

The Effect of Catalyst Loading (Ni-Ce/Al₂O₃) on Coconut Copra Pyrolysis via Thermogravimetric Analyser

Vekes Balasundram^a, Norazana Ibrahim^{*a}, Rafiziana Md. Kasmani^a, Mohd Kamaruddin Abd Hamid^b, Ruzinah Isha^c, Hasrinah Hasbullah^d, Roshafima Rasit Ali^e

^aClean and Energy Research Group (CLAERG), Faculty of Chemical and Energy Engineering, Universiti Teknologi Malaysia (UTM), 81310 UTM Johor Bahru, Johor, Malaysia.

^bProcess Systems Engineering Centre (PROSPECT), Research Institute for Sustainable Environment, Universiti Teknologi Malaysia (UTM), 81310 UTM Johor Bahru, Johor, Malaysia.

^cFaculty of Chemical & Natural Resources Engineering, Universiti Malaysia Pahang, 26300, Gambang, Pahang, Malaysia.

^dAdvanced Membrane Technology Centre (AMTEC), Faculty of Chemical and Energy Engineering, Universiti Teknologi Malaysia (UTM), 81310 UTM Johor Bahru, Johor, Malaysia.

^eMalaysia-Japan International Institute of Technology (MJIIT), Universiti Teknologi Malaysia, Jalan Sultan Yahya Petra, 54100 Kuala Lumpur, Malaysia.

norazana@utm.my

The aim of this study is to investigate the influence of catalyst weight loading on pyrolysis of coconut copra via thermogravimetric analyser (TGA). The pyrolysis process is conducted up to 700 °C at a heating rate of 10 °C/min in nitrogen (N₂) atmosphere flowing at 150 mL/min. The catalyst was successfully prepared via wet impregnation method, with alumina (Al₂O₃) used as support, while cerium (Ce) and nickel (Ni) act as promoter. The feedstock samples for TGA were prepared accordingly with biomass to catalyst weight loading ratio as follows: CC-1 (1 : 0.05), CC-2 (1 : 0.10), CC-3 (1 : 0.15), CC-4 (1 : 0.20), CC-5 (1 : 0.50), and CC-6 (1 : 1). For comparison, the pyrolysis of coconut copra without catalyst is also determined at the same operating condition and labelled as CC-7 (1 : 0). The TGA-DTG curves shows that, the presences of catalyst significantly affect the degradation rate of volatile matter than lignin degradation. In this study, the CC-3 sample has achieved high mass loss at 83.27 % and also high degradation rate at 0.0107 mg/s. For lignin decomposition, it shows that, CC-1 to CC-6 samples has achieved lignin mass loss percentage below 12.7 %. The non-catalytic sample (CC-7) has exhibited 80.33 % of volatile matter of mass loss and 13.92 % of lignin mass loss. The optimum catalyst loading was observed at 1 : 0.15 (CC-3) that work best to degrade volatile matter at highest mass loss, in which attributes to higher yield of pyrolysis oil.

1. Introduction

Biomass applications on the generation of heat and power are of increasing importance. It is also has been recognised as a renewable, sustainable feedstock and received considerable attention around the world (Arumugasamy et al., 2016). In Malaysia, coconut is known to be the fourth important agricultural crop with annual production rate at approximately 6.34 % after oil palm, rubber and paddy (Shafie et al., 2012). Meanwhile, coconut copra is an agricultural waste that produced as a by-product from coconut industry. Therefore, the utilisation of this particular waste through thermochemical conversion or also known as pyrolysis process would solve disposal problem and generate useful energy as well save the environment (Gauthier et al., 2013). Apart from solving the aforementioned problems, pyrolysis of biomass has potential to generate three types of valuable products such as solid (pyrolysis char), liquid (pyrolysis oil) and gas (a mixture of pyrolysis gas) (Volpe et al., 2016). The produced raw pyrolysis oil from biomass is highly oxygenated, viscous, corrosive, relatively unstable and chemically very complex that limits its wide applications (Baniasadi et al., 2016). At the same time, this raw pyrolysis oils have some tremendous advantages: 1) less toxicity, 2) good lubricity and 3) stronger biodegradation. It is necessity to upgrade the raw

pyrolysis oils to extent its applications as fuel engine and gasoline enhancers in petrochemical industry. It has been reviewed that catalytic cracking as one of the promising method to obtain a higher liquid yield with improved physical and chemical properties of pyrolysis oils than hydrodeoxygenation (Gollakota et al., 2016). Catalytic cracking is considered as inexpensive method due to operating under a nitrogen flow and at atmospheric pressure, while hydrodeoxygenation required a hydrogen flow and high pressure that has an additional cost (Gollakota et al., 2016).

Rezaei et al. (2014) reviewed on the types of catalyst used in catalytic cracking of pyrolysis vapor, for example the zeolite materials (HZSM-5, MCM-41, SBA-15, and β -zeolite) and noble metals (Ga, Pd, and Pt) and base metals (Ni, Cu, and Fe). There are many references in the literatures found that transition metals especially nickel (Ni) as promoter on catalyst to be effectively break the bridge bonds in the pyrolysis vapours (Veses et al., 2015). Nickel based catalysts has tendency to increase gas yield and enhance the quality of liquid phase. Similar study by Kantarelis et al. (2014) pointed out that nickel is a reactive metal that increases the H_2 production and reduce the oxygenated compounds during catalytic pyrolysis vapours of biomass performed at 450 °C in a bubbling-bed reactor. It is revealed that the promoter in catalyst needs a support that plays an important role during catalytic cracking and increasing the performance of catalytic pyrolysis of biomass (Grams et al., 2015). The supports may modify the catalyst framework in terms of surface area of the catalyst, its acidity, pore size and volume (Veses et al., 2015).

By considering the above mention modification, alumina (Al_2O_3) has been applied in this study as supports for nickel catalyst in pyrolysis of coconut copra to yield more liquid product. Ferella et al. (2013) proved that alumina is the most widespread supporting carrier of nickel metals and combination of Ni/Al_2O_3 has greater cracking activities and good aromatisation over pyrolysis vapours. Ni/Al_2O_3 catalyst is proved as the best candidate for catalytic pyrolysis of biomass, but the deactivation of catalyst reduces the catalyst's lifetime. This deactivation is due to the blockage of carbonaceous materials deposited on the catalyst surface either on external surface or internal pore channels of catalyst. Previous study suggested that reducible oxides such as cerium (Ce), reduce the coke depositions and increase the catalyst lifetime (Xu et al., 2014). Many researchers investigated the catalytic pyrolysis of biomass using thermogravimetric analyser (TGA) equipment due to easy handling and simplicity (Stefanidis et al., 2014). They also found that, the obtained data from TGA are easy to interpret the thermal behaviours of catalytic pyrolysis of biomass. In detail, the TGA data is presented as the rate of weight change curves with respect to change in temperature; thermogravimetric curve (TGA) and derivative curve (DTG). These curves are used to determine the apparent weight loss of sample with increasing temperature. Previously it is reported that no significant differences between the experimental and calculated TGA curves (Wang et al., 2011). TGA is also preferred for kinetic calculations such as the activation energy, pre-exponential factor and order of reaction of sample.

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 catalytic pyrolysis of coconut copra via thermogravimetric analysis (TGA) is lacking in literature. In this research the coconut copra was catalytically pyrolysed in the thermogravimetric analyser and the results obtained were plotted in two separate curves (TG and DTG curves). From this curves the influence of the coconut copra 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. Materials and methods

2.1 Preparation and characterisation of biomass

Coconut copra is easily available in Malaysia and is collected from local producers. This sample was first sun dried before being dried in an oven at 105 °C for an overnight to reduce moisture content < 10 wt%. Then it was sieved to obtain particle sizes of less than 0.50 mm. The dried samples were kept in a closed container to minimise moisture absorption from the surrounding humidity. The biomass sample was characterised to obtain the ultimate, proximate and high heating value (HHV). The ultimate analysis was carried out by 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 using thermogravimetric analyser (TGA) to measure the amount of volatile matter (VM), moisture content and ash content in the samples. Later, the fixed carbon was then obtained by subtracting from 100 the sum of volatile, ash and moisture content. The HHV of biomass sample was determined using bomb calorimeter. These characterisations can provide early predictions on the amount of pyrolysis oils yield and its characteristics.

2.2 Catalyst preparation

The catalytic material used for pyrolysis experiments via TGA is a $Ni-Ce/Al_2O_3$ which prepared by wet impregnation method. A ratio of 20 wt% Ni, 5 wt% Ce and 75 wt% Al_2O_3 was used to formulate a $Ni-Ce/Al_2O_3$.

Cerium (III) Nitrate Hexahydrate [$\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, 97 %], Nickel (II) Nitrate Hexahydrate [$[(\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O})]$, 99 %] and Alumina [Al_2O_3 , 99 %] were purchased from Sigma Aldrich. First, 20 wt% of Ni, 5 wt% of Ce and balance Al_2O_3 were added to the 80 mL of deionised water (DI) and stirred for 4 h keeping at 80 °C. After 4 h, the catalyst was dried in an oven at 105 °C to evaporate the water. Finally, the catalyst was calcined in a muffle furnace at 750 °C for 4 h and stored in a desiccator. Prior to use, the catalysts were grinded and sieved to the size of 125 μm to ensure high surface area per unit mass that could enhances the product distribution.

2.3 Pyrolysis experimental procedure

Thermogravimetric analyser (TGA) was used to investigate the thermal degradation behaviour of catalytic pyrolysis of coconut copra at different catalyst weight loading. There are six samples used as feedstock for TGA. These samples are added with different catalyst weight loading and labelled as follows: CC-1 (1 : 0.05), CC-2 (1 : 0.10), CC-3 (1 : 0.15), CC-4 (1 : 0.20), CC-5 (1 : 0.50), and CC-6 (1 : 1). Coconut copra without catalyst is also pyrolysed in TGA for comparison and labelled as CC-7 (1 : 0). The prepared samples approximately 5 mg were first heated to 110 °C and kept at that temperature for about 30 min to remove any moisture content from the sample. 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 compositions of coconut copra

The proximate and ultimate analysis of coconut copra is summarised in Table 1. The initial moisture content in coconut copra is recorded at 6.10 wt% and it has a very low ash content at 0.57 wt%. The ash content is proportional to the metal oxide compositions such as Na_2O , MgO , Al_2O_3 , and SiO_2 found in biomass material (Werkelin et al., 2005). Thus, it concludes that coconut copra has low amount of metal oxides that directly influence to have low ash content. Recently, Widayatno et al. (2016) found that the biomass materials with low HHV is due to the presence of highly oxygenated compounds. Biomass sample in this study has a very high HHV of 30.22 MJ/kg that might be due to the low ash and oxygen contents at 0.57 wt% and 32.13 wt% respectively. Previous study by Demirbaş, (2003) investigated on the relationship between lignin contents and fixed carbon content of biomass samples. It is reported that, lignin content is a function of fixed carbon in biomass samples, in which the amount of fixed carbon is solely, depends on the lignin content. In this study, it is observed coconut copra has relatively high value of fixed carbon of 18.58 wt% that might be due to high lignin compositions in coconut copra. Apart from that, coconut copra contains a very high volatile matter at 75.74 wt% and this would give high volatility and reactivity advantages, which is suitable for higher yield of pyrolysis oil. The elemental compositions of carbon (C), hydrogen (H) and oxygen (O) are the main components measured from ultimate analyses of coconut copra. This ultimate analyses shows that 55.84 wt% of carbon and 10.17 wt% of hydrogen contents in coconut copra that explains the higher calorific value found in coconut copra (30.22 MJ/kg). The presence of other elements such as nitrogen and sulphur were at 1.18 wt% and 0.12 wt%, that can be considered as negligible compositions.

Table 1: Physicochemical properties of coconut copra

Analysis	Coconut Copra	
Proximate analysis (d.b. wt%)	Moisture content	6.10
	Ash content	0.57
	Volatile matter	75.74
	Fixed Carbon ^a	17.59
	High heating value (HHV) (MJ/kg)	30.22
Ultimate analysis (d.b. wt%)	Carbon	55.84
	Hydrogen	10.17
	Nitrogen	1.18
	Sulphur	0.12
	Oxygen ^a	32.69

^aCalculated by difference, d.b.: dry basis.

3.2 Catalyst performance on pyrolysis of coconut copra

The influence of catalyst weight loading on pyrolysis of coconut copra was investigated via TGA. TGA-DTG curves show the weight loss and the derivative thermogravimetric evolution profiles of biomass as illustrated in Figure 1. The thermal degradation of biomass is divided into three phases; Phase I is referred to as moisture

and light components evolution that occurred at temperature below 150 °C, Phase II referred as degradation of hemicellulose-cellulose that attained at temperature range of 150 °C to 450 °C and finally lignin decomposes slower, over a broader temperature range (450 – 700 °C) which denoted as Phase III (Gauthier et al., 2013).

The results of Phase I show that, CC-1 (1 : 0.05) and CC-5 (1 : 0.50) samples have achieved the lowest moisture and light component mass loss percentage at 0.28 % and 0.11 %. CC-2 (1 : 0.10), CC-3 (1 : 0.15), CC-4 (1 : 0.20) and CC-6 (1 : 1) samples were observed to have an almost similar moisture loss between 1.03 % up to 1.56 %. Overall, based on TG-DTG plot the mass loss was evolved at less than < 5 % for all investigated samples in the Phase I. It is clearly can be stated that the influence of biomass to catalyst ratio does not play any significant role in the Phase I.

After the Phase I, the biomass continues to degrade in Phase II with more mass loss observed as can be seen in Figure 1 and Figure 2. In general, the main components of biomass are hemicellulose and cellulose, in which required a very high temperature to fracture the chemical bonds of this complex structured component. In Phase II the hemicellulose and cellulose of biomass starts to devolatilise between 150 and 450 °C for all the investigated samples. As illustrated in Figure 1(b), two peaks were observed for CC-1 and CC-7 samples at 0.0078 mg/s and 0.0082 mg/s respectively for first peak and 0.0097 mg/s and 0.0098 mg/s for second peak. In details, the first peak indicates the hemicellulose degradation followed by the second peak showing the cellulose degradation. These peaks start to overlap together and degrade in a single peak for CC-2 to CC-6 samples. This might be due to the influence of catalyst weight loading on coconut copra that enhances and alters the degradation of hemicellulose-cellulose in single peak degradation during pyrolysis. Notably, degradation peak area as plotted in Figure 1(b) attributed to the volatile matter that has evaporated from biomass. At the same time, the single degradation peak was developed at similar degradation temperature of 372 °C for CC-2 to CC-6 samples. Increasing catalyst weight loading on biomass has no effect on the degradation temperature of coconut copra, but it significantly affects the degradation rate of cellulose and hemicellulose compositions. For example, after the CC-3 sample ratio the degradation peak starts to gradually decrease to 0.0097 mg/s, 0.0066 mg/s and 0.0065 mg/s for CC-4, CC-5 and CC-6 respectively. Overall, it can be observed that CC-3 has achieved the highest degradation rate at 0.0107 mg/s as compared to the other samples. The highest mass loss of Phase II was achieved by CC-3 at 83.27 % followed by CC-1 and CC-7 at 82.22 % and 80.33 %. CC-2 with low catalyst weight ratio, but based on the mass loss results from Figure 1(a) and 2 it has higher ability to crack more cellulose-hemicellulose structures at 78.74 % compared to high catalyst loading sample specifically CC-4, CC-5 and CC-6 which were only at 69.21 %, 49.89 % and 44.72 %. From the above-mentioned results, it clearly can be stated that after CC-3 ratio the volatile matter of mass loss starts to decrease with increasing catalyst loading. Based on the TG-DTG results of Phase II, among the entire investigated sample, CC-3 shows the promising results in terms of achieving the highest volatile matter of mass loss that can contribute to higher pyrolysis oil yield.

After the Phase II, the coconut copra continues to degrade in Phase III of lignin decompositions at temperature range of 450 up to 700 °C. Lignin is one of the major components of lignocellulosic structure that are found in the biomass materials. The lignin components are only starts to degrades at temperature above than 450 °C as plotted in Figure 1(a) and 1(b) due to more complex structure than the hemicellulose and cellulose components. In Phase III of lignin decomposition, it shows the non-catalytic sample (CC-1) has achieved the highest mass loss among the samples in this phase (13.91 %). Apart from that, several samples such as CC-5, CC-6 and CC-7 samples were found to have almost similar mass loss ranging from 8.44 to 8.86 %. Low catalyst loading sample specifically CC-2 has degraded at the highest mass loss (12.06 %) among the catalytic samples. Increasing catalyst loading on biomass does not show any significant results in phase III.

The TG analysis on biomass materials were only conducted up to until 700 °C, therefore after Phase III the leftover biomass materials are 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 1(b). In this research, it is mainly focusing on the higher yield of volatile matter with least solid residual leftover. From Figure 2, the lowest solid residue was obtained by CC-7 (non-catalytic) at 2.18 % of mass loss. Among the catalytic samples it is observed that CC-3 has achieved the lowest solid residue value (5.70 %). Increasing catalyst loading on biomass gives negative effects in terms of yielding more solid residue. For example, the CC-7 sample shows the highest solid residue at 45.59 % and even higher than mass loss of Phase II at 44.72 %.

It can be concluded that, CC-3 sample is the optimum biomass to catalyst ratio that gives maximum volatile matter and it works best in cracking cellulose-hemicellulose composition and achieved maximum mass loss at Phase II that attributes for higher pyrolysis oil production. The CC-3 shows the favourable effect on cracking of lignin content in biomass materials with a very low solid residual. Overall from the investigation, the increasing performance of catalyst weight loading ratio on pyrolysis of coconut copra are in the following order: CC3 > CC-1 > CC-7 > CC-2 > CC-4 > CC-5 > CC-6.

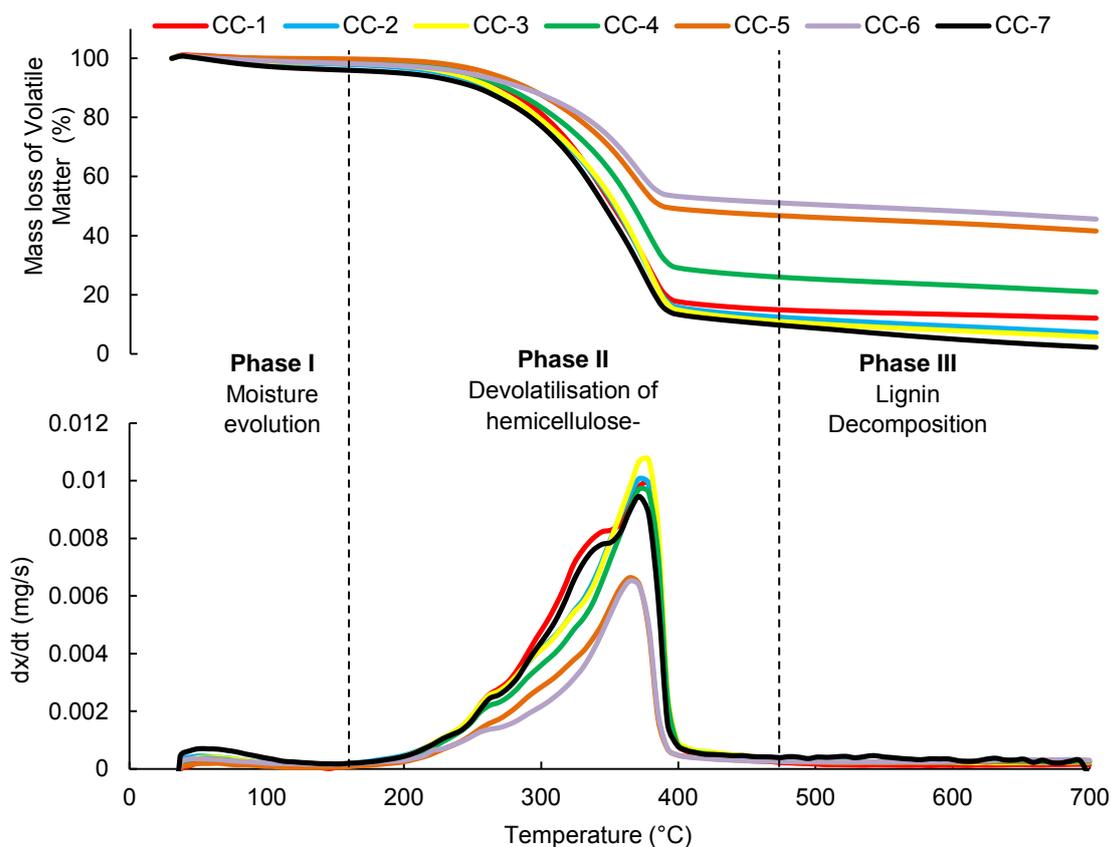


Figure 1: A part of TGA (a) and DTG (b) for CC-1 to CC-7 samples

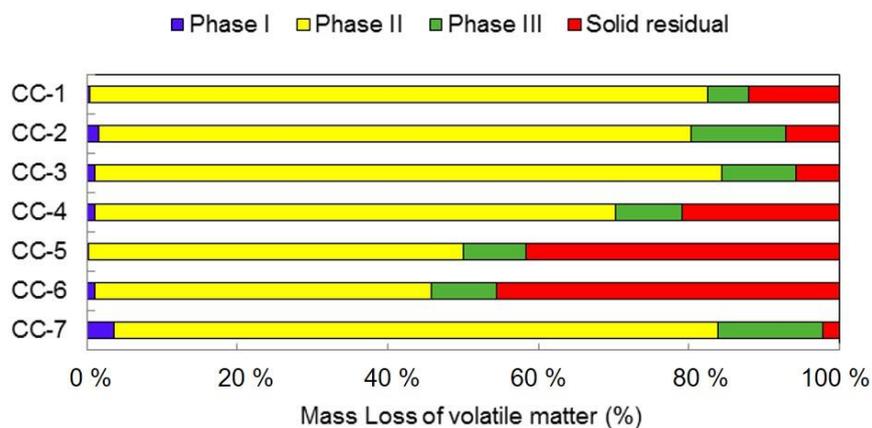


Figure 2: Mass loss of coconut copra's volatile matter

4. Conclusions

The thermogravimetric analysis (TGA) was successfully used to investigate the influence of catalyst weight loading on pyrolysis of coconut copra. The obtained results from TG-DTG plot were divided into three phases of thermal degradation at different temperature range. Based on the obtained data, all the coconut copra samples have shown different thermal behavioural at different ratios. For instance, no significant influence of catalyst weight loading ratio was observed on degradation temperature (372 °C) in Phase II. The catalyst has tremendous effect on the degradation rate of coconut copra and the volatile matter degradation in Phase II. The increment of catalyst loading on coconut copra does not give any positive results towards the high volatile

matter of mass loss, but gradually increases the solid residue. CC-6 sample at highest biomass to catalyst loading ratio proved to yield more solid residue (45.59 %) than mass loss (44.72 %) in Phase II. An optimum biomass to catalyst ratio is necessary to achieve the highest mass loss, in which directly attributed to the pyrolysis products (oil and gas) and at the lowest solid residue leftover. From this study, found that CC-3 sample has achieved the highest mass loss among the entire tested sample at 83.27 % and also highest degradation rate at 0.0107 mg/s from DTG plot. Overall, the optimum ratio was at CC-3 (1 : 0.15) that work best in all three phases of thermal degradation on coconut copra.

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