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Gasification and Properties of Chars Derived Food Waste by Pyrolytic and Hydrothermal Carbonizations

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Abstract. Food waste gasification can be inhibited by high moisture content in food waste. Two common pre-treatments technologies are proposed to treat food waste. The comparative analysis chars derived from different pre-treatments were conducted regarding char properties and gasification reactivity. Cabbage and chicken were pre-treated by two different processes, hydrothermal carbonization at 180-220°C and pyrolytic carbonization at 300-400°C. The result showed that HTC-chars has higher VM but a decrease in O and ash content were seen. The nitrogen content can also be significantly reduced by HTC. However, HTC-chars showed slower char gasification reactivity. To determine the best pre-treatment method for food waste, information from a further study such as the syngas analysis, the tar concentration, and gas emission from gasification should be acquired.

1. Introduction

Due to rapid urbanization, industrialization, and growth in global population, the tremendous amount of food waste is generated throughout the globe, posing a one of the greatest challenges on its management for proper disposal methods. Worldwide, one of the conventional methods of food waste disposal is landfilling [1] which causes not only adverse environmental impacts but also public annoyance [2].

Food waste is an untapped resource and recognized to have great potential for chemical and energy recovery [3]. Recent technologies for energy generation from food waste include biological approaches, such as anaerobic digestion (AD), and thermochemical approaches, such as incineration and gasification. Despite low cost operation of methane production, AD suffers from long duration of its reaction for methane generation [4]. In addition, the consistent performance of AD process can be inhibited by food waste characteristics, namely heterogeneous composition, high concentration of free NH₃, and, especially for cooked food waste, salt [2, 4, 5]. As a result, the two thermochemical processes which require shorter duration to complete the processes and are less susceptible to changes in process conditions have gained increasing attention [6, 7]. In addition to capability to eliminate process-related odors from AD, they also have an ability to reduce larger volume of the waste.

Without proper emission control measures, combustion is harmful to environment and public health, compared to gasification, as it produces highly toxic pollutants, such as dioxins [2, 8]. Gasification is more environmentally friendly due to its low-oxygen atmosphere in a gasifier, where the formation of the dioxins is unfavorable, and, moreover, the efficiency is higher [1]. In this context, gasification became more attractive as the treatment technology for food waste in this research.



Nevertheless, the operation of gasification can be inhibited by the moisture content in food waste due to the high latent heat of evaporation, causing an increase in operation cost and thereby becoming unacceptable [9]. Moreover, the heterogenous and wet characteristics of food waste may lower gasification efficiency and transporting and storing the waste are difficult and uneconomic [10]. The energy harvesting and thermal efficiency could be improved more by pre-treatment of food waste prior to gasification. A pre-treatment of food waste before gasification is then proposed to convert it into a value-added char product with enhanced energy density and upgraded properties concerning fuel quality and emission potential. Two principle thermal pre-treatments to improve inherent properties of biomass are pyrolytic carbonization (PC) and hydrothermal carbonization (HTC) [11]. Not many studies reported on pyrolytic carbonization but hydrothermal carbonization of food waste.

Although there have been many researches on the fuel properties of the pre-treated food waste chars [3,10, 12-21], concerns regarding tar formation and nitrogen emission from gasification as well as interests in the catalytic effect of ash and gasification reactivity are still in existence. This provides encouragement to investigate the effect of the two pre-treatments on gasification performance of food waste chars. Moreover, depending on the characteristics of feedstock and application thereof, the suitable method for food waste was not yet determined and no study refers to the comparison of these two methods with regards to gasification of the respective food waste chars. Owing to the lack of the aforementioned study, a comparative study of properties and gasification of chars produced from the different two pre-treatments should be conducted. To understand the treatment behaviour of nutrient compositions of food waste, Separated-composition food waste was tested separately. The main objective of this research is to investigate and compare yield, properties, and gasification reactivity of food waste chars derived from two different pre-treatment processes. Moreover, an effect of the process temperature in both methods was also tested.

2. Materials and methods

2.1. Materials

In this study, raw cabbage and chicken, bought from a supermarket, are used as representatives for vegetable-type and animal-based fractions of food waste respectively. Nutrient compositions of food waste can be divided into 3 types, namely vegetal, animal-based, and carbohydrate-rich food [21]. These factions generally represent 50, 33, and 17 % of total food waste respectively. To understand the treatment behavior of nutrient composition, Separated-composition food waste was tested separately. Tending to form NO_x emission, animal-based diet is chosen to study while the reason for vegetal one is because of its highest share in the total food waste. Both raw cabbage and chicken are firstly put in an oven at 105°C for at least 24 hours to ensure complete drying. This is to control the moisture of both feedstocks to be the same. The feedstocks were then weighted by mean of an analytical balance. Finally, they were shredded prior to undergoing the pre-treatments. The proximate and ultimate analysis of feedstock is shown in table 1. Raw material and char samples hydrothermally carbonized at 180 °C were further pyrolyzed in the same reactor for pyrolytic carbonization at the temperature of 900 °C for 1 hour to produce samples for Thermal Gravity Analysis (TGA) to determine the gasification reactivity of the samples. The reactivity of the pyrolyzed chars from raw materials is assumed to be similar to that of the pyrolyzed chars from PC-products.

2.2. Pyrolytic and hydrothermal carbonizations

The carbonization was carried out in a fixed-bed reactor, wrapped with heating coils together with insulators. Fifteen grams of the sample was subjected to the left reactor and nitrogen is subjected with controlled flow rate. The sample is heated to the target temperatures which are 300, 350, 400 °C. Being kept for an hour at the target temperature, the reactors were cooled down and the char sample was weighted to measure the productivity.

For HTC, a 500 mL batch type autoclave reactor (MMJ-500, Japan) with a temperature controller, a pressure sensor, and a stirring as illustrated in Nurdawati's study [22]. Forty 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 is 100 rpm. The air inside the reactor was purged by introducing argon gas to create an oxidative-free environment. After the pre-treatment, the solid product was then filtered and put in the oven for drying. The char was weighted after 24 hours of drying.

These PC and HTC conditions are commonly used for biomass feedstock. After the pre-treatment processes, the char samples from different conditions are sealed in the plastic bags to avoid moisture intake before being used for further analysis. The productivity of the chars after PC and HTC is defined as the percentage of dry solids recovered from initial feed stock. This can be calculated by using equation (1).

$$\text{Yield (\%)} = (m_{\text{char}}/m_{\text{feedstock}}) \times 100\% \quad (1)$$

2.3. Proximate and ultimate analysis

The proximate analysis of the samples was carried out using the TGA analyser (Shimadzu D-50 simultaneous TGA/DTA analyser, Japan). The volatile matter, the fixed carbon and the ash of each samples were determined following the ASTM D3172 standard. The ultimate analysis of the char samples was performed using the Vario Micro Cube Elemental Analyzer (Elementary, Japan). The CHNS and Cl contents were determined using the analyser and oxygen was determined by the difference. The higher heating values (HHV) of the samples was calculated using Eq (2) provided by Channiwala et al [23].

$$\text{HHV} = 0.3491C + 1.1783H + 0.1005S - 0.1034O - 0.0151N - 0.0211A \text{ (MJ/kg)} \quad (2)$$

where, C, H, O, N, S and A represents carbon, hydrogen, oxygen, nitrogen, sulphur and ash contents of material, respectively, expressed in mass percentages on dry basis.

2.4. Char gasification

The same TGA analyser used in proximate analysis is used to measure isothermal gasification reactivity of char samples. Approximate ten grams of pyrolyzed char sample was put in an Al₂O₃ crucible pan. Nitrogen was first injected at 150 ml/min, and the sample was heated up to target temperatures, 850, 875, and 900 °C. The condition was then kept for 5 minutes and the gas was auto-switched to CO₂ at 180 ml/min to start gasification process. The mass change was used to calculate the reactivity of gasification.

2.5. Ash analysis

Ash sample was prepared at 575 °C in a muffle furnace, burned for 24 hours, and the ash composition (table 2) was obtained by X-ray fluorescence (XRF, Bruker AXS, Germany)

3. Results and discussions

3.1. Proximate analysis

The proximate analysis of the raw materials and the solid chars are presented in table 1. The result of proximate shows that, compared to PC-chars, HTC-chars showed higher volatile matter (VM) and even higher than raw feedstock for chicken HTC-chars. This indicates that, during the gasification of HTC-char, higher tar may be generated [24], leading to a difficulty to operate gasification in an actual plant. However, reduction in ash content can be seen in HTC-chars while the ash content of PC-chars increased. This result implies the less potential of ash fouling and slagging during the gasification operating at high temperature [25], but the reactivity may be lower. To confirm this explanation, ash analysis should be conducted to see the change in alkali groups, which can act as catalyst during the gasification and promote hydrogen production [7, 26].

Table 1. Proximate and ultimate analysis and solid yield results of raw materials and solid products.

Biomass	Treatment	Temperature	Ultimate analysis (%)				Proximate (%)			Solid Yield (%)	
			C	H	O ^a	N	FC	VM	ASH		
Cabbage	Raw		46.56	4.99	35.22	3.91	20.86	77.04	2.10		
	HTT	180	57.50	5.33	33.13	2.86	29.48	69.09	1.44	51.9	
		200	60.70	5.29	29.66	2.54	34.34	64.68	0.98	45.3	
		220	62.82	5.33	27.26	2.95	38.48	61.20	0.32	45.0	
		PC	300	70.81	4.32	15.24	2.47	51.22	43.69	5.10	45.5
		350	72.91	4.01	10.46	3.68	57.44	37.34	5.22	39.7	
		400	73.35	3.85	9.34	3.16	61.89	31.95	6.15	37.3	
	Chicken	Raw		53.88	7.64	20.57	13.1	10.32	86.21	3.48	
		HTT	180	58.44	8.22	18.82	11.00	9.98	89.92	0.10	22.5
200			61.41	8.7	16.96	9.34	7.53	92.03	0.45	8.0	
220			66.07	9.9	14.57	6.46	4.17	94.81	1.02	4.1	
PC			300	64.82	7.02	9.28	10.6	24.47	71.32	4.21	53.4
		350	66.05	5.46	7.09	10.86	48.65	43.86	7.49	33.5	
		400	60.75	4.22	11.07	10.51	60.17	31.02	8.80	29.3	

^aBy difference

The different degree of decrease in VM after the different pre-treatments comes from the lower process temperature in HTC process as one of the reasons. Another reason is attributed to different reaction pathways and mechanisms of both treatments. Owing to the more removal of volatile matter as a main mechanism in the pyrolytic carbonization [10], the PC-products show higher fixed carbon and ash contents as the compensation. The lower ash content in HTC-chars might also be due to dissolving of inorganics to liquid by-product stream. This indicates, again, HTC-chars may be less reactive than PC-chars during the char gasification process.

The fraction of volatile matter (VM) of cabbage HTC-chars and all PC-chars dropped significantly with an increase in process temperature while the increase of fixed carbon (FC) compensated the loss of VM. This showed the extent of devolatilization of gas products and low molecular weight hydrocarbons highly depended on the increased process temperature [27]. However, chicken HTC-chars did not follow the same trend. The increase in VM of chicken HTC-chars, from 86 in the dried chicken to 94 % in HTC-220 HTC-char, was due to the hydrolysis reaction that breaks protein as a main composition of chicken into amino acids which is generally soluble with water and then went together with water to the aqueous phase [22], leaving more lipid in chicken HTC-char as the temperature increased. This also indicates that hydrolysis is the main reaction during the HTC of high protein-containing feedstock. The result coincided to the significant drop of nitrogen content in chicken HTC-char.

3.2. Ultimate analysis

The result of ultimate analysis demonstrates that, after the pre-treatments, the percentage of C increased while that of O decreased. The carbonization reaction during PC is more severe compared to HTC due to the higher process temperatures. This made O content of PC-chars lower than that of HTC-chars while the C content went to the opposite trend. Later, the authors will conduct the PC at the same temperature with HTC. The same trend was seen by rising the process temperature in PC and HTC. However, chicken PC-char had opposite trend in changes of C and O contents. The reaction pathways (the change in H/C and O/C ratio) of each product can be applied by Van Krevelen diagram in figure 1 [28].

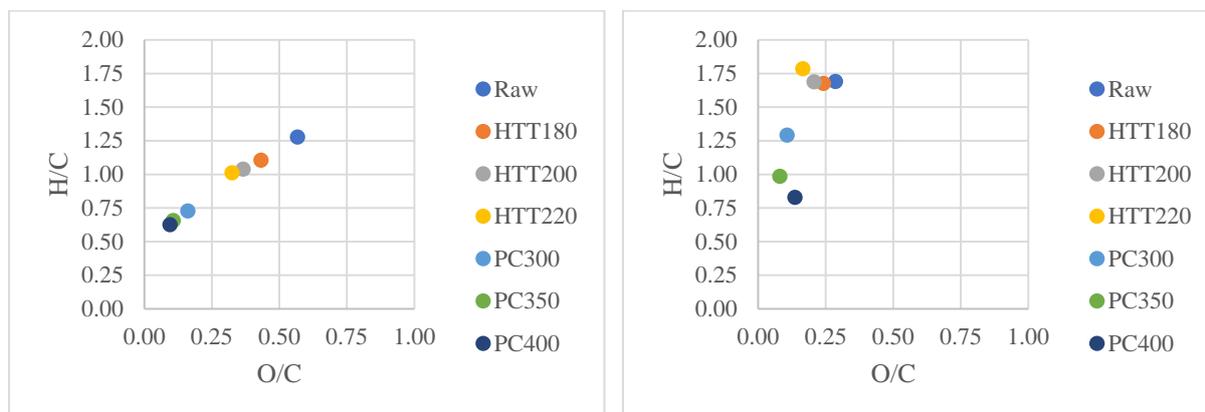


Figure 1. Van Krevelen diagram char products of cabbage (left) and chicken (right).

At 300 °C PC of chicken, it looks like chicken merely went through dehydration. In fact, both decarboxylation and demethanation took place. The CO_2 and CO are the main gases lost as also observed by [29] which study about fixed bed pyrolysis of meat which has similar nutrient compositions (mainly protein and some lipid) to chicken. The release of CO_2 and CO represents the decarboxylation pathways. These light volatiles are from degradation of light aliphatic compounds as said in [12]. The occurrence made the increase in C content but decrease in O content. Not only that, the light nitrogenated tar compounds degraded from protein are also significantly released which state the existence of amination. Most of these compounds should have N/C atomic ratio of 0.25 or above since the result of N/C atomic ratio decrease from 0.21 to 0.14. The chemical formulas of light nitrogenated tar compounds from protein can be seen in [30, 31]. In [29], the result shows that these compounds are the most significant group that reaches its peak of tar production at 300 °C pyrolysis. Moreover, [32] reported that protein derived from microalgae had mass lost the most at around 300 °C. The significant release of light nitrogenated tar compounds then represent the demethanation with nitrogen reduction, which could explain the result from ultimate analysis of chicken PC-chars at 300 °C.

The same phenomenon happened when the chicken was pyrolytic carbonized at 350 °C. However, at this temperature, the degree of demethanation was stronger due to the heavier volatile compounds from protein and lipid releasing. The study [30] shows that the highest mass loss of lipid is at 350 °C. This indicates volatile compounds from lipid are degraded more at this temperature. In contrast, as seen in table 1, the N content was stable from 300 to 400 °C PC. This is attributed to the study that found that the aliphatic N compounds (%) in tar decrease when the temperature rises to 400 °C [29]. Nevertheless, heavier volatile compounds from protein are still released but not much. This means C and H will be removed more from feed stock as the temperature increase while N will be removed less, and it is confirmed by the ultimate analysis result. These higher-molecular compounds, from both protein and lipid, contain more C and H contents, making a drop of H content when compared with chicken 300PC-char as seen in ultimate analysis. Although the release of CO_2 significantly dropped as temperature increase [29], an increase in C content may be due to the enough decarboxylation reaction and the drop of O content can still be seen at 350 °C PC. At 400 °C, even higher volatile compounds from protein and lipid releasing, making demethanation even stronger. Together with the significant decrease of CO_2 , the drop of C and H contents in PC-char are seen. An increase in O content is the compensation of the phenomenon.

For chicken HTC, the main reaction is decarboxylation. This is attribute to the hydrolysis of protein units into amino acids which contain the carboxyl group. Carboxylic group is lost together with amino acids and in a form of CO_2 . However, it should be noted that the gas is only small [33]. As the temperature increased, decarboxylation is more severe. Due to the occurrence of decarboxylation, O content decreased while C and H content increase as compensation.

For cabbage, the decarboxylation and dehydration reactions were essence reaction pathways. The carbonization reaction during PC is more severe compared to HTC due to the higher process temperatures as also seen Van Krevelen diagram. The result show that cabbage hydrochars are in comparison with lignite and the cabbage carbonized chars are even close to the sub-bituminous region.

3.3. Char yield and high heating value

The productivity of and high heating value of the char samples are shown in table 1 and figure 2, respectively.

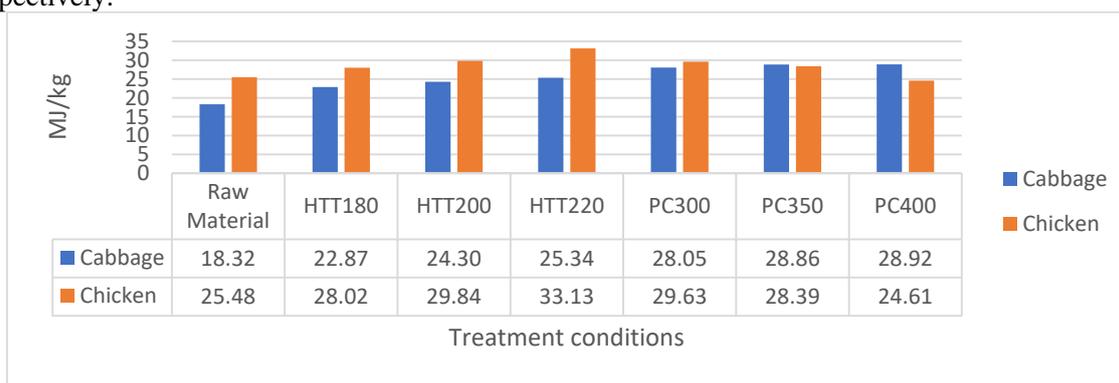


Figure 2. HHV of char products and raw materials.

The productivity of all solid products declined with an increase in temperature. Chicken showed a dramatic decline after HTC. This is, again, due to the hydrolysis the protein. Protein and carbohydrates can be hydrothermally decomposed from 180°C while 280-500 °C is for lignin [33]. The chicken is mainly composed of protein with some lipid. On the other hand, cabbage is similar to lignocellulosic biomass containing lignin. This is the reason behind that cabbage has higher productivity after hydrothermally treated than chicken. For PC, cabbage showed higher productivity at 300 °C but the mass loss of chicken is major when the temperature increases to 350 °C. The result indicates that heavier volatile is contained more in protein than cabbage. In addition, raw chicken contains more volatile matter, so the potential of mass loss is higher when the feedstock go through the process.

HHV of all samples inclined with increased temperature, excepting chicken PC-chars. Since HHV was calculated by Eq. (2), the influence of chemical composition of the samples is high. With raised temperature, C and H contents, major factors, in chicken PC-char reduced, leading to the decrease in HHV. However, HHV of chicken PC-chars showed higher than its raw biomass.

3.4. Change in nitrogen content

Both PC-chars and HTC-chars displayed lower N content after pre-treatments. However, chicken HTC-chars showed more significant decrease in N content which declined as the temperature increase. This phenomenon is because of the hydrolysis reaction of protein which is easier to be hydrolyzed at lower temperature when compared with sugar polymers. Rising temperature did not have an effect on N content for other samples.

3.5. Alkali index

The results from XRF analysis were used to calculate Alkali Index (AI) which is shown in figure 3. This index can be used to explain the potential catalytic effect of the ash in the product. It can be clearly seen that even if hydrothermal has great potential to reduce ash content, it demonstrates very low alkali index. This is due to the loss of alkali group, K and Na. These elements, particularly K could act as catalysts to catalyzed conversion reaction and may increase reactivity [34]. After hydrothermally carbonized, K in ash of products changed significantly. The percentage of K of the total ash decline as the HTC temperature decreases. This indicates that rising HTC temperature may

reduce the reactivity of the gasification. The ash composition after did not change after PC. As the ash content increase with increased PC temperature, the AI inclined. However, other ash indexes should be calculated to see the potential of fouling and slagging during the high temperature process.

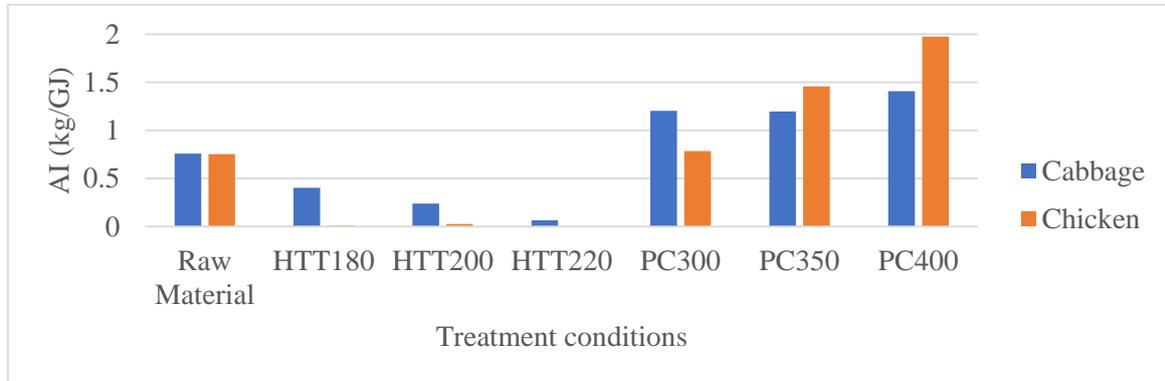


Figure 3. Alkali Index of ash in raw materials and char samples.

3.6. Char gasification reactivity

From the TGA result, HTC-chars demonstrated lower gasification reactivity. This is the consequence of the reduction of alkaline metals in char samples after the HTC process. The alkali elements are known to act as catalysts, thereby increasing the reactivity [2]. During HTC, some of the alkaline salt would be dissolved into liquid phase while it remained in carbonized chars. This was also attributed to lower ash content in HTC-chars than PC-chars. The very slow reactivity of chicken chars may be because of the low surface area and a lack of functional group that can easily react with gasification agent like CO₂ which is less active to gasify feedstock compared to H₂O.

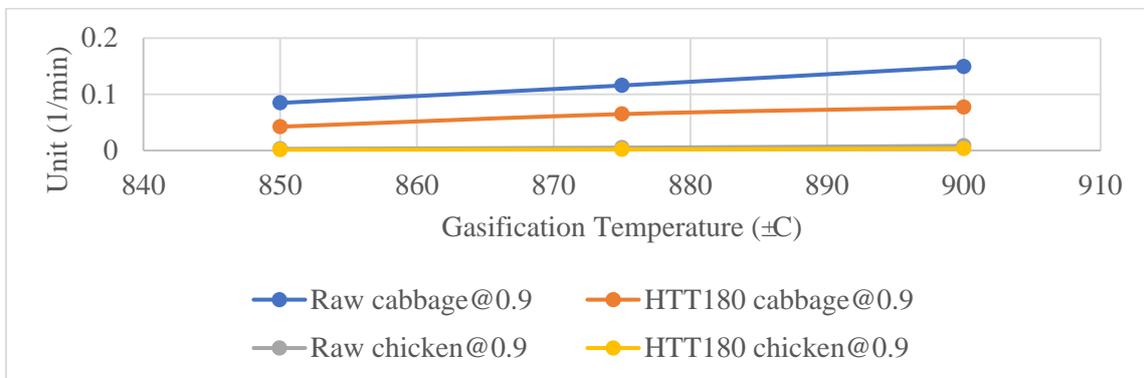


Figure 4. Char gasification reactivity at 90% conversion of pyrolyzed chars.

4. Conclusion

Higher VM can be seen in HTC-chars. However, HTC-chars presented the reduction of both oxygen and ash contents while only that of oxygen can be seen in carbonized chars. The nitrogen content can also be significantly reduced by HTC, especially for high nitrogen-containing feedstock like chicken. HTC-chars clearly showed lower reactivity compared to carbonized chars due to the loss of catalyst during the HTC process. To determine the best pre-treatment method for food waste, information from a further study such as the syngas analysis, the tar concentration, and gas emission from gasification should be acquired

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