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Thermogravimetric Studies on the Catalytic Pyrolysis of Rice Husk

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The main objective of the present work is to study the effect of catalyst weight loading on the catalytic pyrolysis (CP) of rice husk (RH) using thermogravimetric analysis (TGA). The pyrolysis process is conducted at a heating rate of 10 °C/min in nitrogen (N_2) atmosphere flowing at 150 mL/min and heated up to 700 °C. The alumina (Al_2O_3) catalyst was used as the support with addition of nickel (Ni) and cerium (Ce) as promoter at fixed loading by weight percent of 20 wt % Ni: 5 wt % Ce: 75 wt % Al_2O_3. The feedstock samples for TGA were prepared accordingly with biomass to catalyst weight loading ratio as follows: RH-2 (1:0.05), RH-3 (1:0.10), RH-4 (1:0.15), RH-5 (1:0.20), RH-6 (1:0.50), and RH-7 (1:1). For comparison, the pyrolysis of rice husk without catalyst is determined at the same operating condition and labeled as RH-1 (1:0). The TGA-DTG curves shows that, the presence of catalyst has significant effects on the volatile matter of rice husk. Sample RH-4 (1:0.15), was found to be the optimized biomass to catalyst ratio for maximum volatile matter yield. The highest degradation of cellulose and hemicellulose is observed in Phase II for RH-4 at 46.66 %. The results in this study indicated that a proper loading amount of catalyst on rice husk is very important to maximize the yield of volatile matter.

1. Introduction

In the next decades, biomass will be the most meaningful renewable energy source as an alternative to fossil fuels (Achinas and Euverink, 2016). Biomass has been recognized as a renewable, inexpensive sustainable feedstock, environmental friendly and received considerable attention from worldwide (Braz and Cmkovic, 2014). The main source of biomass can be divided into three categories, namely agricultural wastes, annual and perennial dry energy grasses, and forestry waste (Loow et al., 2016). Due to the extensive agricultural activities in various countries, agricultural wastes contribute significantly to the yearly global yield of biomass (Loow et al., 2015). For instance, in Malaysia paddy is known to be as an important agricultural crop with annual production rate at approximately 1.47% after oil palm and rubber crop (Shafie et al., 2012). Rice husk is an agricultural waste that produced as a by-product from paddy mill. Thus, the utilization of rice husk through thermochemical conversion would solve disposal problem and generate useful energy as well save the environment (Gauthier et al., 2013). However, the biomass derived raw pyrolysis oil have undesired properties such as highly oxygenated, viscous, corrosive, relatively unstable and chemically very complex that limits its wide applications (Baniasadi et al., 2016). At the same time, raw pyrolysis oils have some tremendous advantages of less toxicity, good lubricity and stronger biodegradation compared to conventional fuel (Mahsa et al., 2016).

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Hence, it is necessity to upgrade the raw pyrolysis oils to extent its applications as fuel engine and as chemical feedstock. Recently, it has been reviewed that catalytic pyrolysis (CP) of biomass as one of the promising method to obtain higher liquid yields with desirable properties of pyrolysis oils compared to hydrodeoxygenation method (Wu et al., 2016). Moreover, CP is considered as cost effective method due to operating under an inert atmosphere and at atmospheric pressure (1 atm) (Mahsa et al., 2016). Namchot and Jitkarnka (2015) recently reviewed on the types of catalyst used in CP of biomass, for example the zeolite material (HZSM-5), noble metal (Gallium) and transition metal (Nickel). They found that the transition metals especially nickel (Ni) as promoter on catalyst has beneficial effect on breaking the strong bonds of chemical compound in pyrolysis vapours. It is revealed that the promoter in catalyst needs a support that plays an important role during the catalytic cracking of pyrolysis vapours (Grams et al., 2015). The support material could modify the catalyst framework in terms of textural properties and acid contents of a catalyst (Xu et al., 2014).

Alumina (Al_2O_3) has been applied as supports for nickel catalyst in this study to yield more liquid product from CP of rice husk. Goenka et al. (2015) proved that alumina is the most widespread supporting carrier of nickel metals due to its chemical and physical stability. They also found that the combination of Ni/Al_2O_3 has greater cracking ability and good aromatization on biomass derived pyrolysis vapours. Although, Ni/Al_2O_3 catalyst is proved as the best candidate for CP of biomass, but the deactivation limits the lifetime span of catalyst. The deactivation is occurred due to the deposition of carbonaceous materials (coke) on catalyst surface during CP, in which limits the diffusion of mass and heat transfer of pyrolysis vapours. Previous study suggested that addition of reducible oxides such as cerium (Ce) in catalyst could gradually reduce coke depositions and prolonged its lifetime (Xu et al., 2014). Hence, nickel-cerium/alumina ($Ni-Ce/Al_2O_3$) catalyst is synthesized for pyrolysis of rice husk in this study.

Thermogravimetric (TGA) is done on biomass to determine change in weight with respect to change in temperature. TGA depend on critical measurements such as weight, temperature and time (Stefanidis et al., 2014). A derivative thermogravimetric (DTG) curve along with TGA curve is needed to determine the apparent weight loss of sample (Lu et al., 2015). From previous literatures, it is found that investigations on the TGA on biomass mostly were studied on EFB, coconut shell and bagasse (Pinto et al., 2015). In addition, only little information is available about catalytic and non-catalytic thermal degradation behaviour on rice husk. To the best of our knowledge, the comprehensive study on the performance of biomass to catalyst weight loading ratio using $Ni-Ce/Al_2O_3$ as catalyst on CP of rice husk via TGA is lacking in literature. Therefore, in this research the rice husk was catalytically pyrolyzed in the TGA and the results obtained were plotted in two separate curves (TGA and DTG curves). From this curves the influence of the rice husk to catalyst ratios (1:0, 1:0.05, 1:0.10, 1:0.15, 1:0.20, 1:0.50 and 1:1) on the pyrolysis behaviour was examined thoroughly.

2. Experiment

2.1 Preparation and characterization of rice husk

The rice husk samples were abundantly available in Malaysia and supplied by PADIBERAS NASIONAL BERHAD (BERNAS). These samples were sun dried and then crushed into smaller size before being dried in an oven at 105 °C for an overnight to remove any moisture content. Then it was sieved to obtain particle sizes of <0.50 mm. The samples were kept in a closed container to minimize the moisture absorption from the surrounding air moisture. The rice husk samples were characterized to obtain the ultimate, proximate and high heating value (HHV). The ultimate analysis was carried out using an Elemental Analyser, Euro EA 3000 using Callidus Software interface Version 4.1 to determine the amount of carbon, hydrogen, nitrogen and sulphur in the feedstock. Oxygen content was then calculated by difference. Proximate analysis was conducted by using TGA to analyse the amount of volatile matter (VM), moisture content (MC) and ash content (AC) in the samples. The fixed carbon (FC) was then obtained by subtracting from 100 the sum of VM, MC and AC. The HHV of biomass was determined by bomb calorimeter. Thus, these characterizations can provide early predictions on the volatile yields and thermal behaviours of rice husk.

2.2 Catalyst preparation

$Ni-Ce/Al_2O_3$ catalyst was prepared via incipient wet impregnation method for the CP of rice husk (RH) in TGA. Cerium (III) nitrate hexahydrate [$Ce(NO_3)_3 \cdot 6H_2O$, purity = 97 %], nickel (II) nitrate hexahydrate [($Ni(NO_3)_2 \cdot 6H_2O$, purity = 99 %] and alumina [Al_2O_3, purity = 99 %] were purchased from Sigma Aldrich. The amount of chemical was fixed by weight percent at 20 wt % of Ni, 5 wt % of Ce and 75 wt % of Al_2O_3. Ni was set at maximum loading of 20 wt % that could easily crack more strong bonds of chemical compounds in pyrolysis vapour of biomass. However, further Ni loading (>20 wt %) might reduce the surface area and acidity of catalyst (Grams et al., 2015). Meanwhile, Ce was only required at small amount to prolonged the catalyst lifetime and protect the active acid sites of catalyst from coke deposits. Alumina plays the major role as catalyst support, in which required higher loading by weight percent than Ni and Ce. Thus, Ni and Ce metals were added into alumina in order to further enhance the overall catalyst activity towards cracking heavy compounds in pyrolysis vapours. All the three chemicals were added accordingly to the ratio into the 80 mL of deionized water (DI) and stirred for 4 h keeping at 80 °C. After 4 h, the catalyst was further dried in an oven at 105 °C for vaporization of water compounds. Later, the catalyst was calcined in a muffle furnace at 750 °C for 4 h and stored in a desiccator. Lastly, the catalyst (solid powder) was sieved to below 125 µm in order to increase the surface area of catalyst.

2.3 Pyrolysis experimental procedure

TGA was used to investigate the weight loss of catalytic rice husk and the evolution of pyrolysis vapour simultaneously. There are six catalytic samples used as feedstock for TGA. These samples is added with different catalyst weight and labelled as follows: RH-2 (1:0.05), RH-3 (1:0.10), RH-4 (1:0.15), RH-5 (1:0.20), RH-6 (1:0.50), and RH-7 (1:1). In addition, rice husk without catalyst is also pyrolyzed in TGA for comparison and labelled as RH-1 (1:0). The prepared samples between 5 mg were first heated to 110 °C and kept at that temperature for about 30 minutes to remove any moisture content. After that the samples were individually heated to a maximum temperature of 700 °C in an inert (N_2) atmosphere flowing at 150 mL/min at fixed heating rate of 10 °C/min.

3. Results and discussions

3.1 Properties and composition of rice husk

The proximate and ultimate analyses of rice husk are shown in Table 1. The ratios of volatile matter, fixed carbon, ash content and moisture are indicators of pyrolysis product yields. The rice husk contains 6.73 wt % of moisture. Previous study conducted on rice husk by Zhang et al. (2016) shows that no moisture contents was developed due to the samples were dried at 105 °C for 12 h. Thus, by allowing biomass to dry for longer period of time cause the moisture contents to completely evolved from biomass and reduce the effect in the heat transfer. Meanwhile, high ash content was observed for rice husk at 17.06 wt %. In addition, the ash content in biomass is directly proportional to the composition of silica content. Fu et al. (2012) investigated on the chemical analysis of ash in rice husk and found that silica forms the main component at about 87.83 wt % of the rice husk. Rice husk has lower HHV of 17.91 MJ/kg could be due to high ash content. The fixed carbon composition in rice husk is higher at 20.33 wt %, which might have potential to produce higher yield of char. The ultimate analysis of rice husk shows that the elemental ratio of carbon, oxygen, hydrogen and nitrogen also has an important effect on pyrolysis product yields. Rice husk is highly oxygenated (55.15 wt %) due to the presence of carbohydrate structure and influenced to have low HHV. Nitrogen and sulfur were found to be in small amount which less than 1 wt % for rice husk that is favourable for pyrolysis oil and syngas production as reported by Friedl et al. (2005).

Table 1: Physicochemical properties of rice husk sample

Analysis		Rice Husk
Proximate analysis (d.b. wt%)	Moisture content	6.73
	Ash content	17.06
	Volatile matter	55.88
	Fixed Carbon^{a}	20.33
	High heating value (HHV) (MJ/kg)	17.91
Ultimate analysis (d.b. wt%)	Carbon	38.22
	Hydrogen	5.88
	Nitrogen	0.68
	Sulphur	0.07
	Oxygen^{a}	55.15

^{a}Calculated by difference, d.b.: dry basis

3.2 Influence of catalyst weight loading on rice husk

The effect of catalyst loading weight ratio on pyrolysis of rice husk was investigated via TGA. The results of TGA analyses on catalytic and non-catalytic pyrolysis of rice husk are shown in Figure 1(a), which shows the mass loss curves (TGA), for all samples and summarized in Figure 2. Figure 1(b) shows the DTG evolution profiles. In addition these TGA-DTG curves were divided into three phases of thermal degradation of rice husk as follows; Phase I for drying and evaporation of light components (25 - 150 °C), Phase II for devolatilization of hemicellulose and cellulose components (150 - 450 °C) and lastly Phase III for lignin decomposition (450 - 700 °C). Meanwhile, the leftover after 700 °C was labelled as solid residues.

It is observed that in the Phase I, all the samples (RH-1 to RH-7) have evolved at different mass loss as shown in Figure 2. For example, the highest mass loss was achieved by the non-catalytic sample, RH-1 (1:0) at 5.48 %. Meanwhile, RH-7 (1:1) sample has evolved the lowest mass loss at 1.03 % among the other samples in Phase I. In other words, high mass loss was evolved in Phase I at absence of catalyst and tends to decrease with increasing catalyst loading weight on rice husk. Moreover, the moisture is mainly composed of water compounds (H_2O) that has boiling point of 100 °C, thus during the Phase I it is assumed that all the moisture contents were easily evaporated. Therefore, it can be proved that apart from moisture evolution, the evaporation of light components is evolved simultaneously from rice husk in the Phase I.

After Phase I, the samples continue to further degrades in Phase II with more mass loss as shown in Figure 2. In addition, the devolatilization of sample at temperature range from 150 - 450 °C can be divided into two sections of degradation; firstly the degradation of hemicellulose components followed by the degradation of cellulose components as can be seen in DTG curve (Figure 1(b)). For instance, all the samples shows similar pattern of curves with first peak represents the hemicellulose degradation and second peak shows the degradation of cellulose. Both peaks developed at almost similar degradation temperature starting from 296 up to 344 °C for investigated samples. However, the peak of each sample has developed at different degradation rate as shown in Figure 1(b). Therefore, catalyst weight loading does not influence the degradation temperature of rice husk but it has tremendous effect on the degradation rate. In all the samples, it is observed that the first peak shoulder degraded at low degradation rate compared to degradation rate of second peak. It might be due to the high cellulose compositions (41.05 wt %) than the hemicellulose compositions (19.05 wt %) found in rice husk reported by Zhang et al. (2016).

Eventually, the peak shoulders decreasing with increasing biomass to catalyst weight loading ratio as shown in Figure 1(b). However, for RH-4 (1:0.15) sample, there is slightly an increment in degradation rate at both hemicellulose peak (0.0035 mg/s) and cellulose peak (0.0083 mg/s). In addition, RH-4 sample also shows an increment in mass loss at 46.66 % as can be seen in TGA plot (Figure 1) in Phase II. Thus, at this ratio the catalyst works best in cracking the cellulose and hemicellulose components as compared to other six samples. This can further be explained with decreasing in mass loss of volatile matter in Phase II with increasing catalyst weight loading ratio. For example, for non-catalytic RH-1 (1:0) sample higher mass loss was observed at 48.67 % than RH-7 (1:1), which was only at 21.82 % of mass loss. In addition, at low catalyst weight loading sample, RH-2 (1:0.05), the mass loss of hemicellulose and cellulose start to decreases to 48.00 % from 48.67 % (RH-1). Therefore, the performance of catalyst slightly starts to reduce in the Phase II for devolatilization of hemicellulose and cellulose with increasing the amount catalyst weight loading on rice husk.

After the Phase II, the biomass continues to degrade in Phase III of lignin decompositions at temperature range of 450 - 700 °C. Lignin is one of the minor components of lignocellulose structure that are found in the rice husk. The lignin components are only starts to degrade at temperature above than 450 °C as shown in Figure 1 due to composed of complex structure than the hemicellulose and cellulose components. There is no peak was observed from DTG plot (Figure 1(b)) in Phase III, therefore the lignin gradually degraded at higher temperature. Higher degradation of lignin is observed for RH-1 sample at about 18.88 % of mass loss, and it summarizes that as increasing the catalyst weight loading, the mass loss at Phase III starts to decreases. After RH-1, the RH-4 sample was found to have higher mass loss (17.54 %) in Phase III. Meanwhile, RH-7 sample has achieved the lowest mass loss in Phase III. Thus an unfavourable effect was observed with lower mass loss in Phase III at equal weight loading of catalyst and rice husk.

Although TG analysis higher than 700 °C was not done in this experiment, it was predicted that thermal decomposition of carbonate compounds was observed at a temperature higher than 700 °C (Goenka et al., 2015). The leftover biomass materials after Phase III are consider as solid residual that has not been degraded within the temperature range from 30 - 700 °C as shown in Figure 1(a). However, the amount of solid residual is influenced by the catalyst weight loading on biomass samples and it can be attributed as char yield percentage. In detail, RH-7 sample has achieved the highest solid residual left at 65.64 % after 700 °C compared to other samples. This might be due to, at high catalyst loading on rice husk, it is more favourable to produce higher char yields. It can be concluded that, an increasing of biomass to catalyst weight loading ratio directly increases the solid residual. Comparatively, the non-catalytic sample (RH-1) has left over at about 26.97 % that indicates as the lowest solid residual percentage.

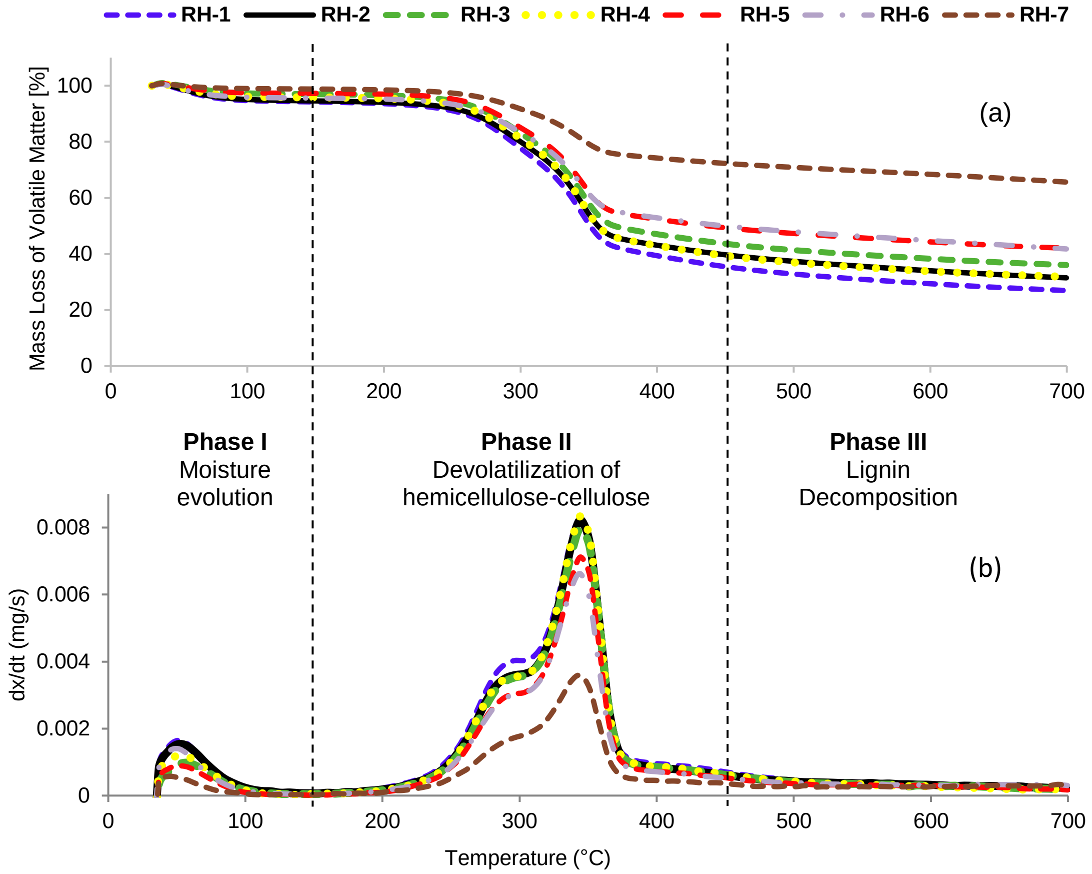

Figure 1: A plot of TGA (a) and DTG (b) for RH-1 to RH-7 samples.

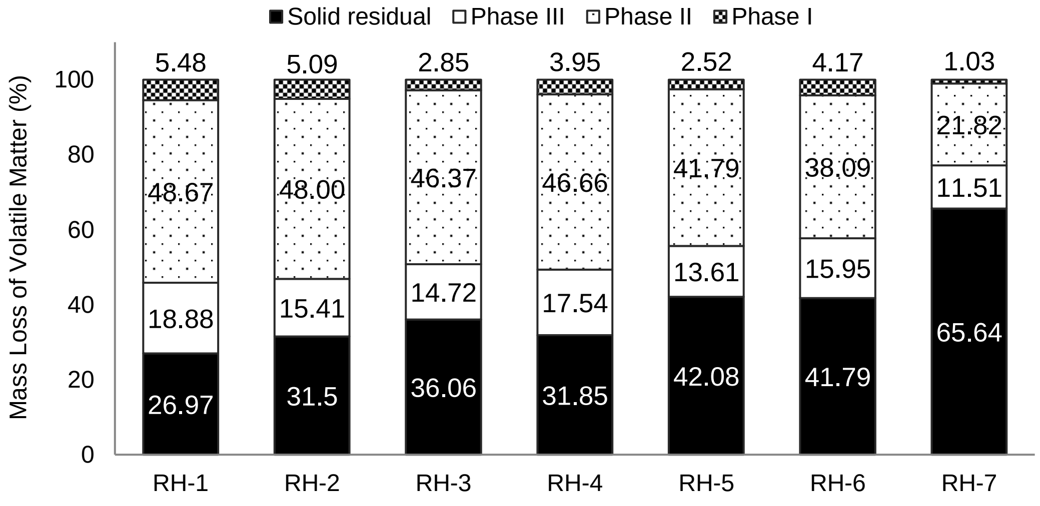

Figure 2: Mass loss of rice husk's volatile matter.

4. Conclusions

The TGA was used to investigate the effect of catalyst weight loading ratio on rice husk. Ni and Ce promoted on Al_2O_3 were prepared by incipient wet impregnation method. It shows that, the catalyst weight ratio does not influence the degradation temperature of rice husk but has an effect on the degradation rate. Therefore, among all the samples it is found that the RH-4 (1:0.15) sample to be the optimal ratio condition for high volatile matter yields from rice husk with mass loss of 46.66 % from TGA plot. Thus, at this ratio the catalyst works best in cracking the cellulose and hemicellulose components compared to other six samples. Hence, it can be concluded that, 20 wt % Ni: 5 wt % Ce: 75 wt % Al_2O_3 catalyst with ratio of biomass to catalyst ratio of 1:0.15 work best in converting the rice husk into volatiles based on the catalyst weight loading on rice husk. The results obtained from this study indicated that the effect of biomass to catalyst weight loading ratio shows good catalytic performance and proper loading amount is very important to enhance the pyrolysis oil production.

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