



Release behavior of arsenic, chromium, and copper during heat treatments of CCA-treated wood

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Abstract

Biomass has been attracting attention as an environmentally friendly energy resource due to concerns about global environmental problems. Chromated copper arsenate-treated wood produced by injecting a solution containing sub-percent of chromium, copper, and arsenic (hereinafter referred to as CCA-treated wood) is one of the construction wastes. As fundamental research on the development of clean gasification process for biomass, pyrolysis (400–800 °C) which is the initial stage of gasification and CO₂ gasification (1000 °C, 0–60 min) characteristics of CCA-treated wood were investigated. The release behavior of high-volatile arsenic during pyrolysis and gasification of CCA-treated wood was followed. When the CCA-treated wood was pyrolyzed, the release of arsenic proceeded with increasing temperature and the release extent was 41% at 800 °C. In the case of gasification, the release extent of arsenic increased with gasification time and 90% of the arsenic was released into gas phase within 60 min. Furthermore, it was possible to suppress the release of arsenic by 800 °C during pyrolysis by mixing organic sludge rich in iron and calcium with CCA-treated wood.

Keywords Biomass · CCA · Organic sludge · Gasification · Arsenic

Introduction

In consideration of global environmental issues, biomass, which is a renewable resource is attracting attention as an environmentally friendly energy with low NO_x and SO_x generation. However, the use of biomass has problems such as high collection and transportation costs, because biomass has a high moisture content and a lower calorific value than fossil fuels and is distributed over a wider area. Therefore, in recent years, a gasification technology has been developed to efficiently and economically recover energy from biomass. The synthesis gas obtained by gasification can be used not only as a fuel for power generation but also as a raw material for chemicals, liquid fuels, and hydrogen sources for fuel cells, which leads to a comprehensive improvement in energy utilization. However, gasification of biomass has many problems such as blockage of equipment due to a large amount of tar generated during pyrolysis stage, corrosion of turbines and environmental pollution due to biomass-derived

alkali metals, chlorides, sulfur oxides and harmful elements, and environmental pollution [1–3].

Construction waste is one of the biomass containing harmful elements. To improve termite resistance and decay resistance of wood, “CCA-treated wood” produced by injecting a solution containing sub-percent of chromium, copper, and arsenic has been used in the world due to its low cost and excellent durability. In Japan, it has been used in our daily lives such as the construction materials, utility poles, railroad ties, and even wooden playground equipment since the late 1960s. Currently, the production and use of CCA-treated wood have already been banned due to its carcinogenicity and consideration for the environment, whereas there is a high possibility that it will be discharged as waste in the future considering the lifetime of buildings and others [4, 5]. In 2000, “Construction Materials Recycling Law” was enforced, and it is obligatory to recycle construction wastes and CCA-treated wood is also covered by this regulation. In the past, unexpected generation of CCA-treated wood wastes has also occurred due to a natural disaster. In 2011, many houses were destroyed by the Great East Japan Earthquake and the subsequent tsunami. About 20 million tons of debris were generated and 75% of which consisted of wood waste. 2.1% of the wood waste was CCA-treated

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wood [6]. Against this background, it is required to develop appropriate disposal and recycling methods for waste wood such as CCA-treated wood. Many studies have been actively carried out on a disposal method of CCA-treated wood based on extraction and, metal recovery and detoxification using microorganisms [7, 8]. However, it is considered that heat and energy recovery by heat treatment are the most appropriate from the viewpoints of volume reduction, cost, and recycling [9–17].

Nishitani et al. investigated the behavior of CCA-treated wood during combustion, and Helsen et al. followed the thermal behavior of arsenic compounds, such as As_2O_3 , As_2O_5 , and CrAsO_4 in the presence of a reducing agent [4, 18–22]. Kercher et al. estimated the reduction mechanism and chemical form by thermogravimetric analysis of a mixture of oxides of chromium, copper, arsenic under different atmospheres and heating conditions [23]. However, although many studies have been conducted on the release of arsenic during heat treatment of CCA-treated wood, the behavior of arsenic during pyrolysis and gasification in high temperature regions has not been clarified yet.

In the previous study, the authors followed the release behavior of arsenic, which is one of the harmful trace elements in the pyrolysis and CO_2 gasification of CCA-treated wood. By applying calcium compound to CCA-treated wood, it was possible to suppress the release of arsenic at temperatures below 800 °C.

In this study, as a basic study for developing a clean gasification process of biomass, the gasification characteristics of CCA-treated wood which is one of the construction waste materials were investigated in the pyrolysis condition (400–800 °C) and CO_2 gasification condition (1000 °C, 0–60 min). The release behavior of arsenic, chromium, and copper during pyrolysis and gasification was also followed. Furthermore, the release of volatile arsenic compound was controlled by mixing organic sludge, which is a biomass resource rich in iron and calcium.

Experimental

Samples

As an experimental sample of CCA-treated wood, American hemlock wood which was injecting a solution containing chromium, copper, and arsenic under pressurized condition to improve termite resistance and decay resistance of wood was used. CCA-treated wood was crushed and sieved to a size smaller than 355 μm . Iron oxide (purity: 95%, extra pure grade, Wako Pure Chemical Industries, Ltd.) and an organic sludge were used as an additive for controlling the release of arsenic. The organic sludge was obtained by dehydrating and drying the sludge which generated by the treatment of

domestic wastewater, sewage sludge, and rainwater through the activated sludge method. The organic sludge was crushed and sieved to a particle size in the range of 350–210 μm .

Pyrolysis

A vertical tubular electric furnace was used for pyrolysis as the heating device, inside of which a fused silica tube with an inner diameter of 42 mm and a length of 760 mm was placed. Silica wool was set inside the reactor, and 10 g of the sample was filled on the wool. Nitrogen gas was supplied from the bottom of the reactor at a flow rate of 1 L–NTP min^{-1} and then, the sample was heated to a terminal temperature ranging from 400 to 800 °C at a heating rate of 20 °C min^{-1} . After the heat treatment, the sample was cooled to lower than 30 °C. Tar generated by thermal decomposition of the sample was collected by a low-temperature trap at minus 70 °C using dry ice–methanol. The gaseous products, CO , CO_2 , CH_4 , and C_2H_6 were determined by GC/MS (AGILENT 5973, AGILENT Technologies, Inc.). Based on the yield of products and amount of carbon in products, partitioning of carbon was calculated using following equation.

Partitioning of carbon [%] =

$$\left(\frac{\text{Carbon in product}}{\text{Carbon in raw CCA - treated wood}} \right) \times 100.$$

Gasification

An infrared image furnace (RHL–E44VHT, SHINKU–RIKO Inc.) was used as the heating device. The size of the fused silica reactor was the same as for pyrolysis. The sample (0.7 g) was placed on an alumina board and inserted into the reactor and nitrogen gas was supplied at a flow rate of 1L–NTP min^{-1} . After the temperature was raised to 1000 °C at a heating rate of 20 °C min^{-1} , the supply gas was changed to CO_2 (gas flow rate: 1L–NTP min^{-1}) and the gasification was carried out for 0–60 min. A gasified char was obtained by immediately cooling under nitrogen gas stream. The identification of the gasified char was carried out by X–ray diffraction (Rigaku Corporation, RAD).

Analyses

Elemental and proximate analyses of CCA-treated wood and the organic sludge and ash composition of the sludge are shown in Tables 1–2. Elemental analysis was conducted by Yanaco MT–700 HCN Corder and a carbon and sulfur analyzer (EMIA–520, HORIBA Ltd.). Contents of volatile matter and ash, and calorific value were determined by a magnetic suspension balance for gravimetric measurements (FMS TG, RUBOTHERM GmbH, Germany) and a bomb

Table 1 Analyses of biomass sample

Sample	Ultimate							Proximate		H.H.V (kcal/kg)
	C	H	N	S	As	Cu	Cr	V.M	Ash	
	(wt.%, d.a.f)				(ppmw)			(wt.%, d.b.)		
CCA	44.6	5.9	0.1	0.2	4200	2200	2200	80.8	0.9	4600
Sludge	52.0	8.0	5.5	1.5	18.6			67.4	21.6	4050

Table 2 Ash composition of sludge

Fe ₂ O ₃	SiO ₂	P ₂ O ₅	Al ₂ O ₃	CaO	MgO	K ₂ O	SO ₃	Na ₂ O
29.3	28.2	17.8	11.2	5.5	1.9	1.8	1.2	1.2

calorimeter (AUTO-CALCULATIG BOMB CALORIMETER CA-XPJ, SHIMADZU Corp.). Ash composition of the sludge was determined by wavelength dispersive X-ray fluorescence apparatus (ZSX Primus IV, Rigaku Corp.). In the co-pyrolysis and co-gasification experiment, the mixing ratio of CCA-treated wood and organic sludge was set to 1:1 and 1:4 by weight.

The CCA-treated wood, pyrolyzed and gasified samples were dissolved by heating with sulfuric acid and hydrogen peroxide in a Digesdahl Digestion Apparatus (23130–20, HACH Company). The tar was heated stepwise according to JIS K 0083 (Methods for determination of metals in flue gas) in a mixed acid of nitric acid and sulfuric acid, nitric acid, a mixed acid of nitric acid and perchloric acid to completely dissolve arsenic, chromium, and copper. The reagents used to digestion and dissolution were sulfuric acid (GR, Nacalai Tesque, Inc.), hydrogen peroxide (GR, SANTOKU CHEMICAL INDUSTRIES, Co, Ltd.), nitric acid (GR, Nacalai Tesque, Inc.), perchloric acid (60%) (GR, Nacalai Tesque, Inc.). Concentration of metals in the dissolved solution was determined by atomic absorption spectrometer (AA-6800, SHIMADZU Corp.). A hydrogen vapor generator (HVG-1, SHIMADZU Corp.) was used to hydrogenate arsenic for the analysis of arsenic.

To investigate the influence of change in arsenic form on the release behavior during pyrolysis, the arsenic form in the CCA-treated wood and its pyrolyzed sample was classified according to their solubility into various leaching solutions [24–29]. Ammonium acetate (GR, Nacalai Tesque, Inc.), sodium chloride (GR, Nacalai Tesque, Inc.), hydrochloric acid (GR, Nacalai Tesque, Inc.), and nitric acid (GR, Nacalai Tesque, Inc.) were used to prepare leaching solutions. The water-soluble and ion-exchangeable forms of arsenic were dissolved in 1 mol/L ammonium acetate aqueous solution. The residue was immersed in 1 mol/L sodium chloride aqueous solution to dissolve the arsenic weakly bound to copper. The arsenic bound to chromium and iron was dissolved by heating the residue in 5 mol/L hydrochloric acid and 2 mol/L nitric acid, respectively. The arsenic remaining in the residue

was dissolved by using the Digesdahl Digestion Apparatus. Concentration of arsenic dissolved in the solutions was determined by the atomic absorption spectrometer equipped with the hydrogen vapor generator. Arsenic leached by each leaching solutions and remained after leaching are defined as CH₃COONH₃-soluble, NaCl-soluble, HCl-soluble, HNO₃-soluble, and H₂SO₄-soluble, respectively.

Thermodynamic equilibrium calculations for As₂O₅, As₂O₅-C, and the sludge-mixed sample was conducted under an atmosphere of nitrogen gas were carried out using the software HSC Chemistry (ver. 5.0, Outokumpu Research Oy). The nitrogen gas was assumed to be present in excess. In the case of the sludge-mixed sample, the calculation was based on the elemental composition and ash content of samples shown in Table 1, and the ash composition of the sludge shown in Table 2. The ash contained in the wood with less than 1 wt% is assumed to be negligible here.

Results and discussion

Pyrolysis and gasification of CCA-treated wood

Figure 1 shows effect of temperature on partitioning of carbon into products during pyrolysis of CCA-treated wood. The amount of carbon distributed to the char decreased significantly up to 400 °C and reached a constant value at temperatures above 400 °C. Tar was generated by decomposition of char, and then gradually decreased with increasing temperature at temperatures above 400 °C. The decrease of char and formation of tar up to 400 °C are considered to be due to the decomposition of wood since the decomposition temperatures of cellulose, lignin, and hemicellulose as components of wood, are 240–400 °C, 280–550 °C, and 180–300 °C, respectively [30]. Formation of gaseous species, such as CO, CO₂, CH₄, C₂H₆ was confirmed with the decrease of char and tar.

Figure 2 shows release extent of arsenic, chromium, and copper during pyrolysis of CCA-treated wood. When the

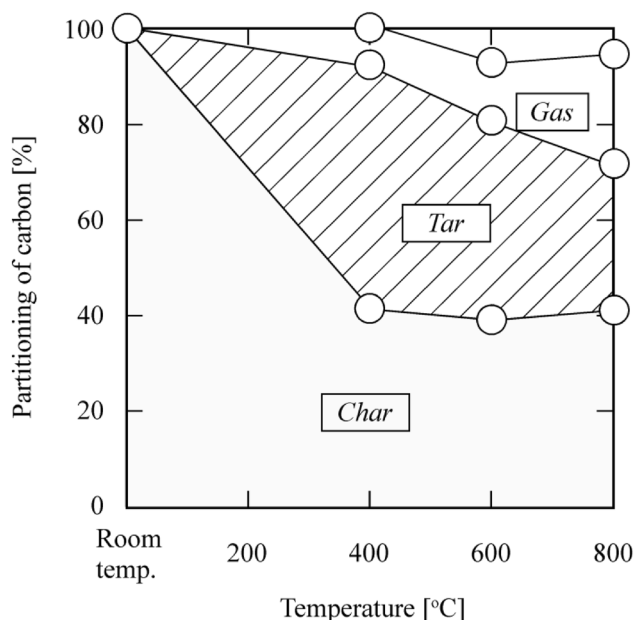


Fig. 1 Partitioning of carbon into char, tar, and gas during pyrolysis of CCA

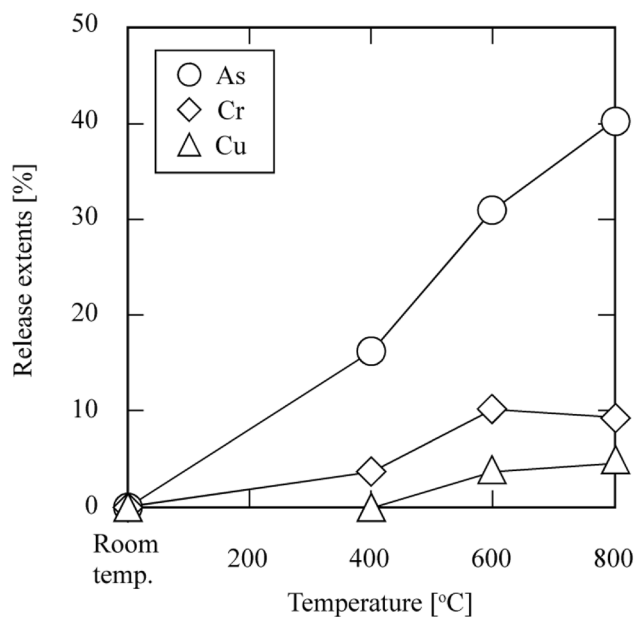


Fig. 2 Change in release extents of As, Cr and Cu during pyrolysis

CCA-treated wood is heated, appreciable release of arsenic is observed at temperatures from 400 to 800 °C. Release of 15% of arsenic was confirmed at 400 °C and the release extent was increased with temperature, reaching 41% at 800 °C. On the other hand, the most of copper and chromium remained in the char during pyrolysis. Figure 3 shows the partitioning of arsenic into char and tar during pyrolysis. It was confirmed that the amount of arsenic in char decreased

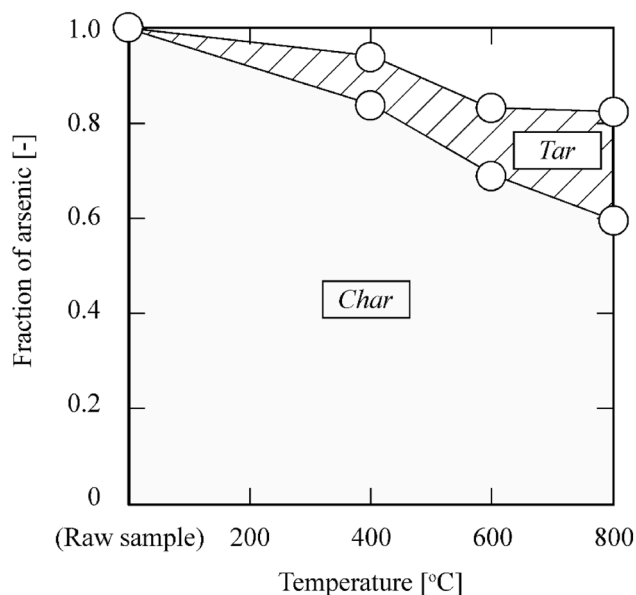
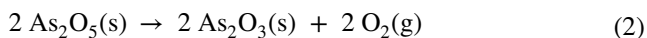
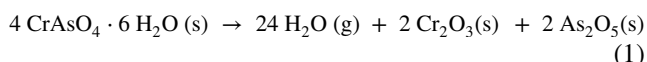


Fig. 3 Change in distribution of arsenic during pyrolysis

with increasing temperature and the extent distributed into tar increased correspondingly.

CCA-treated wood had been prepared by impregnating wood with $As_2O_5 \cdot 2H_2O$, $Na_2Cr_2O_7 \cdot 7H_2O$ (or $K_2Cr_2O_7 \cdot 7H_2O$), and $CuSO_4 \cdot 5H_2O$ under high temperature and pressure conditions. These metals are reported to be present as insoluble $CrAsO_4$ ($Cr_2As_4O_{12}$) and $CuCrO_4$ on the surface of cellulose and the inside of lignin complexes in wood [31–35].

The reactions related to the release of arsenic in pyrolysis proposed by Helsen et al. [20–22] are shown in Eqs. (1)–(3). Many researchers have reported that $CrAsO_4$ decomposes at 300–



400 °C during pyrolysis to generate As_2O_5 and Cr_2O_3 [18, 19, 23, 36–38]. $As_2O_5 (s)$ is stable in an inert atmosphere and volatilizes at temperatures higher than 600 °C when it is heated alone in a nitrogen atmosphere at heating rate of 10 °C/min [21]. However, it is considered that As_2O_5 is reduced to As_2O_3 at temperatures below 600 °C by the carbon in wood and gaseous products such as carbon monoxide and hydrogen, and arsenic volatilizes during pyrolysis process. Figure 4 shows the thermodynamic equilibrium of $As_2O_3-N_2 (g)$ system. The molar ratio of As_2O_3 and $N_2 (g)$ are shown in the figure. $As_2O_3 (C)$, $As_2O_3 (OR)$ and As_2O_3

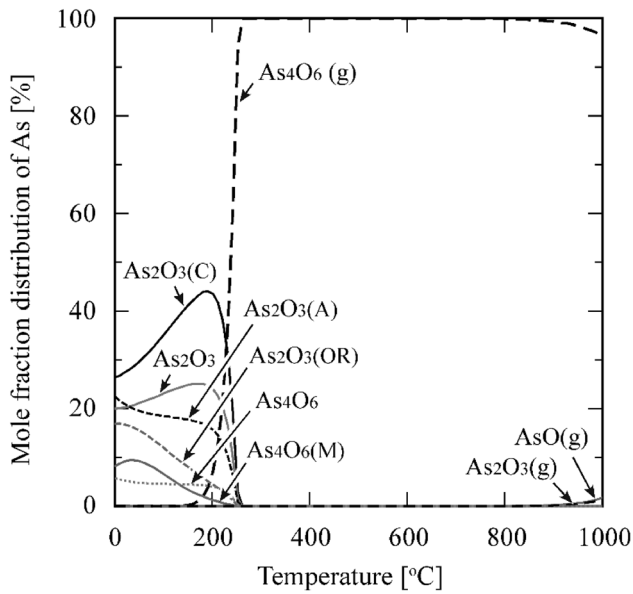


Fig. 4 Calculated thermodynamic equilibrium of $\text{As}_2\text{O}_3\text{-N}_2$ (g) system. Calculation condition (molar ratio): $\text{As}_2\text{O}_3\text{:N}_2$ (g) = 1:1000

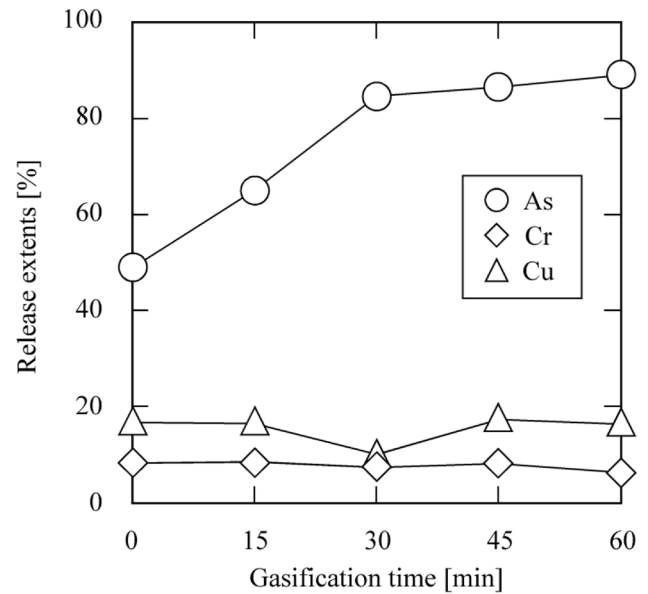


Fig. 6 Change in release extents of As, Cr, and Cu during gasification

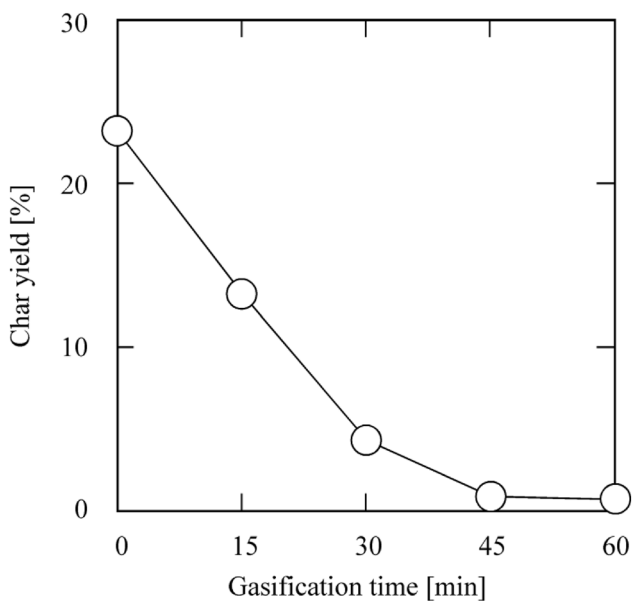


Fig. 5 Change in char yield during gasification

(A) are claudetite, orthorhombic arsenic oxide and arsenolite. It was also suggested that all type of As_2O_3 are released into gas phase as As_4O_6 (g) up to 250 °C. Since As_2O_3 sublimates at 130 °C, it is considered that the release of arsenic in the low-temperature region was caused by the conversion of As_2O_5 (s) to As_2O_3 . The unreacted arsenic compound used during CCA production and the product resulting from the decomposition of CrAsO_4 may be As_2O_5 (s) [20–22, 37, 38].

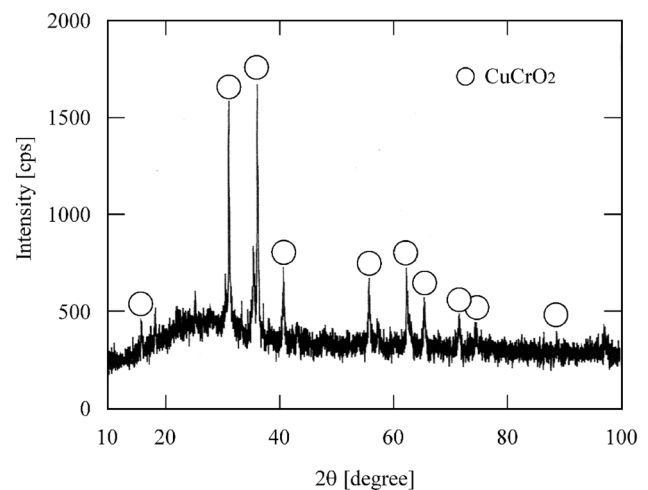


Fig. 7 XRD pattern of gasified char at 60 min

Figure 5 shows the change in char yield when the CCA-treated wood was gasified under CO_2 gas stream at 1000 °C. The char yield decreased significantly with the reaction time, and the gasification was almost completed within 45 min. Figure 6 shows the changes in the release extent of arsenic, chromium and copper during CO_2 gasification. The release extent of arsenic increased with gasification time and reached constant value of approximately 90% after 45 min. On the other hand, chromium and copper showed almost constant release extent regardless of the progress of gasification. To clarify the chemical forms of chromium and copper in the CCA-treated wood, X-ray

diffraction analysis of the gasified char obtained at time of 60 min was carried out. As shown in Fig. 7, copper and chromium were confirmed to exist in the form of thermally stable CuCrO_2 .

Change in chemical form of arsenic during pyrolysis

Arsenic was released during the pyrolysis of CCA-treated wood in the low-temperature regions, whereas a part of arsenic remained in the solid phase even at high temperatures. If arsenic is present in CCA-treated wood as As_2O_3 , which did not react during impregnation, or as compounds of copper and chromium, CuAsO_4 and CrAsO_4 , all arsenic in the wood should be released from the solid phase at high temperatures. Therefore, the chemical forms of arsenic in the solid phase were classified according to their solubilities in various solutions, and the relationship between the release and the quantitative change of these fractions was followed. Figure 8 shows change in distribution of arsenic into solvents with temperature during pyrolysis of CCA-treated wood. CCA-treated wood and pyrolyzed char contained no NH_4Cl -soluble form. NaCl - and HCl -soluble forms, which classified as arsenic bound to copper and chromium, were contained in CCA-treated wood. When pyrolysis of the wood was carried out at 400 °C, the NaCl -soluble arsenic decreased and the formation of HNO_3 -soluble form was confirmed. When the temperature was raised to 800 °C, the

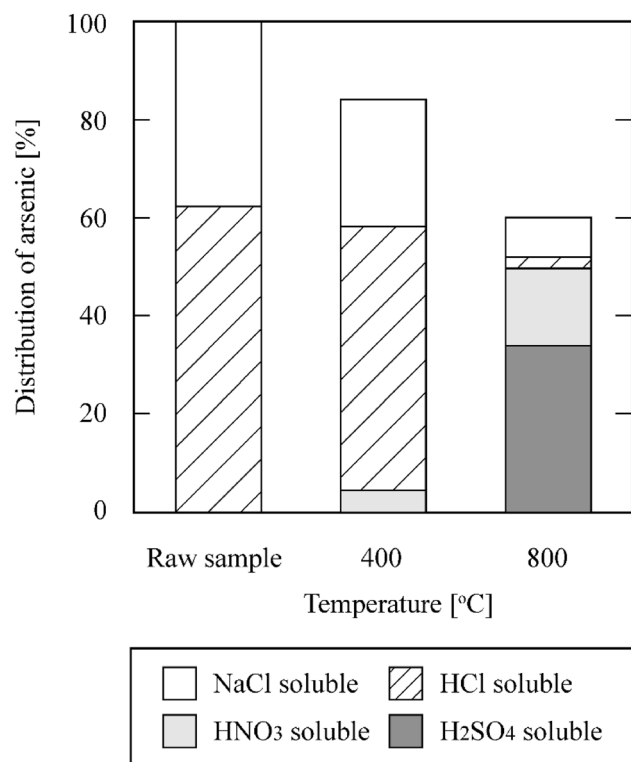


Fig. 8 Change in distribution of arsenic into solvents during pyrolysis

NaCl - and HCl -soluble forms decreased remarkably, and the amount of arsenic in the solid phase decreased. The arsenic remained in the solid phase had changed into HNO_3 - and H_2SO_4 -soluble forms. The former is considered to be arsenic compound such as iron arsenide (FeAs). The latter is a form that dissolves when the char is decomposed with sulfuric acid, and is estimated to be a stable form of arsenic that is included organically [39, 40].

Release control of arsenic during pyrolysis

It has been reported by many researchers that arsenic has a high affinity for iron and calcium [39, 41–44]. In this study, the effect of physically mixing the reagent iron oxide as an iron source with wood was investigated for suppressing the release of arsenic during heat treatment of the CCA-treated wood. Iron oxide was added to the wood at a molar ratio of $\text{Fe}/\text{As} = 20$. Figure 9 shows the change in release extent of arsenic during pyrolysis of the iron oxide mixed sample. The release of arsenic started up to 400 °C, and the release extent was 10%, as in the case of CCA-treated wood without additive. The influence of iron oxide was remarkable at high temperatures, and the release extent at 800 °C was suppressed to 22%. Wang et al. reported that arsenic reacted with iron to form FeAs and remained in solid phase during pyrolysis of coal [45]. Therefore, the thermodynamic equilibrium calculation of $\text{As}_2\text{O}_3\text{--Fe}_2\text{O}_3\text{--N}_2$ (g) system was

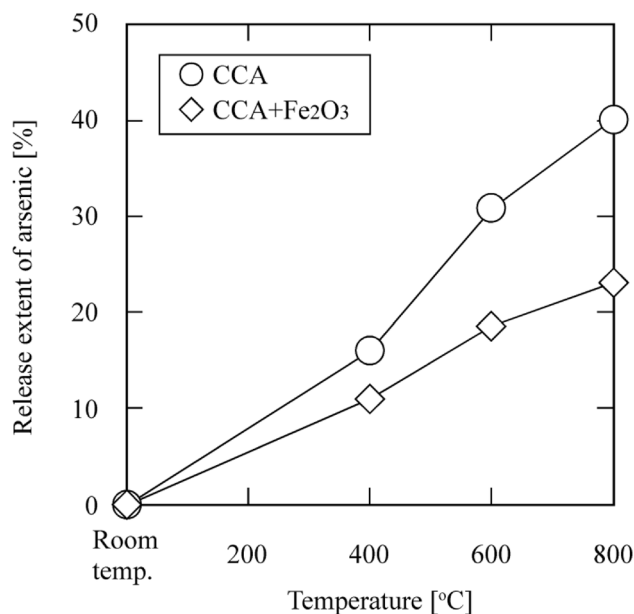


Fig. 9 Change in release extent of arsenic during pyrolysis

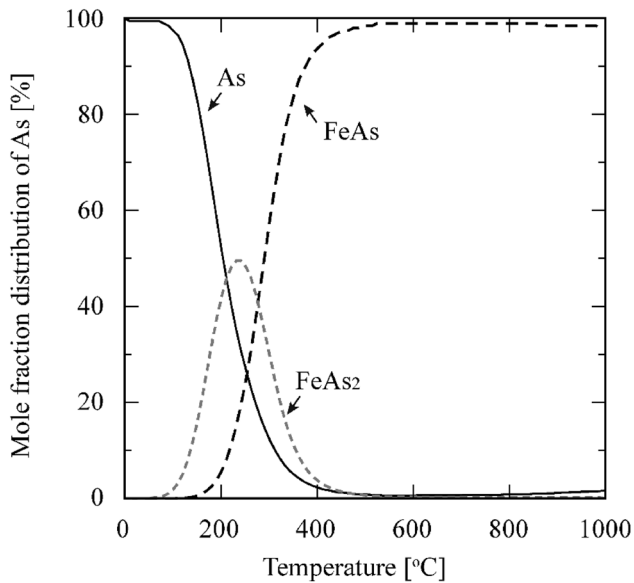


Fig. 10 Calculated thermodynamic equilibrium of $\text{As}_2\text{O}_5\text{-Fe}_2\text{O}_3\text{-C-N}_2(\text{g})$ system. Calculation condition (molar ratio): $\text{As}_2\text{O}_5\text{:Fe}_2\text{O}_3\text{:C:N}_2(\text{g})=1\text{:}20\text{:}100\text{:}1000$

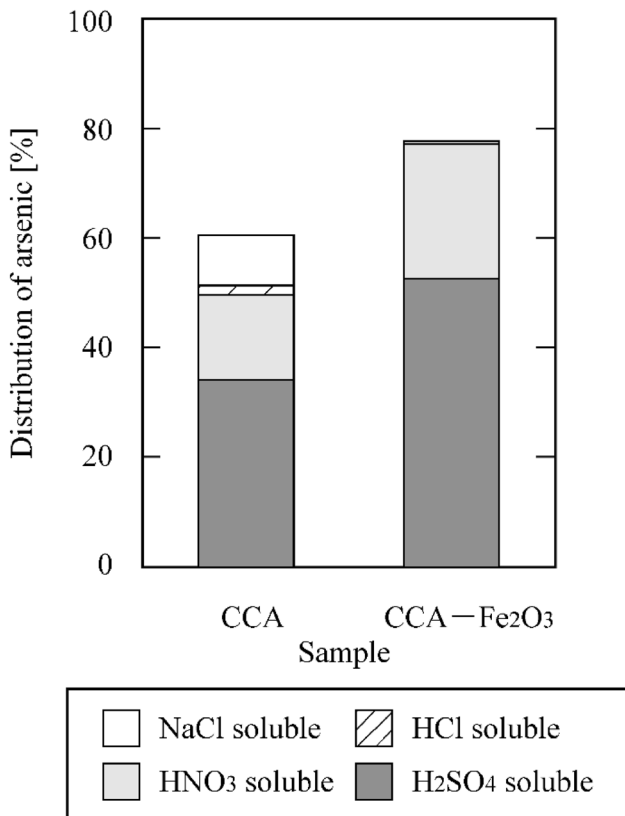


Fig. 11 Change in distribution of arsenic into solvents during pyrolysis for $\text{CCA} + \text{Fe}_2\text{O}_3$. (pyrolysis temperature 800°C)

carried out and the result are shown in Fig. 10. Molar ratio of As_2O_5 , Fe_2O_3 , and $\text{N}_2(\text{g})$ was shown in the figure. It was confirmed that arsenic is stable as FeAs_2 at low temperature and as FeAs at high temperature. Figure 11 shows comparison of the soluble form of arsenic in the pyrolyzed sample with and without the addition of iron oxide at 800°C . The addition of iron oxide resulted in an increase in HNO_3 - and H_2SO_4 -soluble forms of arsenic and in a disappearance in NaCl -soluble form. It is considered that $\text{As}_2\text{O}_5(\text{s})$ generated by decomposition of CuAsO_4 and CrAsO_4 soluble in NaCl and HCl reacted with iron oxide and stabilized as HNO_3 -soluble form, FeAs and FeAs_2 . It is estimated that the increase in the H_2SO_4 -soluble form, which is included in organic material, is due to the increase in the extent of arsenic remained in the solid phase by the addition of iron oxide. Similar to the addition of iron compound, calcium compounds are well known to be effective in suppressing the release of arsenic. Lu et al. reported that the release of arsenic in pyrolysis of coal could be suppressed by adding CaO [44]. The effect of adding calcium compound is also high for the CCA-treated wood. It has been confirmed that release of arsenic could be significantly suppressed by a calcium compound during pyrolysis up to 800°C through our preliminary experiment of coating CCA-treated wood with calcium hydroxide.

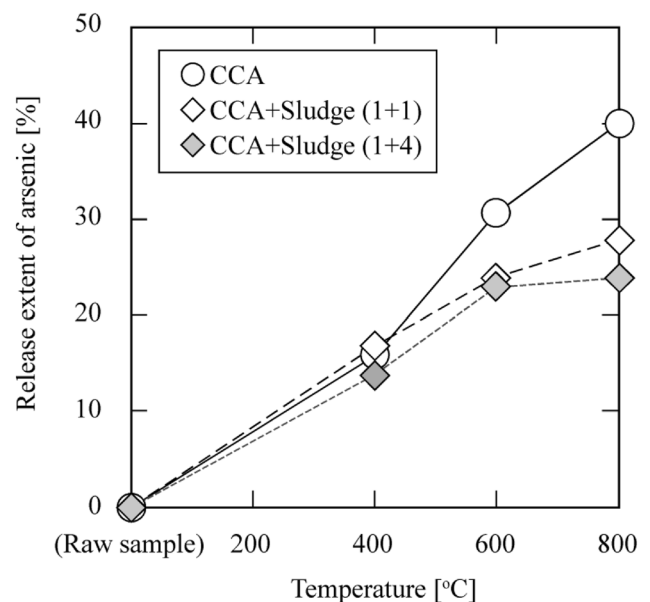


Fig. 12 Change in release extent of arsenic for $\text{CCA} + \text{sludge}$ during pyrolysis

Effect of organic sludge on release control of arsenic during pyrolysis and gasification of CCA-treated wood

Release control of arsenic during heat treatment by mixing organic sludge with high iron and calcium content with the CCA-treated wood was investigated. The organic sludge has a calorific value comparable to that of wood as shown in Table 1, and the reaction rate in pyrolysis and gasification are also similar. Ash content of the sludge is high as 21.6 wt.%, and the Fe_2O_3 occupies over 29 wt.% of the ash (Tables 1 and 2). Figure 12 shows the release behavior of arsenic when CCA-treated wood was co-pyrolyzed with an equal or four times the amount of organic sludge and when the wood was pyrolyzed alone. The addition of organic sludge did not influence the release of arsenic up to 400 °C. The effect of organic sludge on arsenic release was confirmed at temperatures above 400 °C, and the release extent at 800 °C was suppressed at 28 and 24% at the mixing ratios of 1:1 and 1:4, respectively. Figure 13 shows thermodynamic equilibrium calculation carried out for the sludge-mixed sample under nitrogen stream. Calculation condition is shown in the figure. Although arsenic release as As_2 (g), AsP (g), AsS (g) at temperatures higher than 600 °C, a part of arsenic is stable as $FeAs$. In this system, calcium which is abundant in the sludge, is thermodynamically stable as $Ca(OH)_2 \cdot Ca_3(PO_4)_2$ in the temperature range from 600 to 1000 °C. It was, therefore, suggested that suppression of arsenic release by mixing the sludge is due to iron. Figure 14 shows the change in char

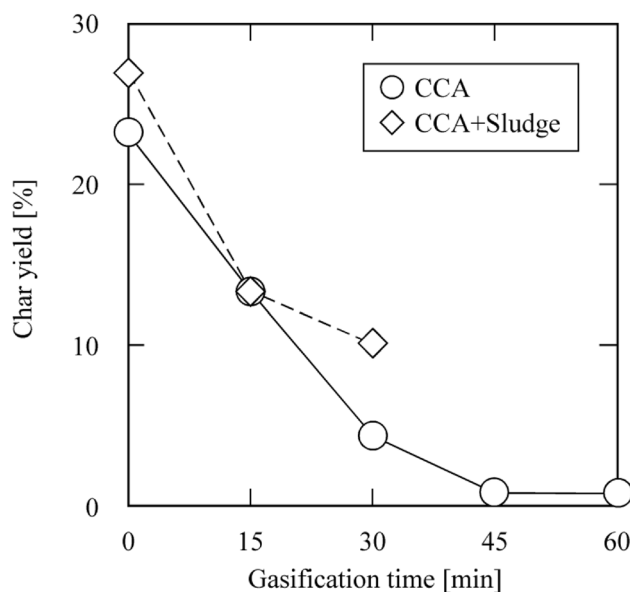


Fig. 14 Change in char yield for CCA + sludge during gasification

yield when the mixture of CCA-treated wood and the sludge at mixing ratio of 1:1 was heated at 1000 °C under CO_2 gas stream. The sludge-mixed sample also showed a drastic change in yield, showing no significant difference from the case of the wood alone. Although the organic sludge is rich in alkali metals as well as iron and calcium, it was confirmed that the coexisting elements do not influence the gasification rate. Figure 15 shows the change in the release extent of

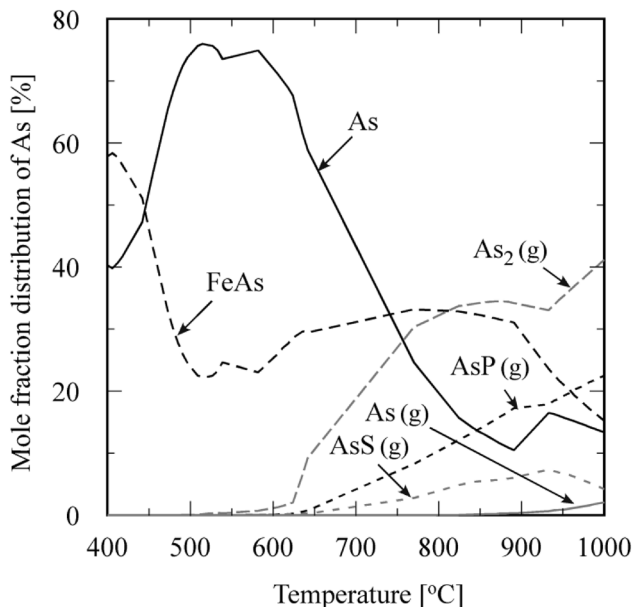


Fig. 13 Calculated thermodynamic equilibrium of sludge-mixed sample. Calculation condition: CCA-treated wood:sludge: N_2 (g)=1 g:1 g:1000 kmol

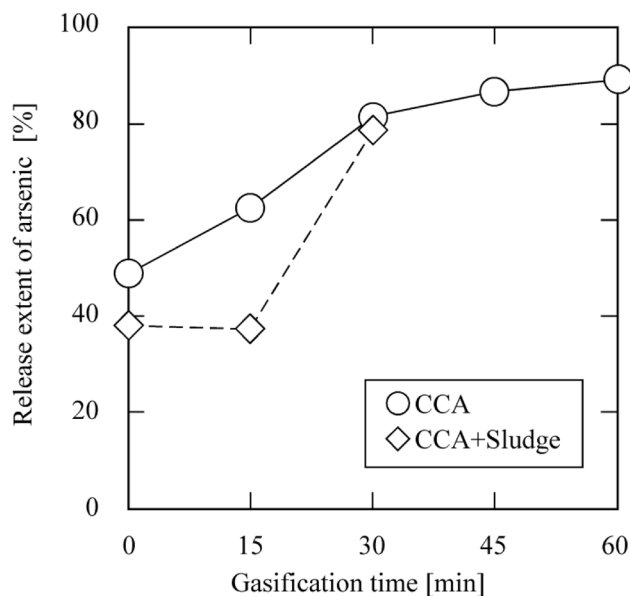


Fig. 15 Change in release extent of arsenic for CCA + sludge during gasification

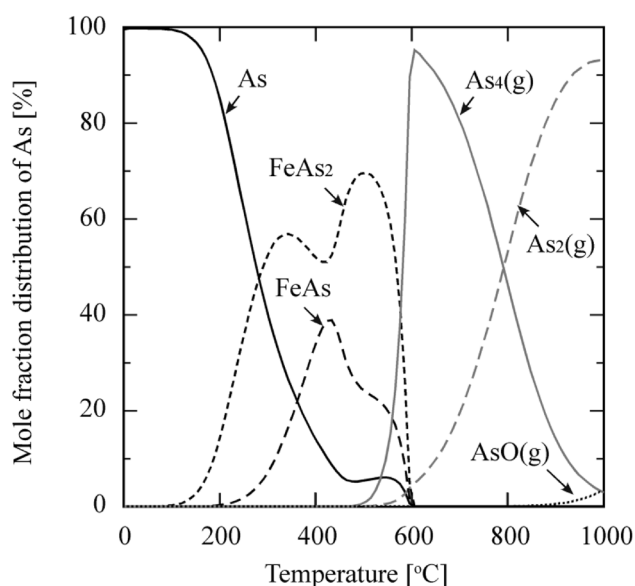


Fig. 16 Calculated thermodynamic equilibrium of FeAs–C–CO₂ (g) system. Calculation condition (molar ratio): FeAs:C:CO₂ (g)=1:10:1000

arsenic during the gasification of the CCA-treated wood and the sludge-mixed sample at 1000 °C. Although the mixing of organic sludge suppressed the release of arsenic within 15 min of gasification time, the release extent was reached the 80% which was the same level as the CCA-treated wood alone at 30 min. To investigate the release of arsenic in the gasification of the sludge-mixed sample, thermodynamic equilibrium calculations were carried out for FeAs which is a stable form of arsenic and iron in pyrolysis step. The result is shown in Fig. 16. Although the arsenic was stable as FeAs and FeAs₂ in the low-temperature region, these forms may decompose and volatilize as As₂ (g) and As₄ (g) at temperatures higher than 800 °C.

Conclusion

As a basic research for developing a clean gasification process of biomass, pyrolysis and gasification behavior of CCA-treated wood were investigated, and the release behavior of arsenic, chromium and copper was followed. In the case of pyrolysis, the most of chromium and copper remained in the solid phase, whereas the release extent of arsenic increased with increasing temperature, reaching 41% at 400 °C. It was also confirmed that the release of arsenic progressed with reaction time and approximately 90% of arsenic released after 45 min when the CCA-treated wood was gasified under CO₂ atmosphere at 1000 °C. Furthermore, the effect of adding organic sludge which contains iron and calcium was investigated

to suppress the release of arsenic during the heat treatment of CCA-treated wood. The effect of addition of the sludge on arsenic release was confirmed above 400 °C, and the release extent of arsenic at 800 °C was suppressed at 24% at the mixing ratio of the wood and the sludge was 1:4.

References

1. Bjorkman E, Stromberg B (1997) Release of chlorine from biomass at pyrolysis and gasification conditions. *Energy Fuels* 11:1026–1032
2. Jensen P, Frandsen F, Hansen J, Johansen K, Henriksen N, Horlyck S (2004) SEM investigation of superheater deposit from biomass-fired boiler. *Energy Fuels* 18:378–384
3. Knudsen J, Jensen P, Lin W, Frandsen J, Johansen K (2004) Sulfur transformations during thermal conversion of herbaceous biomass. *Energy Fuels* 18:810–819
4. Nishitani T, Fukunaga I, Itoh H (1994) Laboratory experiments of heavy metals behaviour on the burning of CCA treated wood. *Osaka City Inst Publ Health Environ Sci* 56:46–52
5. Shalat SL, Solo-Gabriele HM, Fleming L, Buckley B, Black K, Jimenez M, Durbin M, Graygo J, Stephan W, Van de Bogart G (2006) A pilot study of children's exposure to CCA-treated wood from playground equipment. *Sci Total Environ* 367:80–88
6. Ohgami N, Yamanoshita O, Thang ND, Yajima I, Nakano C, Wenting W, Ohnuma S, Kato M (2015) Carcinogenic risk of chromium, copper and arsenic in CCA-treated wood. *Environ Pollut* 206:456–460
7. Coudert L, Blais JF, Mercier G, Cooper P, Janin A, Gastonguay L (2014) Demonstration of the efficiency and robustness of an acid leaching process to remove metals from various CCA-treated wood samples. *J Environ Manage* 132:17–206
8. Ferrarini SF, dos Santos HS, Miranda LG, Nunes Azevedo CM, Maia SM, Pires M (2016) Decontamination of CCA-treated eucalyptus wood waste by acid leaching. *Waste Manage* 49:253–262
9. Hingston J, Collins C, Murphy R, Lester J (2001) Leaching of chromated copper arsenic wood preservatives: a review. *Environ Pollut* 111:53
10. Kazi F, Cooper P (2002) Rapid-extraction oxidation process to recover and reuse copper chromium and arsenic from industrial wood preservative sludge. *Waste Manage* 22:293–301
11. Kazi F, Cooper P (2006) Method to recover and reuse chromated copper arsenate wood preservative from spent treated wood. *Waste Manage* 26:182–188
12. Helsen L, Bluck E (2005) Review of disposal technologies for chromated copper arsenate (CCA) treated wood waste, with detailed analyses of thermochemical conversion processes. *Environ Pollut* 134:301–314
13. Gezer E, Yildiz U, Yildiz S, Dizman E, Temiz A (2006) Removal copper, chromium and arsenic from CCA-treated yellow pine by oleic acid. *Build Environ* 41:380–385
14. Cuypers F, Helsen L (2011) Pyrolysis of chromated copper arsenate (CCA) treated wood waste at elevated pressure: influence of particle size, heating rate, residence time, temperature and pressure. *J Anal Appl Pyrol* 92:111–122
15. Ange N, Brian S (2013) The fate of heavy metals during combustion and gasification of contaminated biomass—a brief review. *J Hazard Mater* 256–257:56–66
16. Kramb J, Kontinen J, Backman R, Salo K (2016) Elimination of arsenic-containing emissions from gasification of chromated copper arsenate wood. *Fuel* 181:319–324

17. Botomé ML, Poletto P, Junges J, Perondi D, Dettmer A, Godinho M (2017) Preparation and characterization of a metal-rich activated carbon from CCA-treated wood for CO₂ capture. *Chem Eng J* 321:614–621
18. Helsen L, Bluck E, Mullens S, Mullens J (1999) Low-temperature pyrolysis of CCA-treated wood. *J Anal Appl Pyrolysis* 52:65–86
19. Helsen L, Bluck E (2000) Kinetic of the low-temperature pyrolysis of chromated copper arsenate-treated wood. *J Anal Appl Pyrolysis* 53:51–79
20. Helsen L, Bluck E, Van Bael MK, Mullens J (2003) Arsenic release during of CCA treated wood waste: current state of knowledge. *J Anal Appl Pyrolysis* 68–69:613–633
21. Helsen L, Bluck E (2003) Metal retention in solid residue after low-temperature pyrolysis of chromated copper arsenic (CCA)—treated wood. *Environ Eng Sci* 20:569–580
22. Helsen L, Bluck E, Bael M, Vanholyland G, Mullens J (2004) Thermal behavior of arsenic oxide (As₂O₃ and As₂O₅) and the influence of reducing agent (glucose and activated carbon). *Thermochim Acta* 414:145–153
23. Kercher A, Nagle D (2001) TGA modeling of the thermal decomposition of CCA treated lumber waste. *Wood Sci Technol* 35:325–341
24. Irvine J, Dahlgren S (1976) Mechanism of leaching of copper chrome arsenic preservatives in saline water. *Holzforchung* 3D:44–50
25. Hingston JA, Moore J, Bacon A, Lester JN, Murphy RJ, Collins CD (2002) The importance of the short-term leaching dynamics of wood preservatives. *Chemosphere* 47:517–523
26. Tessier A, Campbell P, Bisson M (1979) Sequential extraction procedure for the speciation of particulate trace metals. *Anal Chem* 51:844–851
27. Kolker A, Huggins F, Palmer C, Shah N, Crowley A, Huffman G, Finkelman R (2000) Mode of occurrence of arsenic in four US coal. *Fuel Process Technol* 63:167–178
28. Huggins F, Huffman G, Koller A, Mroczkowski S, Palmer C, Finkelman R (2002) Combined application of XAFS spectroscopy and sequential leaching for determination of arsenic speciation in coal. *Energy Fuels* 16:1167–1172
29. Guo R, Yang J, Liu Z (2004) Thermal and chemical stabilities of arsenic in three Chinese coals. *Fuel Process Technol* 85:903–912
30. Migita N, Yonezawa Y, Kondo T (1968) *Wood Chemistry (Mokuzai Kagaku)*, Kyoritsu Shuppan, pp 61–77
31. Pizzi A (1981) The chemistry and kinetic behavior of Cu-Cr-As/B wood preservatives. I. Fixation of chromium on wood. *J Polym Sci* 19:3093–3121
32. Pizzi A (1982) The chemistry and kinetic behavior of Cu-Cr-As/B wood preservatives. II. Fixation of the Cu/Cr system on wood. *J Polym Sci* 20:707–724
33. Pizzi A (1982) The chemistry and kinetic behavior of Cu-Cr-As/B wood preservatives. III. Fixation of a Cr/As system on wood. *J Polym Sci* 20:725–738
34. Pizzi A (1982) The chemistry and kinetic behavior of Cu-Cr-As/B wood preservatives. IV. Fixation of a CCA to wood. *J Polym Sci* 20:739–764
35. Bull D, Harland P, Vallance C, Foran G (2000) EXAFS study of chromated copper arsenate timber preservative in wood. *Journal of Wood-Science* 46:248–252
36. Hata T, Bronsveld P, Ystavel T, Kooi B, Hosson J, Kakitani T, Otono A, Imamura Y (2003) Electron microscopic study on pyrolysis of CCA (chromium, copper and arsenic oxide)—treated wood. *J Anal Appl Pyrol* 68–69:635–643
37. Kakitani T, Hata T, Kajimoto T, Imamura Y (2004) Effect of pyrolysis on solvent extractability of toxic metals from chromated copper arsenate (CCA) treated wood. *J Hazard Mater B* 109:53–57
38. Kakitani T, Hata T, Kajimoto T, Imamura Y (2004) Two possible pathways for the release of arsenic during pyrolysis of chromated copper arsenate (CCA) treated wood. *J Hazard Mater* 113:247–252
39. Wu C, Barton T (2001) A thermodynamic equilibrium analysis to determine the potential sorbent materials for the control of arsenic emissions from combustion sources. *Environ Eng Sci* 18:177–190
40. Diaz-Somoano M, Martine-Tarazona M (2003) Trace element during coal gasification based on a thermodynamic equilibrium calculation approach. *Fuel* 82:137–145
41. Shigematsu K, Kubo J (1982) The vapor pressure measurement of each decomposition reaction of CaO–As₂O₅, 2CaO–As₂O₅, 3CaO–As₂O₅. *J Min Metall Inst Japan* 98:517–522
42. Shigematsu K, Kubo J, Morinaga K, Yanagase T (1982) Reaction of As₂O₅ with Ca, Na and Pb silicates at high temperature. *J Min Metall Inst Japan* 98:611–617
43. Sterling R, Helble J (2003) Reaction of arsenic vapor species with fly ash compounds: kinetics and speciation of the reaction with calcium silicates. *Chemosphere* 51:1111–1119
44. Lu H, Chen H, Li W, Li B (2004) Transformation of arsenic in Yima coal during fluidized-bed pyrolysis. *Fuel* 83:645–650
45. Wang J, Takaya A, Tomita A (2004) Leaching of ashes and chars for examining transformations of trace elements during coal combustion and pyrolysis. *Fuel* 83:651–660

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