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REACTIVITY FOR PYROLYSIS AND CO_2 GASIFICATION OF ALKALI METAL LOADED WASTE WOOD CHAR

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ABSTRACT

In this study, different carbonization processes were performed for thinning wood waste as organic industrial waste and forestry waste biomass to produce waste wood char, which is used as solid and gaseous fuel. Waste biomass samples were added to Na^+ (NaOH) using thermogravimetry with a differential thermal analyser (TG/DTA), where the behaviour of thermal decomposition and the effect of additive amount of alkali metal were investigated. Waste wood char yields were increased at the peak temperature and weight loss was decreased with the increment of Na^+ (NaOH) loaded value. The fixed carbon amount of waste wood char was also increased with the maximum Na^+ (NaOH) loaded value at 100:1, and then it was decreased. Furthermore, in order to evaluate the effect of Na^+ (NaOH) loaded value on char reactivity, an isothermal CO_2 gasification experiment was performed at temperatures between 700°C and 900°C for chars obtained by pyrolysis at 900°C. It was shown that the reaction rate was increased with increasing temperature and the reaction rate of raw char was markedly slower than Na^+ (NaOH) loaded char. The activation energies of char were in decreasing trend with increasing Na loaded value. However, the activation energies of CO_2 gasification of char samples were conversely increased when Na^+ loaded on char sample was more than 50:1. If too large amounts of Na^+ (NaOH) were loaded on char sample, the rate of gasification reaction and the activation energy will be decreased as Na^+ reacts with the char surface covering the gasifying agent.

Keywords: Alkali catalyst, biomass, carbonization, CO_2 gasification, energy recovery.

1 INTRODUCTION

In Japan, the large amounts of organic industrial waste and forestry waste biomass are discharged due to various industrial activities [1]. Recently, very important technical processes have been developed for the volume or weight reduction and detoxification of solid organic wastes that cause environmental pollution and public health problems. Wood waste biomasses in the organic industrial and forestry wastes are discharged over a wide area and are difficult to use as resources due to their low heating values. In general, they have been incinerated by intermediate treatment. While the wood waste is incinerated with low-energy utilization efficiency, a large amount of greenhouse gases such as carbon dioxide is emitted. Besides, incineration of wood waste can cause resources and energy loss. Therefore, from the viewpoint of global warming and recovery of resources and energy from wood wastes, small-scale processing or effective utilizing technologies are used instead of incineration processes [2]. For recycling of forestry wood waste biomass, the system of carbonization technology process, especially for effective utilization of carbon in waste biomass, was implemented in many areas. The wood waste carbonization technology is the waste processing technology based on pyrolytic decomposition for defusing toxicity and volume reduction by heating the organic wastes under the less oxygen or inactive conditions. Carbonization process can reduce CO_2 and CH_4 emission because the easily degradable organic carbons are converted to relatively stable fixed carbon, so-called as immobilized ‘waste wood char’, by pyrolysis [3]. Moreover, highly valuable char can be used as chemical materials or solid fuel for energy. Therefore, more attention has been paid on carbonization process of forestry wood waste biomass than on the intermediate process and incineration [4].

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Wood biomass mainly consists of three major components: hemicellulose, cellulose and lignin. They usually contain trace amount of extractives and minerals. The products generally pyrolyzed from wood biomass consist of gases, liquid (tar) and char [5]. In these products, it is very difficult to use tars directly as fuels because of their high oxygen (40–50 wt%) and moisture (15–30 wt%) contents and low H/C ratios [6]. Furthermore, the large amount of tar has to be reduced for controlling tar trouble as since many studies had not achieved reducing tar generation during pyrolysis because of the requirement of highest temperature for non-catalyst thermal decomposition of tar [7]. Many studies have been carried out by catalytic tar reduction techniques, such as alkali metals and metal oxides [8, 9]. Among them, sodium hydroxide has a significant effect on tar suppression and char yield increment. However, the alkali metals not only decrease the melting point of ash but also cause damage to the furnace wall by attaching to the heat exchanger wall during the carbonization process and char combustion. At the time of the practical application of biomass carbonization process and fuel use process of waste wood char, it is necessary to consider the loading method of alkali metals. In this study, carbonization of wood waste and char for conversion to gaseous fuel was achieved. In addition, after forest wood waste biomass was loaded to Na^+ as NaOH, the thermal decomposition behaviour and the effect of additive amount of alkali metal (optimum addition such as Na^+ (NaOH) loaded value of the alkali metal) were investigated by the thermogravimetry with a differential thermal analyser (TG/DTA). Besides, the reactivity assessment was also carried out on char during its CO_2 gasification reaction.

2 MATERIALS AND METHODS

2.1 Materials

In this experiment, the thinning wood waste samples of Japanese cedar (*Cryptomeria japonica*), which were supplied from STM Co. (thinned cedar, Kitakyushu, Fukuoka, Japan), were investigated. Thinning wood waste biomass samples were ground and sieved to less than 0.25 mm by a crusher (WB-1, 700 W; Osaka Chemical, Co. Ltd., Japan) and a sieve shaker (AS200 digit 50 Hz; Retsch, Co. Ltd., Japan) respectively. Then, they were dried at room temperature with a 1 hour exposure to the laboratory atmosphere to obtain air-dried samples (JIS-M8811). Proximate and ultimate analyses were performed on air-dried sample. Proximate analysis (ash, volatile matter, moisture and fixed carbon) was conducted in accordance with the JIS-M8813. Ultimate analysis was done by using a CHN corder (MT-5 Yanaco, Co. Ltd., Japan). The fundamental analysis of the Japanese cedar is given in Table 1.

As shown in Table 1, the thinning wood waste contained the highest volatile matter (72.4 wt% daf) and at least 0.3% ash content. Na^+ (sodium hydroxide) at the concentration ratio of 1000:1, 500:1, 200:1, 100:1, 50:1 and 20:1 was added to the air-dried samples. Na^+ (NaOH) loaded waste biomass samples were dried at 80°C for 24 hours.

Table 1: Feedstock analyses of Japanese cedar.

Proximate analysis (wt%)				Ultimate analysis (wt%)			
M	VM	Ash	FC	H	C	N	O
8.14	72.4	0.26	19.2	5.85	46.5	0.25	47.4

M: moisture, VM: volatile matter, FC: fixed carbon.

2.2 Methods

2.2.1 Effect of Na^+ (NaOH) loaded value on the pyrolysis of waste biomass samples

Pyrolysis characteristics of waste wood biomass samples and Na loaded biomass samples were analysed by the TG/DTA (Shimadzu DTG-60, Co. Ltd., Japan). The schematic features of the experimental apparatus are shown in Fig. 1. About 10.0 mg of sample was heated at the rate of 15°C/min, starting from room temperature until 900°C in purified nitrogen (99.999% N_2), which was passed at a flow rate of 150 mL/min (s.t.p.). The results of thermogravimetric experiments were expressed as a function of waste wood char yield and decrease in ratio of waste wood char, which were defined by eqns (1) and (2) as follows:

$$\text{Waste wood char yield (\%)} = M_f\,(\text{g})/M_0\,(\text{g}) \times 100 \tag{1}$$

$$\text{Decreasing ratio of waste wood char (\%/s)} = \Delta M_{\text{char}}\,(\%)/\Delta t\,(\text{s}) \tag{2}$$

In eqn (1), M_0 and M_f indicate the initial mass of sample and the mass of the pyrolyzed sample, respectively. In eqn (2), ΔM_{char} indicates the variation in waste wood char samples.

In addition, the carbon contents of waste wood char samples pyrolyzed at 900°C were analysed with a CHN corder (MT-5 Yanaco, Co. Ltd., Japan) and the ratio of carbon immobilized from biomass samples to chars was calculated. Finally, the optimum addition of Na^+ (NaOH) loaded value for the alkali metal was investigated by taking the above results into account.

2.2.2 Effect of Na^+ (NaOH) loaded value on the CO_2 gasification of waste wood char samples

In order to evaluate the effect of Na^+ (NaOH) loaded value on char reactivity, the CO_2 gasification of different waste wood char samples with different Na^+ (NaOH) loaded values were carried out by a differential thermal analyser presented in Fig. 1. The gasification of char samples obtained at 900°C (Section 2.2.1) was performed with the isothermal CO_2 gasification at different temperatures between 700°C and 900°C. The temperature programmes for CO_2 gasification after heating to the gasification temperature under N_2 atmosphere are shown in Fig. 2.

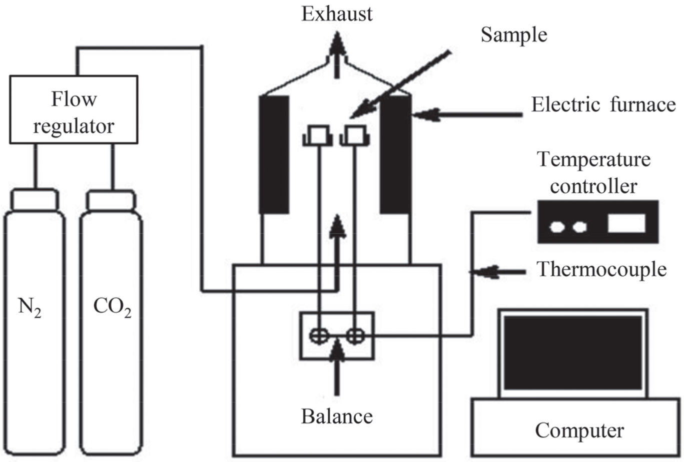

Figure 1: Schematic diagram of the thermogravimetry with a differential thermal analyser used in pyrolysis and gasification process (only N_2 gas was used during pyrolysis).

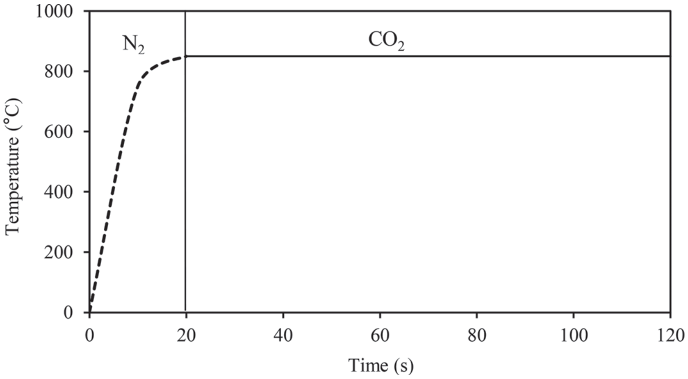

Figure 2: Heating temperature programmes for CO_2 gasification of raw and Na^+ (NaOH) loaded waste wood char samples after heating to the gasification temperature of 900°C under N_2 atmosphere.

In isothermal gasification experiments, the waste wood char samples were heated to the gasification temperature under N_2 atmosphere. Then, the gas feed was switched to purified CO_2 (99.998% CO_2), which was passed at a flow rate of 150 mL/min (s.t.p.). After the switching from N_2 to CO_2, 20.0 mg of initial waste wood char samples were used. The gasification reaction rates were calculated by using the liner curve slopes of thermogravimetry (TG) during the stable period of CO_2 gasification reaction of waste wood char samples after atmospheric gas was changed from N_2 to CO_2 at the different gasification temperatures.

3 RESULTS AND DISCUSSIONS

3.1 Pyrolysis characteristics of mixing thinning waste wood biomass samples

In order to investigate the characteristics of pyrolysis, first all Na^+ (NaOH) loaded biomass samples were prepared by mixing thinning wood waste biomass samples and Na^+ (NaOH) at the concentration ratio of 1000:1, 500:1, 200:1, 100:1, 50:1 and 20:1. Then, biomass samples and Na^+ (NaOH) loaded biomass samples were pyrolyzed at the heating rate of 15°C/min starting from room temperature to 900°C in purified nitrogen atmospheres using the TG/DTA. The pyrolysis behaviour and decreasing ratio of each biomass sample are shown in Fig. 3. From the pyrolysis curve of each waste wood biomass samples, it was found that the loss in sample weight proceeded mainly between 250°C and 400°C in two stages, and it slowly decreased while the temperature was above 500°C. The main components of wood biomass are hemicelluloses, cellulose and lignin, and they account for 20–40, 40–60 and 10–25 wt%, respectively. In general, pyrolysis of hemicelluloses is high at the temperature range of 220°C–315°C. Therefore, the first weight loss peak of the raw biomass sample was found at 280°C, which was considered as decomposition of hemicelluloses [10–12]. The second weight loss peak of the raw biomass sample was found at 360°C, which was considered as decomposition of cellulose because it belonged to the range of cellulose pyrolysis with the temperament ranging from 315°C to 400°C. Decomposition of lignin occurred in whole temperature range from 200°C to 900°C.

Waste wood char yields of raw biomass and Na^+ (NaOH) loaded biomass with mixing ratios of 1000:1, 500:1, 200:1, 100:1, 50:1 and 20:1 consisted of 16.9%, 17.0%, 18.1%, 20.5%, 23.1%, 24.8%

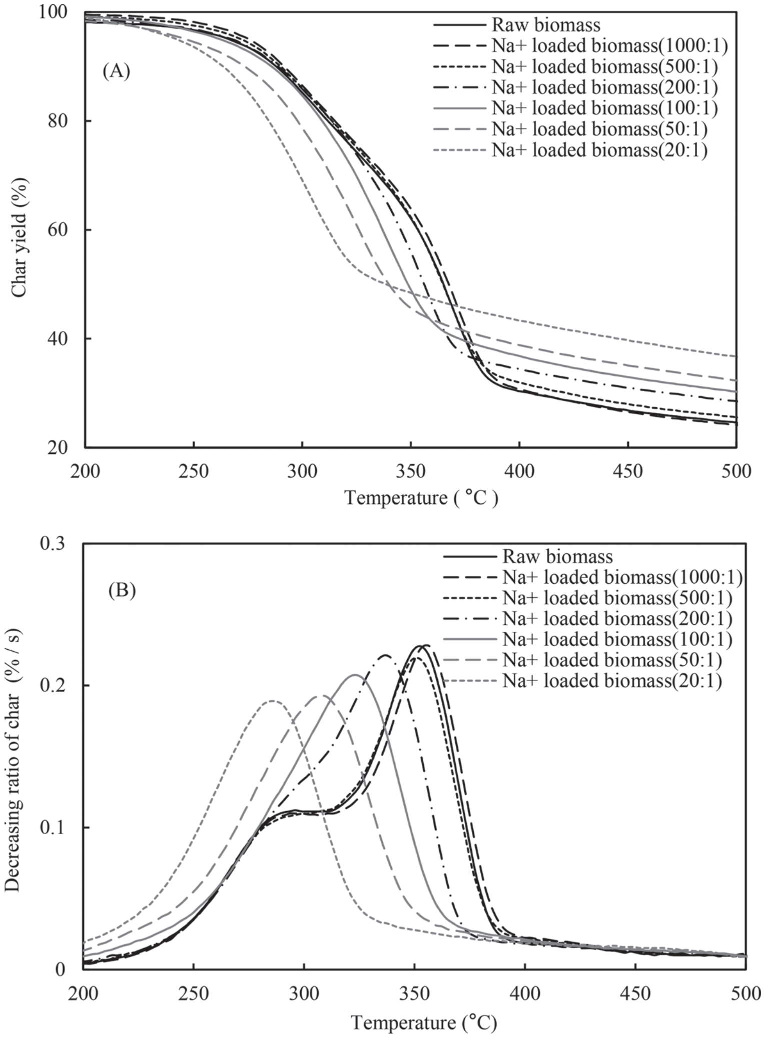

Figure 3: Pyrolysis behaviour and decreasing ratio of raw and Na$^+$ (NaOH) loaded biomass in nitrogen at a heating rate of 15°C/min. (A): Pyrolysis behaviour curve and (B) decreasing ratio of waste wood char.

and 28.2% of biomass, respectively. It was found that Na$^+$ (NaOH) loaded value had a significant effect on the char yield, which increased with the increase in Na$^+$ (NaOH) loaded value. In addition, the weight loss peak of raw biomass was around 360°C, and weight loss peak temperature decreased with the increase in Na$^+$ (NaOH) loaded value. Among them, weight loss peak of 20:1 Na loaded waste wood biomass was found at 280°C. Due to the increment in the char yields and decrement in the weight loss peak temperature, crystal structure of biomass major compound like cellulose was distorted through pyrolysis by Na$^+$ (NaOH) at even lower temperature, which was affected by subsequent thermal decomposition reaction [9]. Further, the elemental analysis of each char sample

Table 2: Ultimate analysis for raw and Na^+ (NaOH) loaded waste wood char samples obtained by pyrolysis at 900°C.

	Raw char	1000:1	500:1	200:1	100:1	50:1	20:1
Char yield (wt%)	16.9	17.0	18.1	20.5	23.1	24.8	28.2
H (wt%)	1.75	1.54	1.33	1.63	1.46	1.51	1.11
C (wt%)	94.3	92.5	92.1	87.4	85.8	78.8	61.8
N (wt%)	0.45	0.56	0.57	0.57	0.54	0.39	0.29

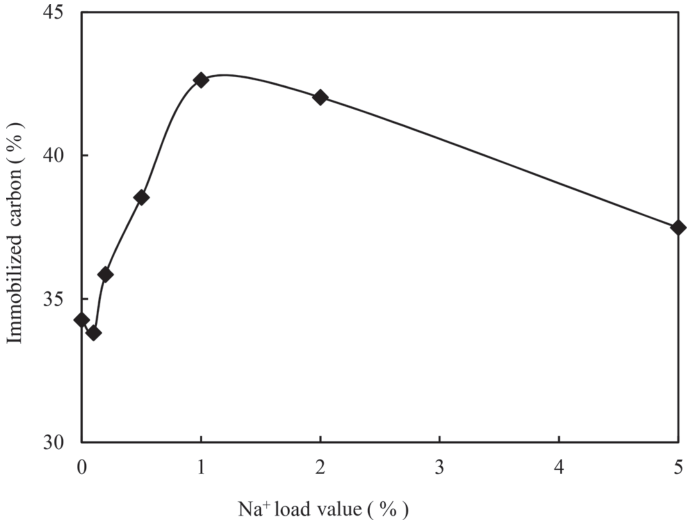

Figure 4: Changes in immobilized carbon at raw and Na^+ loaded waste wood chars pyrolyzed at 900°C, which indicate the relationship with different Na^+ (NaOH) loaded values.

obtained by pyrolysis at 900°C was performed using the CHN corder (Table 2). The results show that the carbon contents were decreased with the increase of Na^+ (NaOH) loaded values.

This represents that they were causally related to the ash increment, because the loaded Na^+ (NaOH) was remained as ash in the char even after pyrolysis. Increment of ash contents was related to the reduction of carbon contents. The ratios of char as carbon immobilized from biomass samples to chars calculated by the elemental analysis are shown in Fig. 4. The amount of immobilized carbon (fixed carbon) as the biomass char was increased because of the increment of the char yield with an increment of Na^+ (NaOH) loaded value. The maximum ratio of immobilized carbon as the biomass char was increased from 34.3% to 42.6% when Na^+ load value was 1 wt % (100:1 biomass/Na^+ (NaOH)). However, on the other hand, the amount of immobilized carbon as the biomass char was conversely decreased when Na^+ load values were more than 2 wt % (50:1 biomass/Na^+ (NaOH)). Immobilized carbon value decreased because it was oxidized by the catalytic action of sodium contained in the char at the higher temperature. From these results, pyrolysis of waste wood biomass sample by loading the Na^+ (NaOH) confirmed to be optimal at 100:1 biomass/Na^+ (NaOH) ratio wt%. In addition, removal of tar can be expected after suitable loading of sodium as Na^+ (NaOH).

3.2 CO_2 gasification reactivity of waste wood char samples

For the utilization of gaseous fuels, which were obtained by gasification of waste wood char, char gasification reactivity was the most important indicator, because the alkali metal loaded to the waste wood char could promote its gasification reactivity. In order to evaluate the effect of Na^+ loaded values on char reactivity, CO_2 gasification experiments were conducted for each char obtained by pyrolysis at 900°C. The curves of CO_2 gasification behaviour obtained through CO_2 gasification of raw char at 825°C, 850°C, 875°C and 900°C are shown in Fig. 5.

The repeatability of the experiments was checked by repeating each test several times for statistical analysis and similar results were achieved. Like raw char, the same CO_2 gasification experiment was conducted for other Na^+ (NaOH) loaded char (Fig. 6).

According to the results, the reaction rate increased with increasing temperature and reaction rate of raw char was obviously slower than Na^+ (NaOH) loaded char. Activation energy is obtained by the gasification rate of CO_2 at every different final temperature of each char. From the gasification weight-time curves, CO_2 gasification reaction of chars can be considered as a zero-order reaction. The constant (k) of reaction rate under different final temperature was obtained by slope of the weight-time curves, which was expressed by the following Arrhenius equation:

$$k = \mathrm{A} \exp(-\mathrm{E}/\mathrm{RT}) \tag{3}$$

Taking a natural logarithm, eqn (3) yields:

$$\ln k = \ln \mathrm{A} - \mathrm{E}/\mathrm{RT} \tag{4}$$

Activation energy (E) in eqn (4) can be determined from the relationship between ln$k$ and 1/T. Thus, from the line of slope, the second term -E/R can be obtained from which the activation energy can be calculated. The plots of 1/T to ln$k$ for CO_2 gasification are shown in Fig. 7. The variations of activation energies of different Na^+ loaded char samples at different temperatures are given in Fig. 8. The activation energies of raw waste wood char and Na^+ loaded waste wood char at concentration ratio of 1000:1, 500:1, 200:1, 100:1, 50:1 and 20:1were 203 kJ/mol, 161 kJ/mol, 150 kJ/mol,

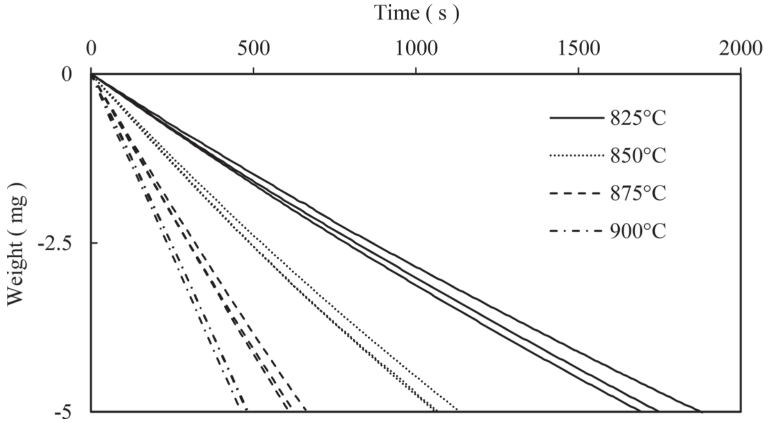

Figure 5: Curves of CO_2 gasification reproducibility for raw char at 825°C, 850°C, 875°C and 900°C.

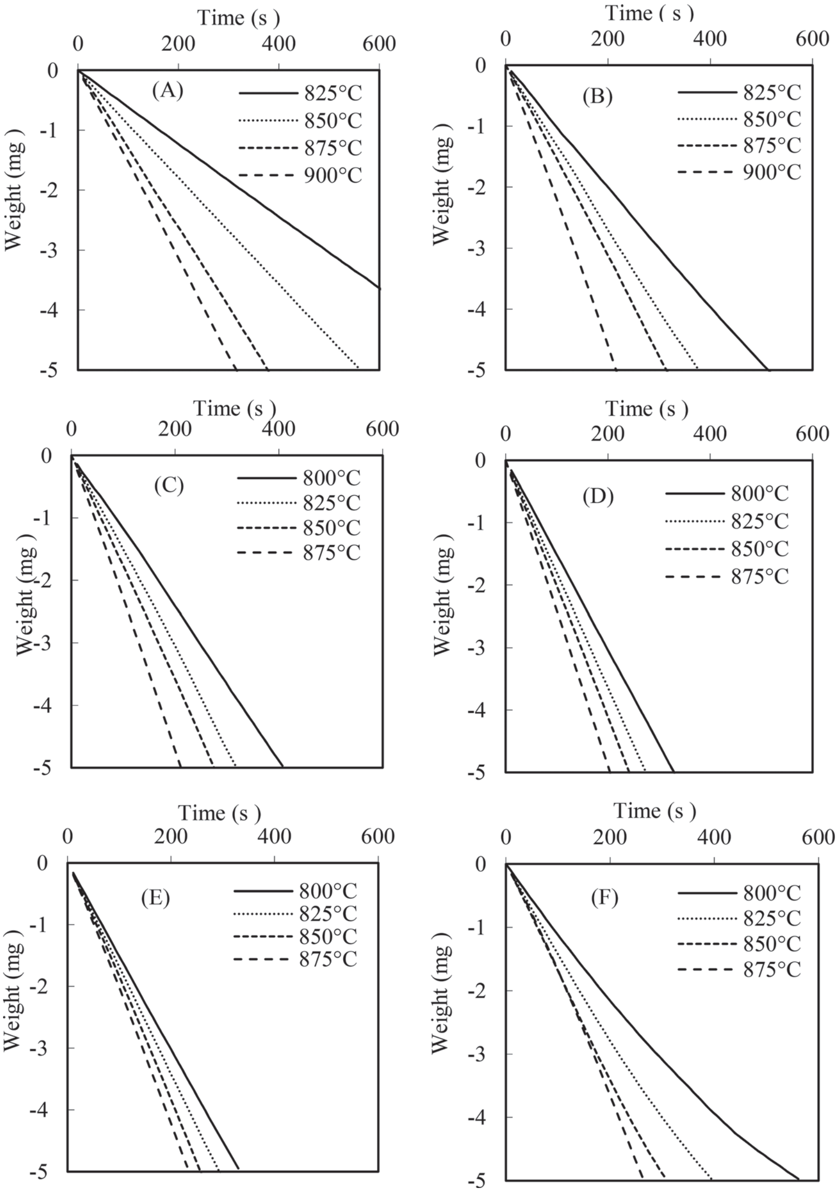

Figure 6: Curves of CO_2 gasification behaviour for different char samples at different temperatures. Biomass/Na^+ (NaOH) ratios are as follows: (A) 1000:1, (B) 1000:2, (C) 1000:5, (D) 100:1, (E) 100:2 and (F) 100:5.

96 kJ/mol, 60 kJ/mol, 62 kJ/mol and 124 kJ/mol, respectively. It was shown that the activation energies were decreasing with increasing Na^+ (NaOH) loaded value. However, it was conversely increased when Na^+ load values were more than 2%.

The CO_2 gasification mechanism of waste wood char samples has not been well understood yet. However, it is generally believed that CO_2 adsorption on the surface of the char followed by

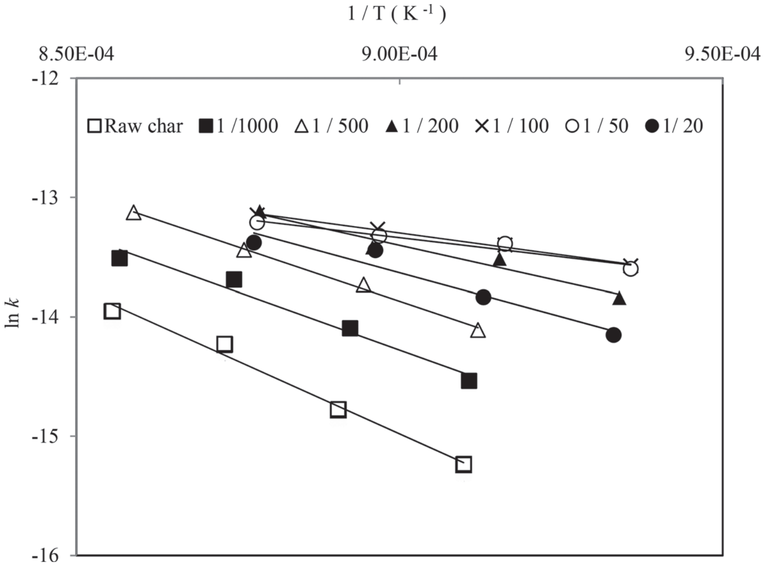

Figure 7: The plots of 1/T to ln*k* for CO_2 gasification at 900°C for different Na^+ loaded char samples at different temperatures.

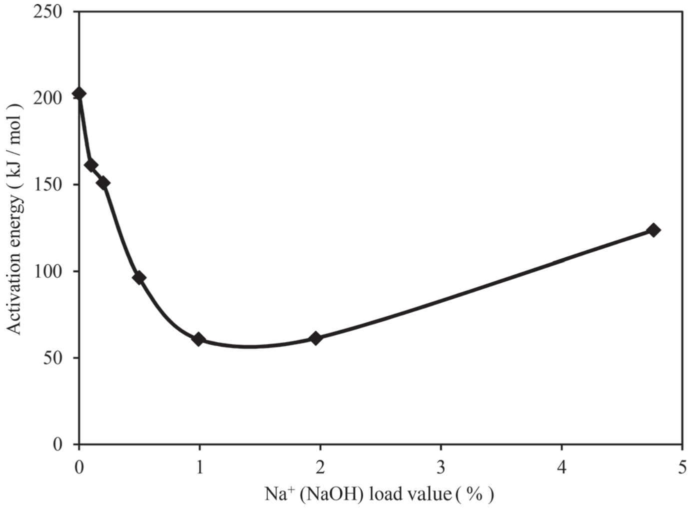

Figure 8: Changes in activation energy of raw and Na^+ loaded waste wood chars pyrolyzed at 900°C, which indicate the relationship with the different Na^+ loaded values.

CO desorption [13, 14] is the main step for determining the gasification rate as the reactivity based on reactions (5)–(7):

$$C_f + CO_2 \rightarrow C\,(O) + CO \tag{5}$$

$$C\,(O) + CO \rightarrow C_f + CO_2 \tag{6}$$

$$C\,(O) \rightarrow CO + C_f \tag{7}$$

In reactions (5)–(7), C_f and C(O) represent an active carbon site and a carbon–oxygen complex, respectively. These spots are central active carbon site that plays an important role in the gasification reaction. It has been shown that C–O complexes are formed through oxygen exchange, and the exchange points are activation sites. Incidentally, the activation energy of CO_2 gasification of char is dependent on C(O), a carbon–oxygen complex. The mechanisms of catalytic metal CO_2 gasification of coal char are given in reactions (8)–(10):

$$MO + CO_2 \rightarrow MO(O) + CO \tag{8}$$

$$MO\ (O) + C_f \rightarrow MO + C\ (O) \tag{9}$$

$$C\ (O) \rightarrow CO \tag{10}$$

In reactions (8)–(10), M is a catalytic metal atom. Incidentally, catalytic metals can increase the gasification reactivity of waste wood char by catalytic effect. Gasification reaction rate of wood char is generally high below the suitable additive amount of Na^+ (NaOH) since the activation energy was decreased with increasing Na^+ (NaOH) loaded values. However, when the amounts of Na^+ (NaOH) loaded values were too high, highly concentrated Na^+ covered and accumulated on wood char surface with the reaction site. Therefore, the gasifying agent was difficult to react with the blockade reaction site at wood char surface covered by Na+ (NaOH). As the result, the rate of gasification reaction was decreased with the increment of the activation energy [15, 16]. This study is performed as the fundamental research to improve the combustion and gasification of waste wood biomass fuel and waste coal. It is worth to develop different technologies for controlling air pollutants emitted from fuel utilization. Some achievements in this study have been applied and linked with other studies reported during the 4th International Conference on Energy and Sustainability [17–19].

4 CONCLUSIONS

In this study, carbonization of thinning wood waste of Japanese cedar and their char samples using solid and gaseous fuel utilization was investigated. The thermal decomposition behaviour and effect of alkali metal additive amount of Na^+ (NaOH) loaded waste wood biomass were also investigated. Furthermore, reactivity assessment of waste wood char samples was carried out using CO_2 gasification experiments. Na^+ (NaOH) loaded values showed that it has a significant effect on the char yields, which increased with an increase of Na^+ (NaOH) loaded values while weight loss peak temperature was decreased. The amount of biomass carbon immobilized as fixed carbon contents of waste wood char samples was increased with the increment of Na^+ (NaOH) loaded values. It was also found to be the reactivity of maximum at 100:1 and then it was decreased.

CO_2 gasification reactivity was increased with increasing temperature, and reaction rate of raw char was obviously slower than Na^+ (NaOH) loaded waste wood char samples. The activation energies were decreased with increasing Na loaded values. On the other hand, it conversely increased when Na^+ (NaOH) loaded values was more than 2%. From these results, pyrolysis of wood waste by loading Na^+ (NaOH) was confirmed to be optimal at 100:1 as biomass/Na^+ (NaOH) ratio (wt%).

From the results of this study, we know that CO_2 gasification reactivity of wood waste can improved effectively by loading only 1 wt% Na^+ (NaOH) as the catalytic metallic content, which may be useful for the application of small-scale processing or be one of the effective alternative utilizing technologies of wood wastes instead of the incineration processes.

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