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COMPARSION ON WET AND DRY CARBONIZATION OF FOOD WASTES: CHAR GASIFICATION REACTIVITY

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ABSTRACT

In this research, dried cabbage, chicken and rice were pre-treated by hydrothermal or pyrolytic carbonizations (HTC or PC). Non-isothermal gasification by thermal gravimetric analyzer (TGA) was conducted to explore gasification behavior of the chars. The maximum gasification rate temperature (T_{max}) was used to explain the comparison of the reactivity and higher T_{max} means lower reactivity. For cabbage and chicken, higher alkaline index of their PC200 char, with T_{max} of 795°C and 910°C respectively, led to higher reactivity compared to their HTC200 chars, with T_{max} of 925°C and 992°C respectively. However, the catalytic effect by alkaline was minimized in the case of rice feedstock and the rice PC200 (T_{max} of 986°C) showed slightly higher reactivity than HC200 (T_{max} of 990°C). Therefore, the higher reactivity of PC chars may not only be correlated with the alkaline index but also with development of the pore structure. Increasing the HTC temperature resulted in a lower alkaline index and thereby lowered the reactivity. However, morphology of the char would be the dominant factor for PC char. Increasing the PC temperature will enhance the stable structure like graphite in the chars, leading to lower reactivity.

Keywords: hydrothermal, pyrolytic carbonization, solid structure, gasification reactivity, food waste.

1. INTRODUCTION

Recent thermochemical approaches for energy generation from food waste include incineration and gasification. However, gasification is more environmentally friendly due to its low-oxygen atmosphere in a gasifier, where the formation of the dioxins is unfavourable and, moreover, the energy efficiency is higher [1]. Nevertheless, the high moisture content in raw food waste may increase operation cost and cause the ignition issue in the gasifier, which thereby becomes unacceptable [2]. As a result, a pre-treatment of food waste before gasification is needed to upgrade its properties before gasification applications. Two principal thermal pre-treatment methods to improve inherent properties of biomass are pyrolytic carbonization (PC) and hydrothermal carbonization (HTC) [3]. Although there were several studies considering both pre-treatment methods, most of them mainly focused on mixed food waste. It should be noted that the compositions of actual food waste widely differs by areas. Furthermore, depending on the characteristics of feedstock and application thereof, the suitable method for food waste pre-treatment was rarely reported, especially with regards to gasification reactivity. Therefore, it is imperative to detailly study the

Table 1 Proximate and ultimate analysis of each feedstock

Biomass	Ultimate analysis (%)				Proximate (%)			HHV
	C	H	O*	N	FC	VM	ASH	(MJ/kg)
Cabbage	46.56	4.99	35.22	3.91	20.86	77.04	2.10	18.32
Chicken	53.88	7.64	20.57	13.1	10.32	86.21	3.48	25.48
Rice	44.33	6.49	47.33	1.2	13.46	86.25	0.29	18.23

effects of two main pre-treatment methods on the following char gasification characteristics. In this study, model compounds were adopted to represent animal-based, vegetal and carbohydrate-rich compositions of food waste, respectively. The char gasification reactivity of the food waste chars derived from two different pre-treatment processes (HTC and PC) was tested by TGA. Meanwhile, some fuel properties of the chars were investigated by Fourier-transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS) analysis to support the result of the gasification reactivity. This research will give comparative insight and information of chars derived from the two pre-treatment methods with regards to the gasification performance.

2. MATERIAL AND METHODS

Raw cabbage and chicken, bought from a supermarket, are used as representatives for vegetable-type and animal-based fractions of food waste, respectively. The carbonization was carried out in a fixed-bed reactor. 15 grams of the sample was used, and nitrogen was supplied with a controlled flow rate. The sample was heated to the target temperatures (200, 300, 400°C) with 1 hour holding time. For HTC, a 500 mL batch type autoclave reactor (MMJ-500, Japan) was used. 40 grams of the sample was hydrothermally carbonized under 180, 200 and 220 °C for 30 min holding time with a feedstock-to-water ratio of 1:5. The stirring speed of the stirrer inside the reactor was 100 rpm. The air inside the reactor was purged in advance. After the pretreatment, the solid product was then filtered and put in the oven for drying 24 hours. TGA was used to measure the non-isothermal gasification reactivity of char samples. Approximately 5 grams of char samples were put in an Al_2O_3 crucible pan. The sample was heated up in an CO_2 atmosphere until the gasification was completed. Data was collected and TG and deferential thermogravimetric (DTG) curves were obtained.

3. RESULT AND DISCUSSION

The DTG curves of cabbage, chicken and rice chars are presented in Figs. 1-3. The chicken HTC220 char was not studied due to the only slurry product after HTC220. Also, it should be noted that the ash of rice sample and its derived chars were not analyzed as the ash content was very low and, assumedly, would not significantly affect the gasification performance. The proximate and ultimate analysis of raw feedstocks are presented in Table 1. It is noted that the gasification process of each

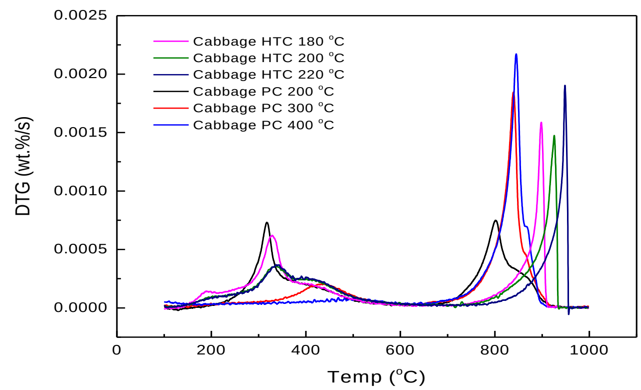

Fig 1 DTG curves of cabbage chars

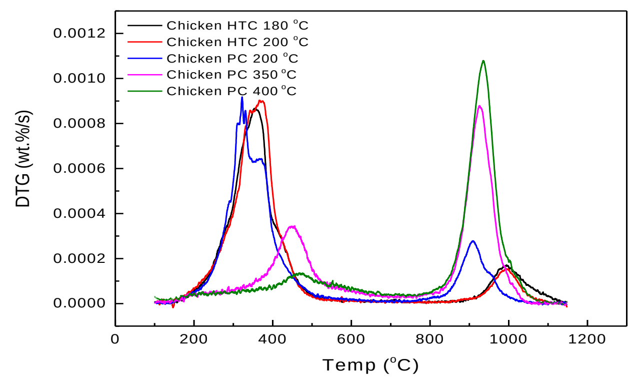

Fig 2 DTG curves of chicken chars

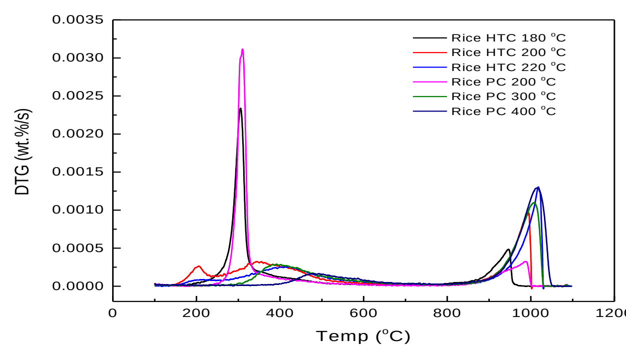

Fig 3 DTG curves of rice chars

char could be divided into two stages, including devolatilization and CO_2 gasification of the remaining chars. The conversion behavior of each stage is explained in the following sections.

3.1 Devolatilization Stage

The curve peak which represents the highest devolatization rate during the devolatilization stage moved forward at a higher temperature with the increase of the pre-treatment temperature for both processes. For PC chars, the significant weight losses were observed after heating over the pre-treatment temperature. This is attributed to decomposition behavior of PC that devolatilization mainly happened during this process. Because of complicated reaction mechanisms during HTC, the weight loss behavior of a char derived from HTC during TG tests varied by its condition and initial feedstock. Cabbage HTC180-char showed two peaks around 190°C and 330°C. Nevertheless, those peaks disappeared, and one peak appeared at around 340°C for both cabbage HTC200- and HTC220- chars. The peak shift from 330°C to 340°C might be partly due to the decrease in the alkaline index (AI) after HTC of cabbage since they presented the same trend. This result is strongly consistent with the work of Daniel [4]. However, the lower reactivity of HTC char produced at a higher temperature might come also from the higher ordered crystalline structure [5]. The value of AI of raw cabbage and chicken and their HTC-chars are presented in Table 1. No important change could be seen but just a small shift of the peak as the feedstock change from chicken HTC180-char to chicken HTC200-char was observed due to main occurrence of hydrolysis. For rice, as the HTC temperature increased to 200°C, the repolymerization happened, leading to the obvious change in the DTG curve at the devolatilization stage. In this research, the noticeable repolymerization of rice under HTC was observed after 190°C as the solid yield started to increase from this temperature (supplementary document). Two peaks can be seen for the rice HTC200-char and those peaks became less intense as the HTC temperature increased to 220°C.

3.2 Char Gasification Stage

The characteristic temperatures, namely the initial reaction temperature, the maximum gasification rate temperature (T_{max}), and the final temperature for complete conversion of each char sample can be obtained from the DTG curves. T_{max} from non-isothermal gasification was used to represent the reactivity of gasification of different char samples [6], which are shown in Fig.4. The lower T_{max} means the higher gasification reactivity of the char.

3.2.1 HTC chars

The reactivity of cabbage and rice HTC-chars decreased with an increase in the HTC pre-treatment temperature. For cabbage, the peak temperatures of cabbage HTC180, HTC200 and HTC220 were 898°C, 952°C and 948°C. This was partly due to the diminishing alkaline index (AI) and thereby decreasing char gasification reactivity. The other factor could be the more stable structure created at higher pretreatment temperature [5]. The peak temperature of rice HTC180, HTC200 and HTC220 were 947°C, 990°C and 1017°C, respectively. The reduction of the reactivity with the HTC severity increase may also come from the repolymerization reaction which forms structures resembling anthracite or even graphite within the biomass body, thereby decreasing the reactivity [7]. On the other hand, the alkaline index of chicken HTC200-char slightly increased compared to HTC180-char due to the higher ash content. This resulted in slightly higher reactivity of HTC200 with the peak temperature of 992°C compared to 996°C for HTC180.

3.2.2 PC chars

All PC chars exhibited the alkaline index in the high regime (>0.34). Therefore, the catalytic effect on the reactivity may be similar for all PC chars. The trend of the alkaline index and the reactivity cannot be the vital factor when comparing the PC chars that were derived from the same initial feedstock with different PC temperatures. Consequently, the morphology was used to explain the gasification reactivity of these chars. Given the same feedstock, the reactivity of PC chars decreased with increasing the PC temperature. The peak temperature of cabbage, chicken, and rice inclined from 800-845°C, 910-937°C, and 986-1018°C, respectively. The declination of the reactivity of PC chars derived at a higher temperature may be due to less amorphous carbon structure during the char gasification stage. Furthermore, more volatiles were released in the chars produced at lower PC temperatures during the gasification, enlarging the pore. Besides these factors, devolatilization under CO_2 atmosphere during the gasification resulted in higher development of pore structure in the remaining char with lower degree of graphitization and higher ratio of small to large aromatic ring systems when compared with that under N_2, as the char graphitization can be inhibited under CO_2 atmosphere. Therefore, the PC char that was produced at a lower temperature under N_2 atmosphere and experienced more devolatilization under CO_2 atmosphere during the gasification process could have more amorphous carbon structure, leading to a higher gasification reactivity.

3.2.3 Comparison between HTC and PC chars

When comparing between HTC and PC chars, the catalytic effect from the alkaline metals plays an essential role on the gasification reactivity. Table 2 shows that HTC chars of chicken and cabbage showed lower reactivity compared to their PC chars partly due to the lower alkaline index. The phenomenon was the consequence of reduction of alkaline metals in char samples after the HTC process. The catalytic effect of alkaline matters was minimized for rice chars due to the very low ash content, and the morphological structure could be the dominant factor for the gasification reactivity of rice chars. The higher reactivity of rice HTC180 char might come from the consequence of more amorphous counterparts created after HTC due to main occurrence of solid-to-solid HTC reaction (primary reaction of HTC). Moreover, PC has been known to increase the crystalline structure of the feedstock, which reduced the gasification reactivity. These causes can be applied for cabbage feedstock also, but catalytic effect seemed to play more important role for the reactivity. However, the reduction of the reactivity of rice HTC char can also be observed when the HTC temperature reached 200°C due to stronger occurrence of repolymerization reaction which forms structures resembling anthracite. Therefore, it can be concluded that PC chars presented higher reactivity than HTC chars for all types of feedstock when assuming the same pre-treatment temperature at 200°C.

Table 2 Ash/FC ratio and alkaline index of each sample

Biomass	Treatment	Temperature	Ash/FC	AI (kg/GJ)
cabbage	Raw		0.10	0.76
	HTC	180	0.05	0.40
		200	0.03	0.24
		220	0.01	0.07
	HTC	200	0.11	1.10
		300	0.10	1.20
		400	0.10	1.41
chicken	Raw		0.34	0.75
		180	0.01	0.01
		200	0.06	0.03
	PC	200	0.20	0.48
		300	0.17	0.78
		400	0.15	1.97

4. CONSLUSION

The gasification behavior could be divided into 2 main stages, devolatilization and char gasification. In the devolatilization stage, the curve peak appeared at a higher temperature with an increase in the pre-treatment temperature for both processes. In the gasification stage, the alkaline index played an important role in the reactivity. HTC chars showed lower reactivity compared to PC chars due to lower alkaline index in the case of cabbage and chicken samples. Yet, the catalytic effect from alkaline was minimized in the case of rice feedstock owing to the very low ash content and HTC showed higher reactivity when compared to PC chars. This index cannot be used as the main factor for the comparison among PC chars from different temperatures. This may be due to the fact that all alkaline index are in high regime, thereby similar influence from catalytic effect. In this case, the morphology of the char would be the dominant factor. The increase in the PC temperature will enhance the stable structure like graphite in the chars, leading to lower reactivity.

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