Decomposition of Tar Derived from Gasification of Fowl Droppings Using Alkaline Materials

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Abstract: The effect of coexistence of alkaline minerals such as, dolomite \(\text{CaMg(CO}_3\text{)}_2\) and mayenite \(\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}\) on the thermal decomposition of tar derived from gasification of fowl droppings was investigated by thermal analysis method. Though the combustion temperature of the tar under dolomite coexistence was 420 ~ 500 °C, the temperature range which was almost equal to self combustion temperature of the tar, the combustion quantity of the tar increased over by two fold. On the combustion behavior under mayenite coexistence, the starting temperature of combustion dropped by about 200 °C, and the combustion quantity of the tar increased to 3.6 times. It was concluded that the oxygen radicals occluded in mayenite were effective and promoted the combustion of the tar.

Keywords: Gasification, Tar, Combustion, Dolomite, Mayenite, Oxygen radicals

1. INTRODUCTION

The creation of a new energy becomes the urgency, when the depletion of fossil fuel such as petroleum becomes serious. Recently the study of the gasification of an organic unused waste such as biomass and waste plastic etc. has been developed rapidly and its achievements have become a center of attraction. When the organic waste is decomposed thermally in the gasification furnace, in addition to the pyrolysis gas containing a mixture of \(\text{CH}_4\), \(\text{CO}\) and \(\text{H}_2\), the main component, tar and char are formed as side products. Though the tar is in gas phase in the high-temperature gasification furnace, it discharges from the furnace in liquid phase at low temperatures. As a result, the tar is adsorbed on pipes, filters and valves of the gas line, and becomes cause of gas blockades. Therefore, the removal of the tar is indispensable in order to operate the gasifier steadily [1]. Combustion is the most widely employed method for removing tar. As combustion is an energy intensive process, it should be performed at lower temperatures in order to reduce the energy consumption [2]. This has been achieved by using catalysts based on \(\text{Ni}\), \(\text{Ru}\), etc. However, deactivation of catalyst by cooking is a serious problem [3-5]. Since the Ru-based catalyst has low coaking and high oxidation activity, it is consider as the promising catalyst. However, the high cost of Ru makes these catalysts unattractive for commercial application to decompose tar [6-8].

In this study, alkaline minerals such as dolomite \(\text{CaMg(CO}_3\text{)}_2\) and mayenite \(\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}\), which are cheaper and readily available materials, have been explored as alternative potential promoter for the decomposition of tar derived from gasification of fowl droppings by means of temperature programmed study.

2. EXPERIMENTAL

2.1. Sample

In this study, the tar recovered from the gasifier of fowl droppings was used as a sample. The chemical analysis of the tar obtained by a CHN coder is shown in Table 1. The main component of the tar is carbon.

The alkaline materials used in this study were dolomite \(\text{CaMg(CO}_3\text{)}_2\) and mayenite \(\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}\). The dolomite was a natural mineral with a Mg/Ca molar ratio of 0.41. The chemical analysis of dolomite is shown in Table 2. Main components are CaO and MgO with a purity of 98.84wt%. The dolomite before and after calcination at 1000 °C for 2 h in air were used as a sample for decomposition of the tar. On the other hand, powder sample of mayenite was prepared by solid state reaction. The stoichiometric quantity of these hydroxides was mixed physically, ground in a pestle and mortar and then, calcined at 1000 °C for 4 h in air.

<table>
<thead>
<tr>
<th>Component</th>
<th>Content / wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>76.36</td>
</tr>
<tr>
<td>MgO</td>
<td>22.48</td>
</tr>
<tr>
<td>SiO2</td>
<td>0.77</td>
</tr>
<tr>
<td>Fe2O3</td>
<td>0.19</td>
</tr>
<tr>
<td>Al2O3</td>
<td>—</td>
</tr>
<tr>
<td>Others</td>
<td>0.20</td>
</tr>
<tr>
<td>Total</td>
<td>100.00</td>
</tr>
</tbody>
</table>

Table 2. Chemical analysis of dolomite.

Table 1. Chemical analysis of tar by a CHN coder.

<table>
<thead>
<tr>
<th>Component</th>
<th>Content / wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>45.21 %</td>
</tr>
<tr>
<td>H</td>
<td>6.43 %</td>
</tr>
<tr>
<td>N</td>
<td>6.20 %</td>
</tr>
<tr>
<td>Ignition loss</td>
<td>42.16 %</td>
</tr>
</tbody>
</table>

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2.2. Characterization of alkaline materials
The crystal structure of alkaline materials was measured by X-ray powder diffractometer (Rigaku, Rint-TTR) by using CuKα radiation (50 kV, 100 mA). The specific surface area was measured by using N2 adsorption / desorption apparatus (Bel Japan, BELSORP 28SP) at 77K. The Raman spectroscopy was measured by using a Laser Raman spectrometer (JASCO, NRS-1000) with the 532.30 nm line from an Ar+ laser for excitation.

2.3. Decomposition of tar
The thermal decomposition behavior of the tar was examined by a thermal analysis apparatus (Rigaku, Thermo Plus TG-8120). The mixture of tar and alkaline material was taken in the sample holder and heated continuously from room temperature to 600 °C at the rate of 2 °C/min in air. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) curves were measured. Since it was very difficult to obtain the tar weight in the mixture because of high viscosity of the tar, the tar weight in the mixture was calculated from the TGA result. The weight at 1000 °C was considered as that corresponds to the alkaline mineral, because the tar completely disappeared at 600 °C as noted from the TGA result of only the tar.

3. RESULTS AND DISCUSSION
3.1. Characterization of alkaline materials
3.1.1 Dolomite
The thermal decomposition behavior of dolomite was measured by a TG-DTA. The thermal decomposition of the material began at 711 °C and ended at 774 °C accompanying both of endothermic reaction and weight loss of 47.96 wt%. The powder XRD patterns of dolomite before and after calcination at 1000 °C for 2 h are shown in Fig.1. The XRD pattern before calcination exhibits only diffraction lines attributed to dolomite (CaMg(CO3)2) mineral. On the other hand, the XRD pattern of dolomite calcined at 1000 °C shows that the diffraction line attributed to dolomite completely disappeared. Only the diffraction lines attributed to CaO, Ca(OH)2 and MgO are observed by decomposition. The formation of Ca(OH)2 seems to indicate that the CaO takes up water vapor in air, because CaO has reacted readily with water. From the above results, it can be concluded that the dolomite mineral decomposes to a mixture of CaO and MgO after calcining at 1000 °C. Specific surface areas of dolomite before and after calcination are 10.4 and 9.6 m2/g, respectively.

3.1.2 Mayenite
There are various important parameters such as particle size of starting materials, mixing degree, calcination temperature and time, calcination atmosphere etc. in the preparation of mayenite. The calcination temperature is one of the most important parameters. It has been observed that calcination at a temperature as high as possible produces mayenite with high crystallinity. In this study, mayenite was prepared by increasing the calcination temperature from 900 to 1350 °C. XRD patterns of mayenite prepared by calcining at 1000°C for 4 h are shown in Fig.2. Though the sample exhibits peaks corresponding to CaO starting material, the sample show a well crystalline phase of mayenite (Ca12Al14O33). The crystallinity of mayenite can be further improved by calcining at higher temperature. However, the high temperature calcination causes severe sintering leading to a drop in specific surface area from 4.8 m2/g to below 1 m2/g with increasing the calcination temperature from 1000 to 1350 °C. In this study, the mayenite prepared by calcining at 1000 °C has been used as a sample for subsequent studies as described below.

3.2. Thermal decomposition behavior of tar
3.2.1. Thermal decomposition of tar without alkaline minerals
The thermal decomposition behavior of tar sample alone has been measured by the thermal analysis apparatus, and the results are shown in Fig.3. From TG curve, there is a weight loss of 30.0 wt% by dehydration and volatilization of high volatile components from room temperature to 110 °C, in addition to, an endothermic peak around 80 °C. Afterwards, a weight loss continued with increasing temperature. The weight loss of 72.9% has also been observed at 258 °C, and the tar completely disappeared at 526 °C. In the elevated temperature process, two exothermic peaks by the self combustion are observed in the temperature range between 335 and 368 °C and between 424 and 526 °C. When both peak areas are...
compared, the latter is larger than the former. The weight loss disappeared in the former combustion, 335 °C ~ 368 °C, and is significantly small, about 4.4 wt%, and that in the latter combustion, 424 °C ~ 526 °C, is 13.9 wt%. We conclude from the experimental result that most component of the tar disappeared by the volatilization, and the disappearance by the combustion is slight, 18.3 wt%, in the elevated temperature process.

3.2.2. Thermal decomposition of tar with dolomite

TG and DTA curves of the tar in the coexistence of dolomite before and after calcination at 1000 °C are shown in Fig.4. TG curves indicated that the weight of dolomite did not change in the temperature range from room temperature to 600 °C. In addition, the tar completely disappeared which heating at 526 °C. Therefore, the weight loss of TG curve was made to be -100 % at 600 °C in order to examine the thermal decomposition behavior of the tar by subtracting the weight of dolomite.

There was a weight loss with endothermic peak caused by evaporation of water and volatilization of high volatility compounds from room temperature to 125 °C on each TG curves. The weight loss was 30.5 and 35.0 wt% for dolomite before and after calcination, respectively, and the results were almost equal to that of the tar alone. Afterwards, there was a large weight loss of about 500 °C. Large exothermic peak was observed in 421 °C ~ 467 °C temperature range, when the dolomite before calcination coexisted. The area of the exothermic peak corresponds to 2.7 times higher than that observed for tar alone. On the other hand, the exothermic peak under the coexistence of dolomite after calcination occurs between 422 and 504 °C, and the area is 2.2 times higher compared to that of the tar alone. The starting temperature of the combustion is not different from that of the tar without dolomite. From the above results, it can be concluded that addition of dolomite improves combustion of the tar. The peak area observed in the dolomite before calcination is 1.2 times as much the area observed in the dolomite after calcination, though their starting temperature of combustion is almost the same. When the experimental error was considered, this difference, 1.2 times, was hard to be regarded as a significant difference. From these results, it was concluded that both of dolomite before and after calcination were effective and act as catalysts for the combustion of tar.

3.2.3. Thermal decomposition of tar with mayenite

The thermal decomposition behavior of the tar, TG and DTA curves, under coexistence of mayenite is shown in Fig.5. In the same figure, the result of only the tar has also been shown. From the DTA curve, there are two exothermic peaks which are related to the combustion of the tar. There was a large exothermic peak in the temperature range between 238 and 371 °C, in addition, a small exothermic peak between 437 and 503 °C. These exotherms for only the tar appear in the temperature range 238 and 371 °C, and in addition, a small exothermic peak between 437 and 503 °C. These exotherms for only the tar appear in the temperature range 238 and 371 °C.
range between 335 and 368 °C and between 424 and 526 °C. Comparison of the quantity of heat released from these exotherms, it is about 3.5 times higher when mayenite coexisted and about 50 % of the tar is combusted. These results conclude that mayenite is suitable for combustion of the tar.

The Raman spectrum of mayenite has been measured, and the spectrum is shown in Fig.6. It is clear that mayenite has occluded superoxide radical (O$_2^-$) and peroxide radical (O$_{2}^{2-}$). It is well known that these oxygen radicals are effective for the oxidative decomposition of organic substances [9-12]. Therefore, when mayenite coexists in the tar, the combustion temperature remarkably falls due to the existence of these oxygen radicals.

4. CONCLUSIONS

The thermal decomposition behavior of the tar derived from gasification of fowl droppings at elevated temperature can be explained as follows: Dehydration and volatilization of highly volatile components with a weight loss of 30.0 % occurred from room temperature to 110 °C. The weight loss of 72.9 % occurred at 258 °C, and the whole quantity of the tar disappeared at 526 °C. Two exothermic peaks by self combustion were observed in the temperature range between 335 and 368 °C and between 424 and 526 °C with a weight loss of 18.3 %.

Next, the thermal decomposition behavior of the tar under dolomite before and after calcination at 1000 °C coexistence was examined. When dolomite before calcination was used, large exothermic peak was observed in the temperature range between 421 and 467 °C. The area of the exothermic peak was 2.7 times higher compared that observed from combustion of tar alone. On the other hand, the exothermic peak under coexistence of dolomite after calcination was obtained in the temperature range between 422 and 504 °C, and the area was higher by 2.2 times. The starting temperature of the combustion was not different from that of the tar without dolomite.

When mayenite coexisted with the tar, there was a large exothermic peak in the temperature range between 238 and 371 °C, in addition to a small exothermic peak in between 437 and 503 °C. The starting temperature of combustion dropped to about 200 °C. The amount of heat released was 3.6 times compared to that obtained when the tar alone was combusted. From Raman spectroscopy measurement, it was confirmed that mayenite has occluded superoxide radical (O$_2^-$) and peroxide radical (O$_{2}^{2-}$). This suggested that these oxygen radicals greatly contribute to the combustion of the tar.

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REFERENCES