Thermal Behaviour and Synergistic Effect Analysis of Co-pyrolysis of Coconut Copra and Eggshell for Biofuels Production

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This research investigates the thermal behaviour and synergistic effect of co-pyrolysis of coconut copra (CC) with eggshell (ES) for biofuels production using thermogravimetric analysis and a lab-scale tubular fixed-bed pyrolyzer at various CC:ES ratios. The TGA-DTG curves revealed that a CC:ES ratio of 1:1 had the highest total weight loss of 96 wt% and a degradation peak of 22 wt%/min. The co-pyrolysis of CC and ES using a tubular fix-bed reactor at temperatures between 350 °C and 600 °C showed that a maximum bio-oil of 74 wt% was produced from CC:ES ratio of 1:1 at 450 °C.I It was observed that as the mass of ES was greater than CC, the bio-oil yield decreased while biochar and pyrolysis gas yields increased. The synergistic effect of higher volatile matter in CC and higher ash content in ES had significantly altered the pyrolysis reactions and yielded different amount of pyrolysis products at different ratios of CC:ES. The presence of high metal content dominated by Ca in ES influenced the devolatilization behaviour of the feedstocks resulting in the increase of bio-oil yield at the suitable ratio of CC:ES. These findings also revealed that the main targeted pyrolysis products can be fine-tuned with the ratio of CC:ES.

1. Introduction

Biomass exists in various forms around the world and they can be utilized to replace the conventional fossil fuels due to their availability and abundancy. Agricultural wastes, generated from harvesting, processing and utilization of agricultural products, are a type of biomass resource that can be an alternative energy resource to meet the current energy consumption demands. Specifically, coconut residues are found in over 90 countries globally with a global production of 62.5 million tons per year (Sarkar and Wang, 2020). Cultivated widely in tropical countries, such as Thailand, India and Nigeria, the extensive cultivation of coconut leads to high generation of coconut residues including coconut shell, husk, fiber and copra that can be used as feedstock for energy conversion (Sarkar and Wang, 2020). Eggshell (ES) waste, which can be categorized as municipal solid waste, are being generated and discarded everyday as it is the basic foodstuffs in every household. ES is mainly composed of 96 % calcium carbonate, 1 % magnesium carbonate, 1 % calcium phosphate, proteins and water, which can be utilized as fertilizer, adsorbent, catalyst and feedstock for energy conversion rather than being discarded (Waheed et al., 2020).

Thermochemical conversion methods can be applied in the energy production from wastes, due to its efficiency compared to biochemical conversion methods. In the past years, pyrolysis has been regarded as the capable thermochemical technology for biomass conversion into biofuels (Uzoejinwa et al., 2018). Pyrolysis of biomass is a simple conversion method where biomass is thermally degraded without the presence of oxygen with suitable operating parameters, such as temperature, reaction time, and heating rate. There are still limitations

of biomass pyrolysis, including high oxygen content and low calorific value of bio-oil, corrosion problems and instability in utilization. The bio-oil produced can be upgraded through other methods such as hydrogenation, hydrodeoxygenation and catalytic cracking to improve its quality (Uzoejinwa et al., 2018). Co-pyrolysis can be one of the alternatives to improve quality and product yield through synergistic effects of the feedstocks used.

Co-pyrolysis process involves two or more different materials as the feedstocks. In co-pyrolysis, the ratio of feedstocks used is very important as each biomass has its own characteristics and chemical composition. Through previous literature, it can be seen that co-pyrolysis is a promising conversion technique to yield high quality biofuels compared to single pyrolysis of biomass. For instance, in a study conducted by Sakulkit et al. (2020), from the co-pyrolysis of oil palm trunk and rubber wood sawdust, the bio-oil yield increased, where undesirable compounds such as aldehydes were reduced.

Co-pyrolysis has widely been studied and utilized for the production of high-quality biofuels using various combination of feedstocks, such as torrefied coconut shell with coal (Zheng et al., 2020), rubber wood with oil palm trunk (Sakulkit et al., 2020) and olive stone with low-density polyethylene (Brachi et al., 2022). To the authors' knowledge, there is lack of study regarding the co-pyrolysis of coconut waste and the study of its potential in energy conversion. Similar to ES, where there is a gap in understanding its ability to be used in co-pyrolysis process to produce biofuels. In this research, coconut copra (CC), a type of coconut waste, was co-pyrolyzed with ES to analyze their thermal degradation behaviour and potential in the production of biofuels.

2. Materials and method

Two types of biomass, coconut copra (CC) and eggshell (ES), were prepared and characterized. Thermogravimetric analysis of the two feedstocks, with different mixing ratios were conducted followed by co-pyrolysis experiment using a fixed-bed reactor.

2.1 Preparation of biomass

CC was collected from leftover of coconut milk extraction obtained from local market while ES were collected from household waste. ES was rinsed with water to remove any impurities. Both CC and ES samples were sun-dried for 6 h to remove moisture content in each sample. The samples were further dried in a laboratory oven at 105 °C for 24 h to reduce the moisture content to less than 10 wt%. Both samples were then grounded and sieved into smaller particle sizes (dp < 0.50 mm). CC and ES were prepared in various ratios (1:1, 1:0.7, 1:0.5, 1:0.3, 1:0.1 and 0.5:1). The samples were stored in a desiccator to avoid moisture absorption from the surroundings.

2.2 Characterization of biomass

Physicochemical characterization of CC and ES was conducted to obtain the ultimate, proximate analysis and high heating value (HHV). Ultimate analysis of both samples were carried out in a thermogravimetric analyzer (TGA) to analyze the moisture content, volatile matter and fixed carbon. The ash content in both samples were determined using AOAC 942.05 17th Edition through complete combustion. Proximate analysis was conducted on both samples to obtain carbon (C), hydrogen (H), nitrogen (N), sulphur (S) and oxygen content using CHNS/O elemental analyzer. HHV of both samples were measured using IKA-Calorimeter.

2.3 Thermogravimetric analysis

Thermogravimetric analysis of CC, ES and mixing ratio of CC:ES (1:1, 1:0.7, 1:0.5, 1:0.3, 1:0.1) were performed in a thermogravimetric analyzer (TGA) to analyse thermal degradation behaviour and their synergistic effect. Each sample was heated gradually from 35 °C to 900 °C at a constant heating rate of 30 °C/min. Nitrogen gas flowing at a rate of 20 mL/min was purged to the TGA furnace.

2.4 Pyrolysis and co-pyrolysis experiment

A tubular fixed-bed reactor system consisting of a vertical tubular reactor (160 mm x 29 mm), furnace, temperature control panel and a condenser, was used to perform the pyrolysis runs under atmospheric pressure. The feedstock was filled accordingly into the reactor while the air in the reactor was purged using nitrogen gas, controlled by a flow controller, throughout the analysis. The thermocouple attached to the reactor showed the skin temperature of the reactor that indicated the pyrolysis temperature. The vapors produced during the pyrolysis and co-pyrolysis runs were condensed in a condenser and collected as bio-oil. The residue remaining in the reactor is the biochar.

Firstly, single pyrolysis of CC was carried out at temperature ranging from 350 °C to 600 °C to determine the optimum temperature for maximum bio-oil yield. Approximately 10 g of sample was weighed and loaded onto the reactor. Nitrogen gas flowing at a rate of 50 mL/min was supplied continuously to the reactor to purge residual air. The reactor was heated to the desired temperature for 30 min. For the co-pyrolysis process,

separate runs of CC and ES with different mixing ratios (CC:ES) of 1:1, 1:0.5, 1:0.1 and 0.5:1 were conducted at the optimum temperature obtained from single pyrolysis of CC. For the pyrolysis products (bio-oil, biochar, gaseous) comparison, bio-oil and biochar yields were determined by weighing while gas yield was determined by subtracting the bio-oil and biochar yield wt% from 100 wt%. The sum of all pyrolysis products is considered 100 wt% based on the mass balance of whole pyrolysis process.

3. Results and discussion

3.1 Physicochemical properties of coconut copra and eggshell

The CC and ES samples were characterized to obtain the ultimate and proximate characteristics as well as high heating value (HHV) as tabulated in Table 1.

Table 1: Physicochemical properties of coconut copra and eggshell

Analysis	Coconut Copra	Eggshell
Proximate Analysis (wt%)		
Volatile Matter	88.8	51.9
Moisture Content	7.1	0.7
Ash Content	3.3	47.1
Fixed Carbon	0.8	0.3
Ultimate Analysis (wt%)		
Carbon	47.4	13.0
Hydrogen	7.8	0.5
Nitrogen	0.6	0.7
Sulphur	0.5	0.5
Oxygen	43.7	85.3
High Heating Value (HHV) (MJ/kg)	20.1	3.4

From the proximate analysis, the moisture content in both CC and ES samples was relatively low, as it did not exceed 10 wt%, where a higher moisture content would affect the heating rate during pyrolysis as stated by Vasu et al. (2020). Volatile matter is the main component in pyrolysis feedstock for producing bio-oil while fixed carbon contained in the feedstock sample is the component that can be converted into biochar. From Table 1, CC contained the highest volatile matter (88.8 wt%) and fixed carbon (0.8 wt%) compared to the ES (51.9 wt% volatile matter and 0.3 wt% fixed carbon). The high volatile matter and low fixed carbon in both CC and ES would favour the high production of bio-oil as volatile matter can be further condensed into bio-oil. Ash content in the samples can impact its high heating value (HHV), where high ash content will result in lower HHV. The low ash content in CC (3.3 wt%) resulted in a higher HHV of 20.11 MJ/kg compared to ES (3.40 MJ/kg), which had 47.1 wt% ash content. From ultimate analysis, carbon content of 47.4 wt% and hydrogen content of 7.8 wt% in CC, contributing to higher HHV, can enhance combustion efficiency. When compared to CC, ES had lower carbon and hydrogen content and higher oxygen content, resulting in low HHV. Nitrogen and sulphur content in both samples of CC and ES are less than 2 wt% which can be considered as negligible compositions.

3.2 Thermal degradation behavior of coconut copra and eggshell

The thermal degradation behaviour of CC (1:0), ES (0:1) and CC:ES ratios of 1:1, 1:0.7, 1:0.5, 1:0.3 and 1:0.1 were carried out by thermogravimetric analysis (TGA) and shown in Figure 1 and 2. From Figure 1 and 2, it can be observed that the thermal degradation of CC, ES and their mixed ratio can be divided into three different phases. In phase I, occurring below 150 °C, moisture and light components are vaporized followed by devolatilization of hemicellulose, cellulose and lignin at phase II, occurring between 150 °C and 450 °C, and lastly, the decomposition of remaining lignin occurred at phase III, occurring above 450 °C (Escalante et al., 2022). Among the three phases, the greatest weight loss occurred in phase II as a result of the decomposition of cellulose and hemicellulose to condensable and incondensable vapors (Sakulkit et al., 2020).

The thermal degradation of ES alone, CC:ES-(0:1), there was a slight decrease in phase I (1.81 wt% of weight loss) and II (9.30 wt% of weight loss), then the sample started to decompose significantly between 400 °C and 850 °C due to the decomposition of calcium carbonate ($CaCO_3$), a major component of ES, to CaO (Razali et al., 2022). From Figure 2, a small peak occurring at 640 °C was observed, indicating the rapid decomposition of $CaCO_3$ in ES (Fayyazi et al., 2018).
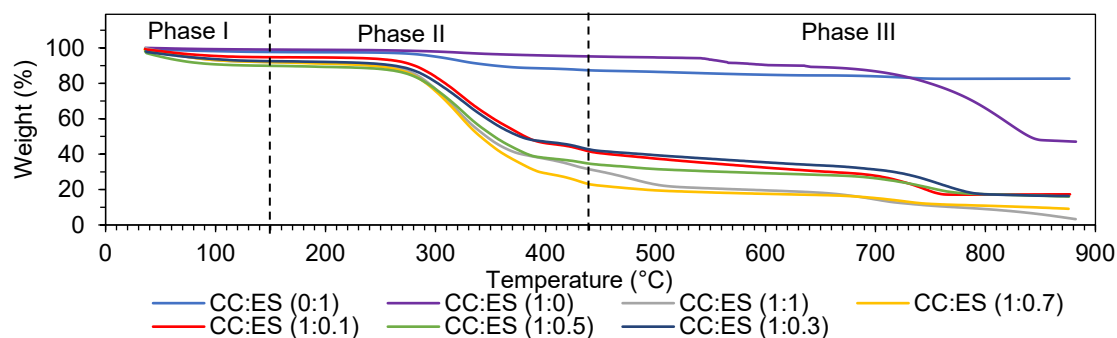
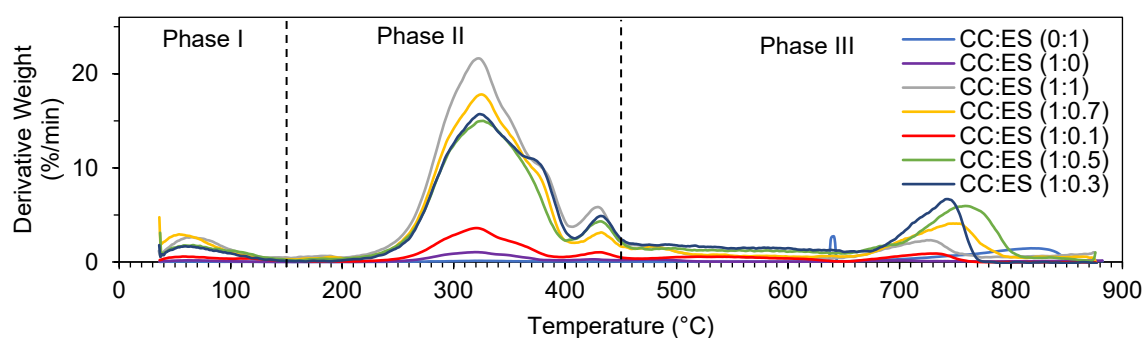Figure 1: TG curves of coconut copra, eggshell and mixed ratio of CC:ES

Figure 2: DTG curves of coconut copra, eggshell and mixed ratio of CC:ES

From Figure 1, it can be seen that ES had a significant influence on the thermal degradation behaviour of CC, as the total weight loss of CC mixed with ES was higher compared to that of the individual CC and ES runs. The highest total weight loss was achieved by CC:ES-(1:1) with 96.71 wt% weight loss, followed by CC:ES-(1:0.7) (90.88 wt%), CC:ES-(1:0.5) (83.95 wt%), CC:ES-(1:0.3) (83.63 wt%) and CC:ES-(1:0.1) (82.69 wt%). Compared to CC:ES-(1:1), thermal decomposition of CC sample alone, CC:ES-(1:0), only achieved 79.83 wt% weight loss. This could indicate that the presence of CaO in ES promoted the decomposition of the biomass components, leading to higher weight loss. It can also be concluded that the more ES was mixed with CC, the more the weight loss achieved by the samples.

In Figure 2, regarding peaks attributed to the degradation of cellulose as mentioned by Escalante et al. (2022), CC:ES-(1:1) showed the highest peak around 330 °C with degradation rate of 21.53 %/min in phase II while CC:ES-(1:0) showed the lowest peak at 320°C with lower degradation rate of 1.04 %/min. This implied that the higher amount of ES mixed with CC contributed to the faster degradation of cellulose. In phase III, the highest degradation rate of lignin in all samples were observed between 400 °C and 500 °C. Interestingly, another shoulder peak was observed for all samples except for CC:ES-(1:0) at between 650 °C and 850 °C, which can be attributed to the decomposition of $CaCO_3$ to CaO, where the presence of CaO would boost the decomposition of CC.

3.3 Pyrolysis of coconut copra

Single pyrolysis of CC has been carried out at various temperatures ranging from 350 °C to 600 °C via the fixed-bed reactor and the product yield distribution is shown in Figure 3. From Figure 3, it can be observed that bio-oil yield increased and attained a maximum value of 67.5 wt% at 400 °C, then decreased to a minimum yield of 51.0 wt% at 600°C. The increase and decrease pattern of the bio-oil yield from pyrolysis is typically caused by the multiple type of reactions. The primary reactions generally start at lower temperatures, and the increase in temperature increases the formation of vapors, resulting in the increase of vapor condensation and liquid yield (Jalalifar et al., 2018). Further increase in temperature promotes the secondary reactions which results in higher gaseous products. The maximum bio-oil yield at 400 °C seen in Figure 3 is mainly contributed by the maximum devolatilization of condensable volatile matters into liquid products. Meanwhile, the gaseous yield increases with temperature steadily from 17.0 wt% at 350 °C to 37.8 wt% at 600 °C due to the secondary decomposition of volatiles and char into lighter components, generating more gaseous products (Wu et al., 2020). The decrease

in biochar yield is observed with an increase in pyrolysis temperature due to the release of more volatile materials from the feedstock.
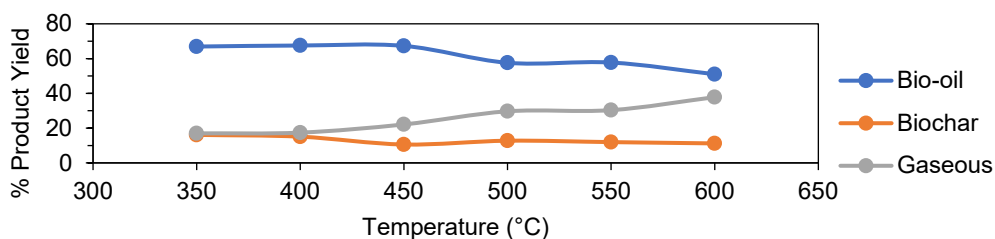

Figure 3: Pyrolysis products yield from single pyrolysis of coconut copra

3.4 Co-pyrolysis of coconut copra and eggshell

Co-pyrolysis of CC and ES were conducted at various mixing ratio of CC:ES of 1:1, 1:0.5, 1:0.1 and 0.5:1. The pyrolysis was carried out at the optimum temperature of 400 °C, obtained from the previous section, and the product yield distribution is shown in Figure 4.
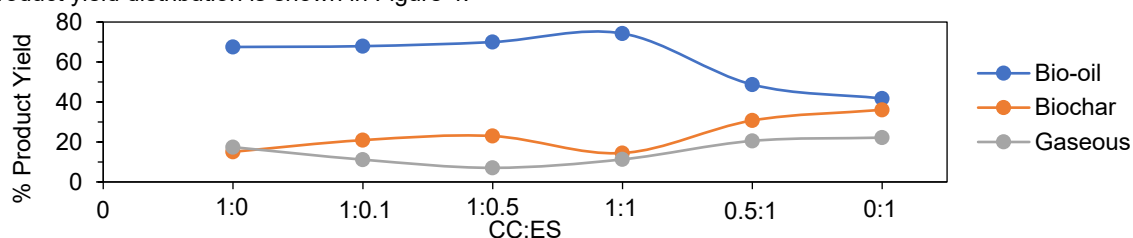

Figure 4: Pyrolysis product yields at various mixing ratio of CC:ES

From Figure 4, the single pyrolysis of CC, CC:ES-(1:0), produced higher bio-oil yield (67.5 wt%) compared to the single pyrolysis of ES, CC:ES-(0:1) (41.8 wt%), due to the presence of higher volatile matter in CC. The biochar yield of CC:ES-(0:1) (36.1 wt%) was higher than that of CC:ES-(1:0) (15.1 wt%) due to the higher ash content in ES. The gaseous yield of CC:ES-(1:0) (17.4 wt%) was lower than that of CC:ES-(0:1) (22.2 wt%). From the investigated mixing ratio samples, CC:ES-(1:1) yielded the highest bio-oil yield (74.3 wt%). The increase in bio-oil yield when CC was co-pyrolyzed with ES was due to the improvement of the cracking reactions of the heavy molecules in pyrolysis vapors from the presence of ES (Rohim et al., 2015). The higher bio-oil yield obtained in co-pyrolysis for CC:ES-(1:1) also may be due to synergetic effect of high volatile content in CC and high ash content in ES, promoting the volatilization reaction (Li et al., 2017).

From Figure 4, bio-oil yield gradually increased from 67.5 wt% (CC:ES-(1:0)) and reached a maximum of 74.3 wt% at a CC:ES ratio of 1:1 before decreasing as the ES was further added to a CC:ES ratio of 0.5:1. The presence of CaO in the ES was able to increase the production of bio-oil due to the presence of acid sites that breaks down heavy compounds into non-condensable vapors (Mohamad Dzol et al., 2022). The bio-oil yield was further decreased from 48.7 wt% at ratio of CC:ES-(0.5:1) to 41.8 wt% at ratio CC:ES-(0:1). Interestingly, the biochar yield significantly increased after the mass of ES exceeded the mass of CC. This could be due to the absorption of CO_2 by CaO at lower temperatures which caused the CO_2 fixation from non-condensable vapors to solid residue (biochar and used CaO). Furthermore, high CaO might also catalyze the pyrolysis process by cracking pyrolytic volatiles, resulting in the decrease of bio-oil yield and the increase biochar yield (Li et al., 2017). The decreasing biochar yield can be ranked as follows: CC:ES-(0.5:1) with 30.7 wt% > CC:ES-(1:0.5) with 23.0 wt% > CC:ES-(1:0.1) with 20.9 wt% > CC:ES-(1:1) with 14.5 wt%. The gaseous yield was maximum at ratio CC:ES-(0.5:1) with 20.5 wt% due to the higher amount of ES in the feedstock mixture, accelerating the cracking of pyrolytic volatiles to produce more gaseous yield (Li et al., 2017). From this finding, it can be concluded that the increment of ES resulted in a higher bio-oil production but after the mass of ES is higher than the mass of CC, the bio-oil yield starts to decrease.

4. Conclusions

In conclusion, the thermal degradation and synergistic effect of CC and ES and their potential for biofuel production have been successfully analyzed and conducted for different mixing ratios of CC and ES. The co-

pyrolysis experiment results showed that equal mass proportion of CC and ES fed to the reactor yielded maximum bio-oil yield of 74.3 wt% which was 6.7 wt% higher compared to pyrolysis of CC alone. It can be deduced that ES is a suitable co-feeding material in co-pyrolysis process as it is able to increase the bio-oil yield. For future work, it is recommended to conduct an analysis on the bio-oil chemical composition to observe the impact of the presence of ES on the bio-oil.

Acknowledgments

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