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Study on pyrolysis behavior and gas formation rate of washed rice straw

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Abstract: Three washing techniques namely water at room temperature, hot water, and hydrochloric acid were applied to rice straw to remove the inorganic matters. The ash content and elemental composition of washed rice straw were examined in detail. Then, the pyrolysis behaviors and gas formation rate during the pyrolysis of washed biomass were examined using TGA and TG-MS techniques. It was found that water could easily remove alkali metal and Cl, but water could not remove alkaline earth metals. On the other hand, hydrochloric acid could significantly remove alkali and alkaline earth metals. However, silicon cannot be removed by washing because of the strong bonding between amorphous silica and biomass matrix. Washing significantly affected the pyrolysis behavior of biomass. The weight change curves during the pyrolysis of washed biomass increased by approximately 20°C in temperature. It was found that the amount of tar produced during the pyrolysis increased significantly, whereas the amount of H_2O decreased significantly by washing. From these measurements, the effect of inorganic matters on the pyrolysis behavior of biomass was examined in detail.

Keywords: Rice straw, washing, pyrolysis behavior, gas formation rate.

1. Introduction

Biomass is a promising renewable energy resource with high potential. Rice straw is considered to be the most important agricultural residue, particularly in Thailand, where massive amounts of rice straw are generated. Rice straw can be converted to energy by thermo-chemical conversion. Pyrolysis is a basic thermochemical decomposition by heating organic matters in the absence of oxygen, which produces gas, char and bio-oil [1-2]. Pyrolysis behavior demonstrates the typical decomposition of components in the biomass. Each kind of biomass has a characteristic pyrolysis behavior based on a mixture of cellulose, hemicellulose, lignin, extractive and inorganic components [3].

Inorganic components, particularly K, Na, S and Cl are known to cause environmental and technological problems during thermal processes such as fouling and slagging [4-6]. An inorganic components act as a catalyst, which affect to pyrolysis degradation and the yield of pyrolysis products [5, 7]. Several washing pretreatment methods have been reported to effectively remove ash and inorganic components. Washing with water is the mildest washing technique that has the ability to remove some elements such as K and Cl. Jenkin et al. [8] tested the removal of inorganic elements by laboratory washing using many techniques included spraying, flushing and soaking. The results showed that some ash, K, Na and Cl are easily removed by washing. Soaking seems to be a controllable techniques. Deng et al. [9] investigated the effect of washing temperatures at 30°C, 60°C and 90°C and found that the higher water temperature, the smaller sample size and lower ratio of sample to water making inorganic elements and ash removal more effective. Jensen et al. [10] suggested washing with tap water and distilled water make no difference to element removal and 3 hours was long enough to complete the elemental extraction. However, it is difficult to remove Ca and Fe because these metallic species dissolve only partially in water [11]. It is well established from many research articles that acid washing is more effective to remove ash [12]. The solutions for acid washing include mainly inorganic acids (hydrochloric acid, HCl) [13-14] and organic acids (acetic acid) [15].

Washing can remove a large part of ash, alkali and alkaline earth metals. In addition, the chemical composition of biomass would change after washing. Therefore, it is necessary to study the pyrolysis behavior of washed biomass to investigate their positive or negative influence during pyrolysis and gas production. However, in the view point of the fundamental data, there are few studies studying the effects of inorganic matters on pyrolysis behavior and gas formation behavior during pyrolysis by using the TG-MS technique. Therefore, these data are attractive and may useful to the research community.

In this work, rice straw was washed by three techniques: water at room temperature, hot water, and hydrochloric acid. Then, the pyrolysis behaviors of washed rice straw were examined by TGA technique. The gas formation rates during the pyrolysis were examined by TG-MS method. The ash content, elemental compositions of biomass after washing were analyzed. From these measurements, the effects of inorganic matters on the pyrolysis behavior of biomass were examined in details. The fouling tendency of the washed biomass was calculated.

2. Experimental section

2.1 Sample

Rice straw (RS) was selected as a biomass sample. After milling and sieving into size less than 250 µm, the sample was dried at 105°C for 12 hours before experimental use. Table 1 shows the results of solid yield, proximate and ultimate analyses of the sample. The raw rice straw after drying was labeled as Raw-RS.

2.2 Washing experiments

Three laboratory washing techniques were used in this study namely water at room temperature (30°C), hot water (80°C) and 1 molar of hydrochloric acid (HCl). Biomass about 5 g was taken in a 250 ml of solution (biomass: solution = 1g: 50ml) and stirred continuously for 1 hour as a control factor. The solid sample was collected by filtration and washed by distilled water until pH of solution become neutral. Then, washed samples were dried at

110°C for 24 hours before analyses. The rice straw after washing with water at room temperature, hot water and hydrochloric acid were labeled as H_2O-RT-RS, H_2O-HT-RS and HCl-RS respectively.

2.3 Pyrolysis behavior

Pyrolysis behavior of Raw-RS, H_2O-RT-RS, H_2O-HT-RS and HCl-RS samples were analyzed by Thermo Gravimetric Analyzer or TGA (PerkinElmer, Pyris1). The flow rate of nitrogen gas was 100 ml/min and about 5-10 mg was used for each run. Samples were heated from room temperature (30°C) to 110°C held 10 minutes to remove moisture content and heated again to 800°C with a rate of 10°C/min to examine the decomposition behavior and decomposition temperature of the samples.

2.4 Analysis of gas formation rates during the pyrolysis

A mass spectrometer (Perkin-Elmer, Clarus 500MS) coupled to the thermobalance (Perkin-Elmer, Pyris1 TGA) was used for the evolved gas analysis. The 20-30 mg samples were heated in a nitrogen atmosphere with a 10°C/min heating rate up to the final temperature at 600°C. The transfer lines between TGA and MS were heated to 200°C to avoid cold spots and also prevent the condensation of the gaseous product. The signals for the mass numbers of 2, 15, 18, 28 and 44 were continuously detected and subsequently converted into concentrations of H_2, CH_4, H_2O, CO and CO_2 by referring to the calibration curve constructed using the standard gases.

3. Results and Discussion

3.1 Chemical properties of washed rice straw

First, chemical properties of Raw-RS, H_2O-RT-RS, H_2O-HT-RS and HCl-RS were analyzed. Table 1 shows the solid yields and the proximate analyses are on dry basis, and the ultimate analyses is on dry ash free basis. It was found that the solid yields were slightly decreased to 85.97%, 83.15% and 81.50% after washed with water at room temperature, hot water and HCl respectively. The volatile matters of washed rice straw increased significantly while the fixed carbon decreased. The results of the ultimate analyses of washed rice straw were not significant different to Raw-RS.

The ash content of washed rice straw decreased from 16.6% (Raw-RS) to 15.2% and 13.2% by water at room temperature and hot water, hence 1.4% and 3.4% of this lost ash component is water-soluble. After HCl was washed the ash content decreased to 12.6%, and 3.9% of the lost ash component consisted of both water-soluble and acid-soluble components. Ash reduction was due to washing techniques extracts large amount of soluble component which are alkali metals, chlorides, nitrates and sulfate [16-17]. Hot water can remove more of ash than water at room temperature, because increased temperatures led to increased solubility in the washing medium [7]. It was well established from many research articles that acid washing has high efficiency for ash removal. Acid washing opens up or loosens the structure of the biomass, which facilitates mass transfer and higher levels of ash removal [12]. However acid washing not only removes water-soluble and acid-soluble components but it also removes organic components from biomass matrix [18] so the behavior of pyrolysis is necessary for further study.

3.2 The elemental compositions of rice straw ash

Table 2 shows the elemental compositions in ash of Raw-RS, H_2O-RT-RS, H_2O-HT-RS and HCl-RS which analyzed by XRF technique. It was found that, SiO_2 64.70%, K_2O 17.00% and Cl 3.88% was three main elements of Raw-RS. After washing, the amounts of K_2O, Cl, SO_3 and Na_2O decreased greatly when using water at room temperature and decreased even more after using hot water and HCl. In general, the light metals (K and Na) easily removed ash. The amount of ash removal is similar with each tested washing solution. For example, K_2O decreased from17.00% to 4.04%, 2.74 and 0.44% after washing with water at room temperature, hot water and HCl respectively. The types of solutions used play a minor role, as light metals can be efficiently removed by all washing solution. Heavy metals (Ca and Mg) and SiO_2 cannot be removed by water but they have a higher solubility in acid solutions than water. These results agree with the analysis of Jenkins et al. [8], Cen et al. [14] and Davisson et al. [19].

Table 1. Solid yield and chemical properties of raw and washed rice straw.

Washing techniques	Solid yields [wt%, d.b]	Proximate analyses (wt%, d.b)			Ultimate analyses (wt%,d.a.f)			
		%VM	%FC	%Ash	C	H	N	O(diff)
Raw-RS	100.00	66.9	16.5	16.6	42.4	6.4	0.6	50.6
H_2O-RT-RS	85.97	72.4	12.4	15.2	42.6	6.4	0.6	50.4
H_2O-HT-RS	83.15	74.9	11.9	13.2	42.6	6.4	0.5	50.5
HCl-RS	81.50	76.0	11.4	12.6	43.5	6.4	0.6	49.5

Table 2. Elemental compositions of rice straw ash and fouling tendency.

	Washing techniques			
	Raw-RS	H_2O-RT-RS	H_2O-HT-RS	HCl-RS
Ash at 575°C	15.40	13.34	12.49	10.08
Elemental composition in ash (% ash at 575°C)				
SiO_2	64.70	83.50	82.50	93.30
K_2O	17.00	4.04	2.74	0.44
Cl	3.88	0.00	0.00	0.00
CaO	3.36	4.39	4.00	0.22
MgO	1.97	1.46	1.47	0.00
SO_3	1.33	0.32	0.30	0.07
P_2O_5	1.30	0.29	0.32	0.33
Na_2O	0.65	0.19	0.12	0.00
MnO	0.40	0.40	0.45	0.02
Al_2O_3	0.17	0.23	0.22	0.18
Fe_2O_3	0.13	0.29	0.27	0.14
TiO_2	0.00	0.00	0.00	0.00
Base-acid oxide ($R_{B/A}$)	0.36	0.11	0.10	0.01
Fouling tendency (F_u)*	6.29 (medium)	0.37 (Low)	0.30 (Low)	0.00 (Low)

* $F_u \leq 0.6$, low fouling inclination, $0.6 \leq F_u < 40$ medium, $F_u > 40$ high [20]

Ash of Raw-RS has a very high content of SiO_2 about 64.70% and SiO_2 increased to 83.50% after washing with water at room temperature and increased to 93.30% after washing with HCl. This occurs because water-soluble elements (K, Na and Cl) have been removed from the biomass. RS maintain a strong bond between amorphous silica and biomass matrix [9]. SiO_2 cannot be removed by washing. Therefore it makes the proportion of SiO_2 increase after washing.

Undesirable effects of biomass ash in thermal processes include ash sintering, slagging and fouling. These side effects are related to the concentration of K and Si in biomass ash [21-22]. One of the most common indicators that correlates with base-acid oxide ($R_{B/A}$) is calculated from Eq. (1) [23-24]. Fouling tendency are calculated from Eq. (2) [23-24]. The fouling tendency of washed rice straw was calculated and compared with Raw-RS as shown in Table 2. (Slagging index was not calculated in this study)

$$R_{B/A} = \frac{Fe_2O_3+CaO+MgO+K_2O+Na_2O}{SiO_2+TiO_2+AL_2O_3} \quad (1)$$

$$\text{fouling tendency} = R_{B/A} \times (Na_2O + K_2O) \quad (2)$$

It was found that the fouling tendency decreased from medium to low inclination range. The fouling tendency decreased from 6.29 to 0.37 using water at room temperature, 0.30 with hot water and 0.00 after washing with HCl. This result indicates that HCl is the most effective technique to reduce thermal problems by removing inorganic matters.

3.3 Pyrolysis behavior of washed rice straw

Figure 1 shows the weight change behavior (TG curves) and rate of decomposition during the pyrolysis (DTG curves) of washed rice straw compared with Raw-RS. TG and DTG curves were demonstrated in dry-ash-free basis.

It was found that the weight change curve of Raw-RS started to decrease at 200°C and char formation occurring at 800°C was about 20%. After washing, the weight change behavior was significantly different from the Raw-RS. The weight change curve of washed rice straw started to decrease at higher temperature approximately 20°C and char formation was reduced. It meant that washed rice straw started to decompose at higher temperature. The DTG curve demonstrated more obvious differences than the TG curve. The maximum devolatilization rate of all washed rice straw was faster than Raw-RS and HCl-RS demonstrating the fastest devolatilization rate. It can be explained by alkali and alkaline earth metals inherent in the main biomass components, which acted as catalysts to promote volatile releases and char formation. The catalytic elements have been removed by washing and the main components of washed samples are more resistant to thermos-chemical decomposition. Pyrolysis shifts can be found in washed rice straw. Although HCl can remove more alkali and alkaline earth metals than water, the pyrolysis of HCl-RS has no significant difference to H_2O-RT-RS and H_2O-HT-RS on TG and DTG curves. It only found a small difference in DTG curves for HCl-RS. Deng et al. [9] also found the similar results. The biomass type and washing experiment in this work are probably not intense enough to distinguish the difference from pyrolysis.

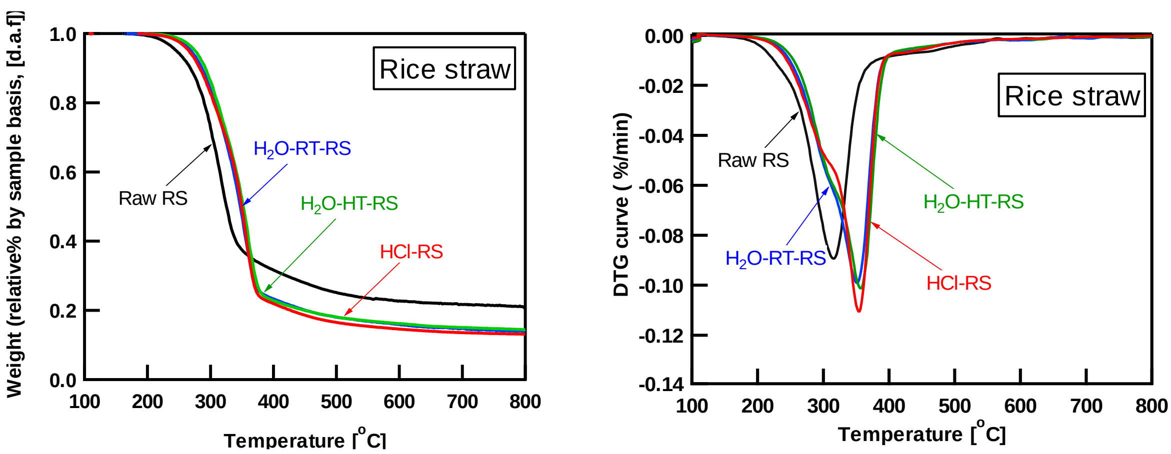

Figure 1. (a) TG curves and (b) DTG curves of washed and Raw-RS.

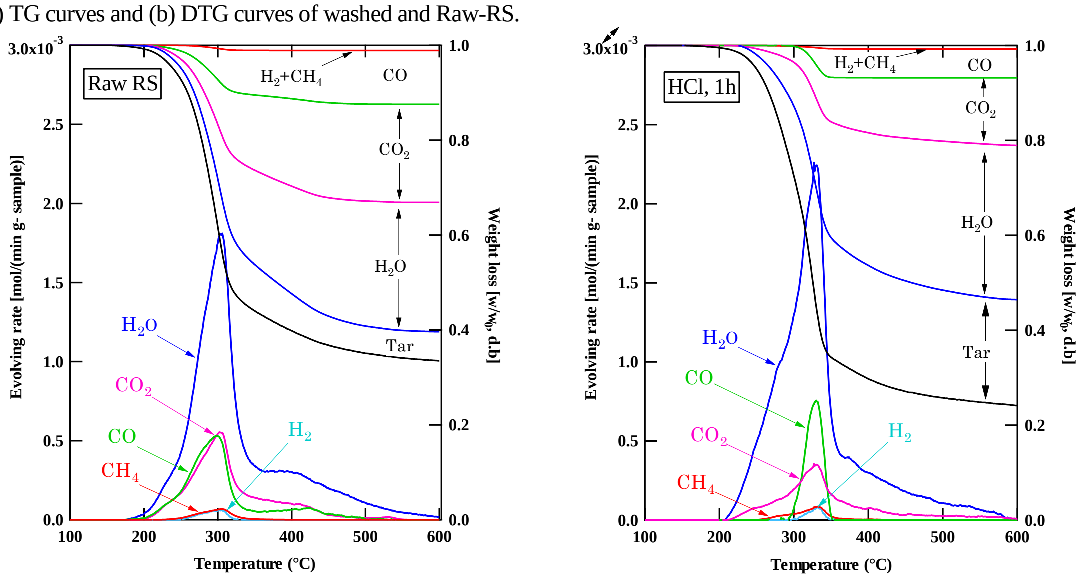

Figure 2. TG curve, gas formation rate and product distribution during the pyrolysis of raw of Raw-RS and HCl.

3.4 Gas formation rates during the pyrolysis of washed rice straw

The TG-MS technique was used to study the pyrolysis behavior of biomass to gain more details than TG curve. Both the weight change curve and the evolving rate of product gas during pyrolysis of Raw-RS and HCl-RS are shown in Figure 2. The integrated products and distributions of products are shown in the figure. The amount of tar equated to the difference between the weight loss and the sum of the evolved amounts of H_2, CH_4, CO, CO_2 and H_2O. The weight loss curves are on dry basis. Cen et al. [14] reported that washing by water had no obvious effect on the mass yield of pyrolysis gas products. This study investigated on HCl-RS and compared the result with Raw-RS. It was found that weight loss curves and the evolving rate behavior of HCl washing found clear differences from Raw-RS.

The major weight decrease of Raw-RS was observed at 250-300°C. The char yield at 600°C was 33% while the major weight decrease of HCl-RS was observed at higher temperature (270-350°C) and char yield decreased. As mentioned in section 3.2 and 3.3, acid washing can remove a large part of alkali and alkaline earth metals. The pyrolysis shift will demonstrate the weight loss curve and the peak of evolving rate. Gas formation behavior during pyrolysis of H_2O, CO and CO_2 were well accompanied by the sharp decomposition seen in weight loss curves. However, CH_4 and H_2 formation behavior was not accompanied by any sharp decomposition. The H_2O was a main product formed for Raw-RS and HCl-RS. It started to evolve at 190°C for Raw-RS while HCl-RS started to evolve at 210°C. The same result was found in other gases (H_2, CH_4, CO, CO_2) after washing these gases started to evolve at higher temperature.

Figure 3 shows the yield products (H_2, CH_4, CO, CO_2, H_2O and tar) for Raw-RS and HCl-RS. Among condensable gases such as H_2, CH_4, CO, CO_2, it was found that CO_2 and CO are dominant gas products, while H_2 and CH_4 are minor products during pyrolysis. These results agree with previous studies [2, 14]. The amount of CO_2 and CO in Raw-RS was 0.207 g/g-sample and 0.113 g/g-sample. After washing with HCl, the amounts of CO_2 and CO decreased to 0.143 g/g-sample and 0.061 g/g-sample and both gas species CO and CO_2 were released at shorter time. Alkali and alkaline earth metals had remarkably different effects on the yields of pyrolysis gas products. This occurred by altering reaction pathways of main biomass components. These elements acted as catalysts, which reacted with vapor during pyrolysis. They also promoted ring opening reactions of carbohydrates [14, 17], resulting in the formation non-condensable gases. Since HCl can remove high amount of alkali and alkaline earth metals, the formation non-condensable gases decreased.

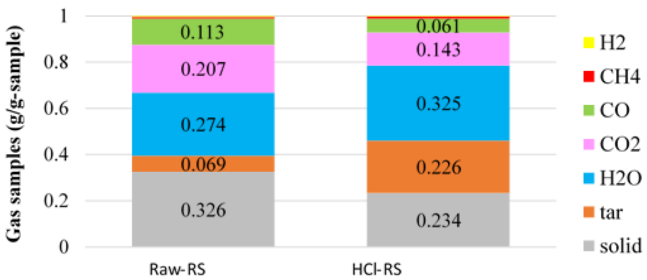

Figure 3. Product yield (H_2, CH_4, CO, CO_2, H_2O and tar) of Raw-RS and HCl-RS.

The most significant difference from pyrolysis products between the Raw-RS and HCl-RS was the amount of tar. Tar increased remarkably from 0.069 g/g-sample to 0.226 g/g-sample after washing with HCl. The amount of tar was related with the amount of volatile matters in samples [25]. After washing with HCl, the amount of fixed carbon decreased, while the amount of volatile matters increased as shown in section 3.1. This same phenomena was found in Blasi et al. [22] and Cen et al. [14].

4. Conclusions

The washing technique had a remarkable influence on pyrolysis behavior and gas formation of rice straw. Among the three washing techniques, hydrochloric acid washing demonstrated the highest removal efficiency for ash, alkali and alkaline earth metals (especially K, Na and Cl) and further reduced catalytic effects on pyrolysis. That resulted in the pyrolysis behavior of washing rice straw shifting to a higher temperature and a completely different weight change curve from raw rice straw. In addition the pyrolysis of rice straw after washing with hydrochloric acid has no significant difference to rice straw after washing with room temperature water and hot water. Gas formation was analyzed by using the TG-MS technique. It was found that the amount of CO_2 and CO decreased after washing with hydrochloric acid. The most significant difference in the pyrolysis product between the raw rice straw and hydrochloric acid washing is the amount of tar. Tar increased remarkably and tar production is related directly with the amount of volatile matters present. Since hydrochloric acid washing demonstrated the highest volatile matters that resulted in increased tar production. Furthermore, acid washing can mitigate thermal process problems in by reducing the ash content, alkali, alkaline earth metals and by reducing the fouling inclination.

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