Effect of Tar-adsorbing Particles on Tar Components Generated by Lignite Gasification in a Fluidized Bed Gasifier

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In a dual fluidized bed gasifier suitable for gasification of lignite, tar is generated as the raw material is gasified because the gasification reaction has at 1073-1173 K, which is a relatively low temperature, and there is a problem such as tar adhering to the piping of the cooling system in the subsequent stage. In this study, in order to reduce tar in the gasification of lignite, porous alumina particles were applied as a tar adsorbent to the upper stage of a laboratory-scale two-stage fluidized bed gasifier, and the gasification characteristics of the produced gas and the tar components were analyzed and its effect was investigated. From the analysis results of tar components using gas chromatograph mass spectrometry (GC/MS) and field desorption mass spectrometry (FD-MS), the tar components obtained under the respective gasification conditions of pyrolysis and steam were almost no difference, and the main components of tar were polycyclic aromatic hydrocarbons without substituents. It was also found that the main components of tar can be sufficiently identified by GC/MS analysis alone. The application of the porous alumina particles increased the gas yields due to the cracking effect of tar. Furthermore, it was confirmed that the gas yields increased under the steam gasification condition rather than pyrolysis condition, and the gasification reactions were promoted by steam. From these results, it is considered that the porous alumina particles are effective in reducing tar, and as a reformer using this, a dual-type reformer capable of using the tar adsorbent for a long period of time is suitable.

Keywords
Tar component, Tar-adsorbing particle, Lignite gasification, Porous alumina, GC/MS, FD-MS

1. Introduction
Gasification technology, which converts lignite into gas and then uses it, has received increasing attention in recent years. A dual fluidized bed gasifier is suitable for the gasification of lignite1). In this gasifier, the gasifier and combustor are separated, and steam is used as the gasifying agent. Since the gasifier operates at low temperatures (1073-1173 K), tar is generated with the syngas after gasification3,4). It is important to identify the tar components to stabilize the gasification system; this is because tar may have limitations, such as adhering to the piping of the cooling system in the subsequent stage of the gasifier. Okumura previously investigated the dependence of tar components on coal types by gas chromatograph mass spectrometry (GC/MS) analysis5,6). Zeng et al. have investigated the effects of temperature and residence time of tar abatement by char catalyst in a two-stage fluidized bed gasifier7). Studies on tar components have been mainly performed by GC/MS analysis8-12). In this study, to accurately identify the tar components, we have proposed an analysis method combining GC/MS and field desorption mass spectrometry (FD-MS), which can measure the molecular weight distribution of tar13), and the tar components have been analyzed by steam gasifying lignite at a practical temperature of 1123 K14,15). The main tar components were found to be unsubstituted polycyclic aromatic hydrocarbons (PAHs), and there was almost no difference on changing the amount of steam supplied in the gasifier16,17). To further reduce the tar components by steam, it is necessary to use a temperature that exceeds the operating temperature of the dual fluidized bed gasifier18). As one of the methods for reducing tar, a high-temperature reformer, which is operated at 1373-1573 K, is installed in the subsequent stage of the gasifier19,20). In addition, catalytic studies have been conducted as another means of reducing tar21,22), and it has been reported that a Ni-based catalyst has a significant tar reduction effect. In this study, we used porous alumina, which is a tar-adsorbing particle that is cheaper than expensive catalysts such as Ni. We conducted fundamental experiments on a tar reformer utilizing the
porous alumina particles, to obtain a tar reformer that can operate at the same level as or on a lower level than a gasifier. The effect of the tar-adsorbing particles on the gasification characteristics and the tar components by lignite gasification using a laboratory-scale two-stage bubbling fluidized bed gasifier was analyzed.

2. Experimental

A schematic of the laboratory-scale two-stage bubbling fluidized bed gasifier is illustrated in Fig. 1. The reactor is made of quartz glass, and the inner diameters of both the lower stage and upper stage are 65 mm. Silica sand with approximately 0.15 mm particles was used in the lower stage as a bed material, while porous alumina particles (Mizusawa Industrial Chemicals, Ltd.; average particle size: approximately 0.11 mm; pore volume: 0.44 cm$^3$/g; specific surface area: 200 m$^2$/g) were used in the upper stage as the tar-adsorbing particles. The static bed heights were 100 mm in both stages. The fluidizing gas supplied steam primarily from the lower portion of the gasifier under the steam gasification experiment; conversely, the gas supplied only nitrogen under pyrolysis. The molar ratio of the steam feed rate to the carbon content in the raw fuel (S/C) was set to approximately 1.5, which is practical operating conditions. The temperatures in both fluidized beds were controlled at 1123 K using an electric furnace. Lignite was continuously supplied at a rate of 1.0 g/min for 60 min using a screw feeder. The fuel properties are listed in Table 1, and the diameter of the fuel was 0.5-1.0 mm. The tar generated with the syngas after gasification was cooled and captured using a cold trap (iced water at 273 K and an acetone/liquid nitrogen mixture at 205 K). The syngas composition (H$_2$, CO, CO$_2$, CH$_4$, C$_2$H$_4$, and C$_2$H$_6$) was analyzed by gas chromatograph (CP-4900, Varian Inc., CA) after capturing the fine particles with a filter paper thimble$^{23}$.

The tar-containing sample collected in the cold trap was washed with acetone and then recovered as an acetone solution. This solution was filtered with a glass filter to remove particles such as sand and char. The residue on the glass filter was then washed with fresh acetone. These filtrates were collected, and the solvent was removed to obtain the condensate sample. In this study, the thus-obtained final sample was considered the “tar.” The collected tar was diluted with toluene and the tar components were analyzed using GC/MS (HP-6890/HP-5973N, Agilent Technologies); the main analytical conditions are listed in Table 2. The tar compounds were identified by comparing the obtained mass spectra with a mass spectral database (Chem Station/NIST14) and with the mass spectra obtained for standard PAH reagents (PAH solution mix, Associates of Cape Cod, Inc.). Subsequently, the molecular weight distribution of the tar was measured using FD-MS (JMS-T100GCV, JEOL Ltd.) with the analysis conditions listed in Table 3.

3. Results and Discussion

The gas yields, which is the average value of 10 to 60 min after the fuel is supplied, obtained in this experiment are shown in Fig. 2, along with the gas yields previously obtained at 1123 K in the one-stage fluidized
bed employing only silica sand as a reference\textsuperscript{16,17}. The steam gasification condition for the one-stage fluidized bed was the same as that for the two-stage fluidized bed, S/C is 1.5. The gas yields obtained under steam gasification conditions were much higher than those obtained under pyrolysis conditions. This is thought to be because steam gasification caused a steam reforming reaction (Eq. (1)) and water-gas shift reaction (Eq. (2)), which improved the gas yield.

\begin{align}
C + H_2O & \rightarrow CO + H_2 & (1) \\
CO + H_2O & \rightarrow CO_2 + H_2 & (2)
\end{align}

Additionally, under both pyrolysis and steam gasification conditions, the gas yields obtained in the two-stage were higher than that in the one-stage. This suggests that the tar was cracked on the alumina particles.

The total ion chromatogram obtained by GC/MS analysis of the tar is shown as (a) pyrolysis and (b) steam gasification in Fig. 3. The vertical axis in this figure shows the relative intensity when the maximum strength peak is set as 100 %, and the horizontal axis indicates the retention time. From this figure, 18 main peaks common under both pyrolysis and steam gasification conditions were obtained. The compounds of these main peaks identified by GC/MS are shown in Table 4. Some compounds in this table have the same molecular weight but differ in the bonding positions or number of five- or six-membered rings. Other compounds differ in molecular weight but contain the same number of five- or six-membered rings. Under all conditions, most of the tar components within the detection range of GC/MS were found to be polycyclic aromatic hydrocarbons (PAHs) having no substituent with a five- or six-membered ring structures. Additionally, molecular weight intervals of 24 or 26 from one compound to the next-closest were observed. These results obtained from the GC/MS analysis\textsuperscript{17} were not significantly different from those obtained in the one-stage fluidized bed using only silica sand.

The FD-MS spectra of the tar are shown as (a) pyrolysis and (b) steam gasification in Fig. 4. The vertical axis is the relative intensity, and the horizontal axis is the molecular weight. In FD-MS spectra as well as GC/MS spectra, under both conditions, the main peaks show the same molecular weight pattern with intervals of 24 or 26, and they are predicted to be PAHs without substituent groups. For reference, the results of the one-stage fluidized bed using only silica sand are also shown as (c) and (d) in this figure\textsuperscript{17}. Notably, the molecular weight distribution of the tar in the two-stage was lower than that in the one-stage. It is thought that the lignite formed by the covalent bonding of aromatic rings was fragmented by primary decomposition, and further, mainly PAHs without substituents were formed at 1123 K by condensation reactions of aromatics and
elimination reactions of side chains. Furthermore, due to the effect of the porous alumina particles, most of the main tar components had a molecular weight of 300 or less. It is thought that the tar components having a molecular weight of 300 or more was adsorbed by the porous alumina particles, and a part of the tar was cracked and converted into the syngas. Thus, it was found that most tar components can be analyzed by GC/MS alone.

In this study, the gasification experiments were performed using the laboratory-scale two-stage bubbling fluidized bed; therefore, the structure is such that porous alumina particles cannot be regenerated during the experiment. However, the main components of tar in syngas had a molecular weight of almost 300 or less. For practical utilization, it is desirable to install a tar reformer using the tar-adsorbing particles in the subsequent stage of the gasifier as shown in Fig. 5. The proposed tar reformer has a dual structure, and the technology of the dual fluidized bed gasifier can be utilized. The reformer is separated into a tar adsorber and a tar adsorber regenerator, and the tar-adsorbing particles like porous alumina particles, as a bed material, circulates between the two furnaces. The tar adsorber has a bubbling fluidized bed structure, and the syngas containing the tar generated in the gasifier in the previous stage was introduced from the bottom of the adsorber. The tar-adsorbing particles in the adsorber came into contact with the gas, and tar was adsorbed on the tar-adsorbing particles. Afterward, a part of the adsorbed tar cracked and was reformed into syngas, such as H₂ and CO. The tar-treated syngas was sent to the gas cooler in the subsequent stage. Conversely, the tar-adsorbing particles containing the tar remaining on the particles are transported to the tar adsorber regenerator. The tar adsorber regenerator has the riser structure of a circulating fluidized bed, and the residual tar on the tar-adsorbing particles was combusted by the air supplied from the lower part of the regenerator, and the tar-adsorbing particles were reheated and reactivated. The reactivated tar-adsorbing particles was separated from the exhaust gas by a cyclone and recirculated to the tar adsorber. The tar-adsorbing particles also served as a heat carrier to maintain the temperature in the reformer. By repeating these operations, the tar-adsorbing particles can be used for a long time with high performance. In the high-temperature reformer, which was one of the tar reformers, oxygen was supplied, and the tar in the syngas was treated at approximately 1373-1573 K (19)-(20). Therefore, there is a concern that the cost of oxygen and refractory materials at high temperatures will be relatively high. The dual tar reformer proposed in this study may operate at lower temperatures than high-temperature reformer. This can reduce the material cost. In addition, since exhaust gas is not mixed in the syngas, there is no need to supply oxygen. For the practical use of the dual-type reformer, it will be necessary to carry out experiments to optimize the operating conditions of the reformer.

In the gasification experiment performed in this study, the porous alumina particles could not be reactivated because a two-stage bubbling fluidized bed was used; however, it was found that the main components of tar in syngas generated by lignite gasification had a molecular weight of almost 300 or less by the porous alumina particles. Therefore, FD-MS can be omitted for analysis of tar components, and GC/MS alone can be used for faster identification. In the future, we are going to design and manufacture a laboratory-scale reformer that simulates the dual tar reformer. The reformer will be installed in the subsequent stage of the bubbling fluidized bed gasifier employing only silica sand, used in this study to optimize the operating conditions, such as the temperature in the reformer, and the type and amount of the tar-adsorbing particles.

### Table 4 Tar Components Identified by GC/MS

| No. | Compound          | MW  | Structural formula |
|-----|-------------------|-----|--------------------|
| 1   | Acenaphthylene    | 152 | ![](acenaphthylene.png) |
| 2   | 1,2-Diphenylethane| 182 | ![](1,2-Diphenylethane.png) |
| 3   | Fluorene          | 166 | ![](fluorene.png) |
| 4   | Phenanthrene      | 178 | ![](phenanthrene.png) |
| 5   | Anthracene        | 178 | ![](anthracene.png) |
| 6   | Benzo[def]fluorene| 190 | ![](benzo[def]fluorene.png) |
| 7   | Fluoranthene      | 202 | ![](fluoranthene.png) |
| 8   | Pyrene            | 202 | ![](pyrene.png) |
| 9   | Benzo[a]anthracene| 228 | ![](benzo[a]anthracene.png) |
| 10  | Triphenylene      | 228 | ![](triphenylene.png) |
| 11  | Chrysene          | 228 | ![](chrysene.png) |
| 12  | Benzo[b]fluoranthene| 252 | ![](benzo[b]fluoranthene.png) |
| 13  | Benzo[k]fluoranthene| 252 | ![](benzo[k]fluoranthene.png) |
| 14  | Benzo[j]fluoranthene| 252 | ![](benzo[j]fluoranthene.png) |
| 15  | Benzo[c]pyrene    | 252 | ![](benzo[c]pyrene.png) |
| 16  | Benzo[a]pyrene    | 252 | ![](benzo[a]pyrene.png) |
| 17  | Indeno[1,2,3-cd]pyrene| 276 | ![](indeno[1,2,3-cd]pyrene.png) |
| 18  | Benzo[ghi]pyrene  | 276 | ![](benzo[ghi]pyrene.png) |

Numbers 1 to 18 in this table are same as Fig. 3.
thermore, we would like to consider the quantification of each tar component, and coke adsorbed on tar-ad-
sorbing particles. From these experimental results, we
would like to clarify the conditions under which the
power generation system is established.

4. Conclusions

Steam gasification and pyrolysis experiments of lig-
nite were carried out at 1123 K by a laboratory-scale
two-stage bubbling fluidized bed gasifier. Of the two

Fig. 4 Examples of Tar Compounds Inferred by the Combined GC/MS and FD-MS Method

Fig. 5 Schematic Diagram of a Fluidized Bed Gasification System with Tar Reformer
stages, the lower stage, which is a conventional gasifier, used silica sand, and the upper stage used porous alumina assuming a tar reformer. As a result of analyzing the tar components by combining GC/MS and FD-MS, it was observed that the main component was PAHs without substituents, and there was almost no difference in the results for steam gasification and pyrolysis. However, it was found that the main components of tar in the syngas had a molecular weight of almost 300 or less by the porous alumina particles. It can be said that this is because tar in the syngas was adsorbed on the porous alumina, and a part of the tar was cracked and converted into the syngas. The dual tar reformer proposed in this study can be operated at a lower temperature than the high-temperature reformer and does not require oxygen. Therefore, there is a possibility that the cost can be further reduced.

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要 旨

流動層ガス化炉における褐炭ガス化によって生成するタール成分に対するタール吸着粒子の影響
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