



Title	Characterization of char derived from various types of solid wastes from the standpoint of fuel recovery and pretreatment before landfilling
Author(s)	Hwang, I.H.; Matsuto, T.; Tanaka, N.; Sasaki, Y.; Tanaami, K.
Citation	Waste Management, 27(9), 1155-1166 <a href="https://doi.org/10.1016/j.wasman.2006.05.013">https://doi.org/10.1016/j.wasman.2006.05.013</a>
Issue Date	2007
Doc URL	<a href="http://hdl.handle.net/2115/33050">http://hdl.handle.net/2115/33050</a>
Type	article (author version)
File Information	matsuto2.pdf



[Instructions for use](#)

**Characterization of char derived from various  
types of solid wastes from the standpoint of fuel  
recovery and pretreatment before landfilling**

**I.H. Hwang, T. Matsuto\*, N. Tanaka, Y. Sasaki, and K. Tanaami**

**Laboratory of Solid Waste Disposal Engineering  
Graduate School of Engineering  
Hokkaido University  
Kita 13, Nishi 8, Kita-ku  
Sapporo 060-8628, Japan**

**\*Corresponding author. Tel./fax: +81-11-706-6828.**

***E-mail address:* matsuto@eng.hokudai.ac.jp (T. Matsuto).**

## **Abstract**

Carbonization is a kind of pyrolysis process to produce char from organic materials under an inert atmosphere. In this work, chars derived from various solid wastes were characterized from the standpoint of fuel recovery and pretreatment of waste before landfilling. Sixteen kinds of municipal and industrial solid wastes such as residential combustible wastes, non-combustible wastes, bulky wastes, construction and demolition wastes, auto shredder residue, and sludges were carbonized at 500 °C for 1 h under nitrogen atmosphere.

In order to evaluate the quality of char as fuel, proximate analysis and heating value were examined. The composition of raw waste had a significant influence on the quality of produced char. The higher the ratio of woody biomass in waste, the higher heating value of char produced. Moreover, an equation to estimate heating value of char was developed by using the weight fraction of fixed carbon and volatile matter in char.

De-ashing and chlorine removal were performed to improve the quality of char. The pulverization and sieving method seems to be effective for separation of incombustibles such as metal rather than ash. Most char met a 0.5 wt% chlorine criterion for utilization as fuel in a shaft blast furnace after it was subjected to repeated water-washing.

Carbonization could remove a considerable amount of organic matter from raw waste. In addition, the leaching of heavy metals such as chrome, cadmium, and lead appears to be significantly suppressed by carbonization regardless of the type of raw waste.

From these results, carbonization could be considered as a pre-treatment of waste before landfilling as well as for fuel recovery.

*Key words:* Carbonization; Char; Solid wastes; Fuel recovery; Pre-treatment before landfilling

## **1. Introduction**

When MSWIs (municipal solid waste incinerators) were reported to be a major source of dioxins in the 1990s, it was a considerable shock to Japanese society since until that time Japan had treated nearly 80% of its waste by incineration. Since then, small or medium scale incinerators have been restricted or replaced by large scale ones equipped with expensive air-pollution control systems and ash melting processes. At the same time, various processes which can substitute for mass-burn incineration started to be studied actively. The pyrolysis-melting system was also introduced as a process to minimize the discharge of pollutants such as dioxins and heavy metals into the environment. Carbonaceous materials produced in the pyrolysis process become energy sources as well as treatment objects in melting process. However, there is still much controversy over its excessive energy consumption, difficulties in maintenance, unmarketability of slag and so on.

With this background, we focus on pyrolysis, excluding the melting process, and consider its role as a unique process in integrated solid waste management systems. In this work, pyrolysis will be called “*carbonization*” because we are

interested in solid residues, known as “*char*”, obtained by thermal treatment under an inert atmosphere.

Char produced from waste can be used for various purposes such as fuels, adsorbents, soil conditioners, etc. However, the major demand for char appears to be for use as an alternative fuel. From the WTE (waste to energy) standpoint, char is likely to have many advantages compared to waste itself or RDF (refused derived fuel) because of its higher quality, easier handling, and better substitutability in existing coal-fired power boilers (Vassilev et al., 1999). In thermal recycling aspect, MSWIs show significant low energy efficiency (13 to 14%) unlike thermal power plants because they have to keep lower steam temperature to prevent severe boiler corrosion (Malkow, 2004). Besides, RDF or biomass occasionally requires a special boiler system for its combustion (Dayton et al., 1999; Jensen et al., 2001).

Fuels derived from wastes are often faced with obstacles for practical uses owing to their high chlorine or ash content, which is notorious for causing corrosion, fouling, deposition, slagging, sintering, and agglomeration during combustion (Arvelakis and Koukios, 2002). Likewise, their removal is one of the most important tasks to extend char utility. It is necessary for char to satisfy the chlorine criterion of less than 0.5 or 0.1 wt% to be used as fuel for a shaft blast furnace or a cement kiln respectively in Japan.

Even though carbonization is performed at a lower temperature (usually 450-600 °C) compared with incineration or melting, it can also decompose a large amount of organic matter in waste. In Europe, the pretreatment of waste such as mechanical biological treatment is performed to achieve early stabilization of landfills. However, this approach has mainly focused on degradation of organic matter rather than metal control. According to previous researches, char was reported to have a considerable

level of pH buffering and high adsorption capacity (Kistler et al., 1987). This implies that carbonization may have a positive effect on immobility of heavy metals.

Therefore, we intend to consider carbonization as a pre-treatment method before landfilling. To this end, it is necessary to evaluate whether or not carbonization can function as a thermal pre-treatment technique in the scheme of waste treatment and disposal.

In Japan, the annual generation amount of industrial waste was already over eight times that of municipal solid wastes in 2000. The proper treatment and disposal of construction and demolition waste, sludge, or auto shredder residue is especially important because their quantity in industrial waste is much higher than that of other types of waste. Thus, we extended the scope of carbonization subjects from municipal solid waste to industrial wastes: Residential combustible wastes, non-combustible wastes, bulky wastes, construction and demolition wastes, auto shredder residue, and sludges.

The objective of this work is to characterize char obtained from various types of solid waste from the standpoint of fuel recovery and pre-treatment before landfilling.

## **2. Material and Methods**

### **2.1 Sample**

Wastes chosen in this study were, (1) municipal solid wastes: residential combustible wastes, incombustible wastes, and bulky wastes, and (2) industrial

wastes: construction and demolition wastes, auto shredder residues, and sludges.

Sampling and preparation of each type of waste was conducted as follows:

- Residential combustible wastes: *RC1*, *RC2*, and *RC3*. Around 200 kg of combustible waste was sampled at waste collection stations in residential areas. First, it was separated into food, plastics, paper, wood, textiles, and metals, and then each component was shredded to less than 6 cm. After drying them at 60 °C for 24 h, *RC1* was prepared by mixing the waste samples based on the composition of residential combustible wastes generated from Sapporo in 2000. In order to simulate the variation of residential combustible wastes by the enforcement of recycling regulations for food wastes or plastics, *RC2* and *RC3* were prepared by removing food wastes and plastics from *RC1* respectively.

- Non-combustible wastes: *NC*. A sample was obtained from a shredding plant which treated non-combustible waste and bulky waste collected from residential areas in Sapporo. After shredding and metal sorting, the waste was divided into two fractions - combustible and incombustible residue - depending on whether or not it could pass through a screen. About 40 kg of combustible or incombustible residue was sampled respectively and then shredded to less than 6 cm again. *NC* was prepared by mixing these samples on the basis of their weight fraction.

- Bulky wastes: *BW*, *BC*, and *BN*. *BW* were also obtained from the same shredding plant with *NC* and prepared by the same procedure with *NC*. Moreover, shredded combustible and incombustible residue were sampled as *BC* and *BN* respectively. About 40 kg of each one was sampled.

- Construction and demolition wastes: *CDK*, *CDRC*, *CDRN*, *CDT1*, and *CDT2*. The major component of *CDK* is woody waste. After sorting recyclable items, 15 kg of residue passing through screens was obtained as *CDK*.

*CDRC* and *CDRN* were sampled from *R*-Material Recycling Facility (MRF). First bulky or unsuitable item was excluded from commingled waste. After that, the waste went through a screen, magnetic separator, air classifier, and vibration screen. Finally, the waste was divided into combustible and incombustible fractions, which were sampled as *CDRC* and *CDRN* respectively.

On the other hand, both *CDT1* and *CDT2* were sampled at *T*-MRF equipped with a three-stage separation system. First, recyclable items were recovered manually. Next, the waste was divided into combustibles and incombustibles by screening, manual sorting, and air classification. About 9 kg of combustible residue was collected through sampling three times, and noted as *CDT1*. Finally, incombustibles were re-shredded and then divided again into combustible and incombustible residue. About 9 kg of combustible residue was sampled as *CDT2*.

- Auto shredder residue: *ASR*. A sample was obtained from an ELV (End of life vehicle) plant. ELV was crushed coarsely and then shredded again. Ferrous and non-ferrous recyclable metal were recovered and finally, the remaining residue was sampled as *ASR*. Around 3 kg of *ASR* was sampled.

- Sludges: *OS*, *SS*, and *PS*. *OS* was obtained from a drying plant of organic sludge. This was mixed with coffee bean husks for improvement of handling during landfilling. *SS* and *PS* were dewatered sludges discharged from a sewage water treatment plant and a paper-mill plant respectively. About 15 kg of each type of sludge was sampled and dried at 60 °C until variation of moisture content was not observed. Details of these wastes are summarized in Table 1.

## 2.2 Experimental method

### *2.2.1 Physical and chemical composition of wastes*

With the exception of sludges, the physical composition and its weight fraction were investigated to characterize raw wastes. Each sample was shredded again below 5 mm using a cutting mill to ensure homogeneity of the sample for proximate analysis. The measurement of fixed carbon, volatile matter, and ash followed proximate analysis for coal and coke (JIS M 8812).

### *2.2.2 Carbonization*

Prepared waste was loaded into a rotary kiln type of reactor by a screw feeder and then carbonized at 500 °C for 1 h. In the preliminary test of carbonization under 400-600 °C, it was proven that the yield of fixed carbon was highest at 500 °C, whereas the concentration of total organic carbon in filtrate decreased sharply in the leaching test. Actually, most makers operate their carbonization processes in the range of 400-500 °C for 1 h of retention time with taking account of char quality, energy balance, various systematic conditions, etc. In this work, the slope angle and rotation rate of the kiln were also adjusted to 0.8-2.3 ° and 1-2 rpm respectively depending on input wastes to maintain 1 h of retention time. Nitrogen was used as the carrier gas at the rate of 11 L/min. Figure 1 shows the entire carbonation system used in this work.

### *2.2.3 Characterization of char*

The weight of raw waste and char were checked to determine the yield of char in each run. Char was pulverized by ball-mill for 1 h and then sieved using a 100 mesh. A fraction passing through 100 mesh ( $\leq 1$ mm) was provided as sample char to be characterized. Proximate and ultimate analysis were performed to investigate char composition. Carbon, hydrogen, and nitrogen were measured by elementary analyzer

(CHN recorder MT-5, Yanaco Co.). Sulfur was absorbed in hydrogen peroxide solution during the incineration of sample and its concentration was measured by ion chromatography (DX-500, Dionex Co.). Chlorine analysis was performed by the incineration method using a tubular quartz reactor (JIS Z 7302-6) and its concentration was measured by the mercuric thiocyanate method (JIS K 0107) using an absorption spectrophotometer (U-1101, Hitachi Co.). The heating value was measured using a bomb calorimeter (Auto-calculating calorimeter CA-4PJ, Shimadzu Co.). The microwave-assisted acid digestion method was used to measure metal content in char (SW-846 Method 3052, EPA). The concentration of cadmium, chromium, lead, zinc, copper, potassium, sodium, magnesium, and calcium were analyzed by atomic absorption spectrometry (Z-8200, Hitachi Co.).

#### *2.2.4 Ash separation and chlorine removal*

Ash separation and chlorine removal accounted for improvement of char quality. Pulverization and sieving were performed to separate ash from char. Pulverization was carried out to break the char aggregate into single carbon or ash particles as far as possible. Milled char was simply divided into two fractions, above- and below 1 mm using a 100 mesh. The weight fraction of ash in char before and after removal of the fraction above 1 mm was compared to ascertain the quality improvement.

For chlorine removal, around 10 g of char below 1 mm was rinsed with 100 ml distilled water repeatedly. The entire procedure of water washing followed the previous study (Hwang et al., 2006). After washing, the chlorine content in char was measured to estimate the efficiency of chlorine removal.

#### *2.2.5 Estimation of organic matter and metal*

For a comparative study, raw waste and ash were tested along with char. Around 200 g of waste was heated to obtain ash in an electric muffle furnace at 900 °C for 2 h. However, the ash of sludge was obtained by heating at 600 °C for 2 h.

The quantity of organic matter in waste and char was estimated by adding together the amount of fixed carbon and volatile matter.

The leaching concentration of dissolved organic matter and metal from raw waste, char, and ash was investigated by Japanese leaching test No.13 (Environment Agency of Japan, 1973). In this test 10 g of char was immersed in a flask containing 100 mL of distilled water (L/S=10), which was capped and shaken horizontally for 6 h at 200 rpm. After the sample was filtered using 1 µm pore size filter paper, the filtrate was provided for measuring pH and total organic carbon (TOC). TOC was measured using a simultaneous TOC-TN analyzer (TOC-V CPH/CPN, Shimadzu Co.).

In addition, the concentrations of cadmium, chromium, lead, zinc, copper, potassium, sodium, magnesium, and calcium in the filtrate were analyzed by atomic absorption spectrometry (Z-8200, Hitachi Co.).

The entire experimental flow is presented in Figure 2.

### **3. Results and Discussion**

#### 3.1 Characteristics of char obtained from various wastes

The physical and chemical compositions of each type of waste are summarized in Table 2. Describing waste components more simply, they are likely to be classified into, (1) biomasses such as foods, papers, woods, and sludges, (2) synthetic high

molecular substances such as plastics, textiles, and rubbers mainly produced from petroleum, and (3) incombustibles such as glasses and metals.

The yield, proximate and ultimate analyses, heating value, and metal content of char below 1 mm in size are presented in Table 3. The yield of char was in the range of 21-86% depending on the type of raw wastes. As the portion of woody biomass was larger in raw wastes, the amount of fixed carbon also increased in char and thus the higher heating value of char could be obtained. Chars produced from *BW*, *CDK*, and *OS* had a high fixed carbon level but low ash content. The superior quality of *OS* char also was attributed to the presence of mingled coffee bean husks. On the other hand, the yields of char derived from *CDRN*, *CDT2*, and *PS* were high but these were certainly due to their high ash content.

Table 4 shows the physical composition of char over 1 mm. Their compositions absolutely rely on the original components of the raw waste, however, they mostly correspond to incombustibles such as glasses, metals, and so on.

Chlorine content in char was in the range of 0.2-4.9 wt%, which is high enough to cause various problems during combustion when it is used as a fuel (Table 3). In particular, char produced from *CDRC* or *ASR* had higher chlorine content compared to other char. Such high chlorine content of char seems to be inevitable because it is a sort of “inheritance problem” originating from the composition of raw waste. Release of chlorine from Cl containing polymer such as PVC almost completes under 400 °C whereas inorganic salts such as sodium chloride or potassium chloride would remain in char despite carbonization at 500 °C because their boiling points are much higher than 500 °C. Thus, a good deal of chlorine might remain in char owing to incomplete volatilization of inorganic salts in some cases.

In addition, alkali metals associated with chlorides also have a serious effect on corrosion, fouling, and deposition in incinerators (Arvelakis and Koukios, 2002). As shown in Table 3, the content of potassium, magnesium, sodium, and calcium was also remarkably high, regardless of the kind of char. In particular, the content of potassium and sodium was higher in *RC1*, *RC3*, and *OS* char. From the fact that *RC1* and *RC3* contained food wastes and *OS* was discharged from a food processing plant, the presence of K and Na might be originated from the ingredients of food wastes. On the other hand, the high calcium content in *CDRN* and *PS* char appears to be caused by ceramic tiles and calcium carbonate used as filler for paper manufacturing respectively.

The content of heavy metals such as cadmium, chrome, lead, and zinc is also higher than that of general coal. For instance, the Clarke No. of bituminous coal is as follows: Cd, Cr, Pb, and Zn are 0.3, 12, 2.5, and 18 mg/kg respectively (Vassilev and Braekman-Danheux, 1999). Chrome generally comes from paints, pigments, alloys, electronics, and surface metal coatings etc. (Vassilev and Braekman-Danheux, 1999). Since *CDK* comprises a large amount of woody waste generated from construction and demolition areas, its high chrome content might be originated from paints or pigments on the wood surface. As *BC*, *BN*, and *ASR* char were derived from wastes containing a considerable amount of plastics, additives in the plastics might be responsible for the high lead and zinc content.

## 3.2 Evaluation of char from a fuel recovery standpoint

### 3.2.1 Classification of char based on chemical composition and heating value

According to the ternary diagram of ash, fixed carbon, and volatile matter in Figure 3, chars were visually divided into four groups as follows: (1) G1: *BW*, *CDK*, and *OS* char, (2) G2: *RC1*, *RC2*, *RC3*, *BC*, and *CDRC* char, (3) G3: *BN*, *CDT1*, *CDT2*, *ASR*, and *SS* char, and (4) G4: *NC*, *CDRN*, and *PS* char.

In comparison to general coals, the quality of chars that belong to G1 seems to be a match for sub-bituminous or bituminous coal (Figure 3). As shown in Table 3, their heating value was also more than 22,000 kJ/kg and the fuel ratio ranged from 2.19 to 3.38. Chars that belong to G2 or G3 may be required to improve quality if they are under consideration to use as fuel. Finally, chars classified to G4 have 64-72 wt% of high ash content, which is likely to be an obstacle for fuel utilization.

### 3.2.2 Development of an equation to estimate heating value of char

From the results in Table 3, it can be supposed that fixed carbon and volatile matter have a close correlation with the heating value of char. Assuming that fixed carbon is composed of pure carbon, we can estimate the heating value of volatile matter by subtracting the combustion heat of fixed carbon from the measured heating value as follows:

$$HV_{VM} [\text{kJ/kg}] = HV_{Measured} - HV_{FC} = HV_{Measured} - (32,750 \times FC) \div 100 \quad (1)$$

where 32,750 kJ/kg is the combustion heat of carbon. From the linear regression of volatile matter and  $HV_{VM}$  in Figure 4, we can develop an equation to estimate the heating value by means of substituting the weight fraction of fixed carbon ( $FC$ ) and volatile matter ( $VM$ ) in char as follows:

$$HV_{Estimated} \text{ [kJ/kg]} = (32,750 \times FC + 19,598 \times VM) \div 100 \quad (2)$$

The correlation coefficient and the average error between  $HV_{Measured}$  and  $HV_{Estimated}$  were 0.957 and  $\pm 1,031$  kJ/kg respectively. However, the volatile matter presented a bad correlation with  $HV_{VM}$  as shown in Figure 4. This is probably due to errors caused by the measurement of fixed carbon and volatile matter, the assumption of heating value of fixed carbon as combustion heat of carbon, the variation of volatile matter in char etc.. Equivalent curves of heating values in Figure 3 were also predicted by equation 2.

### 3.2.3 Quality improvement of char by ash separation

As shown in Table 4, 78-100 wt% of char  $> 1$  mm corresponded to incombustibles such as glasses or metals rather than ash, which suggested that pulverization and simple sieving could be a feasible tool to separate ash from char. In order to determine the improvement of char quality by ash separation, the ash reduction ratio ( $\eta$ ) was estimated as follows.

$$\eta \text{ (\%)} = \left( \frac{A_R}{A_0} \right) \times 100 \quad (3)$$

Where,  $A_0$  and  $A_R$  mean the weight fraction of ash in char before and after ash separation respectively. Table 5 shows the ash reduction ratio by application of pulverization-simple sieving or high media separation (HMS). The HMS is an ore separation technique using the difference of specific gravity among particles in liquid

media such as calcium chloride solution. The data of ash separation by HMS was referred from previous study (Matsuto et al., 2004).

After the application of pulverization and sieving, the ash in char was decreased to 44-96% of initial content (Table 5). The quality of *BW* char was fairly improved among the various chars. According to the results of HMS application, the ash in *BW* char was normally transferred into sinks so a considerable amount of ash could be separated. However, HMS had almost no effect on *RCI* char because it was so light as to float up completely (Matsuto et al., 2004).

#### *3.2.4 Chlorine removal of char by water washing*

Chlorine in char was denoted in this work as follows: (1) volatile chlorine, (2) residual chlorine, and (3) water-soluble chlorine. Volatile and residual chlorine was analyzed to determine how much chlorine would volatilize or not during incineration of char. Water-soluble chlorine means chlorine removed by repeated water washing.

As shown in Figure 5, through four cycles of water washing, 67-97 % of chlorine was removed from the char that belong to the group of G1 and G2 in Figure 3 . Above all, volatile chlorine, which can cause various problems during combustion, was remarkably decreased in the char. With the exception of char derived from *BC*, the washed char met a criterion of 0.5 wt% of chlorine content, enabling it to be utilized as shaft blast furnace fuel. However, it was difficult to satisfy the criterion of 0.1 wt% of chlorine that would allow the char to be used as fuel for cement kilns in Japan. Hwang et al. (2006) suggested that carbonation or heating could be effective to promote the release of difficult-to-dissolve chlorine compounds during water-washing without excessive chemical or energy input.

### 3.3 Evaluation of char from a standpoint of pre-treatment before landfilling

Chars that belong to the group of G3 or G4 in Figure 3 are ranked as low grade fuel owing to their high ash content as well as low heating value. In this case, they can be considered as “pretreated wastes” before disposal in landfills instead of fuels for thermal recycling. In order to determine whether or not carbonization can function as a pretreatment process before landfilling, the load of organic matter and metal into landfills should first be evaluated.

#### 3.3.1 *Effect of carbonization on reduction of organic matter*

Both volatile matter and fixed carbon were determined as total organic matter included in samples. The reduction efficiency of organic matter was estimated to know how much the organic matter in raw wastes decreased by carbonization (Table 6). To this end, the organic matter in char was re-calculated by multiplying char yield, assuming that the weight of raw waste was 100. With the exception of *CDRN* containing low organic matter originally, 65-86% of organic matter was reduced by carbonization, which suggested that the absolute amount of organic matter could be decreased by carbonization (Table 6).

On the other hand, the concentration of total organic carbon (TOC) in filtrate of char ranged from 99 to 148mg/L, which was commonly higher than that of ash, 0.7-128 mg/L. The TOC released during JLT-13 might represent just an easily leachable organic matter during the initial period of landfills because there is no consideration about the biological degradation of organic matter by microorganism.

Despite the result for TOC concentration, it was certain that the load of organic matter could be largely reduced by carbonization compared to direct landfills of waste.

### 3.3.2 Comparison of metal leaching from waste, char, and ash

The pH and metal concentrations in filtrate of raw waste, char, and ash obtained from JLT-13 are shown in Table 7.

The variation of pH showed a distinct tendency according to waste, char, and ash regardless of waste types: Ash > char > raw waste. Except for *CDT1*, *CDT2*, and *PS*, filtrate obtained from waste and char had a pH in a neutral range, whereas the pH of filtrate from ash was 10-13 excluding ash of *SS*. A high pH value may cause a retardation of landfill stabilization because it can adversely affect the biological activity of microorganisms. Moreover, leaching of amphoteric metals such as lead can be accelerated under high pH conditions ( $\text{pH} \geq 10$ ).

Metal leaching also seems to show trends depending on raw waste, char, and ash rather than kinds of wastes (Table 7). Chrome and lead were detected in filtrate of raw waste or ash whereas heavy metals such as cadmium, chrome, and lead were nearly zero or not detected in filtrate of char except that about 0.01 mg/L of lead was released from *PS* char (Table 7). From these results, it was found that char has a considerable ability to suppress leaching of heavy metals. There might be two reasons. First, the pH of filtrate of char is chemically neutral. According to the relationship between pH and metal leaching, metal concentration generally tends to decrease in a neutral range. However, the pH of raw waste was also in a neutral range and *CDT1*, *CDT2*, and *PS* char had a high pH value of 9.48-12.08. Thus, the suppression of metal leaching could not be described only by pH dependency. Honda et al. (1993) noted that iodine adsorptive capacity of 680-720 mg/g was achieved by carbonization of waste ion exchange resin. Sainz-Diaz and Griffiths (2000) reported that straw and furniture waste chars produced at 500 °C had 50 m<sup>2</sup>/g and 40 m<sup>2</sup>/g of BET surface

respectively. According to above references, the adsorptive capacity of char by its specific surface area and pore structure might be considered as another reason for restraining metal leaching.

On the other hand, almost alkali metals, apart from magnesium, showed a tendency to release easily regardless of raw waste, char, or ash. Leaching of magnesium was conspicuously decreased in ash.

Using the yield of char and ash in Table 3 with the concentration of metal released from raw waste, char, and ash in Table 7, the leaching amount of metals according to disposal methods can be estimated. Figure 6 exhibits the leaching amounts of metals supposing 1 t of waste disposed of in a landfill, without pretreatment and with pretreatment such as carbonization or incineration.

Of the three treatment methods, carbonization had the most remarkable effect on the suppression of leaching of chrome, cadmium, and lead. Although the control of zinc and copper by carbonization was inadequate, their release amount was relatively smaller than that occurs under direct landfilling. However, the leaching amounts of alkali metal appear to be nearly same to one another.

As already mentioned, the pH and specific surface or porous structure of char can be considered as the most probable cause of restrained metal release. However, a further study seems to be necessary to clarify the mechanism related to the suppression of metal leaching.

#### **4. Conclusions**

In this work, we investigated the carbonization from the standpoint of fuel recovery and as a pre-treatment method before landfilling. Residential combustible wastes, non-combustible wastes, bulky wastes, construction and demolition wastes, auto shredder residue, and sludges were carbonized at 500 °C for 1 h under nitrogen atmosphere.

The composition of input wastes definitely influenced the quality of char as a fuel; the higher the ratio of woody biomass in raw wastes, the higher heating value of char produced. Heating value of char estimated by using its weight fraction of fixed carbon (*FC*) and volatile matter (*VM*) showed a good correlation with measured heating value ( $R^2=0.957$ ).

Regarding quality improvement of char, the pulverization and sieving method did not have a significant effect on improvement of char quality, however, it is likely to be effective in separation of incombustibles rather than ash. Most char met a 0.5 wt% chlorine criterion to be utilized as shaft blast furnace fuel after repeatedly water washing.

Leaching of heavy metals such as chrome, cadmium, and lead decreased remarkably with carbonization regardless of the type of raw waste. Although the concentration of TOC released from char was higher than that of ash, carbonization had an excellent effect on reduction of organic matter destined for landfills.

From these results, carbonization might be considered as a feasible option for pre-treatment before landfills, as well as for fuel recovery.

## **Acknowledgements**

This work was performed with the financial support of the Ministry of the Environment, Japan.

## References

- Arvelakis, S., Koukios, E.G., 2002. Physicochemical upgrading of agroresidues as feedstocks for energy production via thermochemical conversion methods. *Biomass and Bioenergy*, 22, 331-348
- Dayton, D.C., Jenkins, B.M., Turn, S.Q., Bakker, R.R., Williams, R.B., Belle-Oudry, D., Hill, L.M., 1999. Release of inorganic constituents from leached biomass during thermal conversion. *Energy and Fuels*, 13, 860-870
- Honda, I., Seno, M., Ochiai, Y., Shibata, A., Nozaki, M., 1993. Production of activated carbon from waste ion exchange resin. *Proceedings of 4<sup>th</sup> Annual Conference of the Japan Society of Waste Management Experts*, 285-288
- Hwang, I.H., Matsuto, T., Tanaka, N., 2006. Water-soluble characteristics of chlorine in char derived from municipal solid wastes. *Waste Management*, 26, 571-579
- Jensen, P.A., Sander, B., Dam-Johansen, K., 2001. Pretreatment of straw for power production by pyrolysis and char wash. *Biomass and Bioenergy*, 20, 431-446
- Kistler, R.C., Widmer, F., Brunner, P.H., 1987. Behavior of chromium, nickel, copper, zinc, cadmium, mercury, and lead during the pyrolysis of sewage sludge. *Environmental Science and Technology*, 21, 704-708
- Malkow, T., 2004. Novel and innovative pyrolysis and gasification technologies for energy efficient and environmentally sound MSW disposal. *Waste management*, 24, 53-79

- Matsuto, T., Tanaka, N., Kakuta, Y., Tojo, Y., Matsuo, T., 2004. Carbonization of household waste for recycling and thermal pre-treatment for landfill disposal. *Journal of the Japan Society of Waste Management Experts*, 15, 408-417
- Sainz-Diaz, C.I., Griffiths, A.J., 2000. Activated carbon from solid wastes using a pilot-scale batch flaming pyrolyser. *Fuel*, 79, 1863-1871
- Vassilev, S.V., Braekman-Danheux, C., Laurent, P., 1999. Characterization of refuse-derived char from municipal solid waste. 1. Phase-mineral and chemical composition. *Fuel processing technology*, 59, 95-134
- Vassilev, S.V., Braekman-Danheux, C., 1999. Characterization of refuse-derived char from municipal solid waste. 2. Occurrence, abundance and source of trace elements. *Fuel processing technology*, 59, 135-161

Table 1. Summarization of waste chosen in this work

Types	Abbreviation	Typicals
Residential combustible wastes	<i>RC1</i>	Combustible wastes collected at waste collection stations in a residential area
	<i>RC2</i>	Excluding food wastes from <i>RC1</i>
	<i>RC3</i>	Excluding plastics from <i>RC1</i>
Non-combustible wastes	<i>NC</i>	Shredded non-combustible wastes obtained from a shredding plant
Bulky wastes	<i>BW</i>	Shredded bulky wastes obtained from a shredding plant
	<i>BC</i>	Combustible residues of shredded bulky wastes, <i>BW</i>
	<i>BN</i>	Non-combustible residues of shredded bulky wastes, <i>BW</i>
Construction and demolition wastes	<i>CDK</i>	Mainly wood C&D wastes collected after screening at <i>K</i> -MRF <sup>a</sup>
	<i>CDRC</i>	Combustible residues of commingled C&D wastes at <i>R</i> -MRF <sup>b</sup>
	<i>CDRN</i>	Non-combustible residues of commingled C&D wastes at <i>R</i> - MRF <sup>b</sup>
	<i>CDT1</i>	Combustible residues collected after screening of commingled C&D wastes at <i>T</i> - MRF <sup>c</sup>
	<i>CDT2</i>	Combustible residues collected after screening of non-combustible C&D wastes at <i>T</i> - MRF <sup>c</sup>
Auto shredder residue	<i>ASR</i>	Auto shredder residues obtained from an end of life vehicle treatment plant
Sludges	<i>SS</i>	Dewatered digested sewage sludges
	<i>PS</i>	Dewatered sludges discharged from a paper-mill plant
	<i>OS</i>	Organic sludges mixed with coffee bean husks, which are discharged from food processing industries

<sup>a-c</sup>: *K*-, *R*-, and *T*- are initials of facility names

Table 2. Physical and chemical composition of waste used in this work

	RC1	RC 2	RC 3	NC	BW	BC	BN	CD K	CD RC	CD RN	CD T1	CD T2	ASR	SS	PS	OS
Moisture content (wt %-wet)	39.7	15.7	45.6	6.2	7.0	4.8	12.2	16.6	24.8	19.7	20.3	24.6	-	77.7	61.4	63.7
Component (wt %-dry)																
<i>Food</i>	17.3	0	22.0	0	0	0	0	0	0	0	0	0	0	-	-	-
<i>Paper</i>	51.2	61.1	65.5	11.9	1.4	19.1	6.2	1.0	39.1	5.8	22.3	31.4	0	-	-	-
<i>Wood</i>	2.6	3.2	3.6	6.1	61.6	19.0	31.1	77.7	32.2	12.5	37.9	21.9	0	-	-	-
<i>Plastic</i>	22.4	27.5	0	31.2	10.9	44.5	34.0	0.8	11.8	5.4	17.7	11.8	42.6	-	-	-
<i>Textile</i>	4.8	5.7	7.1	8.3	1.8	0	0	0	0	0	0	0	33.5	-	-	-
<i>Rubber</i>	0	0	0	1.5	1.8	0	0	0	0	0	0	0	0	-	-	-
<i>Glass</i>	0	0	0	13.1	3.4	0	1.3	16.2	9.2	54.7	13.9	16.0	1.7	-	-	-
<i>Metal</i>	1.7	2.4	1.8	3.6	8.4	12.3	3.7	0	0	2.5	0	0	11.4	-	-	-
<i>Miscellaneous (<math>\leq 2</math> mm)</i>	0	0	0	24.2	10.7	5.1	23.6	4.2	7.6	19.1	8.2	19.0	10.7	-	-	-
<i>Sum</i>	100	100	100	100	100	100	100	100	100	100	100	100	100	-	-	-
Proximate analysis (wt %-dry)																
<i>Ash</i>	13.6	9.1	13.0	40.6	9.5	29.9	28.0	7.8	33.8	72.6	31.0	36.4	42.1	22.1	45.4	3.6
<i>Fixed carbon</i>	7.7	10.0	12.3	4.4	16.4	8.6	8.5	12.9	8.0	5.3	10.1	10.0	6.0	5.7	2.1	10.6
<i>Volatile matter</i>	78.7	80.9	74.7	55.0	74.1	61.5	63.4	79.3	58.2	22.1	58.9	53.5	51.9	72.2	52.5	85.8

-: Not measured.

Table 3. Char yield and the composition, heating value, fuel ratio, and metal content of char below 1 mm

	RC 1	RC 2	RC 3	NC	BW	BC	BN	CD K	CD RC	CD RN	CD T1	CD T2	ASR	SS	PS	OS
Char yield (wt %-dry)	24.0	21.1	30.1	47.5	30.4	34.0	45.0	28.4	34.6	85.8	46.9	53.8	35.6	37.5	61.1	25.5
<i>1 mm or under</i> <sup>a</sup>	88.6	83.5	92.7	63.5	79.2	58.7	77.9	85.5	88.6	51.9	94.5	92.3	57.3	95.4	99.6	100.0
<i>1 mm over</i> <sup>b</sup>	11.4	16.5	7.3	36.5	20.8	41.3	22.1	14.5	11.4	48.1	5.5	7.7	42.7	4.6	0.4	0.0
Proximate analysis (wt %-dry)																
<i>Ash</i>	39.0	42.3	40.3	71.9	14.0	40.3	55.8	25.3	41.9	63.6	54.4	57.3	60.3	56.4	68.8	15.7
<i>Fixed carbon</i>	37.0	35.6	36.8	11.8	66.3	39.6	25.8	51.3	31.6	9.8	22.5	19.5	22.0	23.0	5.1	64.5
<i>Volatile matter</i>	24.0	22.1	22.9	16.3	19.6	20.1	18.3	23.4	26.5	26.6	23.2	23.2	17.7	20.6	26.1	19.8
Ultimate analysis (wt %-dry)																
<i>C</i>	43.0	42.3	42.7	18.3	69.8	46.7	33.4	59.0	40.5	22.2	32.0	26.1	29.2	32.5	17.2	67.5
<i>H</i>	1.9	1.8	1.8	1.0	2.6	2.3	1.7	2.9	2.3	1.4	1.5	1.3	1.8	1.7	0.9	2.8
<i>N</i>	1.5	1.3	1.6	0.5	1.9	1.4	0.9	0.9	0.6	0.4	1.1	0.8	0.9	3.8	0.3	3.5
<i>S</i>	0.2	0.3	0.3	0.1	0.2	0.6	0.9	0.6	1.9	5.1	2.5	2.9	0.5	0.5	0.1	0.4
<i>Cl</i>	1.9	1.0	1.6	1.9	1.1	2.3	2.5	1.1	4.9	2.9	1.6	1.3	4.0	0.5	0.2	2.1
High heating value (kJ/kg-dry)																
	15,802	15,065	15,229	5,505	25,932	18,293	13,085	22,931	16,279	8,489	12,880	10,138	11,327	13,071	4,908	24,549
Fuel ratio (-) <sup>c</sup>																
	1.54	1.61	1.61	0.72	3.38	1.97	1.41	2.19	1.19	0.37	0.97	0.84	1.24	1.12	0.20	3.26
Metal content (mg/kg-dry)																
<i>Cd</i>	2.9	2.7	2.7	12.7	14.8	10.5	11.2	1.0	2.0	< 0.05	5.6	1.7	< 0.05	5.5	< 0.05	1.0
<i>Cr</i>	74.8	62.8	24.8	6.2	3.8	3,051	3,472	2,532	249	312	1,156	344	587	70.7	20.7	38.1
<i>Pb</i>	37.0	58.0	55.0	634	1,119	2,273	2,327	673	187	1,333	726	725	4,190	97.6	24.7	101
<i>Zn</i>	540	290	380	2,700	1,380	5,168	4,500	2,593	1,932	1,328	2,110	1,168	12,495	1,593	207	821
<i>Cu</i>	97.0	127	150	627	1,593	612	1,085	422	118	386	403	163	16,090	70.2	666	144
<i>K</i>	4,700	1,800	4,900	1,000	1,200	1,616	1,459	1,767	889	1,293	2,488	2,407	1,196	3,434	482	15,034
<i>Na</i>	9,800	3,700	11,200	5,900	2,500	15,560	8,278	2,346	1,215	2,190	4,877	3,205	2,785	2,140	2,272	40,056
<i>Mg</i>	4,000	3,900	4,600	2,500	1,300	4,215	3,747	3,960	2,265	5,752	7,220	7,644	4,707	5,473	12,347	4,995
<i>Ca</i>	72,300	58,100	80,500	78,300	20,300	32,615	36,252	33,938	91,466	171,052	72,186	88,299	51,938	22,098	168,910	13,204

<sup>a</sup>: Weight fraction of char less than 1 mm based on total weight of obtained char.

<sup>b</sup>: Weight fraction of char more than 1 mm based on total weight of obtained char.

<sup>c</sup>: = (Fixed carbon)/(Volatile matter)

Table 4. Physical composition of char above 1 mm

Composition (wt %)	NC	BW	BC	BN	CDK	CDRC	CDRN	CDT1	CDT2	ASR
<i>Char</i>	0.7	7.9	0.5	0.5	0.0	3.2	0.0	5.3	4.3	0.0
<i>Ferrous metal</i>	11.1	60.4	73.7	5.2	0.0	0.0	0.0	0.0	0.0	6.4
<i>Copper</i>	0.8	6.6	0.0	2.6	0.0	0.0	1.2	14.5	14.3	56.4
<i>Aluminum</i>	7.2	13.3	0.0	6.7	0.0	0.0	0.0	2.6	4.3	13.1
<i>Glass</i>	61.1	7.3	5.3	18.7	15.2	55.3	6.6	0.0	0.0	1.9
<i>Ceramic tiles</i>	0.0	0.0	19.7	16.1	72.2	33.0	89.1	67.1	64.3	0.0
<i>Miscellaneous (less than 2 mm)</i>	19.2 <sup>a</sup>	4.4 <sup>b</sup>	0.9	50.3	12.7	8.5	3.1	10.5	12.9	22.2
<i>Sum</i>	100	100	100	100	100	100	100	100	100	100

<sup>a</sup>: Particle size corresponds to 2-5.6 mm.

<sup>b</sup>: Particle size corresponds to 1-5.6 mm.

Table 5. Ash content of char before and after the application of pulverization and sieving or high media separation and ash reduction ratio  
(Unit: wt %-dry)

	Pulverization and sieving											HMS <sup>a</sup>	
	RC 1	RC 2	RC 3	BW	BC	BN	CD K	CD RC	CD T1	CD T2	ASR	RC 1	BW
Ash content in char before ash separation ( $A_0$ )	46.0	51.8	44.7	31.9	65.0	65.6	36.1	48.5	56.9	60.6	77.3	37.1	49.4
Ash content in char after ash separation ( $A_R$ )	39.0	42.3	40.3	14.0	40.3	55.8	25.3	41.9	54.4	57.3	60.3	30.5	9.1
Ash reduction ratio ( $\eta$ )	84.9	81.6	90.2	43.9	62.0	85.1	70.0	86.4	95.6	94.6	78.1	82.2	18.4

<sup>a</sup>: Referred from Matsuto T. et al. (2004).

Table 6. The total organic matter of waste and char, the reduction efficiency of organic matter by carbonization, and the concentration of total organic carbon of filtrate obtained by the application of JLT-13 to raw waste, char, and ash

	BN	CDRN	CDT1	CDT2	ASR	SS	PS
Total organic matter (wt %-dry) <sup>a</sup>							
<i>Waste</i>	72.0	27.4	69.0	63.6	57.9	77.9	54.6
<i>Char</i> <sup>b</sup>	15.5	16.2	20.2	21.2	8.1	15.6	18.9
Reduction efficiency of organic matter by carbonization (%) <sup>c</sup>	78.5	40.9	70.7	66.7	86.0	80.0	65.4
Concentration of total organic carbon released by JLT-13 (mg/L)							
<i>Waste</i>	265.4	138.4	356.8	284.5	153.7	8,848	573.0
<i>Char</i>	127.0	98.8	147.5	140.6	130.5	98.8	113.8
<i>Ash</i>	0.7	2.9	2.6	1.5	5.0	127.9	38.4

<sup>a</sup>: Determined by summing of fixed carbon and volatile matter.

<sup>b</sup>: Calculated assuming that the weight of raw waste was 100.

<sup>c</sup>: = [1-(total organic matter of char)/(total organic matter of waste) ]×100

Table 7. The pH and metal leaching concentration of filtrate obtained by the application of JLT-13 to raw waste, char, and ash

	Type	BN	CDRN	CDT1	CDT2	ASR	SS	PS
pH (-)	<i>Waste</i>	7.00	6.65	9.22	7.60	6.55	6.32	8.06
	<i>Char</i>	7.70	8.35	11.67	12.08	7.65	7.88	9.48
	<i>Ash</i>	10.75	11.90	12.35	13.03	9.80	7.59	11.48
Metal concentration in filtrate (mg/L)								
<i>Cd</i>	<i>Waste</i>	0.025	< 0.0005	< 0.0005	< 0.0005	< 0.0005	0.006	< 0.0005
	<i>Char</i>	< 0.0005	< 0.0005	< 0.0005	< 0.0005	< 0.0005	< 0.0005	< 0.0005
	<i>Ash</i>	< 0.0005	0.010	< 0.0005	< 0.0005	< 0.0005	< 0.0005	0.006
<i>Cr</i>	<i>Waste</i>	< 0.001	0.280	0.140	0.160	0.280	0.068	< 0.001
	<i>Char</i>	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
	<i>Ash</i>	6.920	0.268	0.540	0.725	0.610	< 0.001	0.068
<i>Pb</i>	<i>Waste</i>	1.035	0.115	0.025	0.035	0.190	0.056	0.039
	<i>Char</i>	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	0.011
	<i>Ash</i>	1.260	0.180	0.015	0.055	0.115	0.033	0.017
<i>Zn</i>	<i>Waste</i>	6.900	< 0.05	0.105	< 0.05	3.400	3.444	< 0.05
	<i>Char</i>	< 0.05	< 0.05	< 0.05	< 0.05	2.455	< 0.05	< 0.05
	<i>Ash</i>	< 0.05	0.095	< 0.05	< 0.05	< 0.05	0.083	< 0.05
<i>Cu</i>	<i>Waste</i>	0.530	0.150	< 0.1	0.225	0.455	1.572	0.117
	<i>Char</i>	< 0.1	0.208	0.124	0.106	0.194	< 0.1	< 0.1
	<i>Ash</i>	< 0.1	0.130	< 0.1	< 0.1	< 0.1	0.433	< 0.1
<i>K</i>	<i>Waste</i>	25.6	15.8	30.0	28.0	4.0	75.89	8.43
	<i>Char</i>	33.8	30.7	38.8	20.0	29.5	35.56	0.21
	<i>Ash</i>	35.1	44.4	5.9	18.8	76.6	46.94	< 0.1
<i>Na</i>	<i>Waste</i>	285.0	42.4	115.0	110.0	46.8	41.7	53.9
	<i>Char</i>	355.0	60.3	135.0	53.0	141.0	18.9	25.0
	<i>Ash</i>	700.0	82.1	16.5	24.0	359.4	72.8	1.50
<i>Mg</i>	<i>Waste</i>	9.0	9.1	4.6	7.8	2.4	47.22	10.61
	<i>Char</i>	10.1	1.3	2.0	1.1	19.0	9.83	10.56
	<i>Ash</i>	0.2	0.2	0.2	< 0.05	< 0.05	85.56	0.14
<i>Ca</i>	<i>Waste</i>	171.6	560.5	586.0	618.0	32.1	122.2	89.06
	<i>Char</i>	802.0	2,230	576.0	598.0	988.0	602.2	155.6
	<i>Ash</i>	154.5	1,270	439.5	523.5	259.0	436.7	277.2

Table 8. The yield and metal content of ash obtained by heating wastes at 800 °C for 2 h

	BN	CDRN	CDT1	CDT2	ASR	SS <sup>a</sup>	PS <sup>b</sup>
Ash yield (wt %-dry)	28.0	67.3	31.0	36.4	37.7	23.2	52.7
Metal content (mg/kg)							
<i>Cd</i>	< 0.05	1.00	< 0.05	< 0.05	< 0.05	25.6	1.98
<i>Cr</i>	256	61.9	124	88.4	277	357	30.2
<i>Pb</i>	301	140	12.3	3.01	401	467	100
<i>Zn</i>	3,498	1,001	201	116	17,345	4,029	332
<i>Cu</i>	134,996	2,954	65.2	4,163	98,283	801	900
<i>K</i>	939	1,130	223	315	1,525	5,926	611
<i>Na</i>	5,276	3,437	2,176	4,969	7,842	4,619	2,329
<i>Mg</i>	7,572	7,318	15,803	11,340	12,011	9,926	13,382
<i>Ca</i>	30,438	178,239	212,829	169,868	60,052	45,303	198,749

<sup>a, b</sup>: Obtained by heating at 600 °C for 2 h.

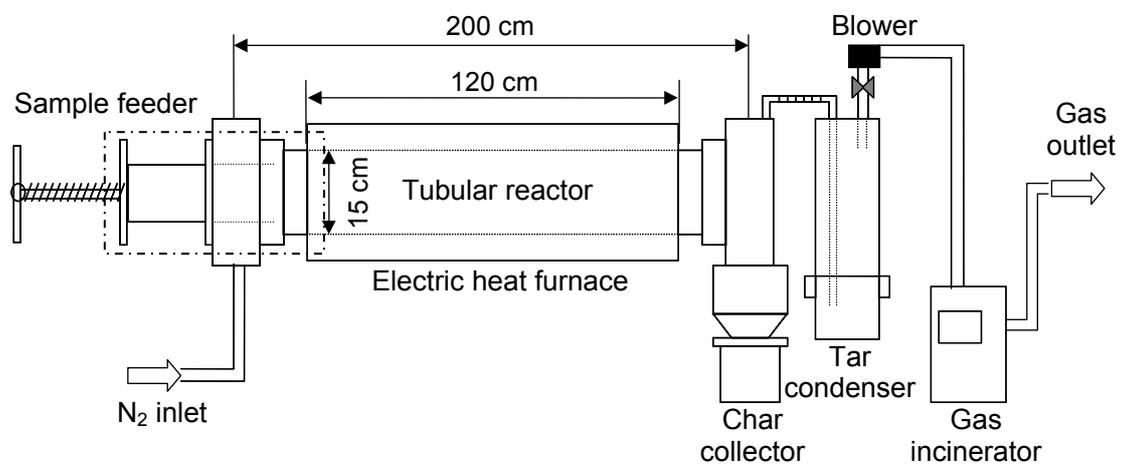


Figure 1. Rotary kiln type of carbonization process

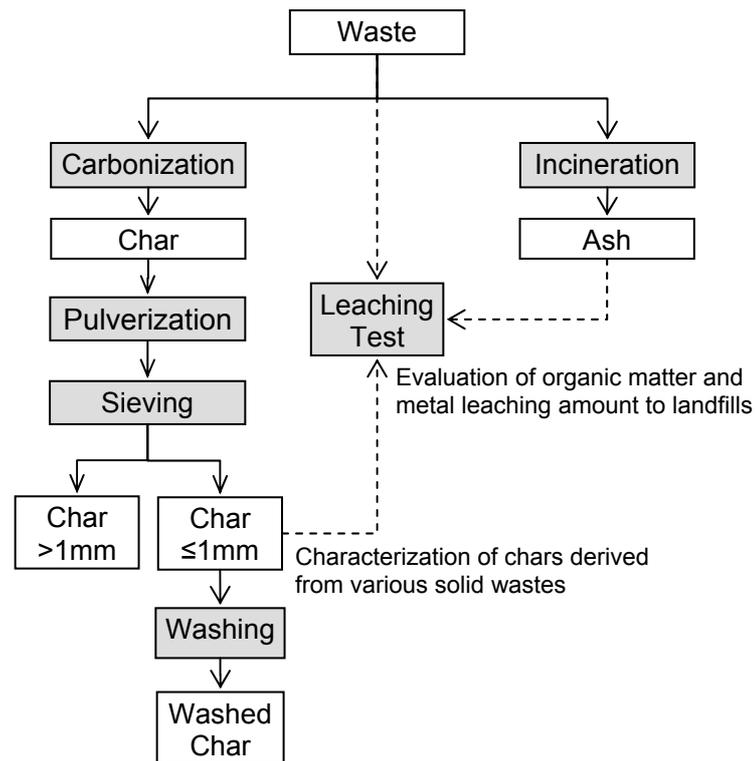


Figure 2. Experimental flow for evaluation of char in this work

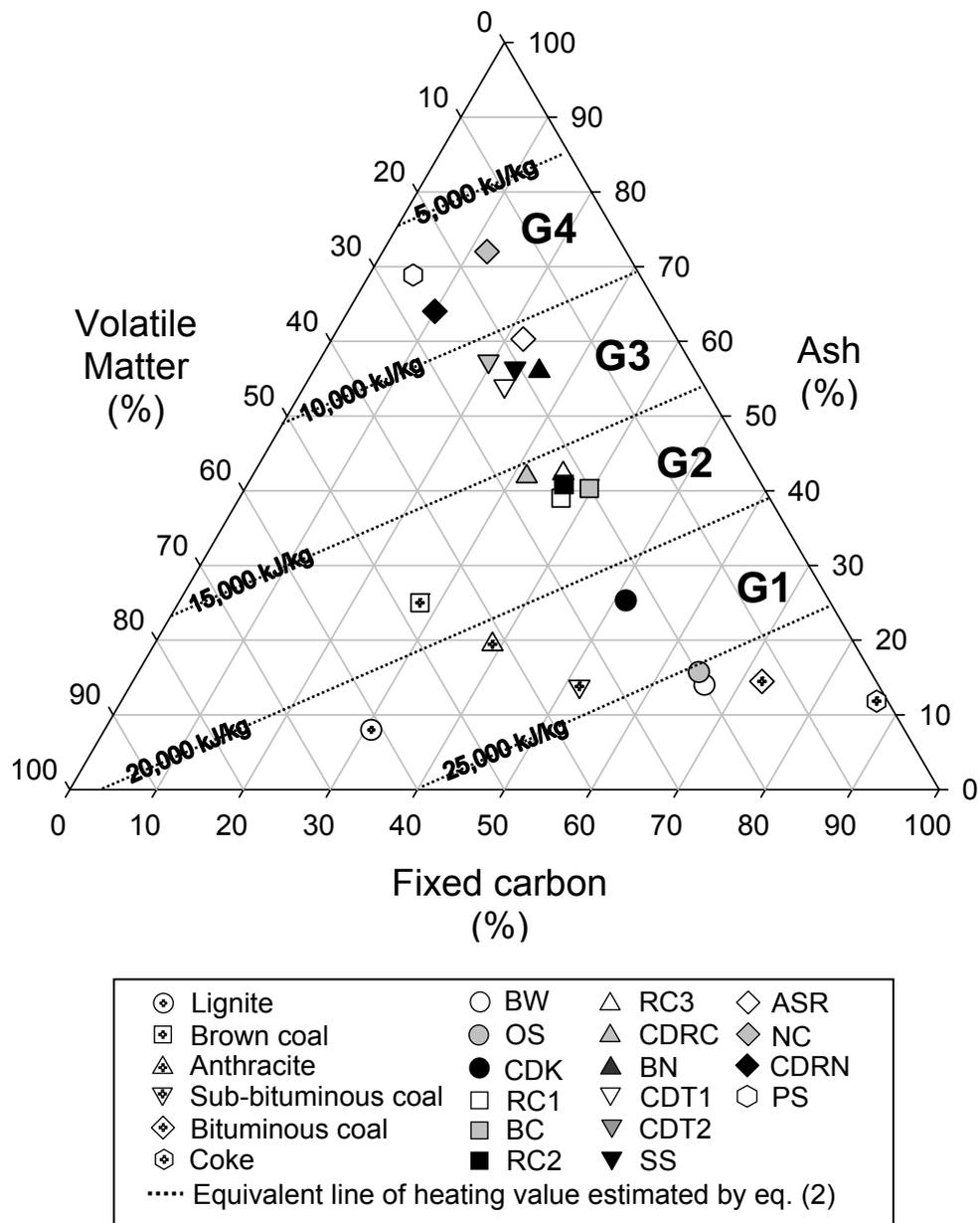


Figure 3. Comparison of char with coal using a ternary plot of volatile matter, fixed carbon, and ash

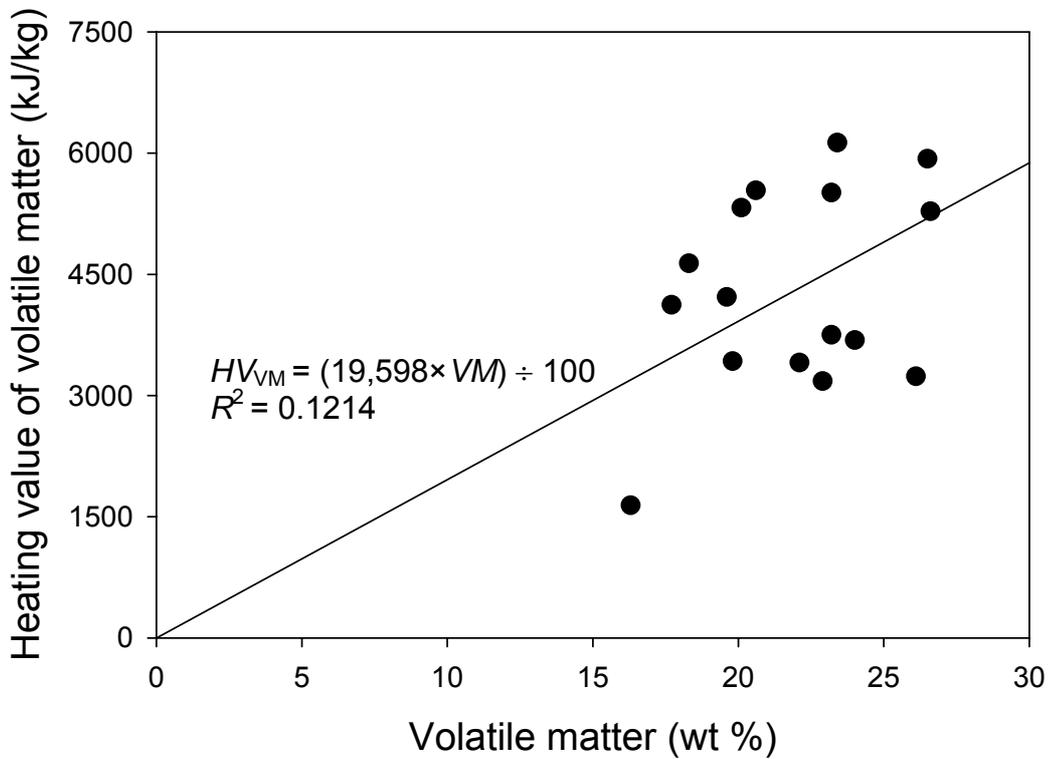


Figure 4. Correlation between volatile matter and heating value of volatile matter estimated by subtracting a heating value of fixed carbon from a heating value measured using a bomb-calorimeter

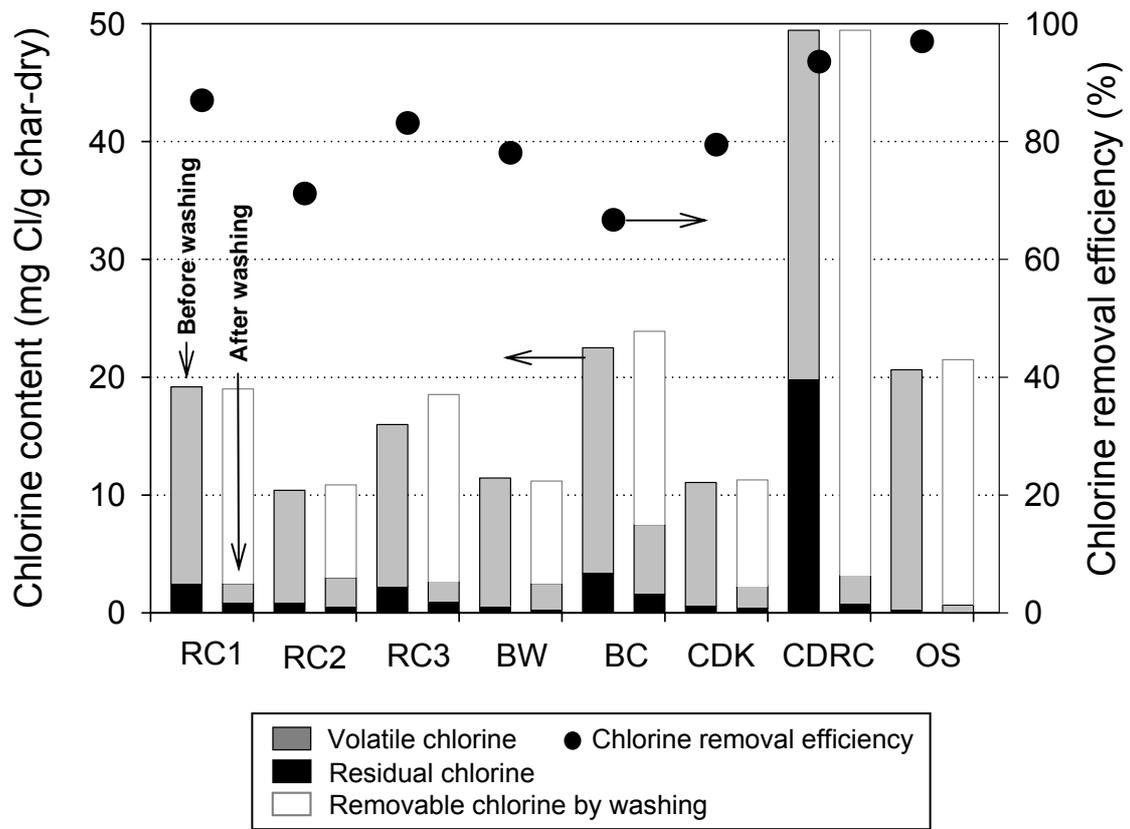


Figure 5. Chlorine balance of char before and after washing and de-chlorination efficiency

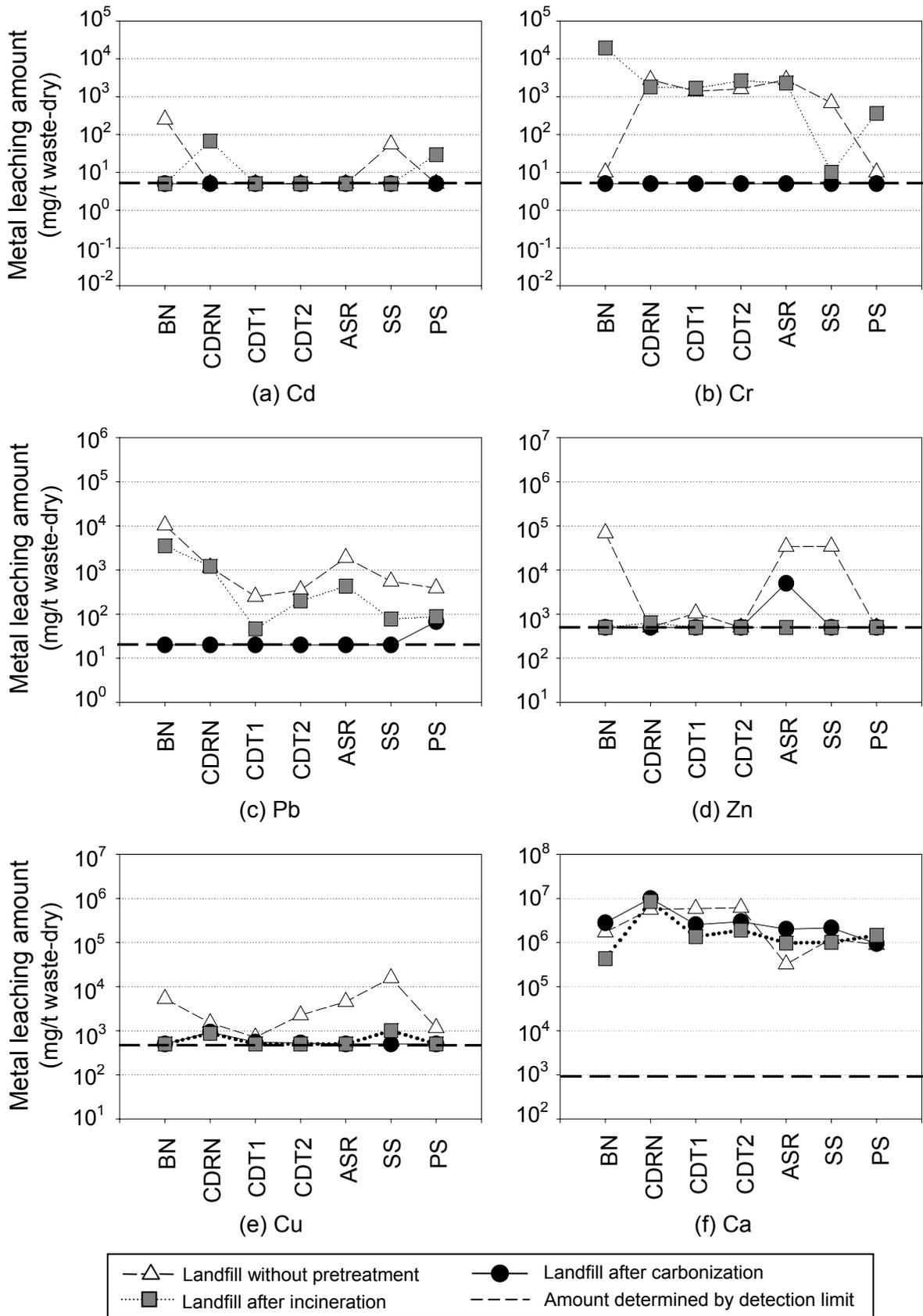


Figure 6. Comparison of leaching amount of cadmium, chrome, lead, zinc, copper, and calcium assuming 1 t of waste disposed in landfill without pretreatment and with pretreatment such as carbonization or incineration