

Thermal Valorization of Wood Waste by Pyrolysis at Low Temperature

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Recycling of waste wood is important for the effective utilization of natural resources. Thermal degradation process seems to be a promising technology for material and energy recuperation out of CCA treated wood waste. The charcoal product resulting from CCA treated wood contain Cu, Cr and As. The research aims at thermal valorisation of CCA treated wood waste using low temperature pyrolysis at different heating rates. During pyrolysis an agglomeration process takes place which results not only the growth of existing mineral agglomerates but also the formation of new agglomerates. The chemical and the physical characterizations of pyrolysis solid products show that the CCA treated wood waste could be used for the production of materials in particular charcoal with high specific area and CCA metal agglomerates.

1. Introduction

Telephone poles, railway sleepers, wooden silos, cable drums and wooden play-ground equipment generate wood waste for which environmentally benign technologies need to be developed. The main part of the wood waste is chromated copper arsenate (CCA) treated one (Zandersons et al. 2006). Each of the components of CCA preservative serves a specific purpose: copper is an effective fungicide and arsenic is an effective insecticide, where as chromium serves to prevent corrosion and bind the chemical preservative to the wood. The number of waste disposal sites decreases and redundant poles, piling and lumber, which constitute a large volume of material, may not be accepted at the limited number of sites in the future. So, recycling of waste wood is important for the effective use of natural resources.

Thermal degradation process seems to be a promising technology for material and energy recuperation out of CCA treated wood waste. Burning CCA-treated wood for energy production is one possible option, but this option faces challenges because it generates toxic gases. Conventional pyrolysis systems operate at temperatures that can potentially volatilize the arsenic. Low-temperature pyrolysis offers a feasible option for wood waste management and the recovery of useful chemicals (Helsen et al. 2005).

Material recuperation is based on the formation of clusters or agglomerates, consisting of metals and minerals during thermal degradation of CCA treated wood. Studies such as scanning electron microscopy coupled with energy dispersive X-ray analysis (SEM-EDS) has shown that during pyrolysis, the metal compounds form agglomerates, and

suggests that the metals can be easily recuperated from the charcoal in a dry way (Hata 2003, Helsen et al. 2006).

To dispose CCA treated wood waste, Thermya S.A. Company uses a novel thermal process called “Chartherisation” based on the low temperature pyrolysis (Helsen 2009). The charcoal resulting from CCA treated wood contains Cu, Cr and As. The metals appear both as agglomerates and diffused in the solid matrix. So, during pyrolysis an agglomeration process takes place which results not only on the growth of existing mineral agglomerates but also on the formation of new ones (Kemiha et al. 2008).

The objective of the present work is the valorization of CCA metals and charcoal from CCA treated wood. To fill the research gap, we performed pyrolysis experiments at low temperature to understand the agglomeration phenomena of CCA metals, as well as the generation of charcoal with high specific surface area from treated wood waste.

2. Materials and Methods

2.1. Pyrolysis procedure

Pyrolysis experiments are carried out on a horizontal tubular furnace (D: 60 mm, L: 600 mm). A few grams of solid samples (5 g) are added in an alumina crucible pushed into a quartz tube in a preheated furnace under nitrogen gas flow rate of 100 L/h (Figure 1).

To study the thermal effect on the agglomerations and the release metals during pyrolysis of wood samples, experiments are carried out following preset temperatures of pyrolysis, 320, 350 and 370 °C. These temperatures are chosen according to the TG curves obtained in thermal characterization and in the limit of Chartherm process.

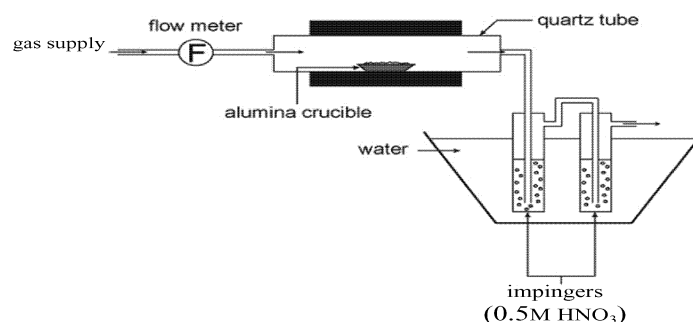


Figure 1: Experimental facility for pyrolysis

The waste samples were heated from room temperature to the preset temperature at a rate of 20°C/min for fast heating and of 5°C/min for a slower one. After that the waste sample is maintained at the preset temperature for duration of 60 min. Finally, the oven is connected to two impingers filled with a solution of 100mL HNO₃ 0.5M allowing the collection of vaporized fraction of the heavy metals. Pyrolysis solid residues were analysed physically and chemically after experiments.

2.2 Characterization Materials

The chemical, physical and thermal characterization of different samples used in this study before and after pyrolysis is carried out by several equipments in the laboratory.

The amounts of As, Cu and Cr in the different samples were measured by inductively coupled plasma spectrometer (ICP-AES). Metals were brought into solution for metal analysis where complete dissolution of the samples in aqua regia solution.

The specific surface area of the samples was determined by adsorption of nitrogen using an automated surface area analyzer (MICROMERITRICS Gemini VacPrep 061). The surface areas were obtained from the BET plots method.

The samples and pyrolysis solid products at different temperatures were examined using environmental scanning electron microscopy (XL 30 ESEM-FEG, FIE Company).

Thermogravimetric analyses (TGA) were performed using TGA analyzer (SETARAM). The wood sample (about 25 mg), was heated from room temperature to 750°C at a heating rate of 5°C/min under nitrogen atmosphere.

3. Characterization Results

3.1 Properties of solid used

Two batches of wood samples are used as polluted (waste) and clean wood respectively: CCA treated wood and wood waste and regular wood. CCA treated wood samples are obtained by impregnation of wood in preservative CCA solution. Regular wood obtained from clean wood (without CCA metals). All the samples pieces used in this work were broken into chips and mixed to produce homogeneous samples.

The solid used characteristics, presented in table1, are similar, notably, density, specific surface area (Sp) and high heating value (HHV). The CCA treated wood samples have higher metal concentrations than the regular wood samples. Chromium and arsenic concentrations are more important than copper concentrations.

Table 1. Physical and chemical characteristics of CCA treated wood and regular wood

Samples	physical characteristics			chemical concentrations		
	Sp (m ² /g)	density (kg/m ³)	HHV (kJ/kg)	As (mg/kg of solid)	Cr (mg/kg of solid)	Cu (mg/kg of solid)
Regular wood	0.9	1452	17302	70	420	850
CCA treated wood	0.8	1482	19982	25770	32150	11520

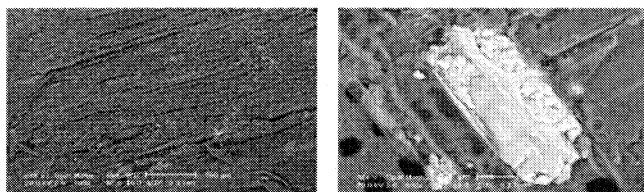


Figure 2: ESEM observations of CCA treated wood

Figure 2 shows the ESEM/EDS investigation of CCA treated wood. The heavy metals were detected as white areas (contrast) at the sample surface. The EDS analyses of the white areas identified arsenic, chromium and copper as the major component of metals. The CCA treated wood had a similar structure to the wood waste, but with more metal precipitates at the surface and agglomerates in the pores of wood matrix.

3.2 Thermo gravimetric analysis (TGA) results

A comparison of the thermal behaviour of the different samples (regular wood and CCA treated wood) obtained by TGA at 5°C/min of heating rate is presented in Figure 3. These curves showed globally same evolutions of weight loss as a function of temperature but at lower decomposition temperature of CCA treated wood compared to wood waste and regular wood. This difference in decomposition temperature is due to the catalytic effects of CCA metals (Helsen et al. 2005; Kercher et al. 2001). So, the CCA metal compounds existing in CCA treated wood act as accelerators to degrade samples at lower temperatures than regular wood. The TGA curves showed three key stages: low temperature volatile loss, main pyrolysis, and carbonization. The char yields for pyrolysis were about 22% and 30% for regular and CCA treated wood respectively.

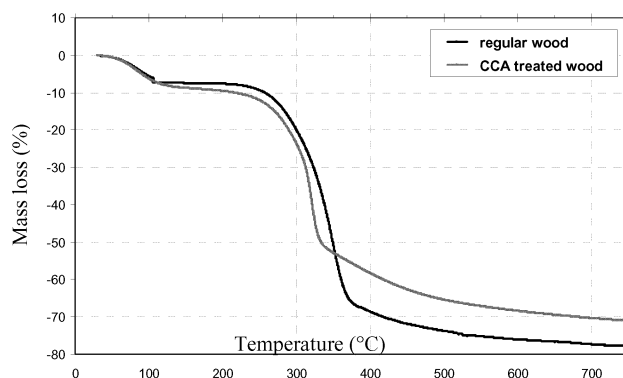


Figure 3: Evolutions of mass loss versus temperature during pyrolysis of regular wood and CCA treated wood, under nitrogen inert gas and 5 °C/min of heating rate

3.3. CCA metals concentration

Figure 4 summarize the results of metal concentrations in the pyrolysis residues by showing the stability of the metals over the range of experimental conditions both for CCA treated wood samples. The initial concentrations of CCA metal in samples are presented in the figure at 20°C. The loss of metals amounts in pyrolysis solid residues show the volatilisation CCA compounds during pyrolysis.

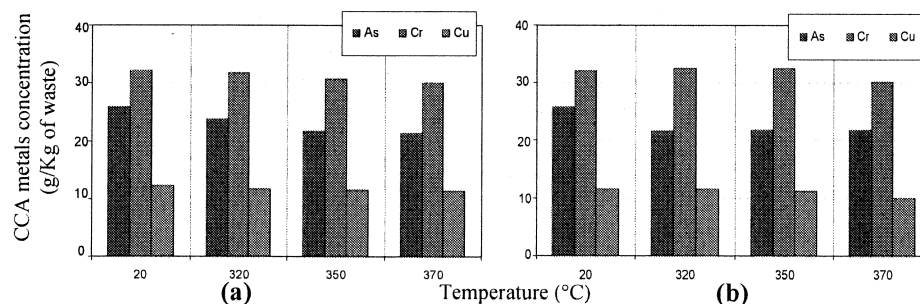


Figure 4: Concentrations of CCA metals in pyrolysis CCA treated wood residues, at different temperatures and heating rates: (a) 5°C/min and (b) 20°C/min.

The concentrations of copper and chromium in pyrolysed CCA treated wood are generally very stable, and the maximum concentration loss in residues is lower than

10% for both copper and chromium in all cases. Arsenic is more volatile during pyrolysis than both copper and chromium because the high initial concentrations of CCA metals. The volatility of arsenic for 5 °C/min heating rate pyrolysis is less than that for 20°C/min especially for 320 °C. In general, the loss percentage of arsenic amount in pyrolysis CCA treated wood residues is less than 15 %. Finally, the pyrolysis of wood waste at low temperature permit to recover until 80 % of the metal amounts initially existing in the CCA treated wood.

This result confirms that it's possible to keep an important amount of CCA metals in the residue matrix using the low temperature pyrolysis of CCA contaminated wood. It is interesting to investigate the distribution of metals in the solid matrix after pyrolysis. Knowledge of the temperature effect on the heavy metals structure in the waste will probably allow choosing the means of separation of metals from the solid matrix.

3.4. Specific surface area evolution

The specific surface area of pyrolysis solid products is measured with BET method. The results of specific surface areas for CCA treated wood are presented in Table 2. Specific surface areas of un-pyrolysed samples are under 1 m²/g for CCA treated.

The results of BET analysis show that specific surface area increase with temperature. This increase can be explained by the higher initial organic content of waste samples. The resulting effect of the decomposition of organic mater content in the waste samples is the liberation of the existent pores and the generation of new one. But this increase of specific surface area is strongly depending on the pyrolysis heating rate. The increase of specific area is higher in the case of 20 °C/min, where it's exceeded 200 m²/g. So for a 5 °C/min heating rate the specific areas are moderate and around 10 m²/g. The SEM analysis at the residue surfaces can provide more explanations for this phenomenon.

Table 2: Specific surface area of residues at different temperatures and heating rates

Temperature	20 °C	320 °C	350 °C	370 °C
5°C/min	0.8	3.5	9.5	11.9
20°C/min	0.8	204	215	215

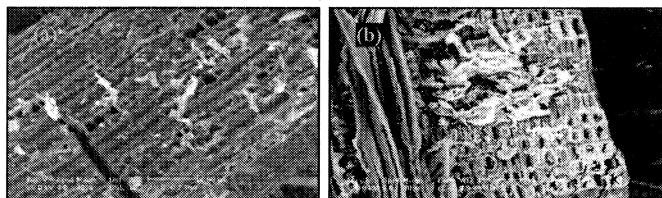


Figure 5: ESEM observations at 370°C of CCA treated wood residues at different pyrolysis heating rates: (a) 20°C/min and (b) 5°C/min

3.5. SEM Observations

The SEM observations in Figure 5, show that the CCA metals agglomerates form the solid films at surface of the residue pyrolysis away from the pores. The metals initially vaporize under thermal effect, concentrated at the residue surface by condensation or nucleation. The difference between values of specific surface area as a function of the heating rate pyrolysis is probably related to the position of metal at the residue surfaces.

For the case of 20°C/min, the amounts of CCA metal leaving the pores are more important. The slow heating rate of pyrolysis promotes the precipitation and the agglomeration of CCA metals at the charcoal surfaces and covering the pores. So Waste residue pyrolysis pores are partially or completely closed by CCA metal agglomerates. These observations explain the low specific surface area in this case.

4. Conclusion

Experimental results of the pyrolysis of CCA treated wood have been presented at different pyrolysis heating rates. The release of CCA metals during decomposition of organics and evaporation of water content from wood pores. The amounts of the CCA metals increase with temperatures. The environmental scanning electronic microscopy observations show that the CCA metals are concentrated at the charcoal surface forming agglomerates with different shape. The size of CCA agglomerates growth significantly at the surface in the case of slow heating rate, and therefore the pores of charcoal were covered with CCA metals and its specific surface area were moderates. At fast heating rate (20 °C/min), CCA metals agglomerate in form of solid films away from the pores, hence the important specific surface area of charcoal.

Finally, the pyrolysis of CCA treated wood is used to generate reactive charcoal with higher specific surface area and to agglomerate CCA metals. Since the treated wood waste could be used for the production of materials (charcoal and CCA metal agglomerates), the approach developed in this study is a promising one.

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