The heterogeneous reaction between tar and ash from waste biomass pyrolysis and gasification


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Abstract

Fossil energy resources that are available in the world are exhaustible. Therefore, renewable biomass has attracted a lot of attention as a future energy resource. In addition, it is an advantage that the biomass grows while absorbing CO$_2$, contributing to prevention of global warming. Biomass utilization technologies are classified as pyrolysis and gasification, fermentation and combustion. Fuel gases and synthesis gases produced by the pyrolysis and gasification are used for power generation, heating and as chemical products. However, pyrolysis and gasification processes also generate condensable organic compounds, so-called “tar”. Most of the tar contents are present as gases at high temperature. However, when they are cooled down at temperatures lower than their boiling point, causing a black oily liquid that leads to equipment failure, appropriate processing is required. As a processing method, the use of catalytic tar decomposition has been widely studied. In the work presented here, thermal decomposition of cellulose was carried out in an experimental apparatus modeling a fluidized bed gasifier. During thermal decomposition of cellulose, tar and gas are generated, tar is collected and cooled, and the gases are measured by a gas-chromatograph with a flame ionization detector (GC-FID) and with a thermal conductivity detector (GC-TCD). Then, K and Ca are selected as the catalysts of alkali metals and alkaline earth metals contained in the waste biomass. They are present in the state of oxide or carbonate during pyrolysis and gasification. A similar experiment was conducted. The amount of condensable products and heavy tar were decreased by installing K$_2$CO$_3$ and Ca(OH)$_2$. Additionally, they brought a further gas production. It can be concluded that alkali metal compound (K$_2$CO$_3$)
and alkaline earth compound (CaO) have a catalytic effect to decompose tar contents, to enhance gaseous production.

**Keywords:** biomass, pyrolysis, heterogeneous reaction, alkali metal, alkaline earth metal, tar decomposition.

## 1 Introduction

Focusing on developing countries, it is expected that the amount of energy consumption is increased in the world. Oil, coal and natural gas are exhaustible resources used to fulfil the energy requirements in the world. Large amounts of carbon dioxide emission occur when these energy sources are used and this promotes global warming. Recently, biomass has attracted attention as a renewable energy resource. Thermal decomposition and gasification are methods used to convert biomass to energy. The gas obtained by the thermal decomposition and gasification is mainly composed of H₂ and CO. From these synthesis ammonia, liquid fuel, methanol and chemical products as well as a variety of derivative products are manufactured [1]. However, an amount of condensable organic compound called tar is produced during thermal decomposition and gasification. The tar clogs the pipe of gasifier and breaks the turbines. Both mechanical methods and thermal cracking have been proposed to remove the tar.

Mechanical methods do not allow energy recovering from tar which is just removed from gaseous products, while thermal cracking requires high temperature (>1100°C) to convert them [2]. Catalytic tar decomposition has been proposed to overcome these drawbacks. In addition, the use of a catalyst can enhance gas formation and modify the gaseous composition promoting the reforming reactions of hydrocarbons. Tar removal using a catalyst has been extensively studied. It is reported that nickel-based catalysts, alkaline metal oxides and alkaline earth metal oxides are suitable to reduce the amount of tar [3]. Alkali metal and alkaline earth metal are present in the ash component of the biomass.

The focus here is on tar reduction in a fluidized bed gasifier such as a fluidized bed and spouted bed system. Even though experiments on thermal decomposition and gasification of biomass in a fixed bed system have been widely studied, studies on the heterogeneous reaction between tar and ash are yet to be performed [4]. Using an experimental system that assumes the heterogeneous reaction of ash and tar in a fluidized bed gasifier, the evaluation of the catalytic effect of the ash is significant. In this study, an experimental thermal decomposition of cellulose has been conducted by constructing an experimental device that assumes the heterogeneous reaction in a fluidized bed gasifier. Cellulose is a major component of wood and plant biomass [5]. By introducing the ash in the experimental thermal decomposition of cellulose, the effect of ash on the heterogeneous reaction with tar has been considered. The yields of char from the results of the thermogravimetry-differential thermal analysis (TG-DTA) experiment have been calculated; the yields of condensable products cooled.
down and collected in the test tube have been measured; the yields of gas by GC-TCD/FID have also been measured.

2 Materials and experimental methods

2.1 Materials

The tested experimental sample was microcrystalline cellulose with an average diameter of 50 μm (SERVA). The chemical formula for this sample polymer could be approximated as \((C_6H_6O_5)_n\), confirming the linearly polymerized structure of the glucopyranose linked by \(\beta-1, 4\)-glycosidic bonds. The analysis of the cellulose had been performed using a CHN corder (Model MT-5, Yanaco Co. Ltd., Japan) for elemental analysis and proximate analysis, which were both performed. The cellulose composition is presented in table 1.

<table>
<thead>
<tr>
<th>Elemental analysis (wt.%)</th>
<th>Proximate analysis (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>H</td>
</tr>
<tr>
<td>43.31</td>
<td>6.23</td>
</tr>
</tbody>
</table>

Potassium and calcium were alkali metal and alkaline earth metal species contained in the biomass. \(K_2CO_3\) (Wako, assay min. 99.5%) and \(Ca(OH)_2\) (Wako, assay min. 96.0%) were used in the study as ash model. Silicon dioxide (Wako) was used as a fluidizing medium [6].

2.2 TG-DTA experiment

The pyrolysis of cellulose was carried out in a TG-DTA (Model DTG-60, Shimadzu Co. Ltd., Japan), in order to calculate the yield of char and survey the pyrolysis behavior. The sample was weighed 5.00–7.00 mg and placed on the scales in the apparatus. The sample was heated up to 900°C at a constant heating rate of 10°C/min. Argon at a flow rate of 70 ml/min was used as the carrier gas to provide an inert atmosphere for pyrolysis and to remove the gaseous and condensable products.

2.3 Thermal decomposition of cellulose

2.3.1 Experimental apparatus for cellulose pyrolysis and gasification

Figure 1 shows the scheme of the experimental setup used for cellulose pyrolysis and gasification. It was composed of a gas feeding system, a pyrolysis system, a tar decomposition system, a condensable products trapping system and a gaseous products measurement system. The pyrolysis and tar decomposition systems consisted of connecting the two stainless reactors (I.D. 21.4 mm, length 500 mm). Cellulose, \(K_2CO_3\), \(Ca(OH)_2\) and silicon dioxide were placed on the mesh (40 μm) in each reactor. This apparatus can be independently heated in two
different electric furnaces while the gas mixture is coming to contact with the catalyst. Therefore, a heterogeneous reaction between tar and ash can be carried out using the apparatus. The lines between the first and second reactor as well as between the second reactor and the condensable products trapping system were heated at between 300 and 400°C to avoid the condensation of tar. The condensable products were collected by cooling the test tube and the collection efficiency was improved by using glass beads. The Cooling bath was kept below –3°C by mixing water, ice and sodium chloride. The Gaseous products were measured by a GC-TCD/FID (Model GC-2014, Shimadzu Co. Ltd., Japan). H₂ and CO, CH₄, CO₂ were measured by a GC-TCD while hydrocarbons (C₂H₆ and C₂H₄, C₃H₈, C₃H₆, iso-C₄H₁₀, n-C₄H₁₀) were measured by a GC-FID.

2.3.2 Experimental procedure
The operative conditions are reported in table 2. The cellulose, catalysts and silicon dioxide were placed in each reactor under the respective conditions of table 2. The second reactor was heated up to a predetermined temperature under argon at constant flow rate. Then, the first reactor was heated up (at 10°C/min up to 900°C) and the gaseous products were measured at every 80°C to 900°C from 180°C by a GC-TCD/FID.

2.3.3 Yields of pyrolysis products
The yields of char were calculated from TG-DTA analysis. The yields of condensable products were determined by the weight difference of the test tube before and after the experiment. The yields of gaseous products were calculated from the measurement results of GC-TCD/FID. Also, the amount obtained by
subtracting the amount of char, the amount of condensable products and the amount of gaseous products from the amount of cellulose was evaluated as a heavy tar. The heavy tar is a tar which remains in the apparatus.

Table 2: Operative conditions used for tests.

<table>
<thead>
<tr>
<th>Item</th>
<th>First reactor</th>
<th>Second reactor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellulose amount (g)</td>
<td>2.00</td>
<td>none</td>
</tr>
<tr>
<td>Catalyst amount (g)</td>
<td>-</td>
<td>K₂CO₃ 0.691</td>
</tr>
<tr>
<td>Silicon dioxide amount (g)</td>
<td>-</td>
<td>Ca(OH)₂ 0.741</td>
</tr>
<tr>
<td>Heating rate (°C/min)</td>
<td>10</td>
<td>-</td>
</tr>
<tr>
<td>Maximum temperature (°C)</td>
<td>900 500, 700,</td>
<td>700, 800 700, 800</td>
</tr>
<tr>
<td>Argon flow rate (ml/min)</td>
<td>70</td>
<td></td>
</tr>
</tbody>
</table>

3 Results and discussion

3.1 Results from TG-DTA analysis

The pyrolysis characteristics, both TG (wt.%) and DTA (μV) curves of cellulose determined with a TG-DTA are shown in fig. 2. Rapid weight loss of cellulose was observed between 300 and 400°C and then the weight loss had progressed slowly. Endothermic peak was observed between 300 and 400°C, indicating that the thermal decomposition of cellulose was occurring within this temperature range [7]. Furthermore, the weight loss was also observed in the same temperature range. Thus, it should be predicted that a large amount of thermal

![Pyrolysis curves of cellulose in the TG-DTA analysis.](image-url)
decomposition products are released at this temperature. As a gradual weight loss continued above 400°C, it should be predicted that a small amount of thermal decomposition products would have been released. Experiments were carried out several times under the same conditions and the measurements were within ± 5% maximum error. Thus, in this study, char yields of cellulose pyrolysis were calculated to be 8.90% (wt.%).

3.2 Thermal decomposition of cellulose

Figures 3 to 6 show the molar quantity (mmol/g-cellulose) of gaseous products generated by thermal decomposition of cellulose under each experimental condition. Also, table 3 shows the total molar quantity (mmol/g-cellulose) of gaseous products generated by thermal decomposition of cellulose under each experimental condition.

![Figure 3](image)

**Figure 3:** Molar quantity of H$_2$ under each second reactor conditions.

At the second reactor temperature of 900°C, the total molar quantity of H$_2$ was maximum while it was minimum at the second reactor temperature of 500°C. At the second reactor temperature of 500°C, the generation of H$_2$ began to increase rapidly above, approximately, 600°C. However, H$_2$ generation was remarkable in between 300 and 500°C under experimental conditions. In the case of second reactor temperature at 500°C, generation of H$_2$ was not observed; only a small amount was generated in that temperature range. The total molar quantity of H$_2$ was increased as the second reactor temperature conditions rose. The total molar quantity of H$_2$ was increased by approximately 7.5% after adding K$_2$CO$_3$ compared to the molar quantity observed with the presence of only silicon dioxide at 700°C. However, the total molar quantity of H$_2$ was increased by nearly 77.6% after installing Ca(OH)$_2$. Compared with the presence of only silicon dioxide in the second reactor at 800°C, the total molar quantity of H$_2$ was increased by about 28.2% and 45.5% with the presence of K$_2$CO$_3$, and Ca(OH)$_2$ respectively.

In the case of Ca(OH)$_2$ being placed in second reactor at 800°C, the total molar quantity of CO was maximum while it was minimum in the case of a
second reactor temperature of 500°C. The generation of CO was significant between 300 and 500°C under all experimental conditions. Compared to the condition where only silicon dioxide was placed in the second reactor at 700°C, the total molar quantity of CO was increased by about 20.4% after adding K₂CO₃. However, it was further increased by nearly 60.4% when Ca(OH)₂ was installed. The quantity of CO was increased by nearly 1.2% and 51.1% with the presence of K₂CO₃ and Ca(OH)₂, respectively, compared to the CO quantity observed when only silicon dioxide was placed in the second reactor at 800°C. The total molar quantity of CO when Ca(OH)₂ was installed without changing the second reactor temperature, was higher than when the second reactor temperature was raised to 700–800°C and 800–900°C. CO was mostly generated in the pyrolysis gaseous products.

![Figure 4: Molar quantity of CO under each second reactor conditions.](image1)

![Figure 5: Molar quantity of CH₄ in each second reactor conditions.](image2)

In the case of Ca(OH)₂ being placed in the second reactor at 800°C, the total molar quantity of CH₄ was maximum and it was minimum at a second reactor temperature of 500°C. The generation of CH₄ was significant between 400 and 800°C when the second reactor temperature was 500°C while it was significant in between 300 and 500°C under other experimental conditions. At the second
reactor temperature of 500°C, generation of CH₄ was not observed; only a small amount was generated within that temperature range. As the second reactor temperature conditions rose, the total molar quantity of CH₄ was increased. Compared to the condition where only silicon dioxide was placed in the second reactor at 700°C, the total molar quantity of CH₄ was increased by about 11.7% and 46.0% by adding K₂CO₃ and Ca(OH)₂, respectively. Compared with only silicon dioxide being placed in the second reactor at 800°C, the total molar quantity of CH₄ was increased by about 9.4% by installing K₂CO₃; on the other hand, the total molar quantity of CH₄ was increased by about 40.4% by installing Ca(OH)₂. The rate of the total molar quantity of CH₄ when Ca(OH)₂ was installed without changing the second reactor temperature, was higher than when the second reactor temperature was raised to 700–800°C and 800–900°C.

In the case of Ca(OH)₂ being placed in the second reactor at 800°C, the total molar quantity of CO₂ was maximum, and it was minimum at a second reactor temperature of 500°C. The generation of CO₂ was significant between 300 and 500°C under all experimental conditions. As the second reactor temperature condition rose, the total molar quantity of CO₂ was increased. Compared to the condition where only silicon dioxide was placed in the second reactor at 700°C, the total molar quantity of CO₂ was increased by about 39.6% by installing K₂CO₃. However it was increased by nearly 39.5% after installing Ca(OH)₂. Compared with only silicon dioxide being placed in the second reactor at 800°C, the total molar quantity of CO₂ was increased by about 49.4% by installing K₂CO₃. However, the total molar quantity of CO₂ was increased by about 62.0% by installing Ca(OH)₂. The amount of the total molar quantity of CO₂ with the presence of K₂CO₃ and Ca(OH)₂ without changing the second reactor temperature was higher than that generated when the second reactor temperature was raised to 800–900°C.

![Figure 6: Molar quantity of hydrocarbons (C₂H₄, C₃H₈, C₃H₆, iso-C₄H₁₀, n-C₄H₁₀) under each second reactor conditions.](image-url)
In the case of Ca(OH)$_2$ being placed in the second reactor at 800°C, the total molar quantity of hydrocarbons was maximum while a minimum quantity of hydrocarbons was observed when the second reactor temperature was 500°C. At a second reactor temperature of 500°C, the generation of hydrocarbons was significant between about 400 and 800°C. However, the generation of hydrocarbons was significant between about 300 and 500°C under the other experimental conditions. At a second reactor temperature of 500°C, generation of hydrocarbons was not observed; only a small amount occurred within that temperature range. As the second reactor temperature conditions rose, the total molar quantity of hydrocarbons was increased. The total molar quantity of hydrocarbons was increased by approximately 6.1% and 42.2% by installing K$_2$CO$_3$ and Ca(OH)$_2$, respectively, compared to the total molar quantity of hydrocarbons when only silicon dioxide was placed in the second reactor at 700°C. Compared with only silicon dioxide being placed in the second reactor at 800°C, the total molar quantity of hydrocarbons was increased by about 15.8% after installing K$_2$CO$_3$ while it was increased by about 25.4% after installing Ca(OH)$_2$. The quantity of the total molar quantity of hydrocarbons when Ca(OH)$_2$ was installed without changing the second reactor temperature, was higher than that generated when the second reactor temperature was raised to 800–900°C.

Table 3: Total molar quantity (mmol/g-cellulose) of gaseous products under each second reactor condition.

<table>
<thead>
<tr>
<th>Second reactor conditions</th>
<th>H$_2$</th>
<th>CO</th>
<th>CH$_4$</th>
<th>CO$_2$</th>
<th>Hydrocarbons</th>
</tr>
</thead>
<tbody>
<tr>
<td>500°C</td>
<td>0.493</td>
<td>3.531</td>
<td>0.333</td>
<td>0.921</td>
<td>0.149</td>
</tr>
<tr>
<td>700°C</td>
<td>1.892</td>
<td>5.059</td>
<td>1.114</td>
<td>1.225</td>
<td>0.979</td>
</tr>
<tr>
<td>700°C-K$_2$CO$_3$</td>
<td>2.033</td>
<td>6.088</td>
<td>1.244</td>
<td>1.710</td>
<td>1.039</td>
</tr>
<tr>
<td>700°C-Ca(OH)$_2$</td>
<td>3.359</td>
<td>8.116</td>
<td>1.626</td>
<td>1.709</td>
<td>1.393</td>
</tr>
<tr>
<td>800°C</td>
<td>3.638</td>
<td>6.411</td>
<td>1.454</td>
<td>1.847</td>
<td>1.112</td>
</tr>
<tr>
<td>800°C-K$_2$CO$_3$</td>
<td>4.665</td>
<td>6.487</td>
<td>1.590</td>
<td>2.759</td>
<td>1.288</td>
</tr>
<tr>
<td>800°C-Ca(OH)$_2$</td>
<td>5.294</td>
<td>9.691</td>
<td>2.040</td>
<td>2.993</td>
<td>1.395</td>
</tr>
<tr>
<td>900°C</td>
<td>5.751</td>
<td>8.673</td>
<td>1.847</td>
<td>2.268</td>
<td>1.146</td>
</tr>
</tbody>
</table>

The total molar quantity of all gas species was increased with the increase of the second reactor temperature; the cause of this should be a secondary pyrolysis reaction of cellulose pyrolysis products in the second reactor. At higher second reactor temperature, heavier tar could be pyrolyzed, thus, the generation of additional gas and carbon constituent is expected. Differences in temperature conditions generated a larger amount of gas from secondary pyrolysis and gasification of tar than from the primary pyrolysis. That could be the reason for the significant difference in the total molar quantity of gas production [8]. In the case of second reactor temperature conditions being the same, the total molar quantity of all gas species increased after installing K$_2$CO$_3$ and Ca(OH)$_2$. Also, under certain experimental conditions, there should be an increase in the total.
molar quantity of gaseous products rather than rising temperature when the catalyst was installed. On the basis of these results, it can be concluded that the addition of K$_2$CO$_3$ and Ca(OH)$_2$ significantly increased gas production. Compared to Ca(OH)$_2$, relatively higher amount of gas is produced in the presence of K$_2$CO$_3$. But the role of K$_2$CO$_3$ might have been underestimated. This is because K$_2$CO$_3$ reacts with silicon dioxide to form glass at a temperature of around 800°C [9]. Furthermore, the weight ratio of K$_2$CO$_3$ and silicon dioxide in the glass in this study is somewhat similar to that in the literature [10]. The melting temperature of K$_2$CO$_3$ is around 900°C, thus, in this study, K$_2$CO$_3$ is not decomposed into K$_2$O and CO$_2$ [11].

At a second reactor temperature of 500°C, the generation behavior of gas was very different from that under other temperature conditions and the molar quantity was also less. On the basis of these reasons, it can be estimated that secondary pyrolysis and gasification of tar did not much occurred. However, under other experimental conditions, it seems that a large amount of pyrolysis products, between 300 and 400°C, have been secondary pyrolyzed and have contributed to the active gas generation between 300 and 500°C.

Figure 7 allows a comparison of mass balance in pyrolysis of cellulose. At a second reactor temperature of 500°C, the largest fragment was condensable products while heavy tar represents the largest fraction at 700°C. On the other hand, the smallest amount of condensable products and heavy tar and total tar were found when Ca(OH)$_2$ was placed in the second reactor at 800°C. The amount of condensable products and total tar decreased, as the second reactor temperature rose. This could be due to the secondary pyrolysis reaction of cellulose pyrolysis products in the second reactor. But the amount of heavy tar in the case of a second reactor temperature of 500°C was less than that at a second reactor temperature of 700 and 800°C. It is surmised that tar composition has gradually changed to heavier one by performing pyrolysis at a high temperature, but this reaction might be insufficient at 500°C. At a second reactor temperature of 700°C, the amount of condensable products and heavy tar and total tar were...
decreased by installing K$_2$CO$_3$ and Ca(OH)$_2$. This result was the same at 800°C. On the basis of current findings, it can be concluded that K$_2$CO$_3$ and Ca(OH)$_2$ have an effect on tar decomposition. Comparing the catalytic effect, Ca(OH)$_2$ was superior to K$_2$CO$_3$. As a comparison, the effect on tar decomposition when Ca(OH)$_2$ was installed without changing the second reactor temperature was higher than that produced when the second reactor temperature was raised to 700–800°C. This result was also observed when the second reactor temperature was raised to 800–900°C and can be considered as the effect of Ca(OH)$_2$. In this study, Ca(OH)$_2$ exists in a state of CaO, such as high temperature, tar and secondary product char adhere to its surface [12]. Adhering material reacts with the pyrolysis product gas, thus gas is further produced. Additionally, the polarity of the active site of CaO can affect the $\pi$-electron cloud’s stability of condensed aromatic compounds, and CaO itself has a cracking active site on both inner and outer surfaces [13].

4 Conclusions

In this study, the experimental apparatus connecting the two reaction tubes has been used for the study of heterogeneous reaction between tar and ash from cellulose pyrolysis and gasification modeling a fluidized bed gasifier. Alkali metal K and alkaline earth metal Ca were selected as the main ash contents that may act as the catalyst for tar decomposition. The catalytic effect of alkali metal K and alkaline earth metal Ca is that, not only they can change in the composition of the tar, but also reduce the condensable organic compounds. Additionally, K and Ca increase the amount of gaseous products. The catalytic effect of Ca(OH)$_2$ was comparatively superior to K$_2$CO$_3$. However, the role of K$_2$CO$_3$ might have been underestimated because K$_2$CO$_3$ reacts with silicon dioxide to form glass at temperature around 800°C. Based on the results of the present study, it can be concluded that K$_2$CO$_3$ and Ca(OH)$_2$ have the catalytic effect to decompose the tar and enhance gaseous production. In the case of using ash as a catalyst, it is necessary to take into account that the chlorides in the biomass are also included so that the change in the thermal decomposition properties is determined in further study.

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References


