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## Release Behavior of Tar and Alkali and Alkaline Earth Metals during Biomass Steam Gasification

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We developed a drop-tube reactor with a separation unit containing a quartz glass filter that is capable of fractionating alkali and alkaline earth metals (AAEMs) released as solid particle, vapor, and combined with water-soluble and water-insoluble tar. The ratio of released AAEMs in pulverized wood chips that had been steam-gasified was examined by changing the temperatures of the reactor and the separation unit independently. We found that approximately 63–80% of the released AAEMs were combined with tar. In addition, as the gasification temperature increased, the yields of the AAEMs combined with water-soluble and water-insoluble tars remained nearly constant, even though the amount of recovered water-soluble tar decreased as a result of secondary decomposition. This finding implies that AAEMs released by the secondary decomposition of water-soluble tar are fine particles that cannot be collected in a quartz glass filter. Additionally, yields of condensed AAEMs substantially increased as the gasification temperature increased, implying that the evolution of AAEMs from char was enhanced at high gasification temperatures. Evaluation of the water-soluble and water-insoluble tar using a Fourier transform infrared spectrometer (FTIR) and an elemental analyzer indicated that AAEMs likely combine with the OH groups of carboxylic acids and phenols in water-soluble tar. This finding infers that the AAEMs recovered from water-insoluble tar are present in aromatic compounds that are derivatives of benzene, xylene, furfural, and naphthalene in the product gas.

### Introduction

Because bioenergy is a carbon-neutral resource, it has the potential to alleviate global environmental problems. Biomass gasification is a promising technology for producing synthetic gas that can be used to power generation systems and chemical synthesis. However, biomass gasification results in the production of tar, ash, and alkali and alkaline earth metals (AAEMs), as well as the desired gas and char. Tar, which contains valuable organic compounds, volatilizes as vapor at gasification temperatures but condenses easily below 623 K.<sup>1</sup> The formation of tar can cause serious problems, such as pipeline plugging, or decreases in the energy conversion efficiency of gasification. To avoid these problems, the concentration of tar in the flue gas should be reduced to less than 600 mg N m<sup>-3</sup>.<sup>1</sup>

The release of AAEMs also causes serious problems, such as fouling, slugging, and corrosion of components in the power generation system, and these problems occur even if the concentration of AAEMs in the flue gas is as low as 24 ppb.<sup>2,3</sup>

Therefore, a hot gas cleaning technology that removes tar and AAEMs from flue gas is necessary. It has been reported that a gas filter unit operating at 673–873 K effectively removes tars, AAEMs, and particulates from product gas.<sup>4</sup>

On the other hand, AAEMs play catalytic roles in the gasification of char derived from biomass<sup>5–9</sup> and brown coals.<sup>9–12</sup> Thus, if the recovered AAEMs are returned to the gasifier, it is considered that the AAEMs can be used as a catalyst for char gasification.

To date, many studies have been conducted to evaluate the mechanism by which AAEMs are evolved during biomass

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**Table 1. Melting and Boiling Points of AAEMs<sup>a</sup>**

		K	Na	Ca	Mg
metal	mp	337	371	1112	924
	bp	1047	1156	1767	1370
chloride	mp	1049	1075	1045	985
	bp	1773	1686	2208	1685

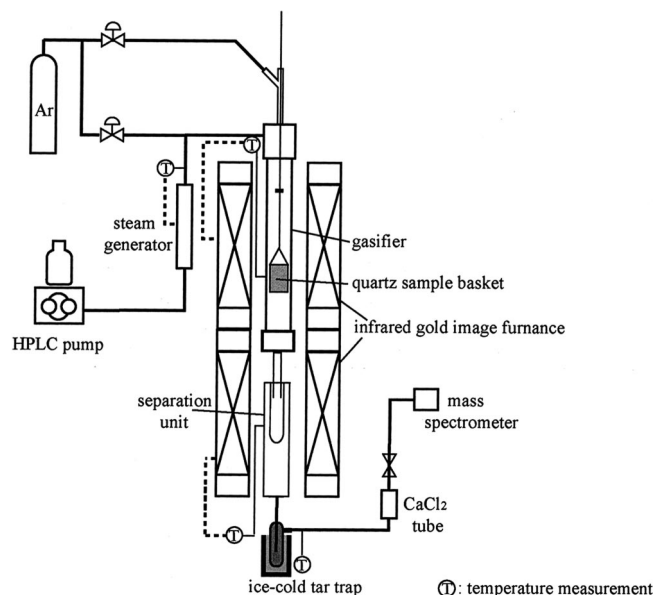
<sup>a</sup> Units in Kelvin.

oxidation<sup>2,4,13–15</sup> and pyrolysis<sup>3,16–20</sup> because hot gas cleaning technology that effectively removes tar and AAEMs from flue gas requires a detailed understanding of their release behavior. It has been reported that only a small amount of AAEMs are emitted from biomass during pyrolysis at low temperatures (up to 773 K), whereas a pronounced release of AAEMs is observed at high temperatures (>773 K).<sup>3,16,17</sup> The release of AAEMs at low and high temperatures is attributed to decomposition of the organic structure of the biomass and to alkali emission from the ash residue, respectively.<sup>3</sup> Kurkela et al.<sup>4</sup> and Dayton et al.<sup>13,14</sup> studied the release behavior of AAEMs during the oxidation of biomass and reported that they primarily volatilize as chlorides into the gas phase. This finding implies that released AAEMs exist as solid particles because the boiling points of AAEM chlorides are above 1600 K (cf. Table 1). In contrast, Keown et al.<sup>18,19</sup> reported that chlorine is volatilized independently from AAEMs. Additionally, Okuno et al.<sup>20</sup> measured the retention of AAEMs in char to investigate their release behaviors during pyrolysis of pulverized pine and sugar cane bagasse and found that AAEMs were primarily released as species other than chlorides.

AAEMs can be removed using a gas filter if they exist as solid particles of inorganic compounds in product gas.<sup>2,15</sup> However, few studies have examined AAEMs released from biomass to determine if they exist as solid particles or vapor or are combined with tar. Therefore, in this study, we developed a drop-tube reactor with a separation unit that is capable of fractionating released AAEMs as solid particles during the steam gasification of pulverized biomass wood chips. This system can analyze the behavior of AAEMs released as solid particles, vapor, and combined with tar during gasification by varying the temperatures of the reactor and the separation unit independently.

## Experimental Section

**Apparatus.** We developed a drop-tube reactor with a separation unit that is capable of collecting AAEMs released as solid particles using a quartz glass filter.<sup>4</sup> Vapor and tar passing through the filter is quenched in an ice-cold tar trap to collect and fractionate the water-soluble and water-insoluble tars. A schematic diagram of the experimental apparatus is shown in Figure 1. The reactor is comprised of a stainless-steel gasifier with an inner diameter of 21.0 mm, a separation unit, a quartz sample basket (inner diameter, 17.0 mm; height, 46.0 mm), and two infrared gold image furnaces.

**Figure 1.** Experimental apparatus.**Table 2. Composition of the Sample**

Proximate Analysis (wt %, Dry Basis)	
ash	0.43
volatiles	81.24
fixed carbon	18.33
Ultimate Analysis (wt %, d.a.f.)	
C	48.21
H	5.79
O	44.99
N	0.25
S	0.76
AAEM Content (wt %, Dry Basis)	
K	0.092
Na	0.015
Ca	0.12
Mg	0.028

The gasifier and separation unit with the quartz glass filter are independently heated with the infrared gold image furnaces (P68C; ULVAC-RICO, Inc.). The lengths of the isothermal zone of the furnaces are approximately 210 and 280 mm, respectively. The solid particles in the product gas stream are removed by a quartz glass wool filter in the separation unit, and the uncollected tar is captured by the ice-cold trap.

The temperatures of the gasifier and the separation unit (hereafter referred to as the gasification temperature and the separation temperature, respectively) are independently measured and controlled using type-K thermocouples and a temperature controller (TPC-1000; ULVAC-RICO, Inc.). In addition, the temperature of the trap is measured using another type-K thermocouple. Water is fed into the system with an HPLC pump (NP-KX-1005; Nihon Seimitsu Kagaku, Co. Ltd.) and then heated with a steam generator. The steam is then mixed with Ar and fed above the sample basket.

**Sample.** Commercial wood chips (Chilean eucalyptus) were pulverized with a mill to obtain a particle size smaller than 0.5 mm. The pulverized samples were then dried at 383 K for at least 10 h prior to use in any experiments. The elemental compositions and moisture contents of the samples are listed in Table 2.

**Procedure.** A total of 2 g of the pulverized wood sample were placed into the sample basket that was hung above the gasifier. Ar gas was then fed from the top of the gasifier at a flow rate of 250 N cm<sup>3</sup> min<sup>-1</sup> to purge the oxygen from the gasifier. Next, the gasifier and separation unit were heated to 873–1073 and 673–823 K, respectively. The boiling points of the AAEMs are above 1600 K (cf. Table 1); therefore, the AAEMs released as metal or chloride should be condensed in the separation unit. When the gasification and separation temperatures were well above 373 K, steam (500

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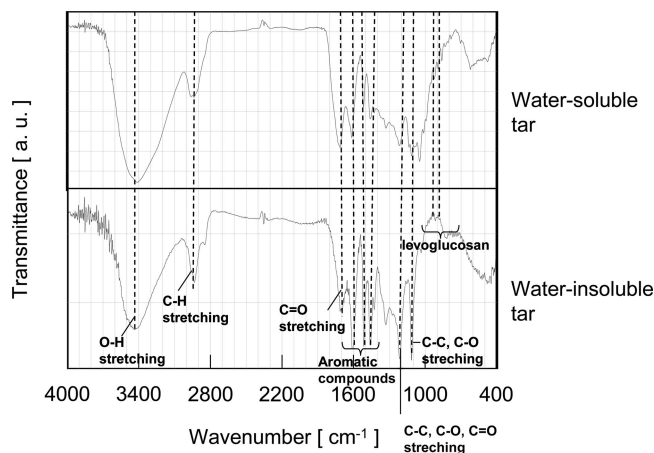
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**Figure 2.** Infrared spectra of water-soluble and water-insoluble tars (gasification temperature, 873 K; separation temperature, 873 K).

**Table 3. Elemental Analysis of Tar**

	water-soluble tar (wt %)	water-insoluble tar (wt %)
C	56.01	67.25
H	5.20	5.46
O	37.79	26.24
N	0.41	0.46
S	0.59	0.59

$\mu\text{L min}^{-1}$  in the liquid state) was introduced into the gasifier with Ar carrier gas ( $250 \text{ N cm}^3 \text{ min}^{-1}$ ). At these flow rates, the estimated residence time of the volatiles was approximately 1 s. After the gasification and separation temperatures stabilized, the sample basket was dropped into the gasifier, which resulted in the sample being heated at an estimated rate of  $100 \text{ K s}^{-1}$ . After 30 min, the basket was raised out of the gasifier to quench the reaction. The completion of the gasification reaction was monitored using a quadrupole mass spectrometer (Standum; ULVAC, Inc.) after eliminating  $\text{H}_2\text{O}$  from the flue gas using a  $\text{CaCl}_2$  column.

**Analysis.** AAEM particles on the filter were immersed in  $50 \text{ cm}^3$  of distilled water that was then heated to 368 K and held at that temperature for 30 min. The solution was then mixed with 6%  $\text{HNO}_3$  (aqueous) to leach out condensed AAEMs.

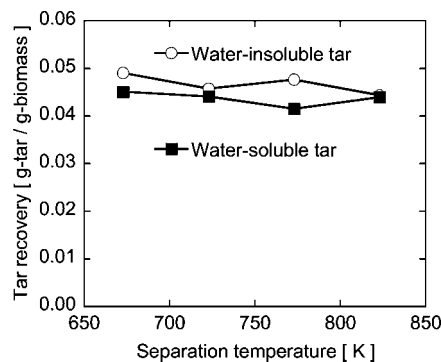
Tar collected in the cold trap was recovered by washing the trap with distilled water and then with acetone to collect the water-soluble tar and water-insoluble tar, respectively. These solvents were then evaporated at 383 K overnight, after which the tar residues were weighed. Next, the tar residues were dissolved in 6%  $\text{HNO}_3$  (aqueous) to quantify the AAEMs as mentioned below. Hereafter, the AAEMs recovered from the water-soluble tar are referred to as water-soluble AAEMs, and those recovered from the water-insoluble tar are referred to as water-insoluble AAEMs.

The Ca and Mg in the particles, the water-soluble tar, and the water-insoluble tar were measured using an inductively coupled plasma atomic emission spectrometer (P4010; Hitachi), whereas the K and Na were measured using an atomic adsorption spectrometer (AAS-825; Japan Jarel Ash, Co. Ltd.).

The composition of each tar was analyzed with a Fourier transform infrared spectrometer (FTIR-230; JASCO) and a CHNS elemental analyzer (2400II CHNS/O; Perkin-Elmer).

## Results and Discussion

**Characteristics of Water-Soluble Tar and Water-Insoluble Tar.** Figure 2 and Table 3 show the infrared spectra and elemental analysis of water-soluble and water-insoluble tar, respectively. The water-soluble tar contains larger peaks corresponding to O–H stretching ( $3412\text{--}3460 \text{ cm}^{-1}$ ) and C=O stretching ( $1709\text{--}1730 \text{ cm}^{-1}$ ) than the water-insoluble tar. These



**Figure 3.** Effects of the separation temperature on tar recovery (gasification temperature, 873 K).

peaks were assigned to phenol, acid, ketones, and carbonyls.<sup>21</sup> In addition, the peaks corresponding to aromatic compounds ( $1500\text{--}1800 \text{ cm}^{-1}$ ) and C–H stretching ( $2800\text{--}3000 \text{ cm}^{-1}$ ) in the water-insoluble tar were stronger than those of the water-soluble tar. These results suggest that water-insoluble tar contains more aromatic compounds than water-soluble tar. This finding is also supported by the results shown in Table 3, which indicate that the ratio of carbon/hydrogen in water-insoluble tar was greater than that of water-soluble tar.

**Effect of the Separation Temperature on Tar Capture and AAEMs Ratio.** Figure 3 illustrates the effects of the separation temperature on tar recovery. The gasification temperature was 873 K, whereas the separation temperature varied from 673 to 873 K. The separation temperature had no significant effect on the recovery of water-soluble or water-insoluble tars, which indicates that water-soluble and water-insoluble tars are not decomposed or condensed in the separation unit at 673–873 K.

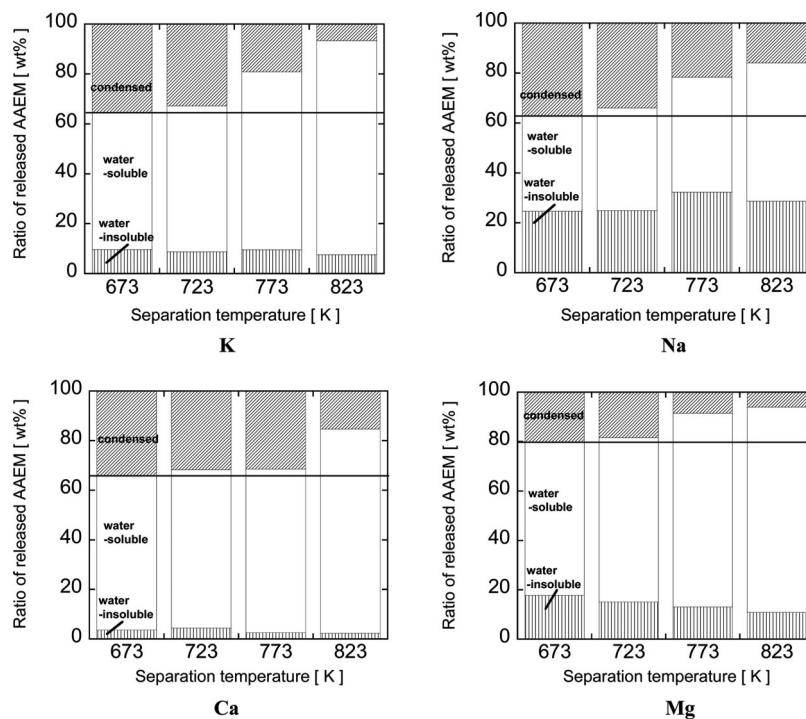
Figure 4 shows the effects of the separation temperature on the ratio of released AAEMs when the gasification temperature was 873 K. The ratio is defined by the following equation:

$$\text{distribution} = \frac{W_i}{(W_c + W_s + W_i)} \times 100\% \quad (1)$$

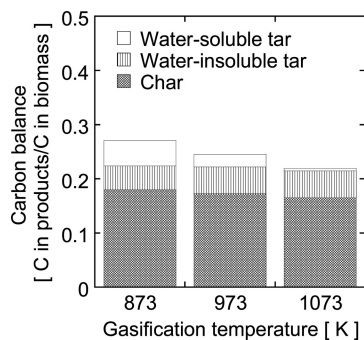
where  $W_c$  is the amount of condensed AAEMs recovered in the filter,  $W_s$  is the amount of water-soluble AAEMs collected in the cold tar trap and recovered using water,  $W_i$  is the amount of water-insoluble AAEMs collected in the cold tar trap and recovered using acetone, and  $W_j$  is  $W_c$ ,  $W_s$ , or  $W_i$  at each separation temperature. Thus,  $W_c$  is the amount of AAEMs released as solid particles and/or vapor condensed at the separation temperature;  $W_s$  is the amount of AAEMs released as vapor, which is not condensed in the separation unit and/or combined with water-soluble tar; and  $W_i$  is the amount of AAEMs combined with water-insoluble tar. Most of the released AAEMs were found to be water-soluble. Assuming that all AAEMs released as vapor condense at 673 K because the boiling points of metals and chlorides are above 1600 K, 35% of K, 37% of Na, 34% of Ca, and 20% of Mg existed as solids at 673 K (shown as a solid line in Figure 4). However, as the separation temperature increased, the ratio of water-soluble AAEMs increased and that of condensed AAEMs decreased. As mentioned previously, the amount of recovered water-soluble tar remained almost constant, regardless of the separation temperature. These results imply that some portions of the released AAEMs exist as vapor, which passes through the separation unit without condensing at higher separation tem-

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**Figure 4.** Effects of the separation temperature on the ratio of released AAEMs (gasification temperature, 873 K).



**Figure 5.** Effects of the gasification temperature on carbon balance (separation temperature, 873 K).

peratures. Therefore, the increase in water-soluble AAEMs can be attributed to water-soluble AAEMs vapor. In addition, the effect of the separation temperature on the ratio of water-insoluble AAEMs was not significant, implying that most of the AAEMs in the vapor were water-soluble. Therefore, it can be said that approximately 65% of K, 63% of Na, 66% of Ca, and 80% of Mg are released as water-soluble and water-insoluble tars (cf. Figure 4).

It has been reported that the primary products formed in reactors at a temperature range of 673–973 K are characterized by the presence of oxygenated compounds, such as acids, ketones, phenols, guaiacols, and furans, and that the secondary products formed at a temperature range of 973–1123 K include phenols, olefins, and light aromatics.<sup>22,23</sup> These findings indicate that AAEMs likely combine chemically with the OH groups of carboxylic acids and phenols in water-soluble tar. In addition, these results infer that water-insoluble AAEMs were present in aromatic compounds, such as derivatives of benzene, xylene, furfural, and naphthalene.

**Effect of the Gasification Temperature on AAEM Evolution.** Figure 5 shows the effects of the gasification temperature on carbon balance when the separation temperature was fixed at 873 K. No significant decrease in the amount of water-insoluble tar was observed in response to increases in the

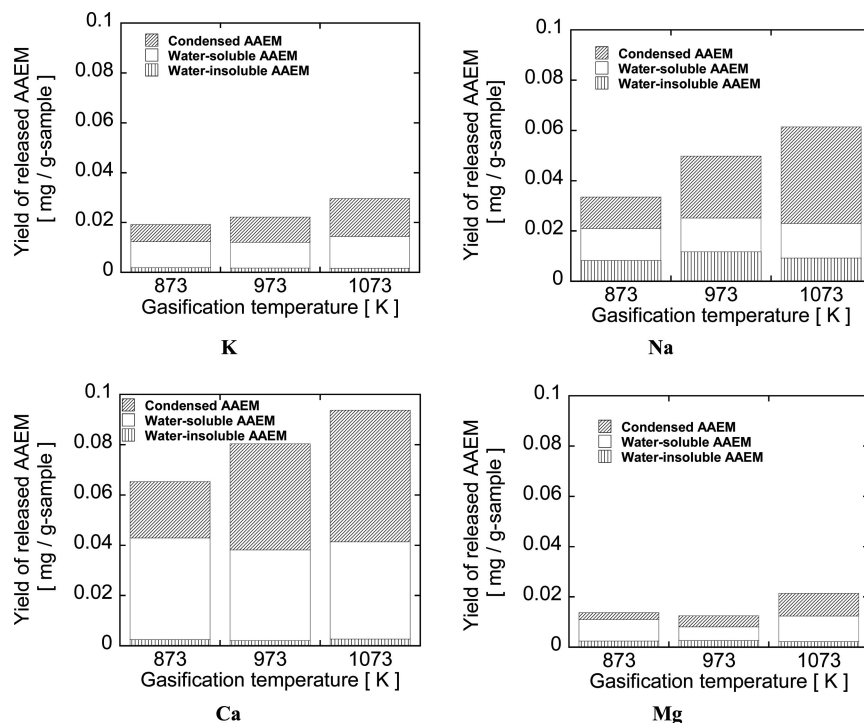
gasification temperature. Conversely, the amounts of water-soluble tar decreased at high temperatures. These findings indicate that the secondary decomposition of water-soluble tar occurs in the gasifier at higher gasification temperatures. The amount of char also decreased slightly as the gasification temperature increased.

The effect of the gasification temperature on AAEM evolution at 873, 973, and 1073 K was measured, while the separation temperature was fixed at 673 K to condense and collect most of AAEMs released as vapor in the quartz glass filter (Figure 6). Changes in the gasification temperature had no significant effect on the yields of AAEMs in water-soluble and water-insoluble tar. As mentioned above, the total amounts of recovered water-soluble tar decreased as the gasification temperature increased because of secondary decomposition in the gasifier (cf. Figure 5). Therefore, it is likely that AAEMs released by the secondary decomposition of water-soluble tar are fine particles that cannot be collected in the quartz glass filter. It is possible that the fine particles are AAEMs produced by the cleavage of chemical bonds containing AAEM species, e.g., –OM and –COOM (M = K, Na, Ca, and Mg), with steam. However, a further study is necessary to investigate the reaction mechanism.

The yields of condensed AAEMs substantially increased as the gasification temperature increased, especially in the case of Na and Ca. The increase in the amount of condensed AAEMs in response to the increase of the gasification temperature is probably caused by enhancement of the AAEM evolution as particles and/or as vapor from char. This finding is in accordance with the results of previous studies, which showed that the evolution of AAEMs from ash was enhanced above 873 K.<sup>2,3,16,17</sup>

## Conclusion

In this study, most of the released AAEMs were found to be combined with tar. Furthermore, most of the AAEMs that were combined with tar were present in the water-soluble fraction of the tar. Assuming that all AAEMs released as the vapor



**Figure 6.** Effects of the gasification temperature on AAEM evolution (separation temperature, 673 K).

condensed at 673 K, 65% of K, 63% of Na, 66% of Ca, and 80% of Mg were released with water-soluble and water-insoluble tars. In addition, as the separation temperature increased, the ratios of the AAEMs released in the water-soluble tar increased, while the ratios of the condensed AAEMs decreased. This implies that some of the released AAEMs exist as vapors that pass through the separation unit at high temperatures.

The yields of AAEMs in water-soluble and water-insoluble tars were nearly constant at gasification temperatures of 873–1073 K; however, the total amounts of recovered water-soluble tar decreased with the rise in the gasification temperature because of secondary decomposition in the gasifier. This finding indicates that AAEMs released by the secondary decomposition of water-soluble tar are fine particles that cannot be collected in the quartz glass filter.

The yields of condensed AAEM substantially increased as the gasification temperature increased, implying that a larger amount of AAEMs exist as small particles at high gasification temperature than at low gasification temperature. This is

probably due to enhancement of the evolution of AAEMs in the form of solid particles and/or vapor from char at high gasification temperatures.

On the basis of the measurements of water-soluble and water-insoluble tars using an FTIR and elemental analyzer, it is likely that AAEMs combine chemically with the OH groups of carboxylic acids and phenols in water-soluble tar. It is inferred that AAEMs recovered from water-insoluble tar were in aromatic compounds, such as derivatives of benzene, xylene, furfural, and naphthalene.

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