Catalytic Pyrolysis of Coconut Copra and Rice Husk for Possible Maximum Production of Bio-Oil

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The main objective of the present work is to study the effect of the nickel catalyst on pyrolysis of coconut copra and rice husk via thermo gravimetric analysis (TGA). The optimisation of catalyst weight ratio on biomass is also determined. The sample is pyrolysed from 30 °C up to 700 °C at 10 °C/min of heating rate in nitrogen (N_2) environment flowing at 150 mL/min. The catalyst ($Ni-Ce/Al_2O_3$) was prepared via wet impregnation method, with alumina (Al_2O_3) as support, while cerium (Ce) and nickel (Ni) act as promoter. The samples were prepared accordingly with biomass to catalyst weight loading ratio and labelled as follows; rice husk as RH-2 (1 : 0.15) and RH-3 (1 : 0.50) including coconut copra as CC-2 (1 : 0.15) and CC-3 (1 : 0.50). For comparison, the pyrolysis of coconut copra and rice husk without catalyst also are conducted at the same operating condition and named as CC-1 (1 : 0) and RH-1 (1 : 0). The TGA-DTG curves show that, the presences of catalyst significantly affect the devolatilisation rate of biomass. The highest volatile matter was achieved by CC-2 at 83.27 % compared to RH-2 at only 46.66 %. Although at similar biomass to catalyst weight ratio of 1 : 0.15, the coconut copra is more favourable to yield a high volatile matter than the rice husk. At the same time, both biomass samples specifically CC-3 and RH-3 have achieved the highest in solid residual yield. Overall, the mass loss of volatile matter decreases in the order of CC-2 > CC-1 > CC-3 > RH-1 > RH-2 > RH-3. In summary, the optimum catalyst loading was at CC-2 and RH-2 that work best to degrade at the highest mass loss of volatile, in which attributes to higher yield of pyrolysis oil.

1. Introduction

Biomass from agricultural waste is considered as one of the renewable energy sources with the highest potential to contribute to the energy needs of modern society (Vasilkovová et al., 2014). In South East Asian countries, specifically Malaysia has established targets for the application of fuels generated from agricultural wastes as an alternative source of energy. Previous study on agricultural production shows that coconut and paddy plantations are among the major agricultural crops grown in Malaysia (Shafie et al., 2012). The solid wastes from these two agricultural sectors produced in large quantities which have no economic values. The utilisation of biomass is very important in order to preserve the environment from the disposal wastes. As reviewed by Zhang et al. (2013), the thermochemical conversion also known as pyrolysis has great potential to generate valuable product from biomass in the form of energy such as bio-char (solid), pyrolysis oil (liquid product) and pyrolysis gas (a mixture of gas product). Another advantage of pyrolysis is it could yield more liquid products

than solid and gas products. Apart from the advantages of biomass pyrolysis, the produced raw pyrolysis oil from biomass has several shortcomings that limit its wide applications such as highly oxygenated, viscous, corrosive, relatively unstable and chemically very complex (Baniasadi et al., 2016). At the same time, the generated raw pyrolysis oils have valuable advantages including less toxicity, good lubricity and stronger biodegradation. It is therefore necessary to upgrade the raw pyrolysis to extent its applications as transportation fuels and as gasoline enhancers in petrochemical industry. Selecting a proper upgrading technique is crucial decision due considering on several factors like costing, efficiency and easy handling of the system. Many researchers studied on the best upgrading method to enhance the physical and chemical properties of raw pyrolysis oils (Arregi et al., 2015). It is found that catalytic cracking method to be most promising method with low cost, higher liquid product yield and straightforward system (Zhang et al., 2013). The catalytic cracking only works at best with suitable catalyst structure to achieve the desired products.

It has been shown that Ni/Al_2O_3 based catalysts are active and selective for conversion of biomass into pyrolysis oils with improved qualities of low oxygenated compounds (Chitsazan et al., 2016). Similar study by Chen et al. (2016) found that Ni loading on Al_2O_3 has greatly improved the product distribution due to NiO as promoter is well dispersed on the surface of support (Al_2O_3). In the absence of catalyst, the concentration of CO and H_2 was at 45 vol% and 18 vol%, while with Ni/Al_2O_3 catalyst, the concentration of H_2 significantly increased to 45 vol% and CO concentration reduced to 30 vol%. This might be due alumina alone itself has greater cracking ability and aromatisation towards the product distribution. Zhang et al. (2013) has reviewed that, nickel (Ni) is most commonly used as catalyst in upgrading process of catalytic pyrolysis of biomass due to their higher reactivity, low cost and high availability. Presences of catalyst in pyrolysis of biomass will increase the coke yield either on external or internal surfaces of catalyst. Coking on catalyst lead to deactivation of catalyst and reduce its lifetime due to blockage on active sites of catalyst by intermediate products of pyrolysis. Previous study proved that the presence of cerium oxide can be helpful in avoiding metal sintering on the catalyst surface (Xu et al., 2014). Similar study by Cheah et al. (2013) found that, cerium was used due its high redox property that able to prevent coking on catalyst. By considering the above mentioned problem, it is decided to incorporate cerium (Ce) as supports for Ni/Al_2O_3 catalyst in this study for pyrolysis of coconut copra and rice husk to increase the catalyst lifetime. Stefanidis et al. (2014) investigated the catalytic pyrolysis of biomass using thermogravimetric analyser (TGA) and found that it is more convenient to predict thermal behaviours. Generally, the TGA data is plotted with y-variables of weight change rates and x-variables of temperatures, in which easy to understand the thermal degradation behaviours. Thus, these curves are used to determine the apparent weight loss of sample with increasing temperature.

The comprehensive study on the optimum weight ratio loading of catalyst on biomass using $Ni-Ce/Al_2O_3$ as catalyst on catalytic pyrolysis of coconut copra and rice husk via thermo gravimetric analysis (TGA) is lacking in literature. In this research coconut copra and rice husk was catalytically pyrolysed in TGA at different weight biomass to catalyst ratio (1 : 0, 1 : 0.15 and 1 : 0.50). The TGA results were plotted in two separate curves (TG and DTG curves). The curves were divided into three phases of thermal degradation to investigate on the thermal behavior of catalytic pyrolysis of biomass. Finally, the optimum value of the biomass to catalyst ratios was discussed.

2. Materials and methods

2.1 Preparation and characterisation of biomass

Coconut copra and rice husk were abundantly found in Malaysia. Coconut copra samples were collected from local producers while, rice husk samples were supplied by Padiberas Nasional Berhad (BERNAS). These samples were dried under sunlight before drying at 105 °C in an oven for an overnight to reduce its moisture contents <10 wt%. Then, it was sieved below than 0.50 mm. The dried samples were kept in a desiccator to prevent moisture absorption from the surrounding humidity. After that, the biomass samples were characterised 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, while oxygen was then calculated by difference. Proximate analysis was conducted using thermogravimetric analysers (TGA) to analyse the amount of volatile matter (VM), moisture content (MC) and ash content (AC), while the fixed carbon (FC) was then obtained by simple subtracting calculation (FC=100-VM-MC-AC). The HHV of biomasses were determined by using bomb calorimeter.

2.2 Catalyst preparation

The $Ni-Ce/Al_2O_3$ catalyst was prepared by wet impregnation method for the catalytic pyrolysis of coconut copra (CC) and rice husk (RH) in TGA. Cerium (III) Nitrate Hexahydrate [$Ce(NO_3)_3 \cdot 6H_2O$, 97 %], Nickel (II) Nitrate Hexahydrate [($Ni(NO_3)_2 \cdot 6H_2O$, 99 %] and Alumina [Al_2O_3, 99 %] were purchased from Sigma Aldrich. The amount chemical weight was fixed at 20 wt% of Ni, 5 wt% of Ce and 75 wt% of Al_2O_3. All the three chemicals

were added accordingly to the ratio into the 80 mL of deionised 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 vaporisation of water compounds. The catalyst was calcined in a muffle furnace at 750 °C for 4 h and stored in a desiccator. The catalyst (solid powder) was sieved to below 125 µm in order to increase the surface area of catalyst.

2.3 TGA-Pyrolysis experimental procedure

The samples for TGA were prepared prior accordingly with biomass to catalyst weight loading ratio. There are six samples were prepared at different weight loading and labelled as follows: CC-1 (1 : 0), RH (1 : 0), CC-2 (1 : 0.15), RH-2 (1 : 0.15), CC-3 (1 : 0.50), and RH-3 (1 : 0.50). Thermogravimetric analyser (TGA) was used to investigate the weight loss of catalytic pyrolysis of biomass and the evolution of pyrolysis vapor simultaneously. The prepared samples approximately 5 mg were first heated to 110 °C and kept at that temperature for about 30 min to remove remaining moisture contents. After that the samples were individually heated to a maximum temperature of 700 °C in nitrogen (N_2) atmosphere flowing at 150 mL/min at fixed heating rate of 10 °C/min.

3. Results and discussions

3.1 Properties and compositions of coconut copra

The feedstock samples were characterised to obtain the ultimate, proximate and high heating value (HHV) as shown in Table 1. The moisture content found in biomass must be removed through evaporation so that heat supply can easily propagated into the biomass structure. The moisture contents of rice husk and coconut copra were almost in similar at 6.73 wt% and 6.10 wt%. Zhang et al. (2013) found that no moisture content was developed from rice husk during the process due to the samples was dried at 105 °C for 12 h. Allowing biomass to dry for long period of time cause the moisture contents to completely evolved from biomass. Coconut Copra has fewer ash content (0.57 wt%) than the rice husk (17.06 wt%). The higher ash content in rice husk is due to higher silica components. Fu et al. (2012) investigated on the chemical analysis of ash in rice husks and found that, silica forms as the main component of ash at 87.33 wt% in the rice husk. Rice husk contains undesirable high amount of oxygen compositions at 38.09 wt% that might influence to generate low HHV (17.91 MJ/kg). Widayatno et al. (2016) reported that biomass materials that generate low HHV is due to the presence of large amount oxygen compounds. Apart of that, rice husk contains the highest fixed carbon composition at 20.33 wt% than that of coconut copra, which is only 17.59 wt%. Demirbaş (2003) investigated on the relationship between lignin and fixed carbon contents of biomass samples. It is reported that lignin contents are a function of fixed carbon in biomass and higher amount of fixed carbon will increase the char yield and decrease the liquid product yield. The volatile matter (VM) is the main concerned in this study, because it can be converted into pyrolysis oil and gases during the pyrolysis process. Among the both samples, coconut copra has the highest volatile matter at 75.74 wt% than rice husk at only 55.88 wt%. It is expected that coconut copra will produce more pyrolysis oil as compared to rice husk. Apart from proximate analysis, ultimate analysis is also taken into account to study the amount of other elements such as carbon, hydrogen, oxygen, nitrogen and sulphur in the biomass. High compositions of carbon and hydrogen with low oxygen compositions are more preferred to obtain more aromatic liquid products. The study shows that 55.84 wt% of carbon and 10.17 wt% of hydrogen contents were found in coconut copra that explains its higher calorific value in coconut copra. The composition of carbon and oxygen in rice husk was at 38.33 wt% and 38.09 wt% shows almost similar values. It might be produced low quality pyrolysis oils (high acidity, corrosive, thermally unstable).

Table 1: Physicochemical properties of biomass

Analysis		Coconut Copra	Rice Husk
Proximate analysis (d.b. wt%)	Moisture content	6.10	6.73
	Ash content	0.57	17.06
	Volatile matter	75.74	55.88
	Fixed Carbon[a]	17.59	20.33
	High heating value (HHV) (MJ/kg)	30.22	17.91
Ultimate analysis (d.b. wt%)	Carbon	55.84	38.22
	Hydrogen	10.17	5.88
	Nitrogen	1.18	0.68
	Sulphur	0.12	0.07
	Oxygen[a]	32.69	55.15

[a]Calculated by difference, d.b.: dry basis.

3.2 Optimisation of catalyst loading on pyrolysis of biomass

The influence of catalyst weight loading ratio on pyrolysis of rice husk and coconut copra was investigated via TGA. Pyrolysis of biomass was divided into three phases; vaporisation of moisture and light components (Phase I) developed at temperature below 150 °C, followed by Phase II of devolatilisation of hemicellulose and cellulose at temperature range of 150 - 450 °C and finally the lignin decomposition denoted as Phase III that degraded at above 450 °C as shown in TG-DTG plot. The weight loss curves of thermo gravimetric (TG) and derivative thermo gravimetric (DTG) evolution profiles for all investigated samples were plotted in Figure 1a and 1b. Leftover of biomass materials after 700 °C was labelled as solid residual.

In Phase I, all the samples developed the curves with less than 5.50 % of mass loss. It considered as negligible amount of mass loss. In general, the moisture is fully composed of water molecules that can easily evaporate once reached its boiling point of 100 °C. At the same time some light components of biomass might evaporate together when further increased the temperature up to 150 °C. increasing the catalyst weight loading on coconut copra has influenced to reduce the amount of mass loss during Phase I. without catalyst, CC-1 (1 : 0) sample has achieved about 3.57 % of total mass loss and it gradually decreases to 1.11 % when the catalyst loading increased as in CC-2 (1 : 0.15) and further increase of catalyst has drastically reduced mass to 0.11 % at CC-3. Loading more catalysts does not show any beneficial effect on coconut copra. In contrast, rice husk samples specifically RH-2 has reduce the mass loss from RH-1 of 5.48 % to 3.95 %, but a little increase in catalyst weight (RH-3) has significantly increased to 4.17 % of mass loss.

After the Phase I, the biomass continues to degrade in Phase II with more mass loss observed as shown in Figure 1 and 2. Hemicellulose and cellulose is known to be the major lignocellulosic components found in biomass, in which requires a very high temperature to fracture the complex bonds. These components were degraded and generate volatile matter in the temperature range of 150 to 450 °C. For example, in DTG plot, two peaks were developed in Phase II; first peak indicate the hemicellulose degradation and second is for cellulose degradation. The first peak shoulder degrades at lower degradation rate than the degradation rate of the second peak as in RH-1, RH-2, RH-3 and CC-1 samples. It might be due to the rice husk contain more cellulose composition than hemicellulose at 34.10 wt% and 27.30 wt% as reported by Goenka et al. (2015). CC-2 and CC-3 samples only exhibit single peak, which both attained at 372 °C. This could be the influence of catalyst activity on thermal behaviour of coconut copra that promotes both hemicellulose and cellulose degrade faster and make the peak overlap and forms only in one single peak. Catalyst weight ratio does not influence the degradation temperature of rice husk and coconut copra but it strongly influences the degradation rate of biomass. The performance of catalyst can be observed for RH-2 and CC-2 where there is little increment in the mass loss for coconut copra at 83.27 % and vice versa for rice husk at 46.66 %. This might be due to the high silica content in rice husk that react with the nickel from catalyst and form amorphous phases that prevent from a complete reaction. CC-2 has also achieved the highest degradation rate at 0.0107 mg/s than the other samples as seen in DTG plot. This catalyst has shown good performance in cracking hemicellulose-cellulose structure in coconut copra than the rice husk. Further increase in catalyst weight loading on coconut copra at ratio of 1 : 0.50 (CC-3) drastically decreased to 49.89 % of mass loss. Catalyst reactivity starts to reduce slowly on coconut copra with increasing catalyst amounts in Phase II.

Finally, the biomass is continued to further degrade the lignin components that are more complex than the hemicellulose-cellulose structure. There is no peak was observed as can be seen in DTG plot (Figure 1b) in Phase III for both biomasses, thus the lignin gradually degraded to high temperature until 700 °C. The highest mass loss of lignin degradation was observed for RH-1 at 18.88 %, and as the catalyst loading increases the lignin mass loss decreases as such RH-2 (17.54 %) and RH-3 (15.95 %). Similar trend of decreasing in mass loss was also observed for coconut copra sample in Phase III.

After Phase III completed the leftover biomass materials were considered as solid residual that has not been degraded within the temperature range from 30 to 700 °C as shown in Figure 1 (a and b). In this research, it is mainly focusing on optimising the yield of volatile matter by altering catalyst weight loading. The char content increases with increasing catalyst weight loading on coconut copra and rice husk. The non-catalytic sample, RH-1 and CC-1 has left 26.97 % and 2.18 % of solid residual. At the highest loading, RH-3 and CC-3 samples shows the highest residual content left at 41.79 % and 41.56 % and this amount is the mixture of solid char and unburnt catalyst. It can be concluded that, CC-2 and RH-2 ratio work best in catalytic cracking of biomass. The CC-2 shows the beneficial effect towards higher yield of volatile matter, in which attributes to the liquid oil production.
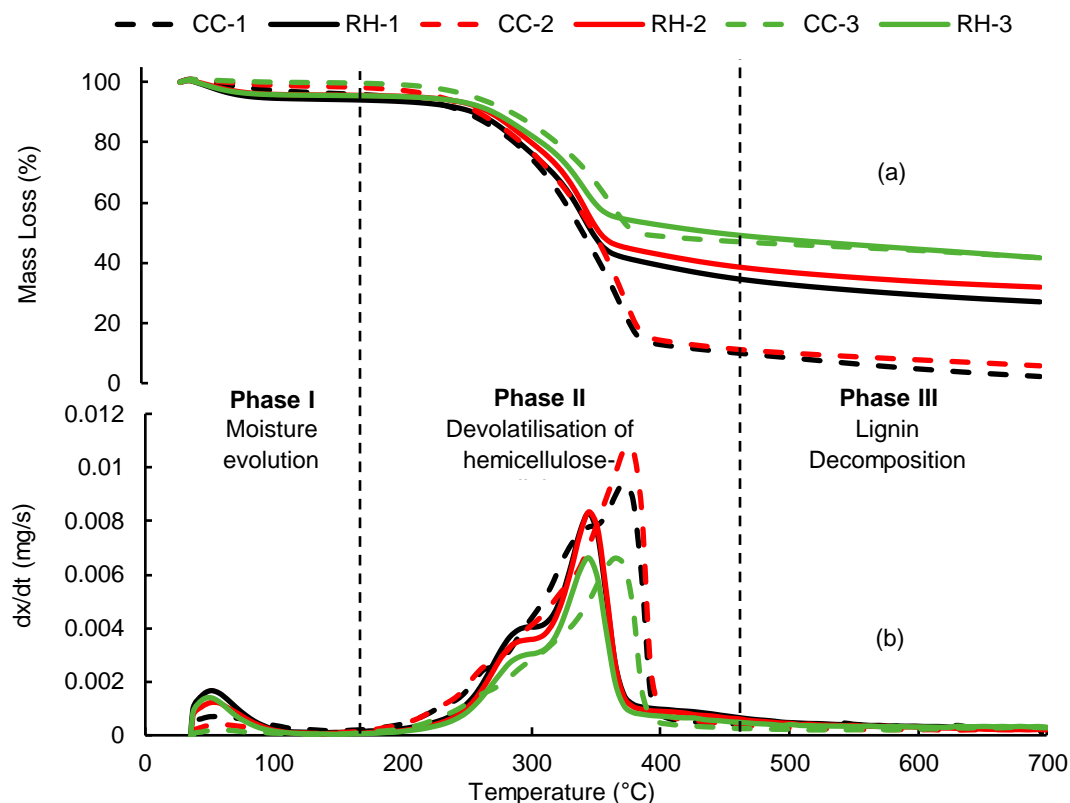
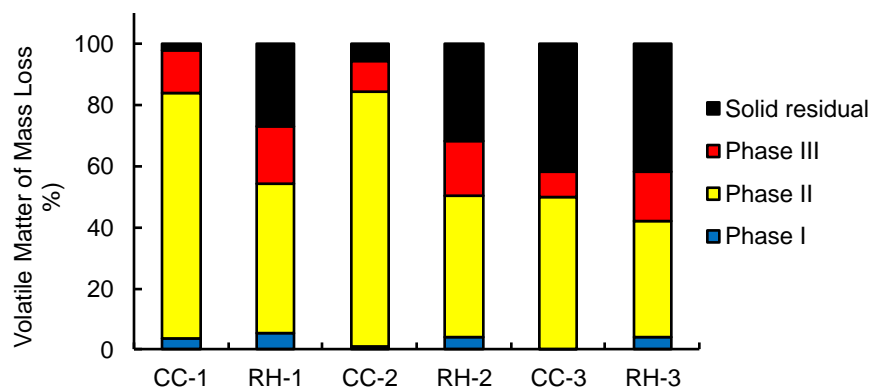Figure 1: A part of TGA (a) and DTG (b) for biomass samples

Figure 2: Volatile matter of mass loss for biomass

4. Conclusions

The thermogravimetric analysis (TGA) was successfully conducted to investigate the influence of catalyst weight loading on pyrolysis of coconut copra and rice husk. The results of the performed studied revealed that Ni-Ce/Al$_2$O$_3$ are strongly active in pyrolysis of both coconut copra and rice husk. The non-catalytic sample of CC-1 has achieved high mass loss in Phase II at 80.33 % than RH-1 at 48.67 %. It shows that coconut copra has high volatility and favourable for liquid oil production. The optimum performance of catalyst can be observed for RH-2 and CC-2 where there is little increment in the mass loss for coconut copra at 83.27 % and decrease in rice husk at 46.66 %. CC-2 has also achieved high degradation rate at 0.0107 mg/s from DTG curve than other samples. This catalyst has efficiently cracked more hemicellulose-cellulose components in coconut copra than rice husk. RH-3 and CC-3 shows almost similar solid residual content at 41.79 % and 41.56 %. The optimum

ratio was found at CC-2 and RH-2 (1 : 0.15) samples that work best in all three phases of thermal degradation on coconut copra and rice husk.

Acknowledgements

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