Study on 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, the renewable biomass resource has attracted a lot of attention as the future energy resource. In addition, it is an advantage that the biomass grows while absorbing CO_2, contributing to the 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 is used as power generation, heating, chemical products, etc. However, pyrolysis and gasification processes also generated condensable organic compounds, so-called “tar”. Most tar contents are present as the gases at high temperature. However, when the temperature is cooled down lower than their boiling point, causing a black oily liquid lead to the equipment failure, the appropriate processing is required. As the processing method, using the catalytic tar decomposition has been widely studied.

In the present study, we have carried out the thermal decomposition of cellulose, in the experimental apparatus modeling a fluidized bed gasifier. The thermal decomposition of cellulose, tar and gas is generated, tar is collected and cooled, and the gases were 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. We conducted a similar experiment. The amount of condensable products and heavy tar were decreased by installing K_2CO_3 and $Ca(OH)_2$. Additionally, they brought further gas

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production. It can be concluded that alkali metal compound (K_2CO_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 fulfill the energy requirement in the world. Large amounts of carbon dioxide emissions occur when these former energy sources are present, promoting global warming. Recently, attention has been attracted by the biomass of renewable energy resource. Features, carbon positive, resources are present all over the world, etc. Thermal decomposition and gasification are methods which are used to convert biomass to energy. The gas obtained by the thermal decomposition and gasification mainly composed of H_2 and CO. These synthesis ammonia, liquid fuel, methanol, and chemical products and a variety of derivative products are manufactured [1]. However, amount of a condensable organic compound called tar is produced during thermal decomposition and gasification. Tar clogs the pipe of gasifier and break turbine. Both mechanical methods and thermal cracking have been proposed to remove tar.

Mechanical methods do not allow energy recovering from tar which are just removed from gaseous products, while thermal cracking requires high temperature (>1100°C) to convert them [2]. The 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 ash component of the biomass.

We focus on the 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 heterogeneous reaction between tar and ash are yet to be studied [4]. Using an experimental system that assumes the heterogeneous reaction of ash and tar in a fluidized bed gasifier, to evaluate the catalytic effect of the ash is significance. In this study, we have conducted an experiment thermal decomposition of cellulose 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]. The thermal decomposition of cellulose experiment by introducing the ash, we have considered the effect of ash is given to the heterogeneous reaction with tar. We have calculated the yields of char from the results of the thermogravimetry-differential thermal analysis (TG-DTA) experiment, have measured the yields of condensable products were cooled down and collected in the test tube, have measured the yields of gas by GC-TCD/FID.

2 Materials and experimental methods

2.1 Matarials

The tested experimental sample was the 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 β-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 were also performed. Cellulose composition is presented in table 1.

Table 1: Elemental analysis and proximate analysis of cellulose.

Elemental analysis (wt.%)				Proximate analysis (wt.%)			
C	H	N	O	Moisture	Volatiles	Fixed carbon	Ash
43.31	6.23	0.00	50.46	7.18	86.90	5.92	0.00

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 of 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 The 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 gas feeding system, pyrolysis system, tar decomposition system, condensable products trapping system and, gaseous products measurement system. Pyrolysis system and tar decomposition system consisted of connecting the two stainless reactor (I.D.; 21.4 mm, length; 500 mm). Cellulose and K_2CO_3, $Ca(OH)_2$, silicon dioxide were placed on the mesh (40 μm) in the each reactor. This apparatus can be independently heated in two different electric furnaces while the gas mixture coming in contact with the catalyst. Therefore, heterogeneous reaction between tar and ash can be carried out by 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 in between 300–400°C to avoid the condensation of tar. 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). H_2 and CO, CH_4, CO_2 were measured by a GC-TCD while hydrocarbons (C_2H_6 and C_2H_4, C_3H_8, C_3H_6, iso-C_4H_{10}, n-C_4H_{10}) were measured by a GC-FID.

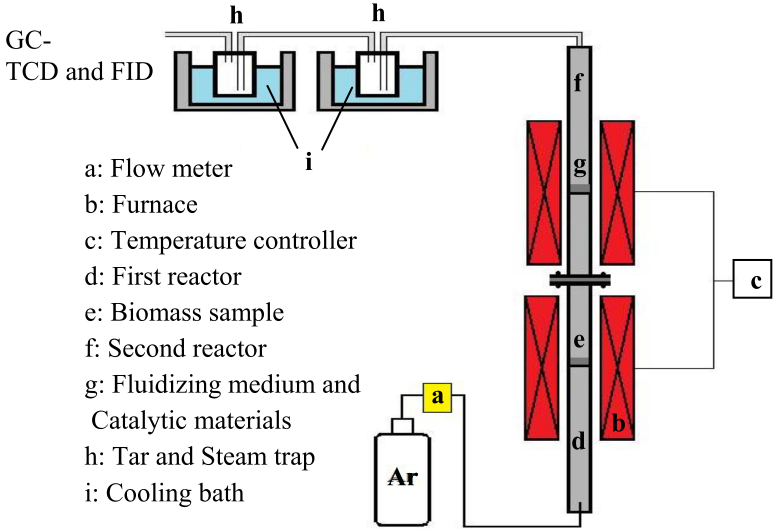

Figure 1: Experimental setup for cellulose pyrolysis and gasification.

2.3.2 The experimental procedure

The operative conditions are reported in table 2. Cellulose, catalysts, silicon dioxide were placed in each reactor under the condition of table 2, respectively. The Second reactor was heated up to a predetermined temperature under argon at constant flow rate. Then, 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 The 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 yield of gaseous products was calculated from the measurement results of GC-TCD/FID. Also, subtracting the amount of char, the amount of condensable products, and the amount of gaseous products

Table 2: Operative conditions used for tests.

Item	First reactor	Second reactor		
		none	K_2CO_3	$Ca(OH)_2$
Cellulose amount (g)	2.00	-		
Catalyst amount (g)	-	-	0.691	0.741
Silicon dioxide amount (g)	-	5.00	4.309	4.259
Heating rate (°C/min)	10	-		
Maximum temperature (°C)	900	500, 700, 800, 900	700, 800	700, 800
Argon flow rate (ml/min)	70			

from the amount of cellulose was evaluated as a heavy tar. The heavy tar is a tar which remains in the apparatus.

3 Results and discussions

3.1 The results from TG-DTA analysis

The pyrolysis characteristics, both TG (wt.%) and DTA (μV) curves of cellulose found out with a TG-DTA has shown in figure 2. Rapid weight loss of cellulose was observed between 300–400°C, and then the weight loss had progressed slowly. Endothermic peak was observed between 300–400°C, indicating that the thermal decomposition of cellulose was occurring in 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 decomposition products released in this temperature. A gradual weight loss was continued after

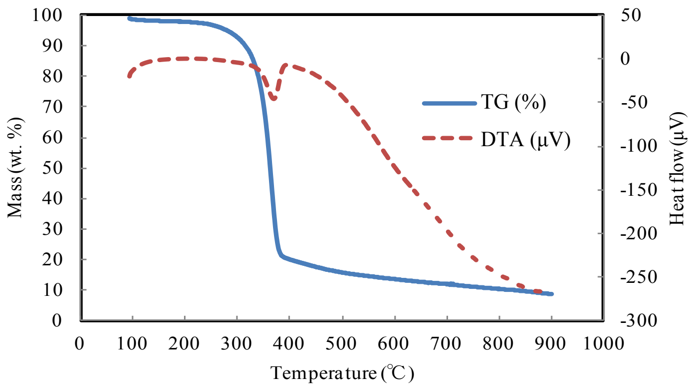

Figure 2: Pyrolysis curves of cellulose in the TG-DTA analysis.

400°C, it should be predicted that a small amount of thermal decomposition products have been released. Experiments were carried out several times under the same conditions and, it was 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 3–6 showed the molar quantity (mmol/g-cellulose) of gaseous products generated by thermal decomposition of cellulose at each experimental condition. Also, table 3 showed the total molar quantity (mmol/g-cellulose) of gaseous products generated by thermal decomposition of cellulose at each experimental condition.

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

Second reactor conditions	H_2	CO	CH_4	CO_2	Hydrocarbons
500°C	0.493	3.531	0.333	0.921	0.149
700°C	1.892	5.059	1.114	1.225	0.979
700°C-K_2CO_3	2.033	6.088	1.244	1.710	1.039
700°C-$Ca(OH)_2$	3.359	8.116	1.626	1.709	1.393
800°C	3.638	6.411	1.454	1.847	1.112
800°C-K_2CO_3	4.665	6.487	1.590	2.759	1.288
800°C-$Ca(OH)_2$	5.294	9.691	2.040	2.993	1.395
900°C	5.751	8.673	1.847	2.268	1.146

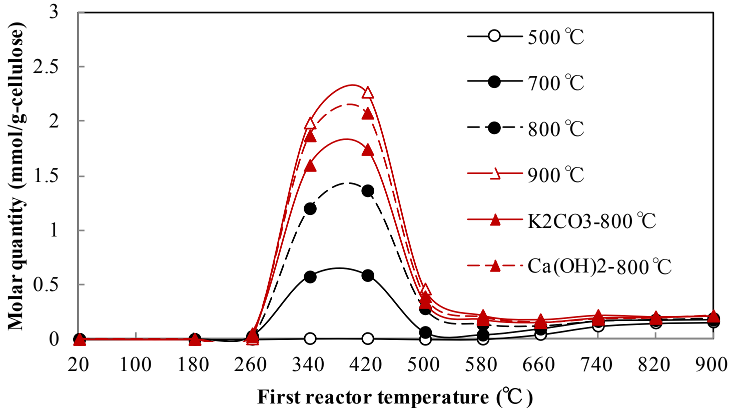

Figure 3: Molar quantity of H_2 in each second reactor conditions.

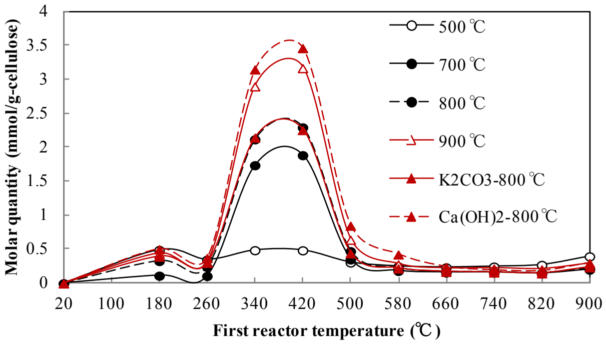

Figure 4: Molar quantity of CO in each second reactor conditions.

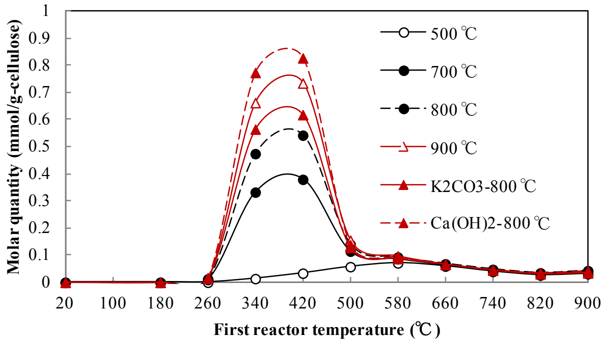

Figure 5: Molar quantity of CH_4 in each second reactor conditions.

In the second reactor temperature at 900°C, total molar quantity of H_2 was maximum while it was minimum at the second reactor temperature at 500°C. At the second reactor temperature at 500°C, the generation of H_2 began to increase rapidly after about 600°C. However, H_2 generation was remarkable in between 300–500°C under experimental conditions. The case of second reactor temperature at 500°C, the generation of H_2 was not observed only a small amount in that temperature range. The total molar quantity of H_2 was increased as the second reactor temperature conditions rise. Total molar quantity of H_2 was increased approximately 7.5% after adding K_2CO_3 compared to the molar quantity observed with the presence of only silicon dioxide at 700°C. However, total molar quantity of H_2 was increased 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 about 28.2% and 45.5% when presence K_2CO_3, and $Ca(OH)_2$ respectively.

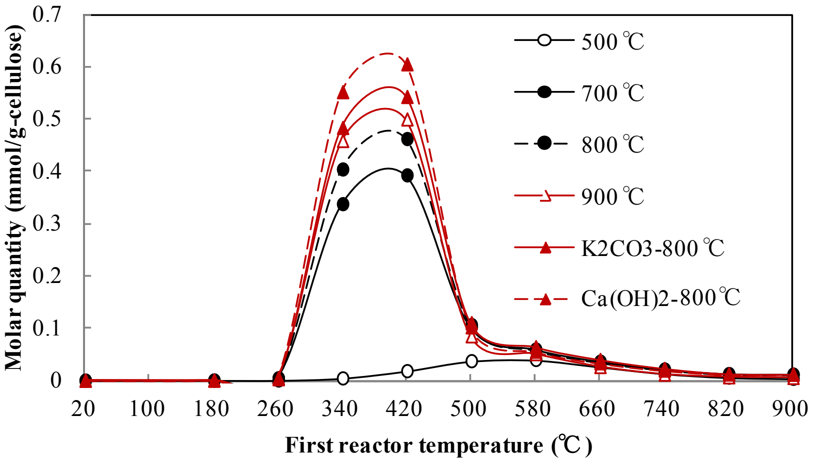

Figure 6: Molar quantity of hydrocarbons[a] in each second reactor conditions. [a]Here, hydrocarbons are C_2H_6 and C_2H_4, C_3H_8, C_3H_6, iso-C_4H_{10}, n-C_4H_{10} in the study.

In the case of $Ca(OH)_2$ was placed in second reactor at 800°C, total molar quantity of CO was maximum while it was minimum, in the case of second reactor temperature at 500°C. The generation of CO was remarkable between 300-500°C in 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 about 20.4% after adding K_2CO_3. However, it was further increased nearly 60.4% when $Ca(OH)_2$ was installed. Quantity of CO was increased nearly 1.2% and 51.1% with the presence of K_2CO_3 and $Ca(OH)_2$ respectively compared to the CO quantity observed at only silicon dioxide placed in the second reactor at 800°C. The total molar quantity of CO when it was installed $Ca(OH)_2$ 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 most generated in the pyrolysis gaseous products.

In the case of $Ca(OH)_2$ was placed in second reactor at 800°C, total molar quantity of CH_4 was maximum and it was minimum in the case of second reactor temperature at 500°C. The generation of CH_4 was remarkable between 400-800°C when the second reactor temperature at 500°C while it was remarkable in between 300-500°C under other experimental conditions. The case of second reactor temperature at 500°C, the generation of CH_4 was not observed only a small amount in that temperature range. As the second reactor temperature conditions to rise, the total molar quantity of CH_4 was increased. Compared to the condition where only silicon dioxide was placed in the second reactor at 700°C, the total molar quantity of CH_4 was increased about 11.7% and 46.0% by adding K_2CO_3 and $Ca(OH)_2$ respectively. Compared with when only silicon dioxide was placed in the second reactor at 800°C, the total molar quantity of CH_4 was increased about 9.4% by installing K_2CO_3, on the other hand, the total molar quantity of CH_4 was increased about 40.4% by installing $Ca(OH)_2$. The rate of the total molar quantity of CH_4 when it was installed $Ca(OH)_2$ 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 $Ca(OH)_2$ was placed in second reactor at 800°C, total molar quantity of CO_2 was maximum, and it was minimum in the case of second reactor temperature at 500°C. The generation of CO_2 was remarkable between 300-500°C in all experimental conditions. As the second reactor temperature condition rise, the total molar quantity of CO_2 was increased. Compared to the condition where only silicon dioxide was placed in the second reactor at 700°C, the total molar quantity of CO_2 was increased about 39.6% by installed K_2CO_3. However it was increased nearly 39.5% after installing $Ca(OH)_2$. Compared with when only silicon dioxide was placed in the second reactor at 800°C, the total molar quantity of CO_2 was increased about 49.4% by installing K_2CO_3. However, the total molar quantity of CO_2 was increased about 62.0% by $Ca(OH)_2$. The amount of the total molar quantity of CO_2 with the presence of K_2CO_3 and $Ca(OH)_2$ without changing the second reactor temperature was higher than that of when the second reactor temperature was raised to 800-900°C.

In the case of $Ca(OH)_2$ was placed in second reactor at 800°C, total molar quantity of hydrocarbons was maximum while minimum quantity of hydrocarbons was observed when second reactor temperature at 500°C. The case of second reactor temperature at 500°C, the generation of hydrocarbons was remarkable between about 400-800°C. However, generation of hydrocarbons was remarkable between about 300-500°C at other experimental conditions, the. The case of second reactor temperature at 500°C, the generation of hydrocarbons was not observed and only a small amount occurred in that temperature range. As the second reactor temperature conditions to rise, the total molar quantity of hydrocarbons was increased. Total molar quantity of hydrocarbons were increased approximately 6.1% and 42.2% by K_2CO_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 when only silicon dioxide was placed in the second reactor at 800°C, the total molar quantity of hydrocarbons was increased about 15.8% after installing K_2CO_3 while it was increased about 25.4% after installing $Ca(OH)_2$. The quantity of the total molar quantity of hydrocarbons when it was installed $Ca(OH)_2$ without changing the second reactor temperature, was higher than that of the second reactor temperature raised to 800-900°C.

Total molar quantity of all gas species were increased with the increase of the second reactor temperature, its cause should be a secondary pyrolysis reaction of cellulose pyrolysis products in 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 large amount of gas from secondary pyrolysis and gasification of tar than 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 are same, total molar quantity of all gas species increased after installing K_2CO_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 addition of K_2CO_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_2CO_3. But the role of K_2CO_3 might have been underestimated. Because, K_2CO_3 reacts with silicon dioxide to form glass at temperature around 800°C [9]. Furthermore, the weight ratio of K_2CO_3 and silicon dioxide in the glass is somewhat similar to this study and the literature [10]. The melting temperature of K_2CO_3 is around 900°C, thus, in this study, K_2CO_3 is not decomposed into K_2O and CO_2 [11].

In the case of second reactor temperature at 500°C, the generation behavior of gas was very different from 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 was not much occurred. However, in other experimental conditions, it seems that a large amount of pyrolysis products between 300-400°C have been secondary pyrolyzed, and have contributed to the active gas generation between 300-500°C.

Figure 7 showed comparison of mass balance on pyrolysis of cellulose. At the second reactor temperature at 500°C, the largest fragment was condensable products while heavy tar represents the largest fraction at 700°C. On the other hand, the fewest amounts of condensable products and heavy tar and total tar were found when $Ca(OH)_2$ was placed in second reactor at 800°C. The amount of condensable products and total tar were decreased, as the second reactor temperature rises. It could be due to the secondary pyrolysis reaction of cellulose pyrolysis products in second reactor. But the amount of heavy tar the case of second reactor temperature at 500°C was less than that of second reactor temperature at 700 and 800°C. It is guessed that tar composition has been gradually changed heavier ones by proceeding pyrolysis at a high temperature, but this reaction might insufficient at 500°C. In the case of second reactor temperature at 700°C, the amount of condensable products and heavy tar and total tar were decreased by installing K_2CO_3 and $Ca(OH)_2$. This result was the same at the 800°C. On the basis of current findings, it can be concluded that K_2CO_3 and $Ca(OH)_2$ effect on tar decomposition. Comparing the catalytic effect, $Ca(OH)_2$ was superior to K_2CO_3. A comparison of the effect of tar decomposition when it was installed $Ca(OH)_2$ without changing the second reactor temperature, which was higher than 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. This result 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, the gas is further produced. Additionally, the polarity of the active site of CaO can affect the π-electron cloud's stability of condensed aromatic compounds, and CaO itself has a cracking active site on both inner and outer surfaces [13].

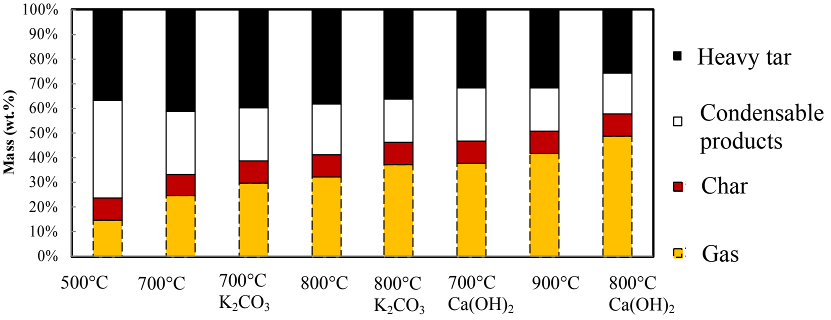

Figure 7: Comparison of mass balance on pyrolysis of cellulose.

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. As the catalytic effect of alkali metal K and alkaline earth metal Ca, they can not only 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_2CO_3. However, the role of K_2CO_3 might have been underestimated. Because K_2CO_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_2CO_3 and $Ca(OH)_2$ have the catalytic effect to decompose the tar, to enhance gaseous production. In the case of using ash as a catalyst, it is necessary to take into account that it is also included the chlorides in the biomass to give the change in the thermal decomposition properties in the further study.

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