in Section 2.4.1, a number of studies have recommended using pyrolysis-derived oil for this purpose. If the derived arsenic-rich bio-oil is proven to be an effective preservative for wood treatment, further investigation and process development are warranted.

It is suggested that any such work should be directed at maximising the arsenic content in the liquid product and increasing the liquid yield; through using continuous fast pyrolysis.

For the purpose of this investigation, it is assumed that the pyrolysis oil will be fractionated to produce a light oil fraction with a boiling point in the range analogous to that of a typical LOSPs (Light Organic Solvent-borne Preservatives) as per the fractionation scheme shown in Figure 6.2. The proposed fractionation scheme was historically used for the production of tar, terpenes, turpentine, methanol and other products; however, the wood distillation and fractionation processes were superseded by coal-tar products and chemical treatment of wood (e.g. through CCA). However, still used today are Light Organic Solvent Preservatives, which utilise white spirits as a solvent. Fractionation of the oil may allow for a product to be recovered similar to that of white spirits.

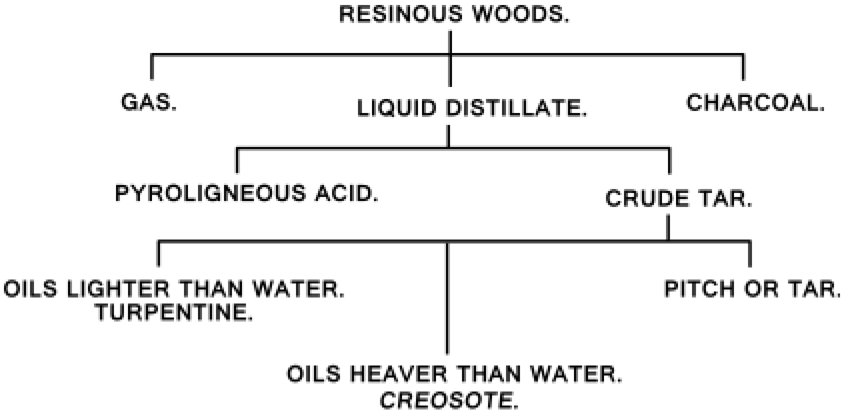

Figure 6.2: Pyrolysis oil fractionation products [10]

As shown in the above figure, a liquid distillate from the pyrolysis of CCA-treated timber is first separated into pyroligneous acid and crude tar fractions. From the experimental results, the majority of the liquid distillate is suggested to be crude tar, as the formation of pyroligneous acid from the breakdown of lignin is assumed to be inhibited Section 4.3.1. The crude tar is then further fractionated into an oil fraction lighter than water, a fraction heavier than water and pitch or tar components.

For this investigation, the proposed process shown in Figure 6.1 has been used to develop a model to simulate industrial-scale operation, thus allowing an initial comparison of the properties of the oil fraction lighter-than-water against those of LOSP.

Furthermore, as recovery and recycle of the pyrolysis oil is the preferred waste management approach, for process modelling purposes it was decided to use the literature-reported results of liquid yields with high arsenic levels, as found in the fast pyrolysis process. In this study, the experimental results and pyrolysis modelling predictions were based on a conventional pyrolysis process which resulted in much lower oil yields and arsenic concentrations than those of the above. Therefore, going forward, the findings of Kim et al. [1] (shown in Figure 6.3 for product yield and arsenic content) are used. These data were determined experimentally using fast pyrolysis with a residence time of 2 s at pyrolysis temperature of 500°C. The proposed process model and process design in this chapter is conceived so that it can be adapted for new data for a more accurate analysis in the future, when fast pyrolysis experiments have been performed with CCA-treated *Pinus radiata* timber waste.

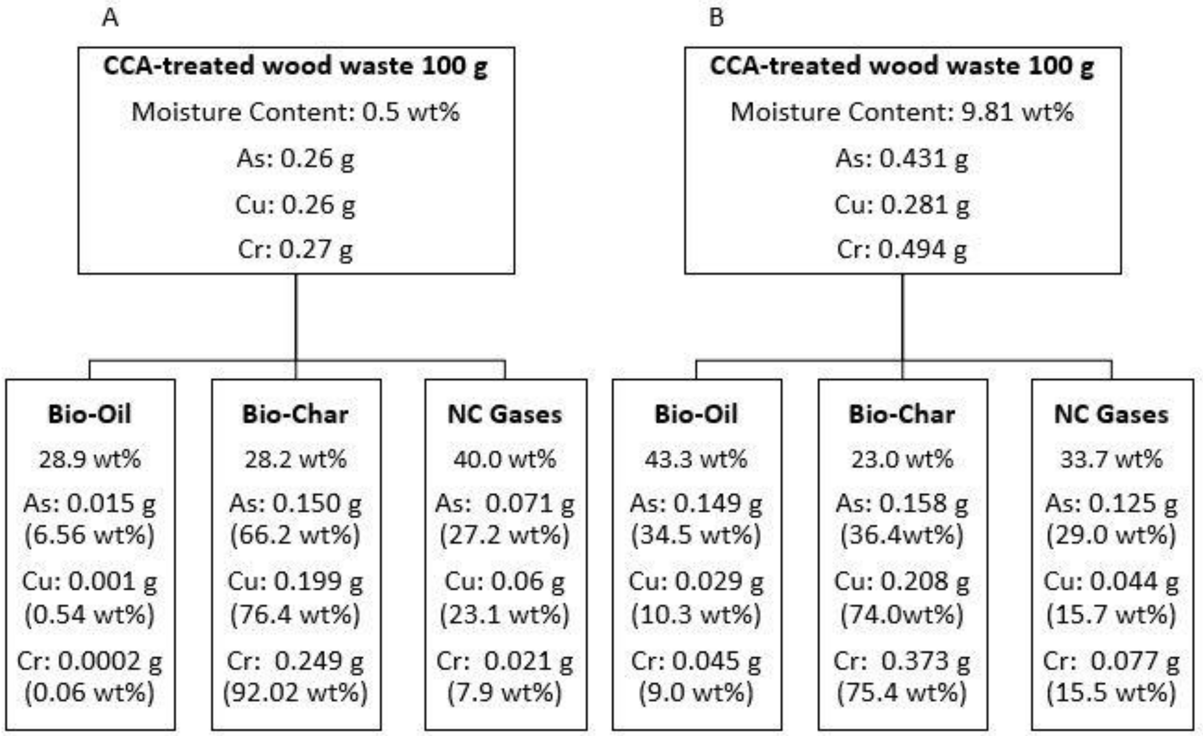

Figure 6.3: Experimentally determined pyrolysis product yields and CCA disposition, where the non-condensable (NC) gases include the unaccounted fraction. Left side (A) shows the experimental findings of this study as presented in Chapter 4 (477°C) using conventional pyrolysis; right side (B) shows the findings from Kim et al. [1] (500°C) using fast pyrolysis.

6.3 Design for a Conceptual Process Plant

In an industrial application, consideration will need to be given to the fact that CCA-treated timber wastes will be contaminated with fasteners, paint, and other related detritus. In this case, the char product from pyrolysis will contain the residues from these contaminants, the ash elements and all fixated $CuCrO_4$ and $CrAsO_4$. For simplicity, only the presence of $CuCrO_4$ and $CrAsO_4$ is assumed rather than the full spectrum of chemicals present. The pyrolysis oil will consist of a range of aromatics, water and As_2O_3. The gas product primarily contains CO_2, with some methane, ethane and ethylene, as well as gaseous As_4O_6. To create an inert environment for pyrolysis, nitrogen is used in this model; consequently, the gas stream is diluted. In an industrial setting, the non-condensable gases can be recycled back into the reactor to create an inert environment that promotes oil and char production. However, to stay close to the experimental conditions of this work and that of Kim et al. [1], nitrogen was assumed used continuously throughout the operation.

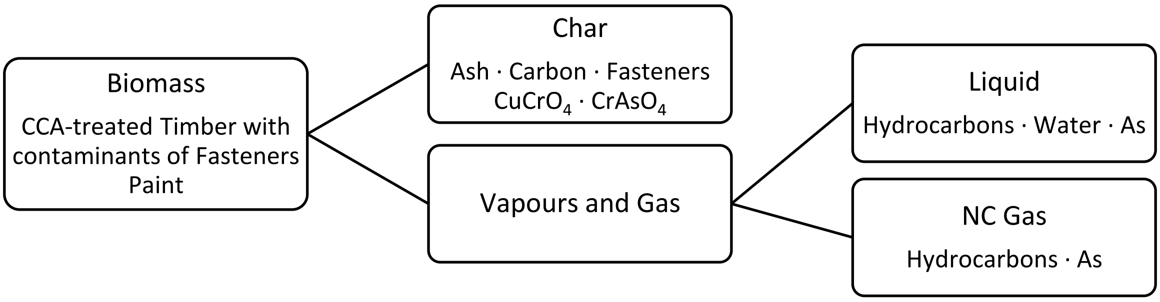

Figure 6.4: Feedstock and products in pyrolysis of CCA-treated timber

If the timber waste is wet – with moisture content of above 10% – drying is needed to remove the excess moisture to below 10% moisture content prior to pyrolysis. Reduction of the feedstock's particle is needed, although this is not modelled at this early stage of design. As grinding operations are energy intensive, future work needs to balance and optimise the grinding energy with the appropriate particle size for heat and mass transfer for a fast pyrolysis system.

In the design adopted, the industrial process begins with grinding to reduce the particle size of the feedstock and a drier to remove excess moisture. As part of this unit operation, fasteners may be removed from the feedstock; however, this is likely a labour-intensive step. Ideally, the fasteners would be removed after pyrolysis from the brittle char product. Thereafter, the biomass is converted to char and vapours via a fast pyrolysis reactor. A downstream condenser allows for the separation of the vapour stream into a liquid and non-condensable gas fraction. The detailed design of the industrial process is shown in the following flow diagram (Figure 6.5), followed by an explanation of the individual streams and operating steps. The process scheme is modelled using the UniSim software package to simulate mass and energy balances for key operations to recover the described pyrolysis product and arsenic yields.

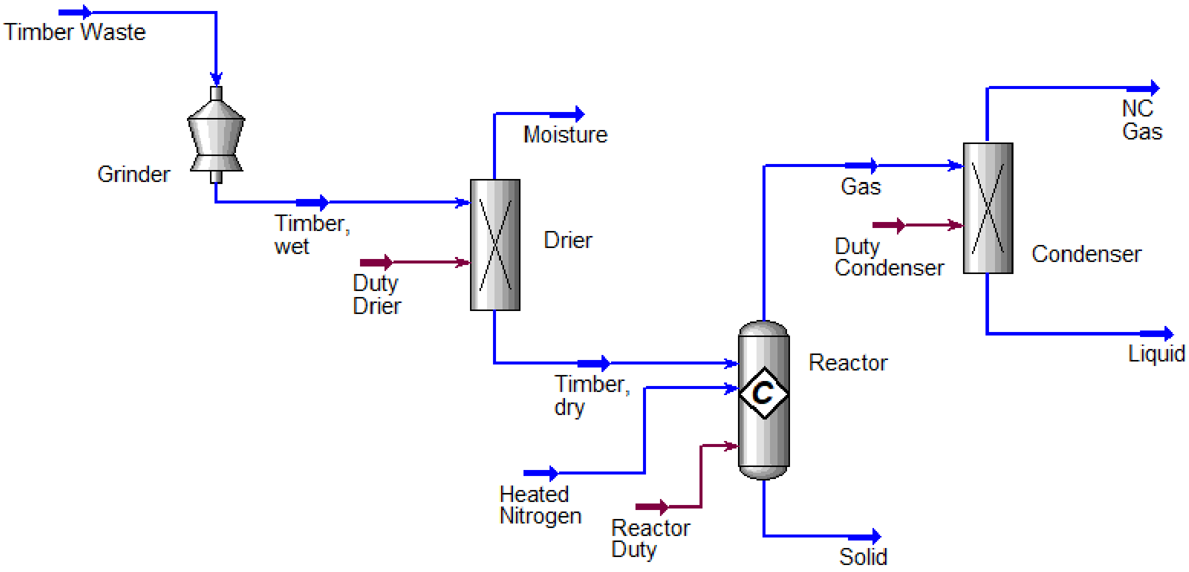

Figure 6.5: Block flow diagram of the industrial process units of pyrolysis of CCA-treated timber for recovery of arsenic compounds.

Detailed stream and energy balance tables are shown in Appendix I.

6.3.1 Feedstock

The feed is assumed to be weathered CCA-treated timber (*Pinus radiata*) which is contaminated with paint and fasteners. The timber composition is assumed to be the same as those presented in Chapter 3 based on the ultimate and proximate analyses. These results are reproduced as shown in Table 6.1 below.

Table 6.1: Results of the ultimate and proximate analysis taken from Table 3.3

Components (wt%)	*Method*	*As Received*	*Dry Basis*
Moisture	(LAD @105degC)	0.5	
Ash	(ISO 1171)	1.3	1.3
Volatile Matter	(ISO 562)	81.7	82.1
Fixed Carbon	(by difference)	16.5	16.6
Carbon	(ASTM D5373)	48.4	48.6
Hydrogen	(ASTM D5373)	5.98	6.01
Nitrogen	(ASTM D5373)	<0.01	<0.01
Oxygen	(by difference)	43.9	44.1

In the process model, the moisture content of the feedstock was set to 8 wt%. Generally, if the wood moisture content is less than 10%, the drying stage is no longer needed in the process. The preservative compounds in the feedstock of CCA-treated timber were included in their fixated form as $CrAsO_4$ and $CuCrO_4$. Additionally, the presence of some As_2O_5 was assumed, as per the findings from the analysis of weathered versus freshly treated timber in Chapters 3 and 4. The assumed feedstock mix was 80% weathered wood and 20% freshly treated wood. Based on this mix, the derived feed comprised 0.15 wt% and 0.18 wt% for $CrAsO_4$ and $CuCrO_4$, respectively, and 0.1 wt% for As_2O_5. The concentrations can be adjusted in the process model for different mixing ratios, if needed.

Contamination of 5 wt% is assumed, of which 4 wt% is metal fasteners, nails and such like; further, 1% contamination with paint or other wood products is assumed. These contaminants are considered in the mass flow calculations through the system.

In the model simulation, the mass flowrate of feedstock was assumed to be 1 tonne per hour and the plant is designed in line with a typical industrial scale plant [11]. For fast pyrolysis, the particle size of the waste wood will be required to be reduced to 1 – 2 mm. The grinding operation is not included in the plant model as it only consumes electricity; the focus is directed at pyrolysis.

6.3.2 Drier

The feedstock is assumed to have a moisture content of 8 wt%, which does not require further drying for industrial operation. For wood feedstock with higher moisture contents, drying would be required. The duty for such an operation would likely be met using the sensible heat contained in the hot off-gases from the pyrolysis reactor.

6.3.3 Pyrolysis Reactor

Collaborating the findings of Chapter 4 and 5 and Kim et al.'s work [1], an empirical model was devised. Feedstock inflows into the pyrolysis reactor are biomass and preheated nitrogen. Furthermore, it is assumed to be at atmospheric pressure and modelled as a conversion reactor. The yields of solid char, liquid oil and gas/vapours from the biomass pyrolysis are determined in accordance with Kim et al.'s findings using fast pyrolysis at a temperature of 500°C (Figure 6.3) [1].

Based on the above variables the conversion of uncontaminated CCA-biomass into pyrolysis products is considered to be:

$$100wt\%\ biomass \longrightarrow 23\ wt\%\ solid + 77\ wt\%\ vapours\ and\ gas \qquad (6.1)$$

Where the vapour and gas stream contain the condensable and non-condensable fractions. This stream is split into a liquid and non-condensable gas fraction through a condenser. This only entails a state change, so no further reactions were assumed to occur.

$$77wt\%\ \ vapours\ and\ gas \longrightarrow 43\ wt\%\ liquid + 34\ wt\%\ NCgas \tag{6.2}$$

Kim et al. [1] report a qualitative list of compounds present in the oil; however, the composition was reported as the GC-MS analysis area percentages. The issues and problematics of GC-MS analysis of pyrolysis oil have been mentioned in Section 4.2.3. Any literature review examining pyrolysis oil compositions shows significant variability in reported oil compositions based on analysis and pyrolysis methods, as well as feedstock choice. After closer examination of the influencing factors, it was ultimately chosen to work with the findings of Chapter 4 for the feedstock, char and gas composition and those reported by Kim et al. [1] for the liquid composition and the CCA disposition within the pyrolysis products, leading to the following assumptions:

- Water concentration in the oil is 27.3wt% (Chapter 4);
- As_2O_3 concentration in the oil is 0.06 wt%;
- The remainder of the oil was comprised of the key compounds listed by Kim et al. [1] in ratios representative of their areas on the GC-MS spectrum.

Compounds which appear in significant area percentages and were also available within the modelling software UniSim are shown in Table 6.2, and are included in the model. To establish the concentration of each compound, the compound's area relative to the total area of the selected representative compounds was calculated.

Kim et al. [1] did not report the produced gas composition, merely its CCA content. Therefore, the non-condensable gas stream was modelled based on the results in Table 4.2. The primary gas component was CO_2. The other low concentration species were CH_4, C_2H_4, C_2H_6 and As_4O_6, respectively, at weight-based contents of 1%, 0.5%, 0.5%, and 0.18%.

By establishing the desired gas and liquid product composition, the vaporous gas stream composition exiting the pyrolysis reactor can be determined. The percentages when divided into condensable and non-condensable gases are determined by the following equation:

$$\%\ of\ species\ in\ gas = \frac{\%\ of species\ in\ liquid \times 43 + \%\ of\ species\ in\ NC\ gas \times 34}{77} \tag{6.3}$$

The stream composition was modelled as displayed in Table 6.2 based on above calculations and assumptions.

Table 6.2: Derived stream compositions for liquid, non-condensable (NC) gas and the total gas stream from experimental findings of Kim et al. – all percentages on a mass basis of a N_2-free stream

		Gas	*Liquid*	*NC-Gas*
Carbon Dioxide	CO_2	43.2%	0%	97.82%
Methane	CH_4	0.44%	0%	1%
Ethane	C_2H_6	0.22%	0%	0.5%
Ethylene	C_2H_4	0.22%	0%	0.5%
Water	H_20	15.39%	27.56%	0%
Acetic Acid	$C_2H_4O_2$	13.57%	24.31%	0%
Levoglucosan	$C_6H_{10}O_5$	8.51%	15.23%	0%
Acetol	$C_3H_6O_2$	4.63%	8.30%	0%
2-Butanone	C_4H_8O	2.94%	5.27%	0%
1,2-Benzenediol	$C_6H_6O_2$	2.71%	4.86%	0%
Ethanol	C_2H_6O	2.46%	4.40%	0%
Methanol	CH_4O	1.28%	2.30%	0%
Fufural	$C_5H_4O_2$	1.18%	2.11%	0%
Phenol	C_6H_6O	1.13%	2.02%	0%
3-Methyl-phenol	C_7H_8O	0.75%	1.34%	0%
4-Methyl-phenol	C_7H_8O	0.69%	1.23%	0%
Ethylene Glycol	$C_2H_6O_2$	0.62%	1.11%	0%
Arsenic Trioxide	As_2O_3	0.034%	0.061%	0%
Tetraarsenic oxide	As_4O_6	0.079%	0%	0.18%
Total		**100%**	**100%**	**100%**

6.3.4 Condenser

The design of the gas stream condenser is based on an exit temperature of 25°C, and the required heat transfer duty determined by the UniSim software based on the gas/vapour flowrate, composition and the condenser inlet and outlet temperatures.

6.3.5 Basis of Design

To summarise, the key design parameters set for the proposed industry plant are:

- Fast pyrolysis at an operating temperature of 500°C and atmospheric pressure (1 atm).
- Mass flowrate of 1 tonne of CCA-treated timber waste per hour.
- Feedstock particle size 1-2mm.
- Feedstock composition as per ultimate and proximate analysis, and CCA content as per ICP-MS:
    - Moisture content of 8 wt%;
    - Carbon and hydrogen contents of 48.6 and 6.01 wt% on the dry basis, respectively;
    - Copper, chromium and arsenic contents of 0.26, 0.27 and 0.23 wt%, respectively, on the dry basis.
- Pyrolysis model is modified to fit the experimental results and derived product composition based on previous studies of Kim et al. [1], and the results were then used in the process model described in the following section.

6.4 Process Modelling and Equipment Sizing

6.4.1 Model Development of the Process in UniSim

The proposed process scheme was modelled using the UniSim (by Honeywell) process modelling software. The UniSim model was built up from the Basis of Design, the biomass's known specifications and from the product analysis described above. Once the pyrolysis reactor model was validated, the drier and condenser with their corresponding streams were included. The model required the use of UniSim's integrated fluid package Peng Robinson – as referred to by several other pyrolysis and gasification models found in literature [12, 13].

From Chapter 5 and Chapter 2 (literature review) of this thesis, it is known that $CrAsO_4$ and $CrCuO_4$ do not decompose at 500°C and thus were modelled as inert, remaining in the solid product (char). Similarly, fasteners and other extraneous materials in the wood waste feed were modelled as inert, forming part of the solid char product.

Furthermore, the following assumptions were set for the process model development:

- All operations were adiabatic: no heat loss was considered at the individual operation units at this conceptual design stage.
- Fasteners, $CrCuO_4$ and $CrAsO_4$ were hypothetical solids within the UniSim software.
- Paint was assumed to be acetone.

A stoichiometric reaction was set up to model biomass conversion into liquid and gaseous products with corresponding compositions as listed in Table 6.2.

Kim et al. [1] provided ultimate analysis results of the CCA-treated wood and pyrolysis char and pyrolysis product yields. The carbon, hydrogen and oxygen contents of the wood that was available to react were calculated on a molar basis. With known char yield and char composition (modelled as $C_{0.72}O_{0.28}H_{0.0019}$), the pyrolysis reaction of biomass to char was established; any remaining carbon, oxygen and hydrogen were then available to form the gas-vapour product. The desired gas-vapour composition as displayed in Table 6.2 was set-up in an Excel file, alongside carbon monoxide gas as the product of incomplete pyrolysis. A molar balance of the remaining carbon, hydrogen and oxygen in the biomass to gas-vapour product and CO was established, where Excel’s built-in Solver was used to minimise the mass balance error through allocating a fraction of the reactants to yield CO. Thereby the calculated data were used as input conditions within the UniSim model.

Once the dry, uncontaminated biomass decomposition was determined, As_2O_5 decomposition reactions were added. The final form of the reaction to describe the biomass decomposition is shown as Reaction (R6.1) below:

$$\begin{aligned}35.8\,C + 17.2\,H_2 + 12.0\,O_2 + 0.0025\,As_2O_5 \longrightarrow\ & 16.95\,Char + 7\,CO_2 + 0.20\,CH_4 \\ & + 0.05\,C_2H_6 + 0.05\,C_2H_4 + 0.38\,C_2H_6O + 6.04\,H_2O + \ 0.41\,C_3H_6O_2 \\ & + 0.19\ \ C_2H_6O_2 + 1.44\,C_2H_4O_2 + 0.24\,C_2H_6O_2 + \ 0.14\,C_5H_4O_2 \\ & + 0.23\,C_4H_8O + 0.04\,C_7H_8O + 0.07C_6H_6O + 0.04C_7H_8O + 0.30\,CH_4O \\ & + 0.38\,C_6H_{10}O_5 + 10.5\,CO + As_2O_3 + As_4O_6\end{aligned} \qquad \textit{(R6.1)}$$

6.4.2 Results from the Process Modelling for Key Unit Operations

This section outlines the unit operations of the process in more detail by describing the process streams and operating conditions associated with each unit. Pressure is atmospheric, with pyrolysis undertaken in an inert atmosphere.

Input Data of the Feed Stream

The composition of feed CCA-treated timber, *as received*, and the mass flowrates of all species in the feed wood are given in Table 6.3. The basis of the feedstock flow was 1000 kg·h^{-1} of dry, uncontaminated CCA biomass. The flow of individual species is based on the ultimate and proximate analysis (Table 3.3); however, the oxygen content was adjusted to accommodate the presence of CCA compounds. An additional 50 kg·h^{-1} of contaminants of fasteners and paint (acetone) was included in the feedstock stream. The moisture content was set to 8 wt% based on the overall weight of the contaminated CCA-treated timber biomass. This allows feed rate into the reactor to be 1000 kg hr^{-1} of dry, uncontaminated CCA-treated timber waste.

Table 6.3: Feed composition of CCA-treated biomass contaminated with fasteners and paint

	Composition, wt%	*Mass flow, kg·h^{-1}*
Carbon	42.6	486
Oxygen	38.2	437
Nitrogen	0.0088	0.1
H_2O	8.0	91.3
Hydrogen	5.3	60.1
Ash	1.1	13
Fasteners	3.5	40
$CrAsO_4$	0.13	1.5
$CuCrO_4$	0.15	1.8
As_2O_5	0.088	1.0
Acetone	0.88	10
Total	**100%**	**1142**

To reflect the findings of Chapter 4 and 5, and those reported by Kim et al. [1] the pyrolysis reactor was modelled on the basis of dry biomass. Therefore, the excess moisture of 8 wt% was removed through a drying operating at 105°C prior to pyrolysis within the UniSim model. However, it is reiterated that in an industrial setting, drying of feedstock with a moisture content less than 10% is not needed as it becomes economically infeasible.

Reactor Section

The modelled pyrolysis reactor schematic is shown in Figure 6.6 in which; the feed stream of dried, contaminated CCA-treated woody biomass is pyrolysed in a nitrogen environment at a known heating duty to produce a contaminated CCA-char stream and a gaseous/vapour product.

Findings from Chapter 5.2 confirm that the release of arsenic into the gaseous and liquid phases follows reaction pathways (*R.2.2 – 2.6*). The results from the equilibrium model as presented in Chapter 4 and those reported by Kim et al. [1] suggest that even with reduced residence time, arsenic in the oil should be present as As(III). Kim et al. [1] further reported that substantial quantities of chromium and copper were found in oil and gas products, which for the purpose of this study have not been considered. Chapter 5 explored some chromium decomposition and did not establish its gaseous release. Copper compounds were not considered as part of this study. The release of these compounds and the reaction mechanics ought to be established in future work.

A nitrogen flowrate of 3.5 L·min^{-1} was used throughout the lab-scale experiments for pyrolysing of approximately 25 g of CCA-treated timber particles (approximate residence time of 30 minutes). Similarly, Kim et al. [1] used a nitrogen flowrate of 10 L·min^{-1} for 150 g·h^{-1}. In the process modelling using UniSim software, a similar ratio of nitrogen to wood was chosen resulting in a nitrogen gas flow rate 2.3 m^{3}·h^{-1} at standard conditions. The nitrogen stream entering the reactor was at atmospheric pressure and preheated to 500°C. In an industrial setting such high N_2 to feedstock ratio would be economically unfeasible; hence, the recycle of the non-condensable gas stream has been proposed (page 162).

The heating duty required for the pyrolysis reactor to heat the feedstock and maintain a temperature of 500°C is calculated by UniSim software. The results calculated a 5,982 MJ·h^{-1} (1.67 MW) heat supply requirement for the pyrolysis conditions adopted.

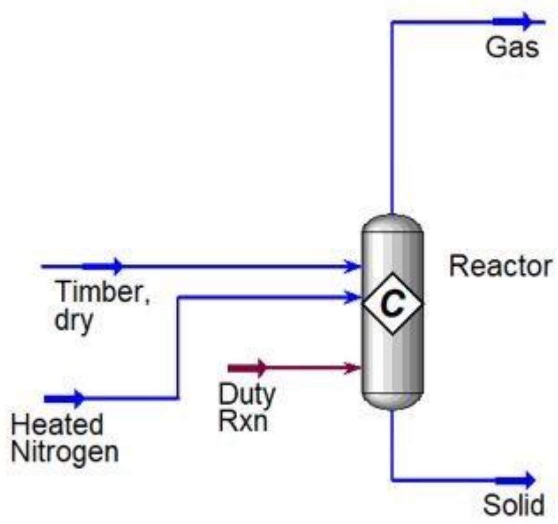

Figure 6.6: The pyrolysis reactor of the model with woody biomass and nitrogen entering the reactor, producing solid and vapour/gas products.

Pyrolysis conversion is described by the stoichiometric reaction (R6.1). The simulation results arrived at for both the composition and flow rates of reactants and products are shown in Table 6.4. A small fraction (less than 2%) of the carbon contained within the biomass did not convert and remained within the char.

Table 6.4: The model predicted product composition and mass flowrates into and out of the fast pyrolysis reactor.

	Wood, dry	*N_2*	*Char*	*Gas (N_2-free)*	*Gas + N_2*
Temperature, °C	500	500	500	500	500
Molar Flow, kgmole·h^{-1}	84.6	66.2	18	18.9	85
Mass Flow, kg·h^{-1}	1050	1855	293.9	756.1	2611
Enthalpy, MJ·h^{-1}	116	955	443	3,841	4,103
	Composition on weight basis				
Carbon	46.3%	0%	62.7%	0%	0%
Oxygen	42.6%	0%	17.3%	0%	0%
Nitrogen	0%	100%	0%	0%	71%
Hydrogen	5.72%	0%	1.9%	0%	0%
Ash	1.24%	0%	4.4%	0%	0%
Fasteners	3.81%	0%	13.6%	0%	0%
$CrAsO_4$	0.14%	0%	0.51%	0%	0%
$CuCrO_4$	0.17%	0%	0.61%	0%	0%
As_2O_5	0.10%	0%	0%	0%	0%
Acetone	0.95%	0%	0%	1%	0%
CO_2	0%	0%	0%	41%	12%
Methane	0%	0%	0%	0.42%	0.12%
Ethane	0%	0%	0%	0.21%	0.06%
Ethylene	0%	0%	0%	0.21%	0.06%
Water	0%	0%	0%	14%	4%
Acetic Acid	0%	0%	0%	11%	3%
Acetol	0%	0%	0%	4%	1%
Ethanol	0%	0%	0%	2.4%	0.7%
Methanol	0%	0%	0%	1.3%	0.4%
Furfural	0%	0%	0%	1.8%	0.5%
Phenol	0%	0%	0%	0.9%	0.3%
3-Methyl-phenol	0%	0%	0%	0.5%	0.1%
4-Methyl-phenol	0%	0%	0%	0.6%	0.2%
Ethylene Glycol	0%	0%	0%	2.0%	0.6%
As_2O_3	0%	0%	0%	0.1%	0.0%
As_4O_6	0%	0%	0%	0.028%	0.01%
2-Butanone	0%	0%	0%	2.2%	0.6%
Levoglucosan	0%	0%	0%	8.2%	2.4%
1,2-Benzenediol	0%	0%	0%	2.8%	0.8%
CO	0%	0%	0%	4.5%	1.3%
Total	100%	100%	100%	100%	100%

In this simulation the solid char composition - as given in Table 6.4 - is in its final form, and no further solid processing is considered in the model.

Condenser and Liquid Product

Following the pyrolysis reactor, the vapour product stream is condensed from 500°C to 25°C. The UniSim simulation predicts the condenser to require a cooling duty of -2,238 MJ·h^{-1} (0.36 MW). This could be potentially recovered in an integrated heating system. The flowrates and composition of the inlet gas/vapour stream and outlet streams are given in Table 6.5. In the table, the gas streams, both with and without nitrogen, are presented.

As the condenser outlet temperature was set to 25°C, most of the hydrocarbon present were condensed and removed with the liquid stream. Accordingly, the derived gas composition is high in CO_2.

Table 6.5: Flowrates and compositions of the condenser inlet and outlet streams, with gas stream given both with and without inert nitrogen gas

	Gas (N_2-free)	*Gas + N_2*	*NC Gas + N_2*	*NC Gas (N_2-free)*	*Liquid*
Temperature, °C	500	500	25	25	25
Molar Flow, kgmole·h^{-1}	18.9	85	75	8.8	10.1
Mass Flow, kg·h^{-1}	756.1	2,611	2203	348	408
Enthalpy, MJ·h^{-1}	3,841	4,103	2,886	1,930	3,455
	Composition on weight basis				
Carbon	0%	0%	0%	0%	0%
Oxygen	0%	0%	0%	0%	0%
Nitrogen	0.01%	71.0%	84.2%	0%	0%
Hydrogen	0.08%	0%	0%	0.2%	0%
Ash	0%	0%	0%	0%	0%
Fasteners	0%	0%	0%	0%	0%
$CrAsO_4$	0%	0%	0%	0%	0%
$CuCrO_4$	0%	0%	0%	0%	0%
As_2O_5	0%	0%	0%	0%	0%
Acetone	1.32%	0.4%	0%	0%	2.5%
CO_2	40.61%	11.8%	13.9%	88.2%	0%
Methane	0.42%	0.1%	0.1%	0.9%	0%
Ethane	0.21%	0.1%	0.1%	0.5%	0%
Ethylene	0.21%	0.1%	0.1%	0.5%	0%
Water	14.35%	4.2%	0.0%	0%	26.6%
Acetic Acid	11.38%	3.3%	0%	0%	21.1%
Acetol	4.05%	1.2%	0%	0%	7.5%

Ethanol	2.36%	0.7%	0%	0%	4.4%
Methanol	1.30%	0.4%	0%	0%	2.4%
Furfural	1.84%	0.5%	0%	0%	3.4%
Phenol	0.88%	0.3%	0%	0%	1.6%
3-Methyl-phenol	0.50%	0.1%	0%	0%	0.9%
4-Methyl-phenol	0.58%	0.2%	0%	0%	1.1%
Ethylene Glycol	1.97%	0.6%	0%	0%	3.6%
As_2O_3	0.09%	0.02%	0%	0%	0.2%
As_4O_6	0.028%	0.01%	0%	0%	0.1%
2-Butanone	2.22%	0.64%	0%	0%	4.13
Levoglucosan	8.24%	2.4%	0%	0%	15.3%
1,2-Benzenediol	2.81%	0.8%	0%	0%	5.2%
CO	4.51%	1.3%	1.5%	9.8%	0%
Total	100%	100%	100%	100%	100%

In an industrial process, the sensible heat of the non-condensable gas from the pyrolysis at 500°C could be recovered and used in the drier, eliminating the need for further heat requirement. Furthermore, CO_2 also creates an inert reaction environment for pyrolysis, allowing the non-condensable gas stream to be used as a sweep gas to replace nitrogen gas. In this model, this was not considered for the purpose of simplicity and to model experimental work. However, in future the model can be modified to accommodate recycles, which would further reduce the energy requirements through the extraction of heat from the gas.

The liquid stream cut point for downstream fractionation was set to 130°C, as this corresponds to the boiling point of LOSP. As the fractionation efficiency is unknown, its cut of arsenic in the bottom fraction was assumed to be perfect. However, some cross-contamination between light and heavy fractions can be expected in any industrial application. With the assumption of a clean cut, arsenic accumulates in the heavier fraction, whereas the light fraction is free of arsenic contamination. Arsenic in the heavier fraction is present as As(III) as per the findings of Chapter 4 and 5. The implications on product applicability will need to be established once the extent of imperfect separation and cross-contamination is known.

Furthermore, the light LOSP analogue fraction would require its water content to be removed, as the presence of water would be undesirable requiring any wood impregnated with it to be to be re-dried. Removal of the water could possibly be achieved through distillation or stepwise condensation, and the design of any such process would form part of future design work.

From the model simulation, the overheads stream produced 249 kg h^{-1} of target LOSP-grade product from the fractionation unit, whilst the heavier bottom fraction production rate was predicted to be 158 kg·h^{-1}. The composition of each stream is shown below in Table 6.6. The heat duty for heating and fractionating the liquid stream was calculated to be 444.3 MJ·h^{-1} (0.12 MW).

Table 6.6: Stream composition of liquid streams after fractioning at 130°C from pyrolysis of CCA-treated timber waste

	Liquid	*Overheads*	*Bottoms*
Temperature, °C	25	98	176
Molar Flow, kgmole·h^{-1}	10.08	8.55	1.53
Mass Flow, kg·h^{-1}	407.6	249.1	158.5
	Composition on mass basis		
Acetone	2.45%	4.02%	0%
Water	26.62%	43.56%	0%
Acetic Acid	21.10%	34.56%	0%
Acetol	7.52%	0%	19.3%
Ethanol	4.38%	7.17%	0%
Methanol	2.41%	3.94%	0%
Furfural	3.42%	0%	8.79%
Phenol	1.63%	0%	4.18%
3-Methyl-phenol	0.94%	0%	2.40%
4-Methyl-phenol	1.08%	0%	2.78%
Ethylene Glycol	3.65%	0%	9.39%
As_2O_3	0.16%	0%	0.41%
As_4O_6	0%	0%	0%
2-Butanone	4.13%	6.75%	0%
Levoglucosan	15.29%	0%	39.31%
1,2-Benzenediol	5.21%	0%	13.40%
Total	100%	100%	100%

6.5 Heating Duty for Key Operation Units

Table 6.7 summarises the mass throughputs and heat duties for each of the key operating units, including the drier, pyrolysis reactor, condenser, and fractionation unit. To allow a comparison to be made against experimental results of this study and those reported in literature, a drying operation was modelled to remove excess moisture. Therefore, the reported yields and composition are on a dry basis. However, normally wood contains moisture and under practical pyrolysis conditions, this would lead to an increase in water content in the oil.

Table 6.7: Mass flow rates and heating duties for the key operation units

Equipment	*Throughput, kg·h-1*	*Duty, MJ·h-1 [MW]*	*Possible Supply Source*
Drier	1,141	325 [0.09]	Non-condensbale gas stream
Reactor	2,905	5,974 [1.66]	Oil bottoms Pyrolysis gases, other fuels*
Condenser	2,611	(2,238) [0.62]	Water / Air
Fractionation	408	444 [0.12]	Waste Heat

**conventionally, industrial pyrolysis plants are heated using recovered tars (or bottoms) and augmented by pyrolysis gases or other fuels such as landfill gas, LPG or diesel. The preferred energy source is a matter of engineering optimisation. The combustion of tar or gas from pyrolysis for heat supply will require clean up, especially in regards to arsenic, before discharge of the combustion gases to the environment.*

This chapter provides a first insight into a preliminary process scheme for the alternative waste management strategy of processing CCA-treated waste through pyrolysis. As such, the scope of this work does not entail detailed engineering design of process, heat integration and pinch analysis to utilise available waste heat for the thermal processing of the pyrolysis unit or drier. As the proposed technology is designed to be used for waste management, this facility will likely operate as part of a landfill facility. In this case, landfill gas (LFG) can be used as an additional fuel source for this proposed system. It is reported that one million tonnes of landfill waste emit approximately 12,200 m^3 of LFG daily [14]. This is well within the scope of landfills in New Zealand, for example in Auckland, which has an estimated annual waste disposal of 2 million tonnes [15]. LFG consists of ~50 vol% CO_2 and ~50 vol% methane, with small amounts of non-methane organic compounds [16]. The heating value of landfill gas is sufficiently high for use as a fuel in combustion processes – with its calorific value of approximately 13 $MJ \cdot Nm^{-3}$ [17].

Based on this heating value, an LFG demand of approximately 518 $Nm^3 \cdot h^{-1}$ of LFG would be required to meet the total heating duty of the waste timber processing plant. This equates to 6,225 Nm^3 a day, assuming 24 hours a day operation and no energy loss to the environment. This quantity is well within the amounts of LGF produced from a 1 million tonne of landfill per year. However, actual demand will likely be considerably less with appropriate and effective implementation of heat integration within the plant.

A substantial fraction of the cooling duty for condensation (2,238 $MJ \cdot h^{-1}$ (0.62 MW)) could be used to preheat the inert gas prior to it entering the pyrolysis reactor. However, if no heat recovery is considered in the plant, the required cooling water flowrate would be at least 1,123 $m^3 \cdot h^{-1}$.

6.6 Requirements to Achieve Commercial Readiness for Deployment

6.6.1 Technical Readiness and Efficacy

Biomass pyrolysis is a well-researched and established technology, its use as a means of processing CCA-contaminated woody biomass from disposal is nonetheless very much in its infancy. A complete proof-of-concept analysis involving further testing of fast pyrolysis and its products, as well as downstream treatments is required in future ventures to establish its practicality and economic viability.

In this study, a commercial plant is assumed to have a capacity of 1 tonne·h^{-1} of CCA-treated woody biomass (without contamination) which yields 409 kg·h^{-1} of liquid bio-oil, of which 249 kg·h^{-1} is recovered as an LOSP analogue product. Additionally, 254 kg·h^{-1} of char is recovered, containing 13 kg·h^{-1} of ash, 1.5 kg·h^{-1} $CrAsO_4$, and 1.8 kg·h^{-1} of $CuCrO_4$.

As discussed in Section 2.4.2 and at the beginning of this chapter, the char can be applied to several processes or the metal(oid)s can be recovered. There is considerable interest from industry in using the produced char in boilers, provided arsenic limits do not exceed environmental regulations. Golden Bay Cement has successfully trialled and augmented their feed stream with CCA-treated wood waste, while Christchurch City Council's Biosolids Drying Plant trials were unsuccessful [18]. Arsenic emissions and CCA's corrosive nature remain an intractable problem, but some blends of treated and untreated chars may be a future possibility, which has been discussed in more detail in Section 2.2.7.

The non-condensable gases can either be used as a sweep gas replacing nitrogen or combusted with the flue gas as a drying medium for woody biomass. Gas cleaning technologies are available to remove any arsenic emissions to the atmosphere, as discussed in Section2.3.4.

The concept examined here is an initial step towards a comprehensive waste management strategy. Although it is important to state, that the best means to address the reuse of the produced light oil has yet to be proven. Two routes suggested for application of the produced bio-oil as a timber preservative are: firstly, through direct application as an oil preservative or secondly, as an LOSP analogue. As already described in the literature review, pyrolysis liquid from woody biomass shows beneficial antifungal effects and modelling of the bio-oil shows that a light oil fraction can be fractionated from this stream, having similar thermochemical properties to LOSP. To support further development of these concepts, more detailed research is required.

Section 2.4.1 discusses the greater fungal inhibition achieved in bio-oils, derived from lignin-rich fractions. Unfortunately, it is precisely this fraction's decomposition that could be inhibited, as shown by the experimental results presented in Chapter 4 (Section 4.3.1). Nevertheless, the presence of arsenic within a pyrolysis-derived bio-oil could significantly improve its capability to protect against fungal and bacterial decay.

As(III) is more mobile and toxic than As(V) and to prevent any arsenic from leaching out of the bio-oil into the environment may require oxidisation alongside a fixating agent. Alternatively, the bio-oil can be fractionated into a lighter fraction and into a heavier residual fraction. After fractionation, the lighter fraction (the LOSP analogue) is free of any arsenic compounds and thus available for blending with existing LOSP products. Whilst modelling predicts the arsenic compounds to be all retained in the heavy fraction, there may well be some carryover of arsenic compounds into the lighter fraction. The fractionation process and blending of the light fraction with LOSP will need to be further examined to ensure a suitable process scheme.

The thermochemical properties of the modelled light and heavy fractions are compared to those of LOSP as shown in Table 6.8. The parameters described include viscosity, density, and mean average boiling point for the lighter and heavier fractions at normal temperature and pressure.

Table 6.8: Estimated properties of liquid fraction from the pyrolysis of CCA-treated wood at NTP (overheads and bottoms split using a boiling point cut at 130°C)

	Flowrate, $kg \cdot h^{-1}$	*Viscosity, cP*	*Density, $kg \cdot m^{-3}$*
LOSP	-	0.74-1.65	763
Overheads (model estimates)	249	1.676	979.9
Bottoms (model estimates)	159	5.079	1192

From Table 6.8, it can be seen that the overhead product has a comparable viscosity to LOSP; however, density is considerably higher. As the overhead's stream still contains 43 wt% water, these properties are adjusted to be without water, and become 0.92 cP for viscosity and 944 $kg \cdot m^{-3}$ for density. Whilst viscosity is reduced, it remains within the reported range of viscosities for LOSP.

The similarities in viscosity are promising for wood treatment blending. The viscosity values of the light fraction are comparable to those reported in literature [19, 20], see Section 4.2.3. It could be anticipated that the actual density of oil and fractionated oil is higher than those determined by the model. The fixation of chromium to free hydroxyls within lignin and carbohydrate structures inhibiting the breakdown of compounds into smaller ones, leading to an increase in the product's density and viscosity.

As mentioned, the heavy fraction may be used as a fuel source to supply the heating requirement of the pyrolysis reactor. However, as arsenic is present in this fraction is may well be better suited for industrial combustion where there is existing treatment for arsenic removal, e.g. in the cement manufacture. Although the proposed process would only allow for the recovery of the heating value of the heavy fraction, all in all, the process enables the recovery of the CCA compounds from the char alongside the production of an LOSP analogue. There here proposed preliminary engineering design process can be optimised, improved alongside more detailed engineering design, as part of that, the application of the heavy oil deserves further study in due course.

6.6.2 Regulatory Requirements in Respect of the Proposed Process Scheme

Approval Process for Operating Plant

Under the New Zealand Resource Management Act 1991 (RMA), a resource consent will be required to build and operate any commercial facility for the pyrolysis of CCA-treated timbers. This consent will consider the likely environmental, social and economic impacts of the operation. In addition to the resource consent, other approvals in respect to land use, water supply, waste, disposal, transport, health and safety will also be required [21, 22]. Because of the nature of the pyrolysis process and the hazardous chemicals being processed, it can be anticipated that any resource consent for a new facility will attract considerable public interest. In addition, because this will be a first-of-a-kind plant, there is likely to be a heightened concern amongst the general public. This will be an essential consideration for the realisation of any future plant. These concerns fall well outside the realm of this thesis, but are noted here as a matter of record.

A particular area of concern will be the arsenic concentration in any gases or other discharges released through pyrolysis. As previously discussed, there are many options available to mitigate these effects. In a new plant explicitly designed for CCA-treated waste, flue gas cleaning to reduce the arsenic concentration to safe limits is likely to be readily achieved.

Approval Process for Distribution and Use of the Products

The Hazardous Substances and New Organisms Act 1996 (HSNO) requirements will need to be carefully reviewed as a step towards commercial readiness. At this current stage of investigation, testing of a product such as pyrolysis oil for the purpose of research and development, may be applied for under Section 30(ba) of the HSNO. However, the requirements for manufacture, distribution and use of such a product needs to meet the far more onerous requirements of Sections 31 and 32 [23].

Again, this has not been considered here, but it is acknowledged that any new preservative treatment using bio-oil (or a derivative product) will require extensive testing and a regulatory approval process. This is seen as a significant challenge to the technology implementation. As an example, the New Zealand Environmental Protection Authority (EPA) declined an application regarding the import or manufacture of a "creosote-containing substance" for use as a timber preservative in November 2020. In EPA's press release, the intended purpose of the creosote for use in timber treatment trials was seen as presenting an unacceptable risk of exposure to the public, environment and non-targeted animals. The application was declined as containment requirements in respect of the perceived harm were not met [24].

6.6.3 Environmental Life Cycle

A full life cycle analysis has not been completed for the proposed plant; however, the following section reflects on the recycling and recovery methods proposed and sets these into perspective with other waste management methods. Research by Helsen and Van den Bulck [25] discussed the recycling of CCA-treated wood wastes into wood composites and declared it to be simply a deferral of the problem with the ongoing risk of CCA preservatives leaching remaining. This is supported by research by Jones et al. [26] who calculated that wood composite products could at most include 0.03 wt% of recycled CCA-treated wood so that the U.S. EPA standards could still be met.

Pyrolysis opens up the opportunity of recovering the preservatives from CCA-treated timber wastes; and, thereby, diverting the waste away from landfills. Of overarching interest for New Zealand would be moving away from CCA-treatments – a topic researched within the University of Canterbury's Forestry department [27] – which, if acceptable to the public and economic, could create a long term solution. Nonetheless, a waste management scheme for existing CCA-treated wood would still be required. Of utmost importance is that any devised waste management scheme acts to limit the release of CCA-compounds into the environment, either through leaching or air emissions, both during processing and in its subsequent product form.

The following paragraphs discuss the potential benefits in respect of recycling and recovery that might be achieved through the proposed pyrolysis treatment approach. These findings are then compared to commonly deployed waste management methods within New Zealand.

From the proposed plant, 38.8 wt% of dry, contaminated CCA-treated wood waste is recoverable as bio-oil, of which 62.3 wt% can be fractionated to an LOSP analogue. In addition, 27.9 wt% of the waste timber is converted to char containing recoverable preservative metal(oid)s. The recycling options for CCA compounds and energy recovery are visualised in Figure 6.7, where detailed mass and energy flows are shown in Table 6.5 and Table 6.6, with further detail in Appendix I. It is suggested that such an approach offers an underpinning proposition for continued use of *Pinus radiata* in New Zealand and creates a robust value proposition for the wood treatment industry and continued use of CCA-treated timber.

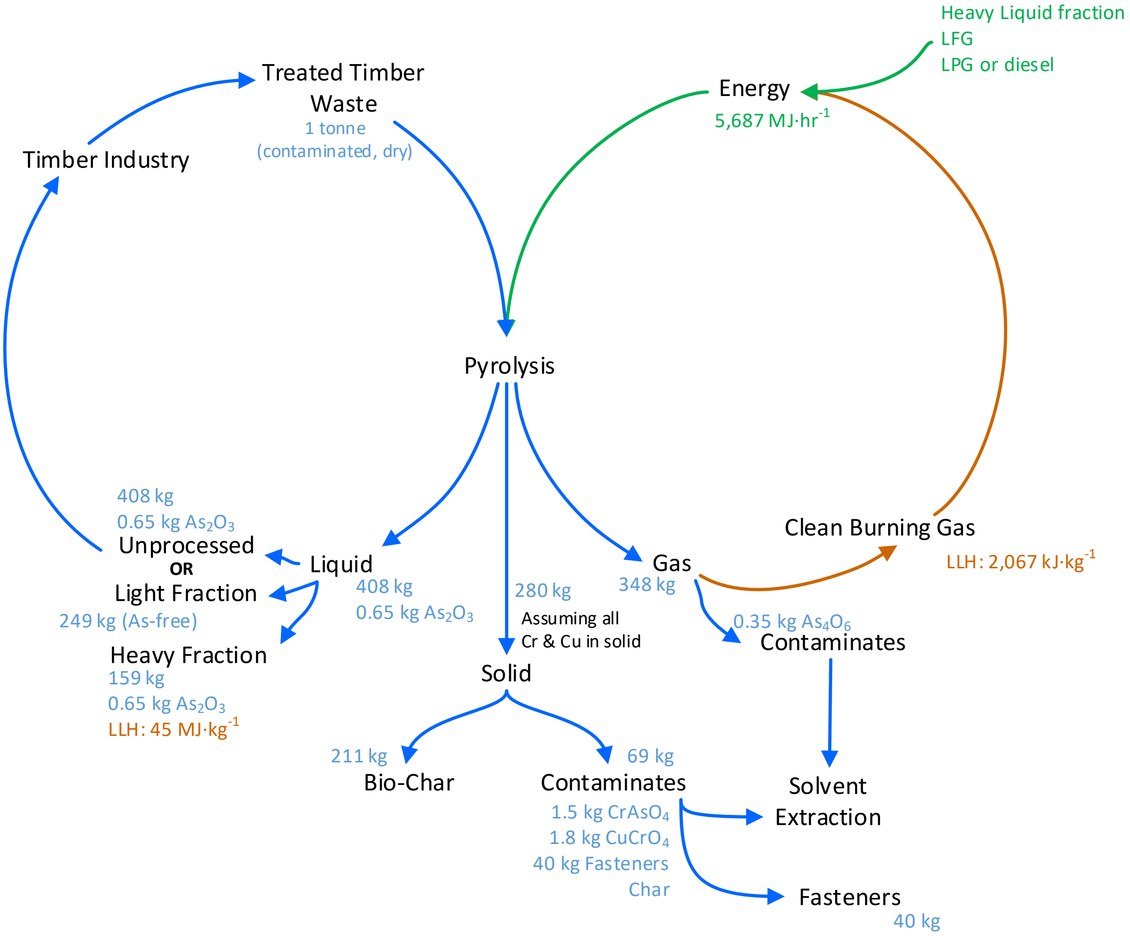

Figure 6.7: Proposed circularity of the pyrolysis liquid product within the wood treatment industry (left circle), alongside possible CCA recovery from the solid product (centre stream) and the recycle of the pyrolysis gas's heating value (right circle)

Figure 6.7 above presents the proposed recycling and recovery scheme – bringing together the findings of this thesis and results from the literature for processing CCA-treated wood waste and preservative recovery with particular attention on arsenic. The CCA compounds can be separated from the char using bead grinding methods, thus producing an uncontaminated char product and a contaminated CCA-rich fraction, which would be further processed to recover the metal(oid)s. Similar leaching and solvent extraction processes to those already researched for CCA-treated wood could be deployed (Section 2.2.4). It can be predicted that overall, less solvent would be required to process CCA-char as the metal(oid) concentration in the char is higher than in the unprocessed CCA-treated wood (see Figure 6.3).

Alternatively, the solid would be processed in ways similar to those deployed in the chromium and copper industry. Through such an approach, it is likely that the arsenic would be volatilised and the gaseous species generated could then be treated similarly to that of the non-condensable gas stream as visualised by the right circle in Figure 6.7.

Gas cleaning will be required to meet air emissions standards, as already stated in Section 2.4.3. Reduction in toxic emissions could be achieved by sorbent addition into the reactor, however, the implications for the recovery of the metal(oid)s from the char and sorbent are unknown. Alternatively, the non-condensable gas can be treated following the same methods as for flue gas treatment which are currently deployed in industrial facilities such as baghouses, electrostatic precipitators, wet scrubbers and multi-cyclones (see Section 2.4.3). With established processes to mitigate arsenic emissions the gas clean-up can be considered to be technologically available. A process engineering assessment will need to be undertaken to find the most suitable technology for any proposed plant.

The produced pyrolysis liquid could be used as an oil based preservative, or fractionated to an LOSP analogue and a heavy oil. An LOSP analogue product could be anticipated to be H1- or H3-capable, as per the introduced hazard classes in Table 2.1; depending on active preservative and retention levels achieved within the timber [28]. Approximately 12 to 15 m^2 of new timber can be treated with 1 L of LOSP [29], indicating that with the recovered quantity of LOSP from 1 tonne of timber waste about 3,815 m^2 of timber can be treated.

The arsenic within the heavy oil fraction could be leached into water, and subsequently removed using zero-valent iron, as described early in Section 2.4.2.

Alternatively, the arsenic contaminated heavier bottoms fraction could be used as a fuel source for the pyrolysis unit, or potentially other industrial processes. As this product is a creosote-like product, any barrier already set by the EPA (see previous Section 6.6.2), needs to carefully be considered and overcome. This arsenic is in the form of As(III), therefore treatment prior to its direct use as a preservative, fuel or other application may be required to oxidise the arsenic to As(V) using methods described in Section 2.4.2 and 6.2.1. Due to As_2O_3's lower volatilisation temperature, any arsenic present as As(III) is expected to be released as a gas. Adequate gas cleaning and flue gas treatment (meeting local environmental conditions) may lead to prior treatment not being required. Although widely used in the past, today, creosote is no longer in widespread use. Therefore, its use as fuel source may well be the bottom's fraction best use, which would not allow for the recovery and reuse of this product stream, yet enable that of the char and the light liquid fraction. Nevertheless, this enables the recovery of the heating value of the heavy oil fraction.

The counterfactual to the above situation is continued disposal of the waste material by landfill. A comparison of the likely environmental impacts of processing CCA-treated wood waste via pyrolysis against landfilling is then presented in Table 6.9. This analysis shows that through implementation of a pyrolysis-based waste management strategy, arsenic leakage into the environment can be significantly reduced. Furthermore, a by-product CCA-free Char, as well as the production of an LOSP analogue preservative oil and other potential recovery options open up new economic opportunities. The proposed pathway allows for the recovery of the arsenic and other preservative metals, reducing the requirement for virgin CCA-preservative, thereby reducing the persistence of the preservative in the immediate environment. In the long term, a cradle-to-cradle product pathway for CCA could become achievable, either within the wood treatment industry through creating a circular economy in respect of CCA use, or deployed as a feedstock material in a different industry.

Table 6.9: Analysis of waste management options for CCA-treated wood waste: comparison between landfilling and pyrolysis processing methods for end-of-life CCA-treated timber.

The CCA-content in waste will vary with age, treatment class, and its in-service application. For landfill calculations the same CCA content of 0.15 wt% and 0.18 wt% for $CrAsO_4$ and $CuCrO_4$ is assumed, respectively, and 0.1 wt% for As_2O_5

Landfill	*Pyrolysis*
Currently, CCA-treated timber waste is destined to Class 2 landfills utilising engineered liners. As such, 109 kt·a^{-1} of CCA-treated waste enters the landfill environment containing: $CrAsO_4$: 164 t $CuCrO_4$: 196 t As_2O_5: 109 t Equivalent to 89.7 t of Cr, 54.9 t of Cu and 194.0 t of As on a metals basis. CCA waste in landfills produce ~55,900 m^3 of leachate annually [d]. Leachate composition data of a Class 2 landfill suggests, that 1,006 kg As, 1.51 kg Cr and 0.06 kg Cu are released as leachate annually. Liner leakages of 10 – 5000 L·(ha·d)$^{-1}$ can be anticipated in a Class 2 landfill. If the liner area is known, the CCA content going directly into environment can be calculated. Although leaching rates decrease over time, CCA wastes accumulating in the landfills continues to leach – see section 2.1.3.	Assuming all CCA-treated timber (109 kt·a^{-1}) is diverted to pyrolysis, the following streams are produced annually: CCA-free char: 23 kt CCA-free LOSP: 25 kt NC gas: 36 kt (2,067 kJ·kg^{-1}, 28 t As) to gas cleaning, then used for its energy content as discussed in Section 2.4.3. Heavy oil: 16.5 kt (containing 50 t As) to recycling and recovery, as discussed in Section 6.2 and 6.6.3. If used as a fuel sources, the exhaust gas must be cleaned prior to its release, comparably to the handing the NC gas stream. Contaminates from char, heavy oil combustion and NC gas: 7.7 kt (containing 114 t As, 101 t Cr and 69 t Cu). If no suitable recovery/recycling application can be determined, the contaminates would produce ~6,130 m^3 of leachate annually [d]. As such, leachate composition data of a Class 2 landfill suggests, that 110 kg As, 0.17 kg Cr and 0.0061 kg Cu would be released as leachate annually.
Occupies large volumes in landfills.	This work proposed possible pathways for arsenic recovery from all pyrolysis products. Through recovery and treatment, Cr, Cu and As could be recycled back into the wood treatment industry or alternatively, into other industries. Neverthess, future work should establish the leach rate of CCA from all pyrolysis productes, so as to mitigate the release of CCA into the environment.
No recycling possibility →New virgin CCA preservative needed.	Possibility of recycling CCA back into a wood preservative product → Less virgin CCA preservative needed.
Linear product life: from *cradle-to-grave*. Increased persistence of CCA in environment.	Possibility for partial or fully circular recycle with in the wood treatment industry. Possibility of recover and application in other industry exist. →*cradle-to-cradle* product pathway

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[d] *Leachate generation is difficult to predict, assumed is 0.2 m^3 per 1 m^3 of waste in a Class 2 landfill [36]*

Currently, there is no product stewardship scheme in place in New Zealand for treated timber. Although in future, this could become a reality; integrated as a levy in addition to the price of the timber to offset the cost of recycling and any perceived environmental harm. However, with the recovery of the metal(oid)s from the char, combined with the application of this char and/or bio-oil as well as heat integration through use of the non-condensable gases, no levy may be required.

In summary, the proposed recycling scheme offers an end-of-life solution for CCA-treated timber with the potential for reduced environmental harm and economic benefit. A full life cycle analysis needs to be carried out to confirm this assumption and would form part of any future work going forward. Additionally, the potential of recycling the bio-oil back into the wood industry shows promise in creating a full recycle with regards to the use of CCA. Moreover, metal(oid)s recovered from the char may be recycled back into a preservative product – if available in a suitable oxidation state.

6.6.4 Development Pathway

The analysis undertaken in this chapter confirms the technical viability of the proposed waste recovery concept scheme. Nonetheless, the proposed scheme still requires experimental and engineering validation as part of a wider proof-of-concept and engineering approval process. In this regard, the key aspects requiring validation are:

- Reactor selection to achieve the desired fast and continuous pyrolysis conditions necessary for a high yield of arsenic-rich bio-oil,
- Preservative performance of the LOSP analogue and its applicability as a timber preservative in industrial use,
- The application of the heavy residual bio-oil fraction as a potential fuel source to supply the heat requirements of pyrolysis,
- Preferred gas cleaning approach for arsenic removal at the small scale typical of the proposed pyrolysis plant,
- Alternative use for the metal(oid) containing char, or other methods to economically separate them from char,
- Life cycle analysis to confirm and quantify the reduction in environmental harm,
- Regulatory requirements, in particular in regard to approvals for use, and health and safety, need to be fully established

In summary, the concept is deemed worthy of further investigation and development.

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7 Conclusions and Outlook

This concluding chapter summarises the key findings related to the research aims and objectives of this thesis and discusses the learnings from the work, their implications and limitations. This leads to a brief discussion of future research opportunities and an outlook regarding the application of pyrolysis as a means of resolving the environmental harm inherent to current disposal methods of CCA-treated timber waste.

7.1 Conclusions

Chromated copper arsenate (CCA) is a wood preservative commonly used for softwood treatment that inhibits its natural decomposition due to weathering and decay caused by fungi, insects and bacteria. To this date, CCA is extensively used within New Zealand as the prevalent treatment for *Pinus radiata* timber.

However, the disposal of the CCA-treated timber waste after its service life has proven problematic due to the toxic nature of the preservative retained in the wood waste. The current practice for its disposal is landfilling; however, leaching of the CCA compounds leads to the requirement of leachate collection systems and subsequent treatment. Additional concerns are the quantity of CCA-treated wood waste, its bulky nature and the availability of future landfill space. Furthermore, with the continued production and use of CCA-treated timber and its linear *cradle-to-grave* product pathway, there continues to be an ongoing requirement for the use of virgin CCA preservative, ultimately allowing more of this preservative to enter and negatively impact the environment. An alternative and sustainable disposal strategy for recovery, reuse and/or recycling of the wood waste and the preservative chemicals is needed.

From the literature review undertaken in this study, pyrolysis was deemed to be the most promising and applicable processing technology for CCA-treated timber wastes within New Zealand. Compared to other end-of-life management schemes, a pyrolysis-based waste management scheme has relatively low capital and operating costs and is an already established technology for untreated waste timber. Furthermore, compared to other thermodynamic conversion processes, such as gasification and incineration, pyrolysis produces less gaseous emissions.

This research project set out to examine pyrolysis as a means of diverting CCA-treated timber waste away from landfills. This entailed an experimental investigation and mathematical modelling of CCA-treated timber waste pyrolysis, as well as forefront work examining the thermodynamic equilibrium of arsenic release during the pyrolysis process. Arsenic is of particular interest, as it is the most volatile and toxic of the three preservative compounds. Through pyrolysis arsenic can be recovered in the liquid product fraction. The reuse of the arsenic-containing bio-oil fraction could open up opportunities for industrial applications that as yet have not been explored. The findings of the research and modelling work undertaken have been conceptualised into an industrial process scheme to allow further use of the bio-oil product to be explored. The recovery and re-use of the preservative, and the ability to utilise the wood waste's energy value are important economic and environmental considerations. A successful realisation of the proposed scheme would do much to support a circular economy for use of arsenic (and the other associated metals) within the wood treatment industry.

The experimental work has shown that the presence of CCA in wood reduces the decomposition temperature in comparison with untreated wood during the pyrolysis process, confirming that the CCA compounds in wood have a catalytic effect on biomass decomposition. Furthermore, the pyrolysis of CCA-treated timber has a higher char yield and a lower oil yield than that of untreated wood. The elevated char yields are reflective of CCA-treated wood's higher ash content. In addition, the presence of CCA compounds promotes secondary cracking leading to higher gas yields at the expense of the liquid yield. The optimum pyrolysis temperature that maximises the total arsenic recovery in the pyrolysis liquid product is 475°C, achieving in this study a liquid yield of 28.9 wt% containing 605 ppm arsenic - 6.7 wt% of the original arsenic content. With a further temperature increase, the liquid yield and the arsenic concentration decreases whilst the gaseous product yield increases.

Arsenic in the produced bio-oil is present as As(III) indicating that the reducing environment of pyrolysis converted As(V) to As(III) at temperatures lower than when in an inert environment.

Literature states that temperature is the key operating parameter that influences arsenic release. However, comparison of this study's findings to those reported in the literature shows that higher liquid yields and arsenic recoveries can be achieved using fast pyrolysis at a similar pyrolysis temperature. This indicates that fast heating rates, short residence time and rapid quenching enhance the liquid yield by hindering the volatilisation of liquid As_2O_3 to gaseous As_4O_6.

It is thus concluded that temperature is the key parameter for the onset of the arsenic release; however, the extent of arsenic release is influenced by heating rate and residence time. Therefore, fast pyrolysis is recommended for practical processing of the CCA-treated timber waste for recovery, reuse and/or recycling of the wood and preservatives.

Using the approach of minimising Gibb's free energy, a thermodynamic equilibrium model was developed to understand the transformation and release mechanisms of arsenic compounds during pyrolysis. The equilibrium model can be used to investigate arsenic release and the effect of temperature on the decomposition of the CCA compounds. The novel work allows for the equilibrium species of arsenic decomposition to be determined independent of proposed reaction pathways. Understanding of the equilibrium species aids in the establishment of the arsenic species and oxidation states present in the pyrolysis products.

The significant decomposition (>1%) of $CrAsO_{4(s)}$ begins at temperatures above 734°C, which is higher than normal pyrolysis conditions and thus, this compound is likely to remain in the solid phase (char) during pyrolysis. Products of its decomposition are $O_{2(g)}$, $As_2O_{5(s)}$ as an intermediate, $As_2O_{3(l)}$ as the product of As_2O_5 decomposition, $As_4O_{6(g)}$, $Cr_2O_{3(s)}$ and $CrO_{2(s)}$.

The decomposition of $As_2O_{5(s)}$, as it is present in freshly treated timber, was modelled, and the decomposition onset was found to be at 336°C. Decomposition products are $O_{2\,(g)}$, $As_2O_{3\,(l)}$ and $As_4O_{6(g)}$. A peak in $As_2O_{3\,(l)}$ yield was recorded at 423°C, after which its yield decreased, concurring with the onset of $As_4O_{6\,(g)}$ release. $As_2O_{3\,(l)}$ (As(III)) is present in its liquid form and most likely also present within the liquid product of pyrolysis.

The thermodynamic model gave credence to the reaction pathways suggested in literature. However, experimental yields were twice as high as those determined by the model, with literature data from fast pyrolysis being twice that again. This underlines the conclusion drawn from the experimental findings that residence time and heating rate play an integral part in determining the extent of arsenic release.

Based on the findings of this study and previous studies reported in the literature, a conceptual waste management scheme for CCA-treated wood waste was developed alongside a preliminary process model to enable conceptual engineering design and to determine mass and energy flows. The adopted scheme was based on continuous fast pyrolysis for the pyrolysis conversion, with the char and bio-oil products further treated and processed to recover the preservative chemicals. The result is a novel end-of-life solution for CCA-treated timber waste for the replacement of current disposal methods.

Application and treatment methods for the various pyrolysis products are suggested that would allow for the CCA to be recycled back into the wood treatment industry, or alternatively, other industries. If future research confirms the suitability of the products for recycle and re-use, a circular economy for the preservative chemical is enabled. The realisation of a partial or complete recycle is positive, as this reduces the usage requirements for virgin chromium, copper and arsenic compounds, thus reducing their presence in the immediate environment and breaking the current linear product pathway of *cradle-to-grave*.

The proposed waste management scheme uses pyrolysis as a means of addressing the growing quantities of CCA-treated timber waste entering landfills. This research is a first step towards a proof-of-concept and indicates that pyrolysis shows promising potential for the recovery of CCA compounds and subsequently the creation of a circular economy. The scheme proposed diverts the toxic waste away from landfills and through recycling and re-use reduces the need for further virgin CCA preservative.

7.2 Outlook and Future Work

Pyrolysis is a well-established technology commercialised to process various types of biomass, including that of woody biomass. However, uncertainties remain about using CCA-treated timber as a feedstock and the application of its pyrolysis products. Adequate gas cleaning and separation of the preservatives' chemicals from the char needs to be explored on an industrial scale. However, immediate work should focus on optimising the design of a fast pyrolysis system to maximise bio-oil yield and total arsenic recovery. The bio-oil suitability as a preservative requires further validation. Two pathways are suggested. Firstly, the applicability of the crude bio-oil directly as a preservative and, secondly, to fractionate the oil to produce a light fraction suitable for industrial use as an LOSP analogue. Both routes deserve further exploration. If the second proves to be effective, the application of the arsenic-contaminated heavy fraction as an energy source for pyrolysis needs to be established. To be effective, and to meet regulatory requirements, treatment of the heavy fraction may be necessary.

It is suggested that if the derived pyrolysis bio-oil can be successfully utilised as a wood preservative, increasing the arsenic content in the oil could be further explored as it would reduce the need for its recovery from the gas and solid products. The produced bio-oil may also be used as a gas scrubbing liquid to capture further arsenic from the off-gas. Alternatively, a second pyrolysis of the char at a high temperature may release further arsenic. These are all opportunities worth pursuing.

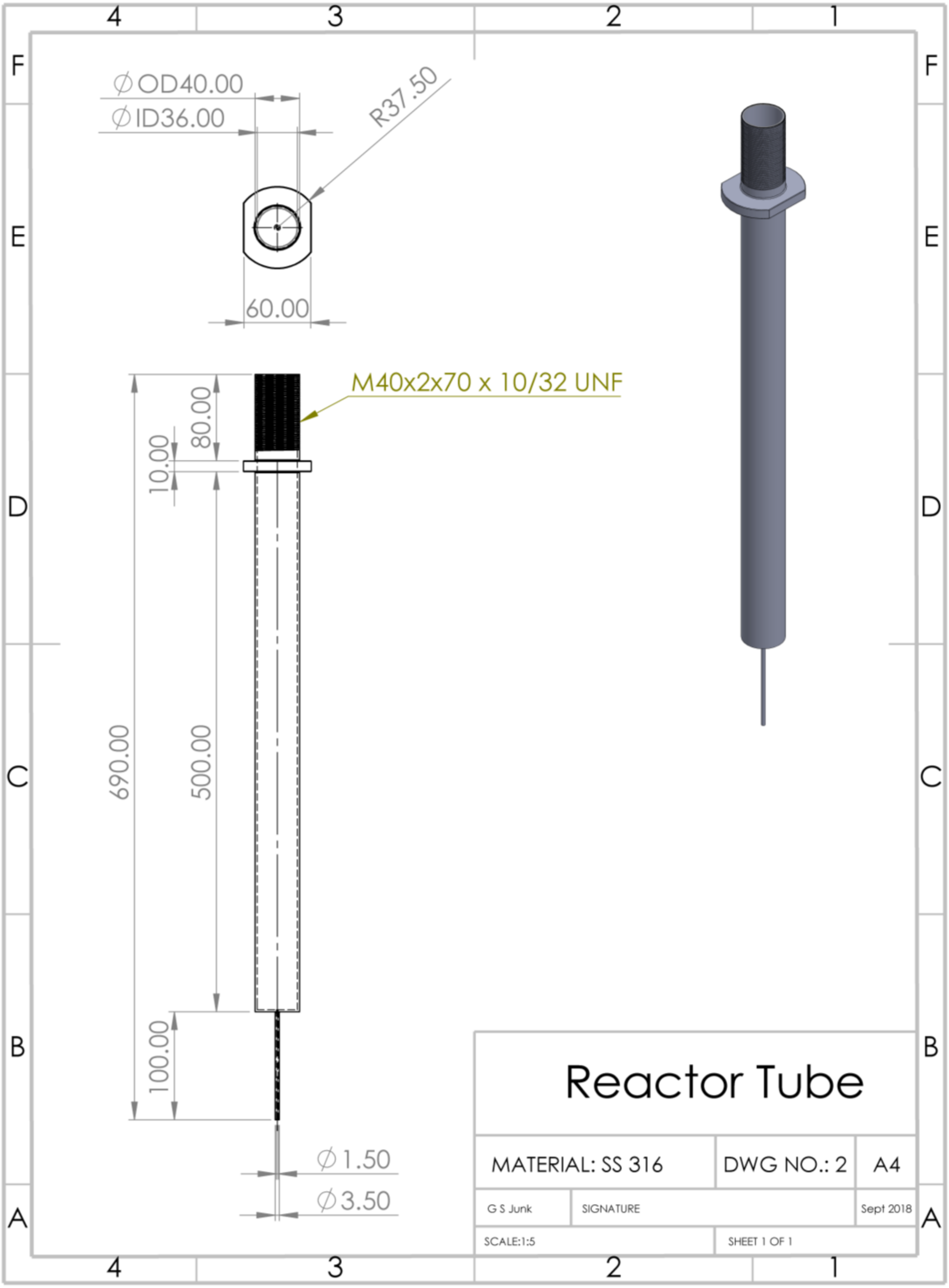
If neither approach proves commercially profitable, but the recovery of CCA from the char can be established on an industrial scale, pyrolysis may still be a valuable tool in reducing the volume of waste going to landfill. Any fractions that might require landfilling (e.g. the residual oil fraction) would require less volume in a landfill, reducing the area at risk of contamination.

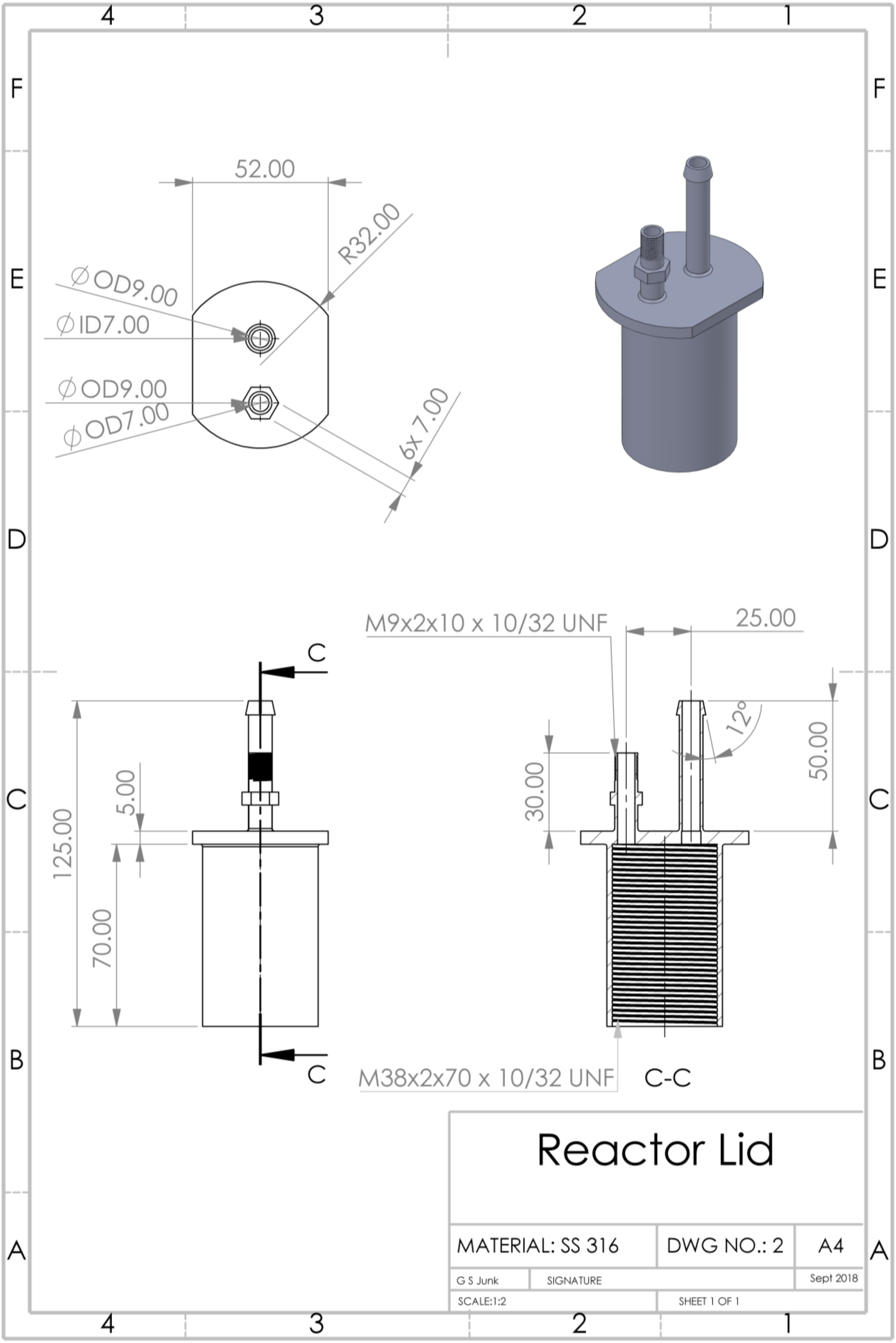
Together these routes offer a potentially viable means of increasing the recovery of arsenic from CCA-treated timbers allowing for the potential to reduce environmental harm through reducing the need to use virgin CCA preservatives.

Appendices

Appendix A: Engineering Drawings

Reactor and Associated Parts





Reactor Lid

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DWG NO.: 2

A4

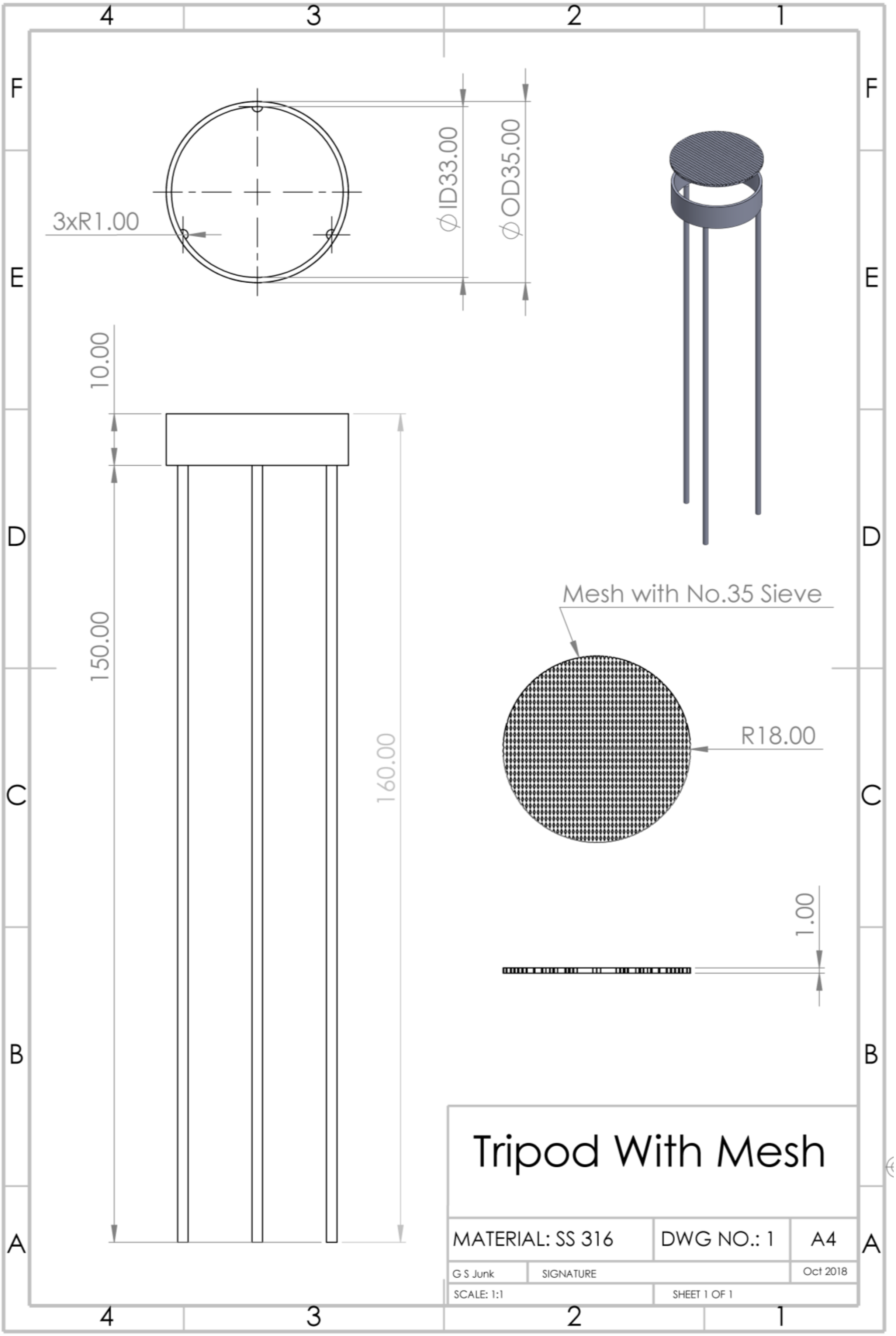
G S Junk

SIGNATURE

Sept 2018

SCALE:1:2

SHEET 1 OF 1



Tripod With Mesh

MATERIAL: SS 316
DWG NO.: 1
A4
G S Junk
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Oct 2018
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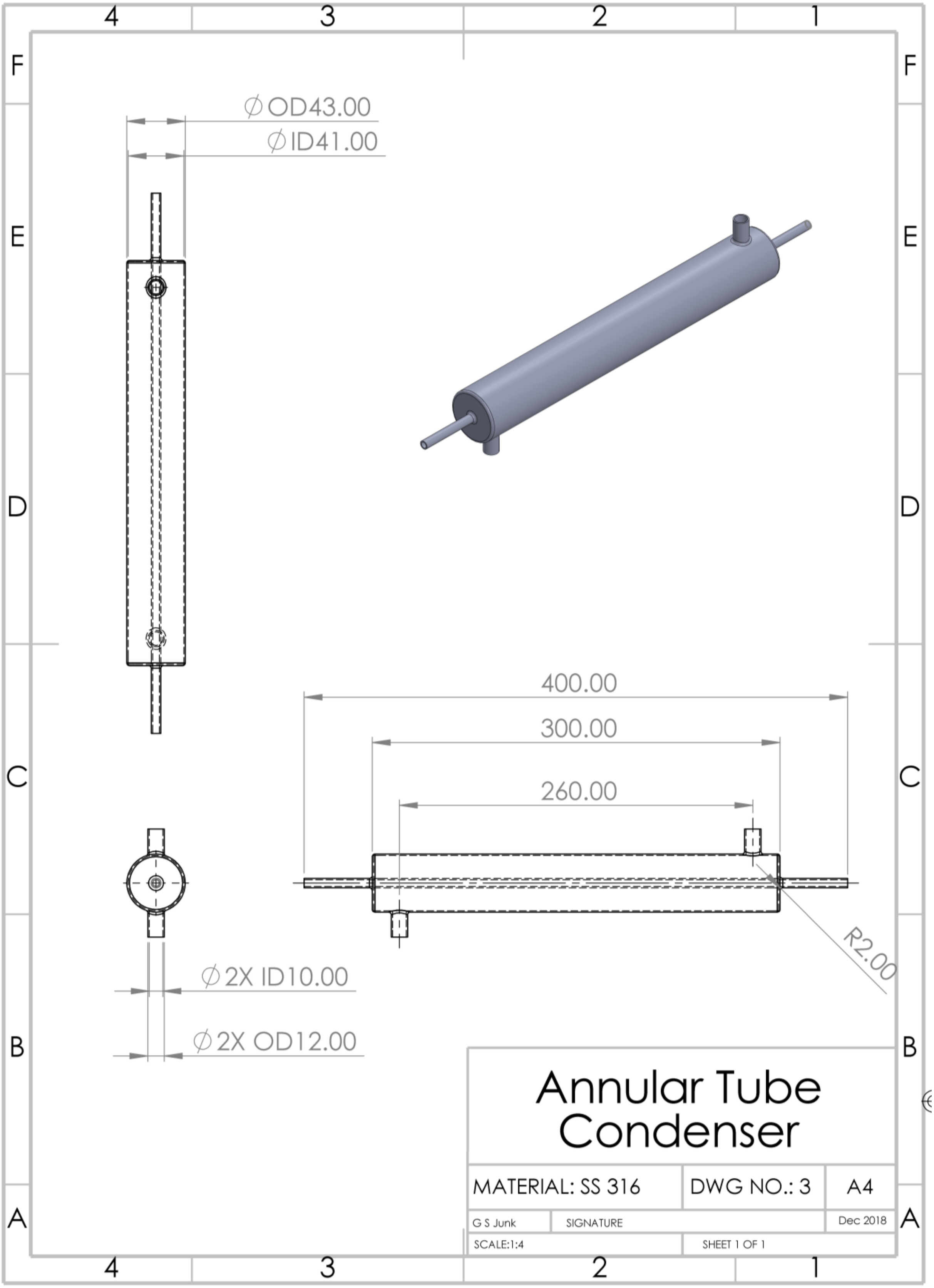
SHEET 1 OF 1

Annular Tube Condenser



Appendix B: Heat Transfer Calculations for Feedstock Sample

Fourier's law in its integrated form:

$$\frac{Q}{\Delta t} = -kA\frac{\Delta T}{\Delta x}$$

where

$$Q = mC_p\Delta T$$

Substituting the second equation into the first and rearranging to find the time *t*, the time it takes for the other side of the sample to reach the same temperature:

$$\Delta t = \frac{m \times C_p \times \Delta x}{k \times A}$$

Q	Heat	J	
Δt	Time	s	To be determined
k	Thermal conductivity of material	W·(m·K)$^{-1}$	0.04 - 0.14
A	Cross-sectional surface area	m^2	(= πr^2)= 0.001018
ΔT	Temperature difference between ends	K (°C)	
Δx	Distance between ends / thickness	m	0.01
m	mass	kg	0.01
C_p	Specific heat capacity	J·(kg·K)$^{-1}$	1,360

Assumptions:

- Sample is 100% dry wood
- Temperature is in the centre, therefore the weight and distance is half of the total: Usual sample mass 20-25 g and space occupied in tube reactor 200 mm

Overall, likely to take less time as these calculations do not considered the external heat supply from the furnace nor that of heated nitrogen.

Appendix C: Micro-GC Calibration

Table 1: Micro-GC calibration data

Retention Time								*Gradient*	*y-Intercept*
N_2	1.101	Area	3.07E8	2.27E8	2.85E8	2.64E8	2.45E8	3.39E8	0.905
		Conc.	100%	77%	96%	90%	83%		
O_2	0.939	Area	3.07E7	5.81E7	8.30E7			3.84E8	1.178
		Conc.	7%	14%	20%				
CO_2	1.18	Area	3.65E7	1.27E7	2.49E7			1.19E9	1.023
		Conc.	3%	1%	2%				
CH_4	1.608	Area	3.52E7	2.35E7	1.25E7			8.53E8	1.032
		Conc.	4%	3%	1%				
C_2H_6	1.263	Area	3.31E7	2.15E7				2.21E8	1.000
		Conc.	15%	7.5%					
C_2H_4	0.917	Area	1.26E7	9.60E6				1.05E8	1.000
		Conc.	12%	6%					
CO	0.924	Area	3.56E7					1.19E8	1.000
		Conc.	30%						

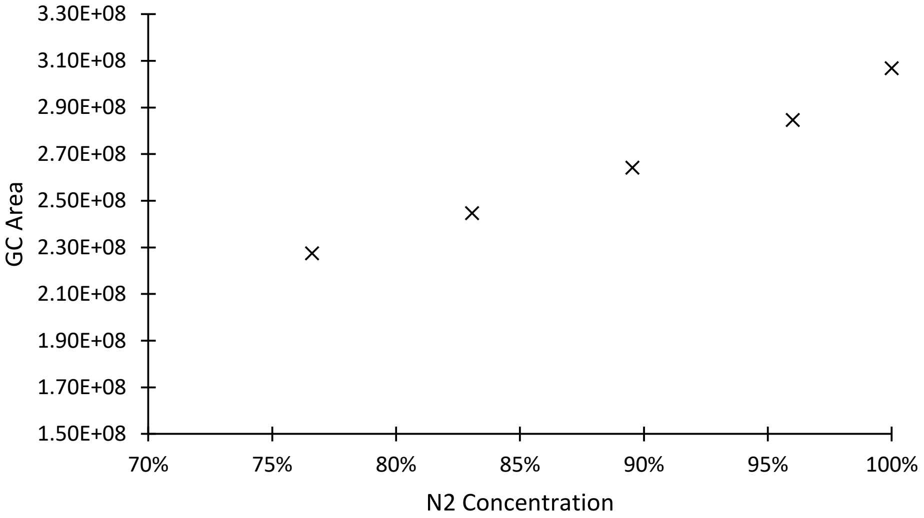


Figure 1: GC Nitrogen calibration data

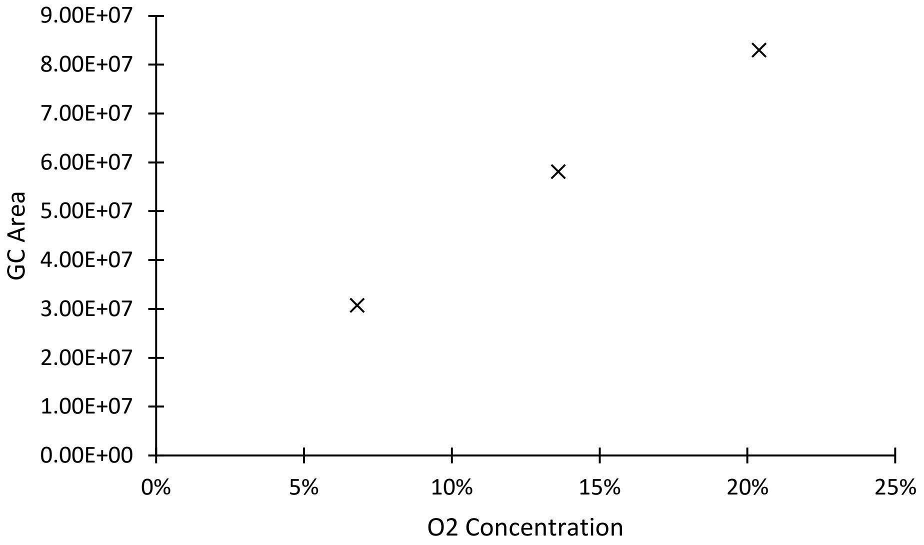


Figure 2: GC Oxygen alibration data

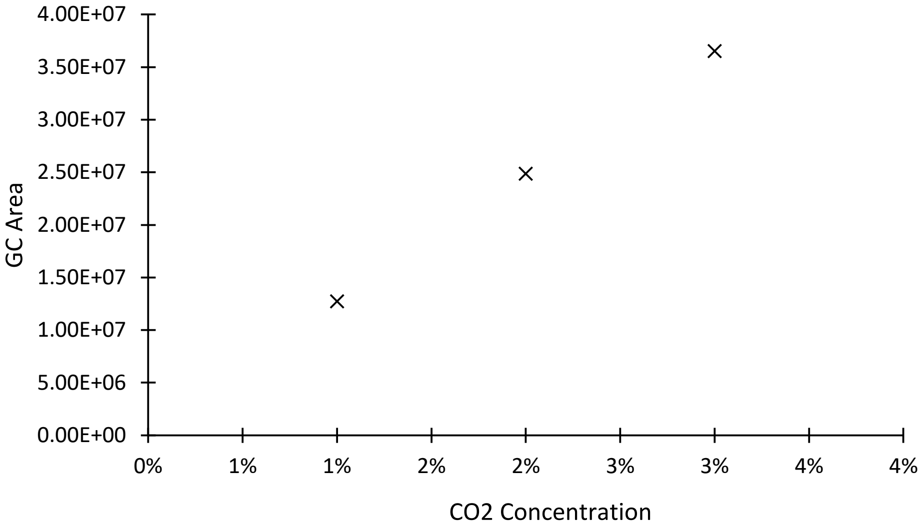


Figure 3: GC CO_2 calibration data

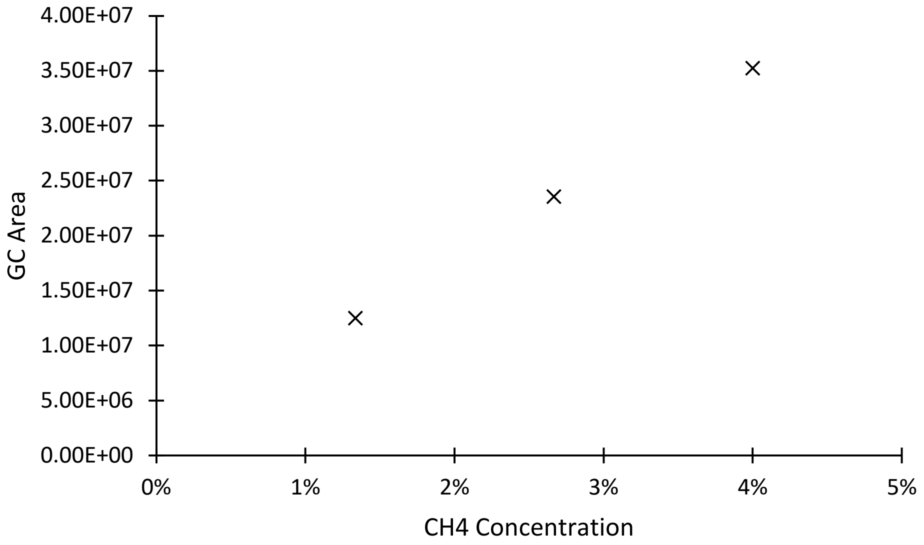


Figure 4: GC Methane calibration data

Appendix D: Total Arsenic Content Procedure

1. In the fumehood, place 0.1 g of dried or pyrolysis residue into a conical flask equipment equipped with a reflux condenser.
2. Add 10 mL of 65% HNO_3 to the conical flask.
3. Place the flask on a heating plate until the sample is fully dissolved. Approximately 2 h for pyrolysis residue, and 4 h for wood.
4. Once fully dissolved, allow to reach room temperature.
5. Add the solution to 100 mL of Milli-Q water.
6. Filter through a fibreglass filter.
7. Transfer the filtrate to a 250 mL volumetric flask and dilute with Milli-Q water.
8. It is likely that the metal content of this sample is above the upper detection limit of the ICP-MS (1 ppm). Hence, further dilution is required.
9. Take a 20 mL sample, place it in a 250 mL volumetric flask, and dilute with Milli-Q water to 250 mL.
10. Transfer samples into vials for analysis using ICP-MS in the chemistry department.

This dilution is set-up to have a Cr content of approximately 0.5 ppm in the second dilution volume (from similar conditions tested in literature).

In the first dilution volume, the acid concentration is approximately 2.6% and in the second dilution volume, the acid content is approximately 0.2%.

Appendix E: Arsenic Speciation Procedure

Standard Preparation

Arsenate solution: Make a 13.3 mmol L^{-1} and a 0.13 mmol L^{-1} arsenate sample

1. In the fume hood, dissolve 0.25 g of sodium arsenate (Na2HAsO4·7H2O) in 250 mL of deionized water.
2. Slowly add 2.5 mL of concentrated HCl to the mixture.
3. Extract a 2 mL sample of the mixture, and using a volumetric flask dilute it to 200 mL with deionized water.

Arsenite solution: Make a 13.3 mmol L^{-1} and a 0.13 mmol L^{-1} arsenite sample

1. In the fume hood, dissolve 0.25 g of sodium m-arsenite (NaAsO2) in 250 mL of water.
2. Add 0.25 g of ascorbic acid to the mixture.
3. Extract a 2 mL sample of the mixture, and using a volumetric flask dilute it to 200 mL with deionized water.

Phosphate solution: Make a 10 mmol L^{-1} and a 1 mmol L^{-1} phosphate sample

1. Add 0.077 g of KH2PO4 to 250 mL of deionized water.
2. Extract a 10 mL sample of the mixture, and using a volumetric flask dilute it to 100 mL with deionized water.

The calibration slope is obtained by two to the replicated analyses of a series of sub-samples that are spike with standard solutions of As(III) and As(V) to increase the total Arsenic concentration by 0.13, 0.67, 2.6, 5.2 and 13.3 µmol L^{-1} (10, 50, 200, 400 and 1000 µg L^{-1}). For the phosphorus calibration slope solution concentrations are increased to 10, 20 and 40 µmol L^{-1}.

Reagent Preparation

Oxidizing Solution: make up a 2 mmol L^{-1} KIO_3 oxidizing solution in the fumehood.

1. Add 2 mL of concentrated HCl to 98 mL of deionized water.
2. Dissolve 0.0425 g of potassium iodate in the HCl-water mixture.

Reducing Solution: make up three solutions in the fumehood:

1. 14% $Na_2S_2O_5$ Solution: Dissolve 28 g of $Na_2S_2O_5$ in 200 mL of deionized water.
2. 1.4% $Na_2S_2O_3$ Solution: Dissolve 2.8 g of Na_2S_2O in 200 mL of deionized water.
3. 10% H_2SO_4 Solution: Dissolve 17.7 g (9.6 mL) of H_2SO_4 in 0.1 L of deionized water. Ensuring to add the acid to the water.
4. Mixing these three solutions together in ratios 2:2:1.

Colour Reagent: make up four solutions:

1. 24 mmol L^{-1} ammonium molybdate solutions: Add 5.59 g of ammonium paramolybdate to 200 mL of deionized water.
2. 2.5 mmol L^{-1} sulphuric acid solution: In the fumehood add 98.08 g of H_2SO_4 to 400 mL deionized water. Ensuring to add the acid to the water.
3. 613 mmol L^{-1} ascobic acid solution: Add 21.59 g of ascorbic acid to 200 mL of deionized water.
4. 8 mmol L^{-1} potassium antimonyl-tartrate: Add 0.53 g of potassium antimony-tartarte to 100 mL of deionized water.
5. The three solutions are then mixed together in a 2:2:1:5 ratio: ascorbic acid, ammonium molybdate, potassium antimonyl tartrate and sulphuric acid, in the fumehood:
    a. Combine the ascorbic acid solution and the ammonium molybdate solution first.
    b. Add the Potassium antimonyl solutions, and immediately add the sulphuric acid solution.

   The solution is stable for 6 h below 30°C. If made up to 500 mL this quantity is suitable for approximately 50 samples.

Sample Pre-Treatment

1. Transfer 2 g of died wood or pyrolysis residue to a 250 mL conical flask.
2. In the fume hood, add 50 mL of H_2SO_4 (2.5 mol dm^{-3}) and 10 mL of H_2O_2 (30% v/v) to the conical flask.
3. Cover the flask and heat at 75°C in a water bath for one hour. Swirl occasionally.
4. Remove from water bath. Add solution to 100 mL of Milli-Q.
5. Once the solution is at room temperature, filter through a fibreglass filter.
6. Transfer the filtrate to a 250 mL volumetric flask and dilute with Milli-Q water.

Standard Addition to Sample

1. Pipet 5 mL aliquots into three 10 mL vials. Use vials that are suitable for UV-vis range up to 900 nm.
2. Add 0.5 mL of oxidizing agent into the first vial.
3. Add 0.5 mL of reducing agent into the second vial.
4. Add 0.5 mL of HCl into the last vial.
5. Wait at least 10 min for the desired redox state to be reached. The samples remain stable for at least 3 hours.
6. After 10 min add 0.5 mL of the colour agent into each vial.
7. Carefully shake the vials to ensure thorough mixing.
8. Wait for a further 10 min before measuring the absorbance data.

Calibration Data

Table 2: UV-vis calibrating data

							Gradient	*y-Intercept*
Arsenate	Molarity mmol·L^{-1}	0.013	0.0065	0.026	0.052	0.13	21.448	0.4329
	Absorbance	0.448	0.283	1.229	2.084	3		
Arsenite	Molarity mmol·L^{-1}	0.013	0.0065	0.026	0.052	0.13	13.501	-0.0683
	Absorbance	0.119	0.058	0.282	0.556	1.715		
Phosphate	Molarity mmol·L^{-1}	0.2	0.1	0.4			0.1486	0.037
	Absorbance	0.068	0.051	0.096				

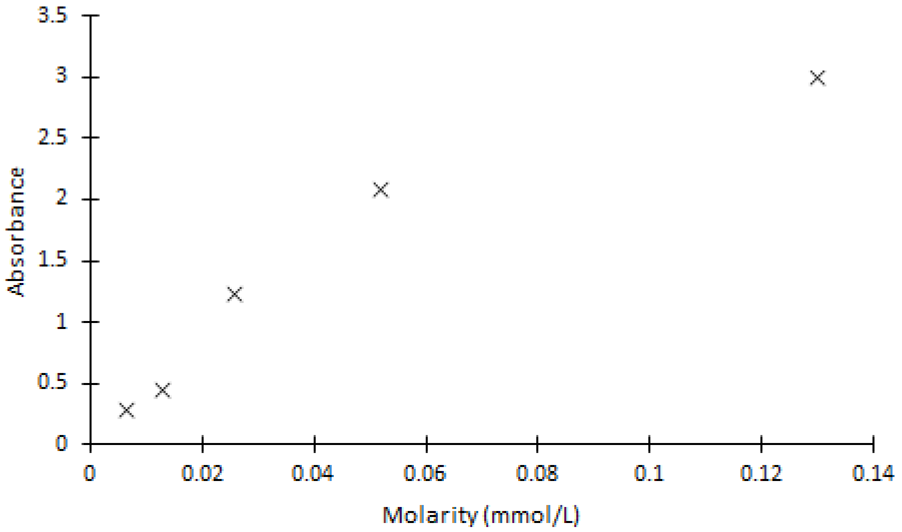


Figure 5: UV-vis calibration data for arsenate

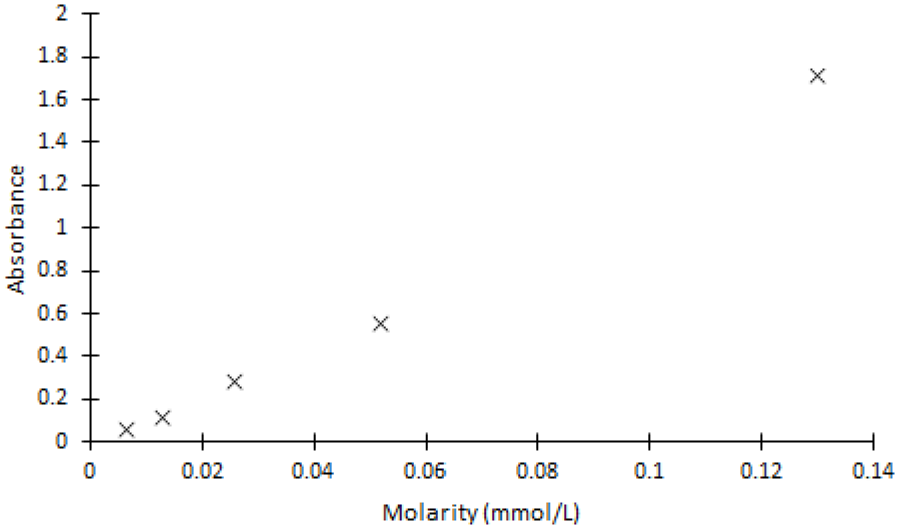


Figure 6: UV-vis calibration for arsenite

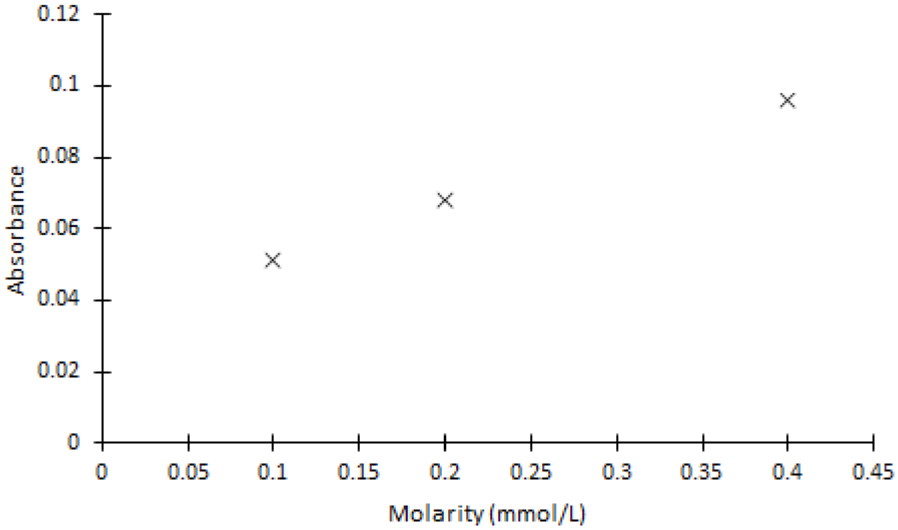


Figure 7: UV-vis calibration for phosphate

Appendix F: Industrial Trial in Timaru - Report

To determine the suitability of pyrolysis oil for wood treatment Koppers Performance Chemicals NZ kindly offer to analyse a sample and determine its compatibility with other existing wood preservatives. For this a 2 L sample of pyrolysis bio-oil was required. Waste Transformation Limited operate a pyrolysis unit at Timaru's Waste Management Facility that processes untreated timber to produce bio-char. The pyrolysis unit is operated batch-wise, in which the chamber is loaded up with waste timber, then heated using a diesel burner to 350°C. The produced gas diverted to an after-burner – photos of the unit are shown below.

Approximately 250 mL of viscous liquid product would be collected at pyrolysis temperatures up to 350°C through a port in the gas outlet line prior to the afterburner. As this was insufficient volume to carry out the desired tests and the consistency of the sample was undesirable, another sampling port was used with at the second attempt. For this a sampling tube consisting of stainless steel pipe containing a ball valve, a quick connect coupling (Mac Union Fitting) and another ball valve was used to direct the gas stream into a conical flask. As the sampling port has approximately 2 meters up the tubing was long enough to cool the gas to ~23°C. The liquid accumulated at the bottom of the flask and the non-condensable gas stream was redirected to the pyrolysis unit.

Using this method approximately 250mL of sample was collected of with 240 mL consists of water and only the remained hydrocarbons. Water/Steam generally indicates that combustion is taking place in the chamber, rather than pyrolysis: the timber is reacting with oxygen producing heat, water and mainly carbon dioxide. Oxygen must be present in the chamber for this to happen, indicating that the chamber is not sealing fully allowing air into it. Through this, little bio-oil and gas is made.

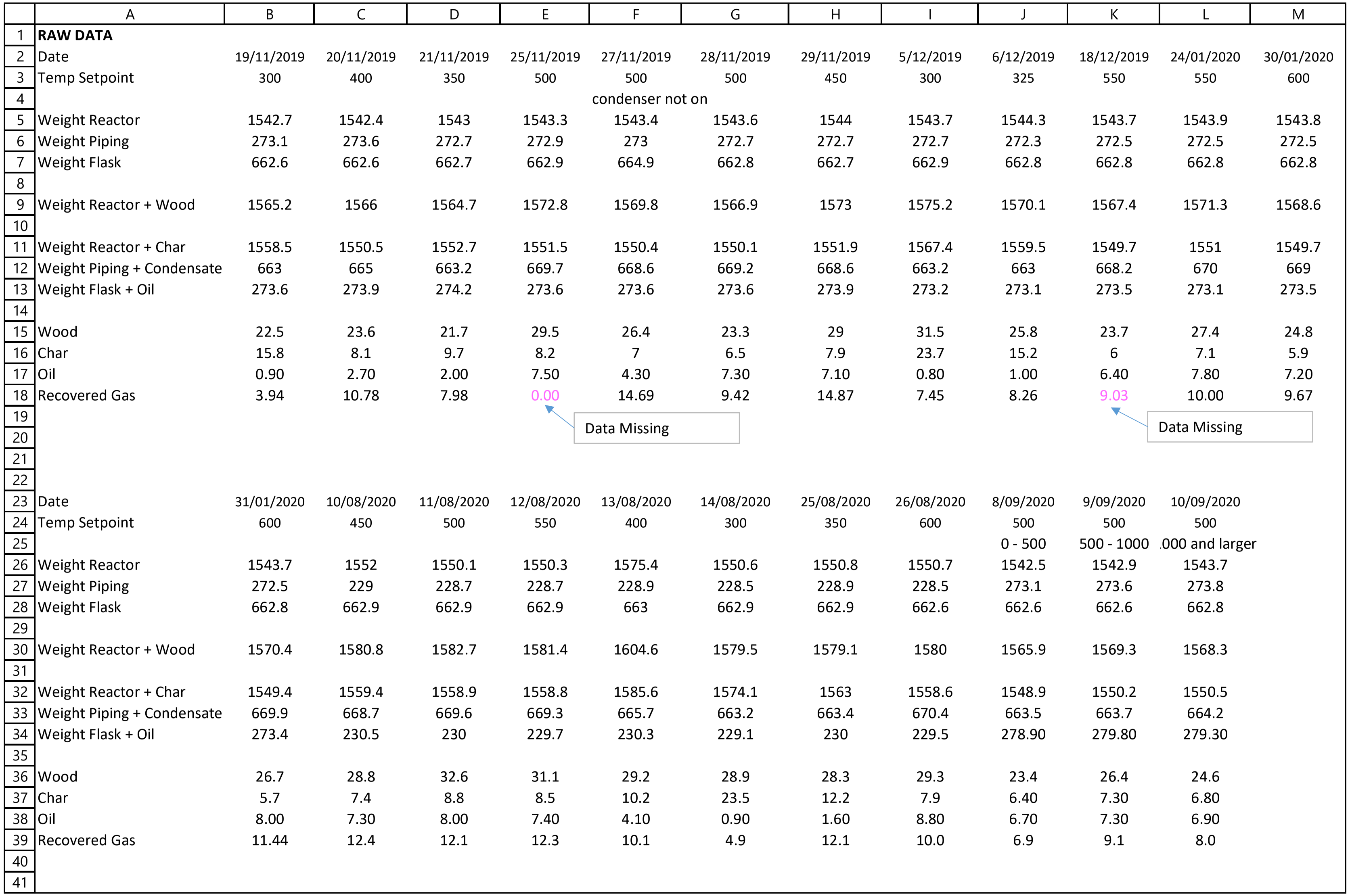
Neither sample was used to carry out tests to determine the bio-oils suitability as a wood preservative.

Appendix G: Raw Experimental Data and Calculations

Pyrolysis Data Using Untreated Timber Particles

	A	B	C	D	E	F	G
1	**RAW DATA**						
2	Date		19/06/2019	21/06/2019	27/06/2019	13/09/2019	24/10/2019
3	Temp Setpoint	C	300	300	300	500	400
4	Condenser Flowrate	L/min	12	0	6	12	12
5							
6	Weight Reactor	g	1542.12	1542.34	1542.16	1542.2	1543.4
7	Weight Piping	g	545.54	533.27	180.39	533.5	534.8
8	Weight Flask	g	662.51	662.67	662.45	662.7	662.6
9							
10	Weight Reactor + Wood	g	1558.24	1564.12	1558.54	1568.3	1567.6
11							
12	Weight Reactor + Char	g	1554.69	1560.07	1555.51	1548	1549.3
13	Weight Piping + Condensate	g	546.99	533.33	180.49	533.6	535
14	Weight Flask + Oil	g	662.58	662.63	662.66	673.1	671.6
15							
16	Wood	g	16.12	21.78	16.38	26.1	24.2
17	Char	g	12.57	17.73	13.35	5.8	5.9
18	Oil	g	1.52	0.02	0.31	10.5	9.2
19	Recovered Gas	g	1.81	3.39	2.40	8.78	8.85
20							
21	Char	wt%	78%	81%	82%	22%	24%
22	Oil	wt%	9%	0%	2%	40%	38%
23	Recovered Gas	wt%	11%	16%	15%	34%	37%
24							

Pyrolysis of CCA-treated Wood Particles – Raw Data



	A	B	C	D	E	F	G	H	I	J	K	L	M
1	**RAW DATA**												
2	Date	19/11/2019	20/11/2019	21/11/2019	25/11/2019	27/11/2019	28/11/2019	29/11/2019	5/12/2019	6/12/2019	18/12/2019	24/01/2020	30/01/2020
3	Temp Setpoint	300	400	350	500	500	500	450	300	325	550	550	600
4						condenser not on							
5	Weight Reactor	1542.7	1542.4	1543	1543.3	1543.4	1543.6	1544	1543.7	1544.3	1543.7	1543.9	1543.8
6	Weight Piping	273.1	273.6	272.7	272.9	273	272.7	272.7	272.7	272.3	272.5	272.5	272.5
7	Weight Flask	662.6	662.6	662.7	662.9	664.9	662.8	662.7	662.9	662.8	662.8	662.8	662.8
8													
9	Weight Reactor + Wood	1565.2	1566	1564.7	1572.8	1569.8	1566.9	1573	1575.2	1570.1	1567.4	1571.3	1568.6
10													
11	Weight Reactor + Char	1558.5	1550.5	1552.7	1551.5	1550.4	1550.1	1551.9	1567.4	1559.5	1549.7	1551	1549.7
12	Weight Piping + Condensate	663	665	663.2	669.7	668.6	669.2	668.6	663.2	663	668.2	670	669
13	Weight Flask + Oil	273.6	273.9	274.2	273.6	273.6	273.6	273.9	273.2	273.1	273.5	273.1	273.5
14													
15	Wood	22.5	23.6	21.7	29.5	26.4	23.3	29	31.5	25.8	23.7	27.4	24.8
16	Char	15.8	8.1	9.7	8.2	7	6.5	7.9	23.7	15.2	6	7.1	5.9
17	Oil	0.90	2.70	2.00	7.50	4.30	7.30	7.10	0.80	1.00	6.40	7.80	7.20
18	Recovered Gas	3.94	10.78	7.98	0.00	14.69	9.42	14.87	7.45	8.26	9.03	10.00	9.67
19													
20						Data Missing						Data Missing	
21													
22													
23	Date	31/01/2020	10/08/2020	11/08/2020	12/08/2020	13/08/2020	14/08/2020	25/08/2020	26/08/2020	8/09/2020	9/09/2020	10/09/2020	
24	Temp Setpoint	600	450	500	550	400	300	350	600	500	500	500	
25										0 - 500	500 - 1000	.000 and larger	
26	Weight Reactor	1543.7	1552	1550.1	1550.3	1575.4	1550.6	1550.8	1550.7	1542.5	1542.9	1543.7	
27	Weight Piping	272.5	229	228.7	228.7	228.9	228.5	228.9	228.5	273.1	273.6	273.8	
28	Weight Flask	662.8	662.9	662.9	662.9	663	662.9	662.9	662.6	662.6	662.6	662.8	
29													
30	Weight Reactor + Wood	1570.4	1580.8	1582.7	1581.4	1604.6	1579.5	1579.1	1580	1565.9	1569.3	1568.3	
31													
32	Weight Reactor + Char	1549.4	1559.4	1558.9	1558.8	1585.6	1574.1	1563	1558.6	1548.9	1550.2	1550.5	
33	Weight Piping + Condensate	669.9	668.7	669.6	669.3	665.7	663.2	663.4	670.4	663.5	663.7	664.2	
34	Weight Flask + Oil	273.4	230.5	230	229.7	230.3	229.1	230	229.5	278.90	279.80	279.30	
35													
36	Wood	26.7	28.8	32.6	31.1	29.2	28.9	28.3	29.3	23.4	26.4	24.6	
37	Char	5.7	7.4	8.8	8.5	10.2	23.5	12.2	7.9	6.40	7.30	6.80	
38	Oil	8.00	7.30	8.00	7.40	4.10	0.90	1.60	8.80	6.70	7.30	6.90	
39	Recovered Gas	11.44	12.4	12.1	12.3	10.1	4.9	12.1	10.0	6.9	9.1	8.0	
40													
41													

ICP-MS Data and Calculations

	A	B	C	D	E	F	G	H	I	J	K	L	M	N
1	**ICP-MS Data and Calculations**					**ICP-MS Results**			**Post Dilution**					
2						In Solution			In Acid			Conc in Sample		
3						As [ug/L]	Cr [ug/L]	Cu [ug/L]	As [ug]	Cr [ug]	Cu [ug]	As [ppm]	Cr [ppm]	Cu [ppm]
4	Sample Mass /g						**Wood**			**Wood**			**Wood**	
5	0.1258	Wood				93.11	114.15	68.10	290.97	356.71	212.82	2313	2836	1692
6	0.1231	Wood				89.43	104.18	132.51	279.46	325.57	414.08	2270	2645	3364
7	0.1252	Wood				88.16	104.06	107.05	275.51	325.18	334.53	2201	2597	2672
8			SP Temp	Py. Date			**Char**			**Char**			**Char**	
9	0.0929	Char	300	14/08/2020		80.15	92.1	52.52	250.46	287.73	164.13	2696	3097	1767
10	0.069	Char	350	25/08/2020		84.18	111.3	73.51	263.06	347.69	229.71	3813	5039	3329
11	0.0987	Char	400	13/08/2020		216.91	272.2	229.96	677.84	850.63	718.62	6868	8618	7281
12	0.0975	Char	450	10/08/2020		207.06	304.6	218.22	647.08	951.78	681.93	6637	9762	6994
13	0.1063	Char	500	11/08/2020		188.76	312.2	247.98	589.88	975.67	774.94	5549	9178	7290
14	0.1177	Char	550	12/08/2020		195.60	367.8	238.29	611.24	1149.31	744.64	5193	9765	6327
15	0.115	Char	600	26/08/2020		175.06	340.3	207.67	547.05	1063.49	648.98	4757	9248	5643
16							**Oil**			**Oil**			**Oil**	
17	0.044	Tar	300	14/08/2020		1.05	0.21	2.85	3.29	0.65	8.90	74.7	14.8	202
18	0.023	Tar	350	25/08/2020		0.35	0.10	1.38	1.10	0.33	4.32	47.8	14.1	188
19	0.132	Tar	400	13/08/2020		10.76	0.28	6.78	33.62	0.86	21.18	255	6.5	160
20	0.164	Tar	450	10/08/2020		19.46	0.37	9.29	60.81	1.16	29.04	371	7.1	177
21	0.115	Tar	500	11/08/2020		22.25	0.23	2.10	69.54	0.72	6.57	605	6.2	57.1
22	0.117	Tar	550	12/08/2020		11.11	0.19	1.96	34.73	0.58	6.12	297	5.0	52.3
23	0.125	Tar	600	26/08/2020		13.71	0.39	7.96	42.85	1.21	24.88	343	9.7	199
24	**Oil Repeats: Complete New Acid Digestion**													
25	0.1243	Tar	400	13/08/2020		9.048	1.872	5.509	28.3	5.85	17.2	227.5	47.1	138.5
26	0.1032	Tar	500	11/08/2020		16.407	0.136	3.063	51.3	0.43	9.6	496.8	4.1	92.8
27	0.1203	Tar	600	26/08/2020		11.359	0.149	2.764	35.5	0.47	8.6	295.1	3.9	71.8
28	0.1203	Tar	600	26/08/2020		11.227	0.094	2.594	35.1	0.29	8.1	291.6	2.4	67.4
29														
30	**Pyrolysis Data**													
31	SP Temp	RXN Temp	Absolute /g				Relative					Averages		
32	°C		Wood	Char	Liquid	Gas	Char Yield	Oil Yield	Gas			Average Char Yield	Average Oil Yield	
33	300	280.5	28.9	23.5	0.9	4.50	81%	3%	16%			76%	3%	
34	350	325	28.3	12.2	1.6	14.50	43%	6%	51%			44%	7%	
35	400	377.5	29.2	10.2	4.1	14.90	35%	14%	51%			35%	13%	
36	450	423.5	28.8	7.4	7.3	14.10	26%	25%	49%			26%	25%	
37	500	475	32.6	8.8	8	15.80	27%	25%	48%			27%	27%	
38	550	527.5	31.1	8.5	7.4	15.20	27%	24%	49%			26%	26%	
39	600	572.5	29.3	7.9	8.8	12.60	27%	30%	43%			24%	30%	
40														

Post Dilution In Acid
(Column I | J | K)

C : Concentration
V : Volume
m_{CCA} : mass (Column I|J|K)
1D : First Dilution
2D : Second Dilution
C_{2D} : ICP-MS Results (Column F|G|H)

$$C_{2D}V_{2D} = C_{1D}V_{1D}$$

$$C_{1D} = \frac{C_{2D} \times 0.25\ L}{0.02\ L}$$

Then concentration was just diluted to 250mL

Conc in Sample
(Column L | M | N)

$$C = \frac{m_{CCA}}{m_{Sample}}$$

$$C = \frac{Column\ (I\ |\ J\ |\ K)}{Column\ A}$$

	A	B	C	D	E	F	G	H	I
41									
42	**Arsenic**			Absolute				Based on 100 g wood	
43	Temp	Actual Temp	Wood	Char	Liquid	Gas - by subtraction	Total As in Liquid	Relative total in liquid	Relative total in char
44	°C		ug	ug	ug	ug	mg	mg	
45	300	280.5	65349	63356	67	1926	0.1	0.2	219.2
46	350	325	63993	46513	77	17404	0.1	0.3	164.4
47	400	377.5	66028	70050	1044	-5067	1.0	3.6	239.9
48	450	423.5	65123	49111	2707	13305	2.7	9.4	170.5
49	500	475	73716	48833	4838	20045	4.8	14.8	149.8
50	550	527.5	70324	44142	2196	23985	2.2	7.1	141.9
51	600	572.5	66254	37580	3016	25658	3.0	10.3	128.3
52									
53	**Chromium**			Absolute					
54		Temp	Wood	Char	Liquid	Gas - by subtraction		Cr Mass Balance	
55		°C	ug	ug	ug	ug		Char	Oil
56	300	281	77813	72783	13.4	5017		94%	0.02%
57	350	325	76198	61476	22.6	14699		81%	0.03%
58	400	378	78621	87907	26.7	-9312		112%	0.03%
59	450	424	77544	72238	51.6	5255		93%	0.07%
60	500	475	87776	80770	49.8	6956		92%	0.06%
61	550	528	83737	83000	37.0	700		99%	0.04%
62	600	573	78890	73057	85.4	5748		93%	0.11%
63									
64	**Copper**			Absolute					
65		Temp	Wood	Char	Liquid				
66		°C	ug	ug	ug				
67		300	74441	41519	182	32740			
68		350	72896	40615	301	31980			
69		400	75214	74265	658	291			
70		450	74184	51757	1293	21134			
71		500	83972	64153	457	19361			
72		550	80108	53776	387	25945			
73		600	75471	44582	1752	29138			
74									

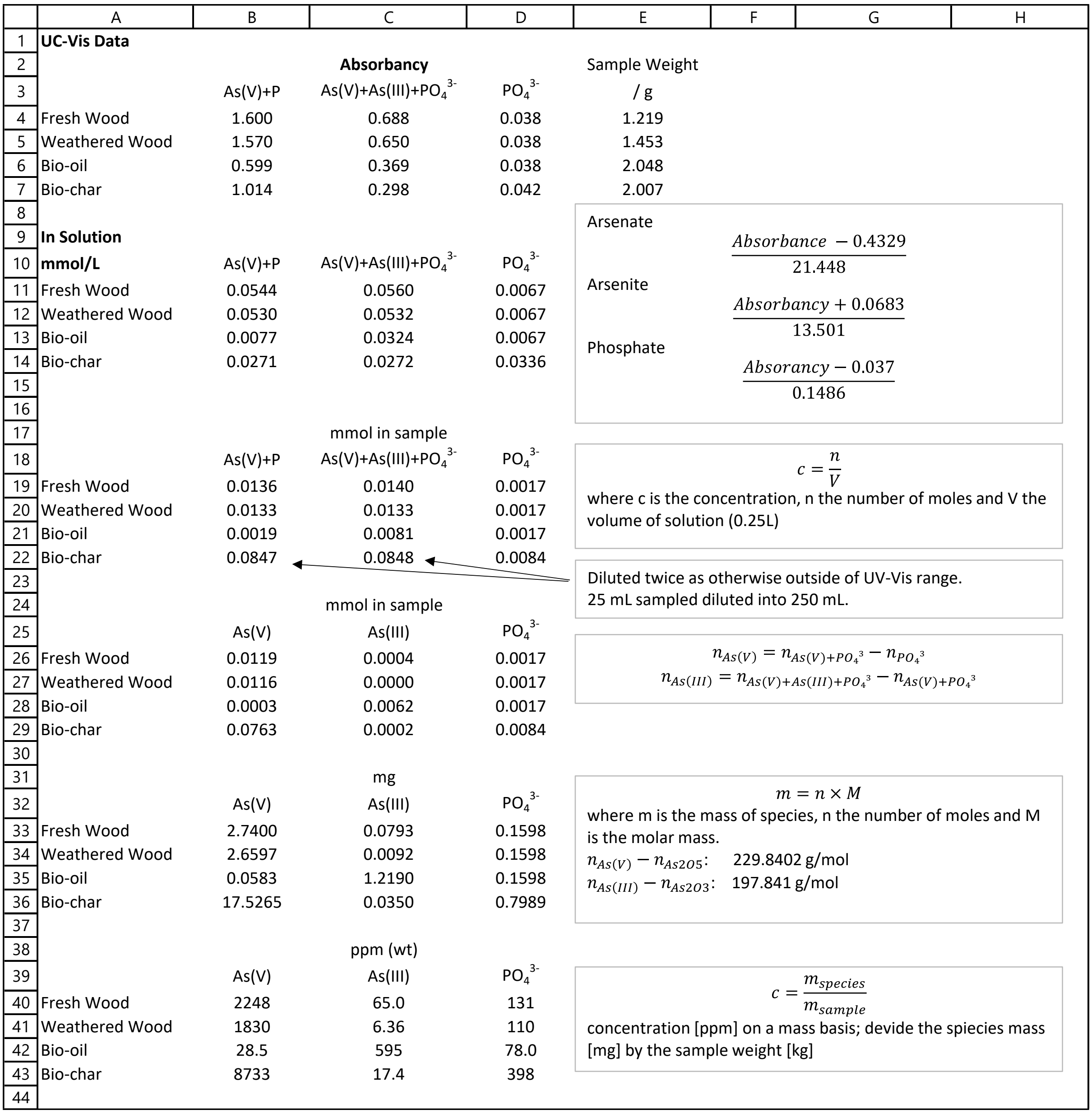
J	K	L	M	N	O	P	Q	R
	Summary for Pyrolysis Product Yield and Arsenic Recovery							
		Char Yield	As recovery in bio-char	Bio-oil Yield	As recovery in bio-oil	Gas Yield	As recovery in gas	
	280.5	73.0%	96.9%	3.3%	0.10%	20.6%	2.9%	
	325	43.8%	72.7%	7.4%	0.12%	42.0%	27.2%	
	377.5	34.3%	106.1%	11.4%	1.6%	45.7%	-7.7%	
	423.5	25.7%	75.4%	25.3%	4.2%	43.0%	20.4%	
	475	28.2%	66.2%	28.9%	6.6%	40.0%	27.2%	
	527.5	25.6%	62.8%	27.7%	3.1%	43.0%	34.1%	
	572.5	23.8%	56.7%	29.0%	4.6%	43.0%	38.7%	

K	L	M
	Char Conc Ratios (Cr Basis)	
Temp	As/Cr	Cu/Cr
280.5	0.87	0.57
325	0.76	0.66
377.5	0.80	0.84
423.5	0.68	0.72
475	0.60	0.79
527.5	0.53	0.65
572.5	0.51	0.61

Gas Composition

Pyrolysis Temperature /°C	*CO_2* /g	*C_2H_6* /g	*C_2H_4* /g	*CH_4* /g	*O_2* /g	*He* /g	*H_2* /g	*CO* /g
280	3.94	0	0	0	0	0	0	0
280	7.43	0	0.02	0	0	0	0	0
302	8.25	0	0.01	0	0	0	0	0
325	7.97	0	0	0	0	0	0	0
377	10.78	0	0	0	0	0	0	0
423	14.85	0	0	0	0	0	0.02	0.13
423	12.30	0	0	0.075	0	0	0	0
475	14.58	0	0	0.05	0.00	0.00	0.06	0.20
475	9.11	0	0	0.09	0.00	0.00	0.00	0.22
527	6.19	0	0	0	2.21	0.60	0.04	0
527	9.83	0.067	0	0.103	0	0	0	0
572	9.51	0	0	0.16	0	0	0	0
572	11.44	0	0	0	0	0	0	0

UV-Vis Data and Calculations



	A	B	C	D	E	F	G	H
1	**UC-Vis Data**							
2			**Absorbancy**		Sample Weight			
3		As(V)+P	As(V)+As(III)+PO_4^{3-}	PO_4^{3-}	/ g			
4	Fresh Wood	1.600	0.688	0.038	1.219			
5	Weathered Wood	1.570	0.650	0.038	1.453			
6	Bio-oil	0.599	0.369	0.038	2.048			
7	Bio-char	1.014	0.298	0.042	2.007			
8								
9	**In Solution**							
10	**mmol/L**	As(V)+P	As(V)+As(III)+PO_4^{3-}	PO_4^{3-}				
11	Fresh Wood	0.0544	0.0560	0.0067				
12	Weathered Wood	0.0530	0.0532	0.0067				
13	Bio-oil	0.0077	0.0324	0.0067				
14	Bio-char	0.0271	0.0272	0.0336				
15								
16								
17			mmol in sample					
18		As(V)+P	As(V)+As(III)+PO_4^{3-}	PO_4^{3-}				
19	Fresh Wood	0.0136	0.0140	0.0017				
20	Weathered Wood	0.0133	0.0133	0.0017				
21	Bio-oil	0.0019	0.0081	0.0017				
22	Bio-char	0.0847	0.0848	0.0084				
23								
24			mmol in sample					
25		As(V)	As(III)	PO_4^{3-}				
26	Fresh Wood	0.0119	0.0004	0.0017				
27	Weathered Wood	0.0116	0.0000	0.0017				
28	Bio-oil	0.0003	0.0062	0.0017				
29	Bio-char	0.0763	0.0002	0.0084				
30								
31			mg					
32		As(V)	As(III)	PO_4^{3-}				
33	Fresh Wood	2.7400	0.0793	0.1598				
34	Weathered Wood	2.6597	0.0092	0.1598				
35	Bio-oil	0.0583	1.2190	0.1598				
36	Bio-char	17.5265	0.0350	0.7989				
37								
38			ppm (wt)					
39		As(V)	As(III)	PO_4^{3-}				
40	Fresh Wood	2248	65.0	131				
41	Weathered Wood	1830	6.36	110				
42	Bio-oil	28.5	595	78.0				
43	Bio-char	8733	17.4	398				
44								

Arsenate

$$\frac{Absorbance\ - 0.4329}{21.448}$$

Arsenite

$$\frac{Absorbancy + 0.0683}{13.501}$$

Phosphate

$$\frac{Absorancy - 0.037}{0.1486}$$

$$c = \frac{n}{V}$$

where c is the concentration, n the number of moles and V the volume of solution (0.25L)

Diluted twice as otherwise outside of UV-Vis range.
25 mL sampled diluted into 250 mL.

$$n_{As(V)} = n_{As(V)+PO_4{}^3} - n_{PO_4{}^3}$$
$$n_{As(III)} = n_{As(V)+As(III)+PO_4{}^3} - n_{As(V)+PO_4{}^3}$$

$$m = n \times M$$

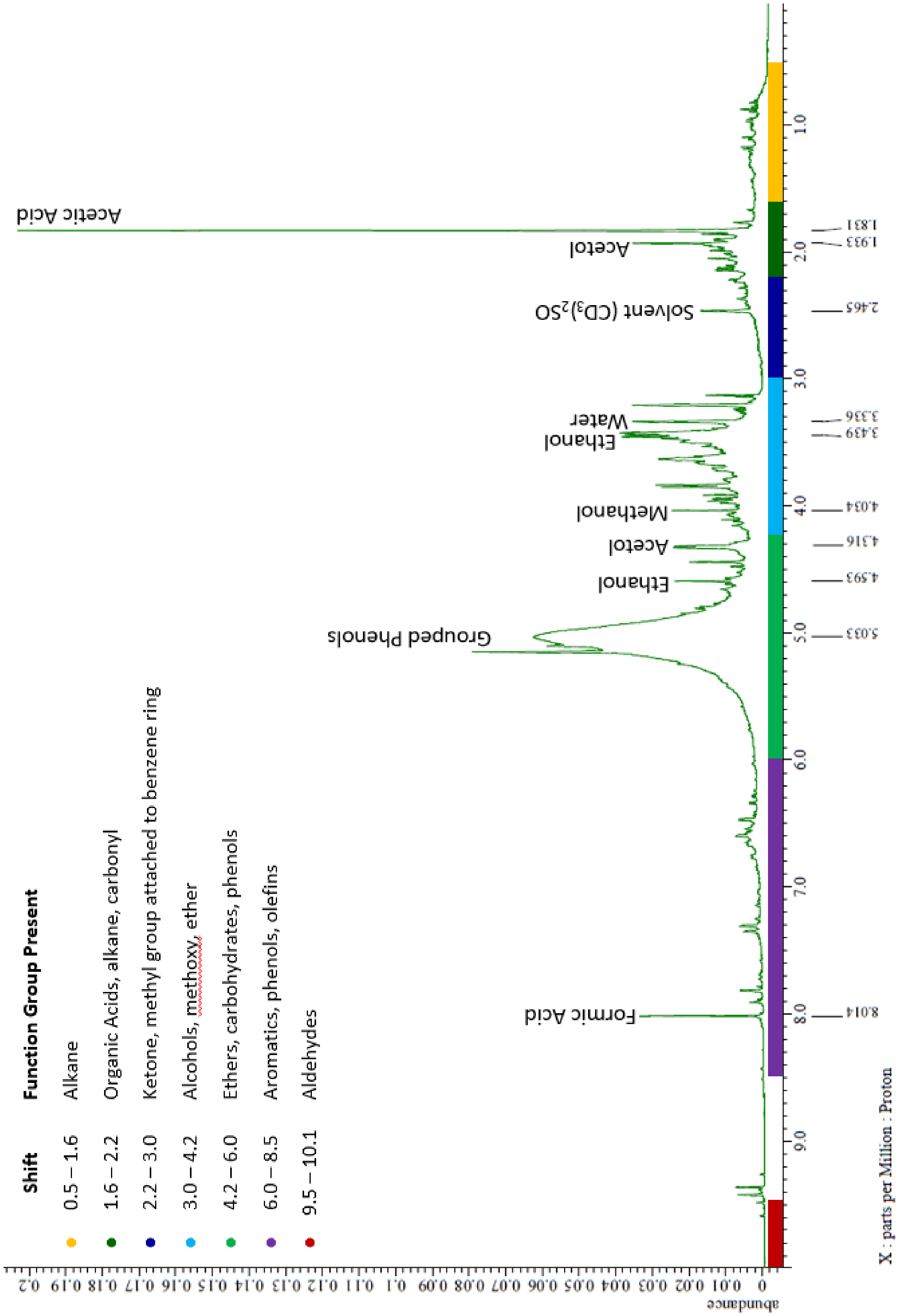
where m is the mass of species, n the number of moles and M is the molar mass.

$n_{As(V)} - n_{As2O5}$: 229.8402 g/mol
$n_{As(III)} - n_{As2O3}$: 197.841 g/mol

$$c = \frac{m_{species}}{m_{sample}}$$

concentration [ppm] on a mass basis; devide the spiecies mass [mg] by the sample weight [kg]

NMR-Spectrum



Appendix H: A Brief Description of MATLAB's Fmincon Solver

The following gives a brief explanation of MATLAB's solver fmincon, deployed in the thermodynamic equilibrium model. A more in-depth explanation can be found elsewhere in mathworks [1] and in the works of Byrd et al. (1999, 2000) [2, 3] and Waltz et al. [4].

Within MATLAB's fmincon solver and interior-point algorithm, this general non-linear problem with equality and inequality constraints was converted into a more general form using slack variables si, where there were as many slack variables as there are inequalities. Next, the inequality constraints were removed by introducing a natural log barrier term ln(si) to the problem, where for each γ > 0, the new function becomes:

$\min\limits_{x,s} f_\gamma(n,s) = \min\limits_{x,s} f(n) - \gamma \sum_i \ln(s_i)$, subject to $\lambda h(n) = 0$ and $g(n) + s = 0$

Where γ is a free parameter and as γ decreases to zero the approximation becomes closer to the original; and the minimum of f_γ(n,s) approaches the minimum of original function f(n) [1, 5].

At each iteration, the solver uses either a direct step or a conjugate gradient step to solve the approximation problem. By default, the direct step approach is attempted first, if not successful the algorithm attempts a conjugate gradient step. To measure the feasibility a merit function is used (Equation (A.1)). At each iteration, the merit function decreases

$$f_\gamma(n,s) + \nu ||(h(n), g(n) + s|| \qquad (\mathrm{A}.1)$$

To force the solution towards feasibility the parameter v may increase with each iteration. If the attempted step does not decrease the merit function, the algorithm rejects the step and forces a new shorter step to be taken. Similarly, a different, shorter step is taken when the objective or constraint function returns a complex value, NaN, Inf or error at an iterate x.

Direct Step

The direct step (Δx, Δs) is defined as

$$\begin{bmatrix} H & 0 & J_h^T & J_g^T \\ 0 & S\Lambda & 0 & -S \\ J_h & 0 & 1 & 0 \\ J_g & -S & 0 & 1 \end{bmatrix} \begin{bmatrix} \Delta n \\ \Delta s \\ -\Delta y \\ -\Delta\lambda \end{bmatrix} = - \begin{bmatrix} \nabla f - J_h^T y - J_g^T \lambda \\ S\lambda - \gamma e \\ h \\ g + s \end{bmatrix} \qquad (\mathrm{A}.2)$$

Equation (A.2) is the result of attempting to solve the two Karush-Kuhn-Tucker (KKT) conditions in the form of Equations (A.3) and (A.4) using a linearized Lagrangian.

$$\nabla_x L(n, \lambda) = 0 \tag{A.3}$$

$$\lambda_{g,i} g_i(n) = 0 \; \forall i \tag{A.4}$$

The algorithm carries out a LDL factorization of the matrix, thereby allowing for (Δn, Δs) to be solved. A further result of this factorization is whether the Hessian is positive or not, if the later the conjugate gradient step approach is carried out.

Conjugate Gradient

The conjugate gradient method aims to minimise the quadratic approximation of the approximated problem within the trust region, through adjusting both n and s, keeping the slack variable s positive.

Lagrangian multipliers are determined by solving the KKT equations using the approach of the method of least-squares, subject to λ being positive; other variables are defined as in the Direct Step approach. The algorithm then takes a step (Δn, Δs) to approximately solve Equation (A.5), subject to the linear constraints of Equation (A.6):

$$\min_{\Delta n, \Delta s} \nabla f^T \Delta n + \frac{1}{2} \Delta x^T \nabla_{nn}^2 L \Delta n + \mu e^T S^{-1} \Delta s + \frac{1}{2} \Delta s^T S^{-1} \Lambda \Delta s \tag{A.5}$$

$$g(n) + J_g \Delta n + \Delta s = 0, \;\; h(n) + J_h \Delta n = 0 \tag{A.6}$$

Equation (A.5) is solved with the aim that its residue matches the residuals of the linear constraint Equation (A.6) while staying within the trust region and keeping the slack variable s strictly positive.

1. MathWorks, I. *Constrained Nonlinear Optimization Algorithms*. 2020 [cited 2020 8.01]; R2019b:[Available from: https://www.mathworks.com/help/optim/ug/constrained-nonlinear-optimization-algorithms.html#brnpd5f.
2. Byrd, R.H., J.C. Gilbert, and J. Nocedal, *A trust region method based on interior point techniques for nonlinear programming.* Mathematical programming, 2000. **89**(1): p. 149-185.
3. Byrd, R.H., M.E. Hribar, and J. Nocedal, *An interior point algorithm for large-scale nonlinear programming.* SIAM Journal on Optimization, 1999. **9**(4): p. 877-900.
4. Waltz, R.A., J.L. Morales, J. Nocedal, and D. Orban, *An interior algorithm for nonlinear optimization that combines line search and trust region steps.* Mathematical programming, 2006. **107**(3): p. 391-408.

5. Vanderbei, R.J., *Linear programming: foundations and extensions*. 2nd ed. Vol. 37. 2001, Boston: Kluwer Academic. ISBN 9780792373421;0792373421;.

Appendix I: Conceptual Model Stream Table

	Timber, as received	*Moisture*	*Timber, dry*	*Heated Nitrogen*	*Char*	*Vapour + Gas*
Temperature [°C]	25	105	105	500	500	499.9
Pressure [kPa]	101.325	101.325	101.325	101.325	101.325	101.325
Molar Flow [kgmole/hr]	89.69	5.07	84.62	66.22	18.04	85.09
Mass Flow [kg/hr]	1141.3	91.3	1050.0	1855.0	293.9	2611.1
Enthalpy Stream [MJ/hr]	1,421	1212	116	955	443	2,886
Carbon	42.58%	0%	46.29%	0%	0%	0%
Oxygen	38.25%	0%	41.57%	0%	61.67%	0%
Nitrogen	0.01%	0%	0.01%	100%	17.29%	71.05%
Hydrogen	5.27%	0%	5.72%	0%	0%	0.02%
Ash	1.14%	0%	1.24%	0%	1.88%	0%
Fasteners	3.50%	0%	3.81%	0%	4.42%	0%
$CrAsO_4$	0.13%	0%	0.14%	0%	13.61%	0%
$CuCrAs_4$	0.16%	0%	0.17%	0%	0.51%	0%
As_2O_5	0.09%	0%	0.10%	0%	0.61%	0%
Acetone	0.88%	0%	0.95%	0%	0%	0.38%
CO_2	0%	0%	0%	0%	0%	11.76%
Methane	0%	0%	0%	0%	0%	0.12%
Ethane	0%	0%	0%	0%	0%	0.06%
Ethylene	0%	0%	0%	0%	0%	0.06%
Water	8.00%	100%	0%	0%	0%	4.15%
Acetic Acid	0%	0%	0%	0%	0%	3.30%
Acetol	0%	0%	0%	0%	0%	1.17%
Ethanol	0%	0%	0%	0%	0%	0.68%
Methanol	0%	0%	0%	0%	0%	0.38%
Furfural	0%	0%	0%	0%	0%	0.53%
Phenol	0%	0%	0%	0%	0%	0.25%
3-Methyl-phenol	0%	0%	0%	0%	0%	0.15%
4-Methyl-phenol	0%	0%	0%	0%	0%	0.17%
Ethylene Glycol	0%	0%	0%	0%	0%	0.57%
As_2O_3	0%	0%	0%	0%	0%	0.02%
As_4O_6	0%	0%	0%	0%	0%	0.01%
2-Butanone	0%	0%	0%	0%	0%	0.64%
Levoglucosan	0%	0%	0%	0%	0%	2.39%
1,2-Benzenediol	0%	0%	0%	0%	0%	0.81%
CO	0%	0%	0%	0%	0%	1.31%

Temperature [°C]	*NC Gas*	*Liquid*	*Overheads*	*Bottoms*	*Cooled Overheads*	*Bottoms Cooled*
Temperature [°C]	25	25	97.95	175.62	20	20
Pressure [kPa]	101.3	101.3	101.3	101.3	101.3	101.3
Molar Flow [kgmole/hr]	75.01	10.08	8.55	1.53	8.55	1.53
Mass Flow [kg/hr]	2203.5	407.6	249.1	158.5	249.1	158.5
Enthaply Stream [MJ/hr]	4,103	3,455	2,293	727	2,684	778
Carbon	0%	0%	0%	0%	0%	0%
Oxygen	0%	0%	0%	0%	0%	0%
Nitrogen	84.19%	0%	0%	0%	0%	0%
Hydrogen	0.03%	0%	0%	0%	0%	0%
Ash	0%	0%	0%	0%	0%	0%
Fasteners	0%	0%	0%	0%	0%	0%
$CrAsO_4$	0%	0%	0%	0%	0%	0%
$CuCrAs_4$	0%	0%	0%	0%	0%	0%
As_2O_5	0%	0%	0%	0%	0%	0%
Acetone	0%	2.45%	4.02%	0%	4.02%	0%
CO_2	13.94%	0%	0%	0%	0%	0%
Methane	0.14%	0%	0%	0%	0%	0%
Ethane	0.07%	0%	0%	0%	0%	0%
Ethylene	0.07%	0%	0%	0%	0%	0%
Water	0%	26.62%	43.6%	0%	43.6%	0%
Acetic Acid	0%	21.1%	34.6%	0%	34.6%	0%
Acetol	0%	7.52%	0%	19.3%	0%	19.3%
Ethanol	0%	4.38%	7.17%	0%	7.2%	0%
Methanol	0%	2.41%	3.94%	0%	3.94%	0%
Furfural	0%	3.42%	0%	8.79%	0%	8.79%
Phenol	0%	1.63%	0%	4.18%	0%	4.18%
3-Methyl-phenol	0%	0.94%	0%	2.40%	0%	2.40%
4-Methyl-phenol	0%	1.08%	0%	2.78%	0%	2.78%
Ethylene Glycol	0%	3.65%	0%	9.39%	0%	9.39%
As_2O_3	0%	0.16%	0%	0.41%	0%	0.41%
As_4O_6	0.028%	0%	0%	0%	0%	0%
2-Butanone	0%	4.13%	6.75%	0%	6.75%	0%
Levoglucosan	0%	15.3%	0%	39.3%	0%	39.3%
1,2-Benzenediol	0%	5.21%	0%	13.4%	0%	13.4%
CO	1.55%	0%	0%	0%	0%	0%