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Pyrolysis of chromated copper arsenate (CCA) treated wood waste at elevated pressure: Influence of particle size, heating rate, residence time, temperature and pressure

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ABSTRACT

Lab-scale pyrolysis experiments with weathered CCA treated wood chips have been performed and the influence of particle size, residence time (10–40 min), heating rate (5–20 °C/min), temperature (330–430 °C) and pressure (0 bar, 5 bar) has been investigated. Few data, covering the pyrolysis of weathered wood was found in the literature and the literature data on pyrolysis experiments with a controlled CCA wood input, showed that results were often highly affected by experimental uncertainty. In order to reduce the uncertainty on the results, a thorough characterization of the wood input has been performed and a ratio method has been proposed which allows to study the effect of particle size on arsenic and chromium volatilization. Larger wood particles show a higher arsenic and chromium retention during pyrolysis which is attributed to the higher mass transfer resistance in these particles. Residence time has a limited effect on arsenic retentions. Increasing heating rate results in a limited increase in arsenic retentions and a more profound increase in chromium retentions. The latter is attributed to a lower average particle temperature during heating caused by the thermal lag in larger particles. Elevated pressure results in a significant increase of arsenic retentions, which is probably due to higher mass transfer resistance. Increasing temperature results in a slight decrease in arsenic retentions till 390 °C, with a sharp decrease at higher temperatures. Chromium retentions are less affected by increasing temperature, especially at higher temperatures. To conclude, a mechanism is proposed for the volatilization of chromium and arsenic during low temperature pyrolysis of CCA wood. Mass transfer resistance and the formation of As_4O_6 are crucial for the control of arsenic volatilization, while heat transfer resistance and thermal lag are more important for the control of chromium volatilization.

1. Introduction

For many years, wood has been preserved with chromated copper arsenate (CCA) to protect the wood against weathering, fungi, insects and bacteria. However, CCA treated wood waste has been classified as hazardous waste, and disposal has become a growing problem [1]. Low temperature pyrolysis, identified as a promising disposal solution [2], combines the recuperation of energy and materials, thanks to the agglomeration of heavy metals. The agglomerates of heavy metals and wood minerals can be separated from the carbon product by centrifugal separation of the solid product, hereby concentrating the heavy metals for recycling or disposal. The main concern is controlling the release of volatile arsenic compounds during pyrolysis. However, this process is complex and not yet fully understood.

Originally, arsenic is present in the CCA treated wood as chromium arsenate ($CrAsO_4$). During pyrolysis $CrAsO_4$ decomposes to chromium(III) trioxide (Cr_2O_3) and arsenic(V) pentoxide (As_2O_5). Hereafter As_2O_5 is reduced by reductive pyrolysis vapors to arsenic(III) trioxide (As_2O_3) which sublimates after desorption from the pyrolysis residue matrix [3–6]. Low temperature pyrolysis aims at controlling or even eliminating this volatilization process by strictly controlling process operating conditions.

However, earlier research revealed some difficulties in studying low temperature pyrolysis or low temperature combustion of CCA treated wood. Table 1 summarizes the type of CCA wood samples used by other researchers, the standard deviation for the heavy metal retentions reported and a short (but inconclusive) summary of reported heavy metal retentions. On the one hand, a large degree of uncertainty on the obtained retention data is often reported due to the heterogeneity of CCA treated wood waste, and the highly complex interaction between wood pyrolysis and heavy

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Table 1
Literature summary of metal retentions during low temperature pyrolysis/combustion of CCA treated wood: type of samples used (freshly impregnated or weathered; wood species; CCA solution used), standard deviation on the metal retentions (σ) and a selection of reported arsenic retention (As ret.), chromium retention (Cr ret.) and copper retention (Cu ret.) at the indicated process conditions (process temperature and oxygen concentration).

Type of sample	Process conditions	σ (%)	As ret. (%)	Cr ret. (%)	Cu ret. (%)	Ref.
Fresh; *Pinus sylvestris* peeling; 2× impregnated with 3.3% CCA 1-C salt	300 °C, 0% O_2	4.3	100	100	N.A.	[3]
Fresh; chipped and powdered; CCA type III salt	300 °C, 0% O_2	N.A.	80	N.A.	N.A.	[7]
CCA treated *Sugi*	400 °C, 0% O_2	N.A.	80	90	90	[8]
Fresh; chipped and powdered; CCA type III salt	400 °C, 0% O_2	12.8[a]	90	N.A.	N.A.	[5]
Fresh; wooden spheres, impregnated *Radiata pine*	500 °C, 5% O_2	As 5, Cr 3	90	N.A.	N.A.	[9]
Aged and weathered CCA wood	600 °C, 21% O_2	As 8.5, Cr 3	86–89	99	99	[10]

N.A.: not available.
[a] Standard deviation for the original sample, no standard deviation reported for results on metal retentions.

metal volatilization. On the other hand, a controlled and homogenized wood input is often used to reduce the heterogeneity of the samples and to reduce the uncertainty on the results.

However, heavy metal volatilization during pyrolysis/combustion is affected by the type of wood samples and the type of treatment. Therefore a controlled and homogenized wood input may show different behaviors with respect to heavy metal retention. Kakitani et al. [5] showed that sawdust impregnated with a CCA solution, without post treatment (aiming at improving heavy metal fixation) showed substantially higher heavy metal volatilization during pyrolysis compared to samples that received post treatment. In addition, due to weathering phenomena, the wood structure of CCA wood waste and the fixation of copper, chromium and arsenic are significantly altered. The particle size of wood samples also has a significant impact. Previous experiments with wood model compounds and heavy metal model compounds [11] showed that physical trapping of heavy metals is an important process in limiting heavy metal volatilization. This physical trapping process may differ in controlled wood input samples, like sawdust or wooden spheres, and therefore may be not representative for wood particles used in an (industrial) application of low temperature pyrolysis of CCA treated wood waste.

In order to represent real wood samples in the present study, wood chips, originating from crushing a weathered CCA treated utility pole, were used. Crushing wooden poles is one of the most efficient ways of downsizing CCA treated wood waste. These wood chips are very heterogeneous in size and metal concentration, however, they closely resemble the type of wood input used in a potential (industrial scale) CCA wood waste treatment plant [12].

Due to the high degree of heterogeneity, it is imperative to perform a thorough characterization of the sample input. To further increase the accuracy of the heavy metal retention data, a ratio method is developed and assessed in this study. This method can also be used to calculate heavy metal retentions in individual wood chips which allow to study the influence of wood chip size on the volatilization of heavy metals during pyrolysis.

Besides the influence of particle size, the influence of elevated pressure (comparison between 0 bar and 5 bar) on heavy metal retention during pyrolysis of real CCA treated wood waste is studied. Elevated pressure is known to have a profound effect on the pyrolysis of wood [13], and is expected to have an influence on heavy metal volatilization. Previous work [11], on wood model compounds, revealed a beneficial effect of elevated pressure on chromium and arsenic retention, in lignin–chromium arsenate–calcium mixtures and glucose–chromium arsenate–calcium mixtures. This effect was mainly attributed to the influence of mass transfer resistance on heavy metal volatilization. A similar effect can be of importance in the pyrolysis of real CCA treated wood samples.

Furthermore, the effect of temperature (330–430 °C), residence time (10–40 min) and heating rate (5–20 °C/min) is studied. Based on these results, an operating window is determined which minimizes or even completely avoids the release of heavy metals. However, the operating conditions have to be chosen in such a way that still a good quality charcoal is obtained, which is brittle and allows the dry separation of heavy metals from the charcoal product. The brittleness is checked by visual observation and by measuring mass retentions. Finally, a mechanism describing chromium and arsenic volatilization during low temperature pyrolysis is proposed.

This study focuses on the volatilization of heavy metals during the low temperature pyrolysis of weathered, real-life wood chips. The aim is threefold: (1) the evaluation of the influence of different process parameters (particle size, residence time, heating rate, temperature and elevated pressure), (2) identification of the mechanisms leading to volatilization of heavy metals during low temperature pyrolysis of CCA treated wood, (3) determination of an operation window which allows the minimization of heavy metal volatilization, while ensuring a good quality of char.

Throughout the manuscript, the term “metal retention” will be used to indicate the amount of heavy metals that is retained in the solid pyrolysis residue, unless stated otherwise (e.g. in the section “ratio method”). “Mass retention” will be used to indicate the mass of solid residue left after pyrolysis relative to the original mass.

2. Materials and methods

2.1. Characterization of CCA-wood waste samples

Wood chips, supplied by the company Thermya (Bordeaux, France), were obtained by crushing a weathered CCA-treated wooden utility pole (>15 years in service). As a result the wood chips were very heterogeneous in size, shape and heavy metal concentration. The type of wood used for the utility poles is *Pinus sylvestris* which has been impregnated with a 3.3% solution of CCA 1-C salt (32.5% $CuSO_4{\cdot}5H_2O$, 41.1% $Na_2Cr_2O_7{\cdot}2H_2O$ and 26.4% $As_2O_5{\cdot}2H_2O$). The poles have been impregnated for class 4, using a full-cell treatment, resulting in a CCA retention of 9 kg/m^3. Approximately 130 g CCA wood chips, oven dried at 105 °C till constant weight, were used in each pyrolysis experiment. Since the heavy metal concentrations of the wood waste input cannot be measured prior to pyrolysis (the analysis method is destructive), the accuracy of the heavy metal retention in the pyrolysis residue relies on a good estimate of the initial heavy metal concentration of the input material. Therefore, a thorough characterization of the wood input has been performed.

A large number (34) of wood chips were analyzed for size, mass and heavy metal concentrations. Inductively coupled plasma-mass spectrometry (ICP-MS) was used for heavy metal analysis. Thereafter the wood chips were classified into 3 classes based on weight. A classification based on size was difficult due to the irregular shapes of the particles which made it difficult to measure thickness, length and width unambiguously. The minimum