Analysis of Tar in Syngas Generated by Lignite Gasification under Conditions of Excess Steam

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Gasification technology converts a solid fuel to syngas, and it has wide utility for power generation and hydrogen production. In a dual fluidized bed gasifier, the fuel is gasified with steam. As the gasifier operates at 1073-1173 K, tar is generated in the syngas, and a tar reformer such as a catalytic reforming tower is normally required. To ensure optimal reformer design, it is important to clarify the components of the tar. In this study, the components of tar were investigated using a laboratory-scale fluidized bed gasifier to gasify lignite at 1123 K, employing wide variations in the amount of supplied steam. As the steam supply increased, the tar concentration decreased. In addition, a prediction method in real time of the tar concentration in the syngas which is varied by the amount of steam supplied to the gasifier from the analysis of the hydrogen and carbon monoxide produced was proposed. The tar components were analyzed using various hyphenated techniques such as gas chromatograph mass spectrometry (GC/MS) and field desorption mass spectrometry (FD-MS). The main components detected were polycyclic aromatic hydrocarbons (PAHs) without any substituent groups. It was shown that even if the steam was supplied at triple the required stoichiometric ratio, the tar composition was unchanged.

Keywords
Tar component, Excess steam, Lignite gasification, Polycyclic aromatic hydrocarbon, GC/MS, FD-MS

1. Introduction

A fluidized bed gasifier is one of the reaction apparatus which is used to gasify solid fuels like lignite and biomass. The dual fluidized bed gasifier in which the gasifier and the combustor are separated makes the fuel gasify with steam4). Since no combustion exhaust gases are mixed with the generated syngas, a high caloric gas can be obtained. However, tar is generated with the syngas due to the operation temperature in the range of 1073-1173 K. It is important to understand the composition of the tar produced as it can cause problems in other parts of the system after the gases cool, primarily by adhering to piping. Furthermore, the amount of steam in the gasifier may control depending upon the operating conditions7). It is necessary to identify the composition of the tar produced under different operating conditions to optimize the design of the tar reformer found in the subsequent stage of the process. In previous studies, tar components of up to a molecular weight of approximately 300 have been identified by gas chromatograph mass spectrometry (GC/MS), under practical steam gasification conditions6,8). To allow the detection of tar components having a wider range of molecular weights, we have devised a method that has enabled us to identify tar components that could not be identified using GC/MS alone. This is accomplished by adding field desorption mass spectrometry (FD-MS) along with GC/MS9,10). We employed this method to analyze the composition of the tar contained in the syngas stream, produced by steam gasification of lignite, under practical operating conditions11). The tar analysis method proposed in this study can contribute to improving the accuracy of the design simulation of the tar reformer. Additionally, it is thought that this tar analysis method can be applied not only to fluidized bed gasifier but also to other gasifiers. However, the composition of the tar produced while employing different amount of steam supplied, especially components that cannot be identified by GC/MS, has not been fully studied. If excess steam is supplied, running cost may be high depending on the amount of water vapor, but the composition of the tar might be changed by decomposition of high molecular weight molecules. If such molecules could be reduced or eliminated, the tar processing load of the system could potentially be reduced. In this paper, lignite was gasified in a laboratory-scale fluidized bed...
gasifier under a wide range of steam conditions. Steam was supplied at up to three times greater than the required stoichiometric ratio. In each case, the composition of the tar was analyzed.

2. Experimental

A schematic of a laboratory-scale bubbling fluidized bed gasifier is illustrated in Fig. 1. The inner diameters of the fluidized bed and the freeboard are 65 mm and 76 mm, respectively. Silica sand (having a mean diameter of 0.15 mm) was used as a bed material. The gasifier was filled with this material to create a static bed height of 100 mm. The fluidizing gas supplied steam primarily from the lower portion of the gasifier. The molar ratio of the steam feed rate and the carbon content of the fuel (the S/C molar ratio) was varied in the range of 1.1-3.2. In addition, it was carried out under pyrolysis (fluidizing gas: only nitrogen) condition. The temperature inside the gasifier was controlled at 1123 K by an electric furnace. Lignite was continuously supplied for 60 min at a rate of 1.0 g/min by a screw feeder. The particle size of the lignite, which is listed in the properties in Table 1, was 0.5-1.0 mm. The tar existing in the syngas after gasification was cooled and captured by a cold trap consisting of iced water at 273 K and an acetone/liquid nitrogen mixture at 205 K. The syngas composition (H₂, CO, CO₂, CH₄, C₂H₄, and C₂H₆) was analyzed with a gas chromatograph (CP-4900, Varian Inc., CA) after capturing the fine particles using a filter paper thimble. The tar-containing sample collected in the cold trap was washed with acetone as a solvent, and then recovered as an acetone solution. This 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 in the filtrate was removed to obtain the condensate sample. In this study, the final sample obtained by the above method was analyzed as “Tar.” The collected tar was diluted with toluene, and the tar components were identified using GC/MS (HP-6890/HP-5973N, Agilent Technologies) employing the analytical conditions listed in Table 2. The tar compounds were identified by comparison of the obtained spectra with a database (WILEY 8th/NIST05) and with spectra obtained for standard PAH reagents (PAH solution mix, Associates of Cape Cod, Inc.). Additionally, to identify the functional groups possessed by the tar components, tar was measured by ¹³C solid-state nuclear magnetic resonance (¹³C NMR) using the CMX Infinity plus NMR Spectrometer System (400 MHz, Varian Inc., CA). The tar obtained under the condition of S/C: 1.1 was placed in a sample tube without dilution. The measurement employed the decoupling magic angle spinning (DD-MAS) method. The frequency of MAS was 6000 Hz.

![Fig. 1 Schematic Diagram of a Laboratory-scale Bubbling Fluidized Bed Gasifier](image)

Table 1 Lignite Properties

| Property                     | VM (dry, wt%) | PC (dry, wt%) | Ash (dry, wt%) |
|------------------------------|---------------|---------------|----------------|
| Proximate analysis           | 49.2          | 49.2          | 1.6            |
| Ultimate analysis            |               |               |                |
| C (dry, wt%)                 | 69.23         |               |                |
| H (dry, wt%)                 | 5.01          |               |                |
| N (dry, wt%)                 | 0.36          |               |                |
| Comb. S (dry, wt%)           | 0.05          |               |                |
| Higher heating value (HHV)   | 27.90         |               |                |

Table 2 Analytical Conditions of GC/MS

| Parameter                  | Specification                               |
|----------------------------|---------------------------------------------|
| Injector                   | 573 K, splitless mode (60 s)                |
| Injection volume           | 1 μL                                        |
| Column                     | Agilent Technology Select PAH              |
| (φ 0.25 mm × 30 m, df/–0.15 μm) |
| Carrier gas                | 1.2 mL/min, He (constant flow)             |
| Column temperature         | 313 K (5 min) - 2 K/min - 573 K (60 min)    |
| Detector                   | mass, EI mode (70 eV), scan mode (m/z 4-700) |

Table 3 Analytical Conditions of FD-MS

| Parameter                  | Specification                               |
|----------------------------|---------------------------------------------|
| Inlet source               | Direct                                      |
| Ionization mode            | FD +                                        |
| Cathode voltage            | −10 kV                                      |
| Ion chamber temperature    | <323 K                                      |
| Emitter current            | 0~40 mA                                     |
| (rate 51.2 mA/min)         |                                            |
| Scan range                 | 20.00-1600.00                               |

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3. Results and Discussion

The relationship between the gas yields and the S/C molar ratio is shown in Fig. 2. As shown in this figure, as the S/C molar ratio increases, the gas yield increases. As the amount of steam supplied increased from 1.1 to 3.2 of the S/C molar ratios, the amount of hydrogen generated during the gasification reaction was increased by about 50%. The reason for this is shown in Eqs. (1) and (2). When the amount of steam increases, the steam reforming reaction (1) and the water-gas shift reaction (2) are more likely to occur.

\[
\begin{align*}
C + H_2O &\rightarrow CO + H_2 \\
CO + H_2O &\rightarrow CO_2 + H_2
\end{align*}
\]

The relationship between the tar concentration and the S/C molar ratio is shown in Fig. 3. As the S/C molar ratio was increased, the tar concentration was decreased. As the amount of steam supplied increased from 1.1 to 3.2 of the S/C molar ratios, the tar concentration generated during the gasification reaction decreased by about 30%. Using the results described above, the relationship between the H$_2$/CO molar ratio and the tar concentration is shown in Fig. 4. The S/C molar ratio is provided as a label on each point in this figure. As shown in this figure, the relationship depends on the fuel and gasifier used, while there is a clear correlation between these parameters. Since the concentrations of H$_2$ and CO are measured by gas chromatograph, their concentrations can be known quickly. Contrarily, several days are required to determine the tar concentration, owing to the time needed for processes such as the aforementioned washing and filtration. By using this figure, it is possible to predict in real time the tar concentration which takes time with direct analysis to become clear by setting the experimental condition of the S/C molar ratio.

The total ion chromatograms for the tar produced at different S/C molar ratios are shown in Fig. 5. 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. These figures show that 23 main peaks were found in common under all conditions. These compounds of main peaks identified by GC/MS are shown in Table 4. Some compounds in the table have the same molecular weight but differ in the bonding positions of the 5- or 6-membered rings or they possess different numbers of 5- or 6-membered rings. Other compounds differed in molecular weight but contained the same number of 5- or 6-membered rings. Under all conditions, most of the tar components within the detection range of GC/MS were found to be PAHs having a 5- or 6-membered ring structure. No attached substituents, such as methyl groups, were observed. Furthermore, a pattern is apparent within the tar components. There is an interval of 24 or 26 in molecular weight from one compound to the next closest in molecular weight.

The FD-MS spectra of the tar components produced with various S/C molar ratios are shown in Fig. 6. The vertical axis is the relative intensity and the horizontal axis is the molecular weight. Under all conditions, the molecular weight of these tar is distributed in...
the range of 178-500, and the main peaks show the same molecular weight pattern of having intervals of 24 or 26. Figure 7 shows the evaluation of compounds of molecular weight over 300 by applying this regularity to a compound of molecular weight 276 that had been identified by GC/MS (Benzo[ghi]perylene in Table 4). As shown in Fig. 7, all tar components produced under all conditions, including components that are outside the detection range of GC/MS, were predicted to be PAHs without substituent groups. It is thought that the lignite, formed by covalent bonding of aromatic rings, is fragmented by primary decomposition and further formed at 1123 K by condensation of fragments and elimination of substituents\(^{14}\)\(^{–}\)\(^{16}\).

The \(^{13}\)C NMR spectrum of the tar is shown in Fig. 8. As shown in this figure, a large peak indicating the double bonds found in aromatic rings, appears in the region of the chemical shift value of 100-150 ppm. However, a small peak indicating a single bond appeared in the region of the chemical shift value of 0-50 ppm. The ratio of these areas shows that the main components of the tar are aromatic compounds. This result agrees with the analysis described in Fig. 7.

The peaks between 2 and 3 of this figure (a), (c), (d) and (e) are compounds derived from toluene solvent.

Fig. 5  Total Ion Chromatogram Produced by GC/MS Analysis of Tar
4. Conclusions

Lignite was gasified using varying amounts of steam at 1123 K. As the amount of steam increased, the tar concentration was decreased. The tar concentration produced in real time at different supplied steam levels can be predicted by gas analysis during operation. The main components of the tar were PAHs that lacked substituent groups, having molecular weights of 152-500, and this was independent of the amount of supplied steam. Even if the S/C molar ratio was increased from 1.1 to 3.2 the composition of the tar was largely unchanged. For the experimental conditions employed in this study, the change in tar composition was extremely small. It appears there is a limit to how much an increase in supplied steam can change the tar’s composition. It seems likely that tar composition may have a large temperature dependence. It is also possible that a suitable catalyst can be found to assist in further reduction of the tar concentration/composition. In future work, we will apply our combined GC/MS and FD-MS analytical method to evaluate the effects of temperature and catalyst.

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Fig. 7  Examples of Tar Compounds Inferred by the Combined GC/MS and FD-MS Method
Table 4  Tar Components Identified by GC/MS

| No. | Compound          | M.W. | Structural formula |
|-----|-------------------|------|-------------------|
| 1   | Acenaphthylene    | 152  | ![Acenaphthylene](image) |
| 2   | 1,2-Diphenylethane | 182 | ![1,2-Diphenylethane](image) |
| 3   | Fluorene          | 166  | ![Fluorene](image) |
| 4   | Phenanthrene      | 178  | ![Phenanthrene](image) |
| 5   | Anthracene        | 178  | ![Anthracene](image) |
| 6   | Benzo[def]fluorene | 190 | ![Benzo[def]fluorene](image) |
| 7   | Fluoranthenne     | 202  | ![Fluoranthenne](image) |
| 8   | Pyrene            | 202  | ![Pyrene](image) |
| 9   | Benzo[ghi]fluoranthene | 226 | ![Benzo[ghi]fluoranthene](image) |
| 10  | Benzo[a]anthracene | 228 | ![Benzo[a]anthracene](image) |
| 11  | Acepyrene         | 226  | ![Acepyrene](image) |
| 12  | Triphenylene      | 228  | ![Triphenylene](image) |
| 13  | Chrysene          | 228  | ![Chrysene](image) |
| 14  | Benzo[b]fluoranthene | 252 | ![Benzo[b]fluoranthene](image) |
| 15  | Benzo[k]fluoranthene | 252 | ![Benzo[k]fluoranthene](image) |
| 16  | Benzo[j]fluoranthane | 252 | ![Benzo[j]fluoranthane](image) |
| 17  | Benzo[e]pyrene    | 252  | ![Benzo[e]pyrene](image) |
| 18  | Benzo[a]pyrene    | 252  | ![Benzo[a]pyrene](image) |
| 19  | Perylene          | 252  | ![Perylene](image) |
| 20  | Indeno[1,2,3-cd]pyrene | 276 | ![Indeno[1,2,3-cd]pyrene](image) |
| 21  | Benzo[ghi]perylene | 276 | ![Benzo[ghi]perylene](image) |
| 22  | Dibenzo[def,mno]chrysene | 276 | ![Dibenzo[def,mno]chrysene](image) |
| 23  | Coronene          | 300  | ![Coronene](image) |

a) Numbers 1 to 23 in this table are same as Fig. 5.

Fig. 8  $^{13}$C NMR Spectrum of Tar (S/C: 1.1 at 1123 K)

References

1) Suda, T., J. Jpn. Inst. Energy, 90, (1), 201 (2011).
2) Yuasa, K., Nakasawa, R., J. IHI Technol., 55, (4), 24 (2015).
3) Kotake, T., J. IHI Technol., 57, (4), 16 (2017).
4) Benedikt, F., Schmid, J. C., Fuchs, J., Maurerhofer, A. M., Müller, S., Hofbauer, H., Energy, 164, 329 (2018).
5) Wang, Y., Dong, W., Dong, L., Yue, J., Guo, S., Suda, T., Xu, G., Energy & Fuels, 24, 2985 (2010).
6) Kern, S., Pfeifer, C., Hofbauer, H., Fuel Process. Technol., 111, 1 (2013).
7) Narukawa, M., Tsuboi, Y., Kumagai, Y., Takafuji, M., Suda, T., Fujimori, T., J. Soc. Powder Technol., 50, 182 (2013).
8) Zhang, L., Zeng, X., Wang, J., Wang, F., Zhang, J., Guo, M., Peng, C., Wu, R., Xu, G., Fuel, 236, 695 (2019).
9) Norisada, K., Murakami, T., Yasuda, H., Energy & Fuels, 31, 249 (2017).
10) Murakami, T., Yasuda, H., Norisada, K., Energy & Fuels, 32, 1110 (2018).
11) Murakami, T., Yasuda, H., Advanced Experimental Mechanics, 4, 38 (2019).
12) Murakami, T., Yang, T., Asai, M., Suzuki, Y., Adv. Powder Technol., 22, 433 (2011).
13) Norisada, K., Murakami, T., Yasuda, H., 93rd Annual Meeting of the Japan Society of Mechanical Engineers Kansai Branch, Osaka, March 2018, Abstr., No. 813.
14) Hüttenger, K. J., Michenfelder, A. W., Fuel, 66, 1164 (1987).
15) Mae, K., J. Jpn. Inst. Energy, 75, 167 (1996).
16) Tanner, J., Kabir, K. B., Müller, M., Bhattacharya, S., Fuel, 154, 107 (2015).
要旨
過剰水蒸気条件下での褐炭ガス化により生成する合成ガス中のタールの分析

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燃料をガス化させて合成ガスに変換し、発電や水素など広範に利用できるガス化技術が注目されている。二塔式流動層ガス化炉では、燃料を水蒸気によりガス化させる。ただし、1073 ～1173 K で運転するため、合成ガス中にタールが生成し、触媒改質のようなタール処理が必要となる。その最適な設計にはタールの成分を明らかにすることが重要である。本研究では、実験室規模の流動層ガス化装置により、埋蔵量が豊富な褐炭を1123 K でガス化させ、供給する水蒸気量を広範に変化させて得たタールの成分を明らかにすることを目的とした。結果として、水蒸気供給量が増加するにつれ、改質効果によりタール濃度は減少した。また、運転中の水素や一酸化炭素のガス分析結果から、ガス化炉への供給する水蒸気量により得られる合成ガス中のタール濃度をリアルタイムに予測する手法を提示した。タール成分においては、ガスクロマトグラフ質量分析（GC/MS）や電界脱離質量分析（FD-MS）など複数の分析装置を組み合わせて解析した結果、主成分は置換基のない多環芳香族炭化水素からなることが分かった。水蒸気を化学量論的ガス化に要する量の3倍まで過剰に与えても、その成分に大きな変化はないことを明らかにした。