Co-pyrolysis of Empty Fruit Bunch and Waste Tire: A Kinetics and Synergism Analysis

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The efforts in discovering new, green and sustainable energy sources have been overwhelming, all with the common aim of combating global warming and environmental pollution while protecting the supply security of conventional energy sources. Pyrolysis is a secure thermo-chemical conversion method suitable for the conversion of biomass waste into a product of higher energy value, aimed for energy production. Co-pyrolysis on a blend of feedstock from different sources has captured the attention of the scientific community as it has been demonstrated to be able to overcome undesirable characteristics of the derived products like high acidity and high ash content. The present study demonstrates the co-pyrolysis of empty fruit bunch (EFB) and waste tire (WT) at a mass ratio of 1:1 using a thermogravimetric analyser. The results were compared with the baseline of pure feedstock pyrolysis. It was reported that EFB is more reactive at a lower temperature region (200-325 °C) due to the composition of cellulose and hemicellulose. WT has a higher temperature degradation zone (300-480 °C), correlating with the compositions of natural rubber, styrene-butadiene rubber and butadiene rubber. A synergism analysis by comparison of theoretical and experimental TG and DTG curve of the blend revealed an inhibitive effect on the decomposition rate on the first peak of the DTG graph (~316 °C) while promoting the decomposition rate on the second peak of the DTG graph (~371 °C). The activation energy of the blend (194.98 kJ/mol) is determined to be lower as compared to EFB (257.29 kJ/mol) and WT (252.92 kJ/mol) obtained through Flynn-Wall-Ozawa (FWO) method, which indicates some form of synergism between both feedstock during co-pyrolysis. Thus, the blending of EFB and WT has been proven to attain synergism during pyrolysis. This finding reports a viable pathway for co-processing of biomass waste (EFB) and rubber waste (WT) while potentially able to generate valuable bio-products of alternate use.

1. Introduction

Pyrolysis has been discovered as a feasible method in processing waste from agriculture (Auta et al., 2014), wastewater (Lin et al., 2016) and rubber manufacturing industry (Banar, 2015). This process reduces the feedstock volume and weight whilst eliminating harmful pathogens. More importantly, the process is also able to produce by products of increased value, bringing this technology to potentially be at the forefront of waste management facilities. Despite the advantages of pyrolysis in processing and managing waste, there are still drawbacks when using this technology, hindering its development and scale up potential. One of the main drawbacks is that pyrolysis is an energy intensive process (Mong et al., 2020) as it relies on heat being imposed to decompose the feedstock. Aside from this, pyrolysis might also not be suitable for feedstocks of low conversion rate (mass loss of 25 wt% at 1,000 °C) due to the composition present in within (Lin et al., 2016).

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Another drawback is that the possibility of obtaining low quality products by the end of the pyrolysis process that requires further pre-treatment prior to direct use (Islam and Nahian, 2016). To overcome the above-mentioned problems, the research focus has been directed to co-pyrolysis of feedstocks. The co-pyrolysis process has been demonstrated in previous studies to be able to improve the yield (Lu et al., 2020) and quality (Idris et al., 2020) of products as compared to the pyrolysis of single feedstock.

To investigate the presence of synergic effect during co-pyrolysis, kinetics study through TGA can be conducted. Insight on the pyrolysis reaction, for instance, the instantaneous mass loss, reactivity and activation energy can be analysed (Chen et al., 2019). A direct comparison on the pyrolysis of pure feedstock with the blend can then be conducted. Positive and negative effects that either promote or inhibit the reaction rate may be detected in the feedstock blend. Chong et al. (2017) states that the synergism interaction can be affected by the type of contact between different components present in the blend, length of pyrolysis period, temperature, heating rate, removal or equilibrium of volatiles formed and presence of solvents or catalyst. In another work on co-pyrolysis of coal and oil shale, an increase in oil (8.20 %) and gas (2.65 %) yield were reported, indicating a positive synergism from the blend. Due to numerous types of waste available, the selection of waste to be co-pyrolysed is crucial as to improve the efficiency of the process. Empty fruit bunch (EFB) from oil palm (Auta et al., 2014) and tyre waste (WT) (Islam and Nahian, 2016) are one of the most abundantly available waste in Southeast Asia due to the geographical location, agricultural practices, industry and domestic demand. Research has been conducted to utilise and valorise these wastes into useful products through pyrolysis. However, there remain problems due to single feedstock pyrolysis as has been reported in literature. For example, EFB contains high amount of oxygen, where the bio-liquid derived are rich in chemicals with high oxygen content and acidity, preventing its direct use as liquid fuel (Auta et al., 2014). WT made from fossil sources has high carbon content and is able to produce diesel-like liquid through pyrolysis that could be used as a bio-fuel. However, the presence of sulphur within the long chain polymer (butadiene, isoprene, and styrene-butadiene) that made up the tyres (Islam and Nahian, 2016) hinders the direct use of the derived pyrolysis oil in combustion engines.

Therefore, as an initial approximation, this work proposes a kinetics analysis for the co-pyrolysis of EFB and WT. The work aims to identify any possible form of synergism when co-pyrolysing these feedstocks, which can potentially be used to address some or all of the abovementioned problems. This work focuses on co-pyrolysing two abundant wastes commonly found in Southeast Asia and identifying possible synergistic interaction that will improve the conversion process. Although there are research studies that focuses on either the pyrolysis of EFB or WT, the co-pyrolysis mechanism, especially on mass loss and kinetics properties has not been conducted before. The findings from this work provides novel insight into the co-pyrolysis mechanism of EFB and WT specifically on the synergism interaction. This will enable the consideration for bulk processing of EFB and WT concurrently while improving the pyrolysis process in terms of feedstock conversion and energy consumption.

2. Materials and methods

Empty fruit bunch (EFB) was supplied by FGV Palm Oil Semanchu Mill situated in Kota Tinggi, Johor Bahru, Malaysia while waste tyre (WT), free of steel wire, was obtained from Eco Power Synergy Sdn Bhd at granular size of approximately 10 mm. Both samples were dried in a conventional oven at 110 °C for 24 h to remove free moisture, followed by grinding to a size of 100-500 μm for further tests. The physiochemical properties of EFB and WT was obtained through proximate analysis, elemental analysis and calorific value analysis. It is to note that the detailed standard procedure is recorded in (Idris et al., 2020). In this work, a feedstock blend of EFB:WT at mass ratio 1:1 was prepared through physical mixing.

2.1 Thermogravimetric analysis (TGA)

The mass loss behaviour of EFB, WT and the EFB:WT=1:1 blend was analysed through a thermogravimetric analyser (TA Instrument Q500). Approximately 10.0 ± 0.5 mg of feedstock was thermally decomposed in a N_2-filled environment at temperature from 30 to 950 °C at a N_2 flow of 20 mL/min. The experiment was conducted at four different heating rates of 2, 10, 20 and 40 °C/min. The mass loss and rate of mass loss of the feedstock were recorded in thermogravimetric (TG) and derivative thermogravimetric (DTG) format.

2.2 Synergistic analysis

The synergistic effect of two feedstock was studied by comparing the experimental value obtained through TGA with the theoretical values for TG and DTG calculated through Eq(1).

$$W = X_{EFB} \cdot W_{EFB} + X_{WT} \cdot W_{WT} \tag{1}$$

where W represents the theoretical weight (wt%), TG_T or DTG_T of the blend; W_{EFB} and W_{WT} represent the experimental TG and DTG values of EFB and WT; X_{EFB} and X_{WT} represent the mass percentage (%) of EFB and WT in the blend (Chong et al., 2017).

2.3 Kinetics analysis

The kinetics of pyrolysis on a feedstock can be analysed through iso-conversional method of which a minimum of three heating rates are conducted by TGA (Gomes et al., 2020).The common solid state reaction that correlates the conversion rate and Arrhenius expansion rate constant is written as in Eq(2).

$$\frac{d\alpha}{dt} = Ae^{\frac{E}{RT}}f(\alpha) \tag{2}$$

The kinetics triplets are represented by A (pre-exponential factor in min^{-1}), E (activation energy in kJ/mol) and f(α) (reaction model). From Eq(1), the conversion rate, α can be described as Eq(3)

$$\alpha = \frac{m_o - m_i}{m_o - m_f} \tag{3}$$

where m_0, m_i and m_f represent the initial, instantaneous and final mass of feedstock at a certain conversion. Flynn-Wall-Ozawa (FWO) is the iso-conversional method implement in this work due to its accuracy in analysing the activation energy at varying conversional level of the feedstock (Mong et al., 2021). The equation that describes the FWO is shown in Eq(4), which is derived from the integration of Eq(2) and Eq(3).

$$\ln \beta = \ln \frac{AE_\alpha}{RG(\alpha)} - \frac{E_\alpha}{RT} \tag{4}$$

G(α) is the integral form of kinetic model, R is the universal gas constant represented by 8.314 Jmol^{-1}K^{-1}, β is the heating rate (K/min) and T is the temperature (K). The activation energy can be determined from the gradient of the graph of lnβ against 1/T.

3. Result and discussion

3.1 Physiochemical properties of EFB and WT

Table 1 shows the physical and chemical characteristics of EFB and WT. Both feedstocks of EFB and WT have high volatile contents, which show the potential of deriving valuable liquid and gaseous product through thermal decomposition process (Mong et al., 2021). Low ash content of 2.3 wt% and 4.2 wt% in EFB and WT portray the potential of transforming this feedstock into solid fuel like charcoal or bio-char. EFB has high oxygen composition (50.4 wt%), which is commonly being reported in biomass feedstock (Chen et al., 2019). WT has high carbon composition (80.3 wt%) due to its fossil-based product (López et al., 2013).

Table 1: Physiochemical characteristics of EFB and WT (obtained from Idris et al. (2020))

	Proximate analysis (wt %)				Ultimate analysis (wt %)					HHV (MJ/kg)
	Moisture	VM	FC	Ash	C	H	N	S	O	
EFB	4.1	69.5	24.1	2.3	42.7	6.2	0.6	0.1	50.4	18.0
WT	0.9	65.4	29.5	4.2	80.3	7.7	0.4	0.9	10.8	39.9

VM: Volatile Matter, FC: Fixed Carbon, HHV: Higher Heating Value

3.2 Mass loss behavior of feedstock and blends

In Figure 1, the initial mass loss at temperature <200 °C is attributed to the evaporation of free moisture and the decomposition of light volatiles (Mong et al., 2021). EFB is observed to decompose at a lower temperature region of 215-500 °C as compared to WT with a main decomposition region between 300 °C and 480 °C. EFB has a sharp DTG peak, indicating a maximum rate of mass loss at 315 °C, followed by a low shoulder at 468 °C. The peak represents the degradation of cellulosic composition, such as cellulose and hemicellulose that makes up about 55-80 wt% of EFB (Chong et al., 2017). The shoulder at a slightly higher temperature region (468 °C) represents the gradual degradation of lignin composition, where it has been reported to have a wider decomposition temperature region (190-900 °C) (Mong et al., 2019).

WT has been demonstrated to have a peak degradation rate at 364 °C and two shoulders at 230 °C and 420 °C, respectively. The degradation of oil and lubricants present in WT is responsible for the first shoulder at the lower temperature region as been reported by Cherbański et al. (2017). The peak degradation (364 °C) is a result of the breaking down of natural rubber composition and the shoulder at the higher temperature region

(420 °C) is attributed to the degradation of styrene-butadiene rubber and butadiene rubber. This is in-line with the work of López et al. (2013), where the maximum rate of decomposition of pure elastomer is reported to be at 373.1 °C for natural rubber, 425.4 °C for styrene-butadiene rubber and 467.3 °C for butadiene rubber.

The feedstock blend at EFB : WT = 1 : 1 is found to exhibit both the decomposition behavior of EFB and WT feedstocks by having two peaks at 316 °C and 371 °C and two shoulders at 221 °C and 422 °C, as shown in Figures 1a and 1b. The TG curve of the blend hovers in between the mass loss range for EFB and WT. Such an occurrence has been reported in co-pyrolysis studies (Lin et al., 2016) as the blend is expected to possess the composition from both feedstocks, naturally inheriting similar mass loss behavior but with a lower reaction rate due the diluted portion of individual composition. This is evident from Figure 1b, where the reactivity of blend (red dotted line) is lower as compared to those of EFB and WT.
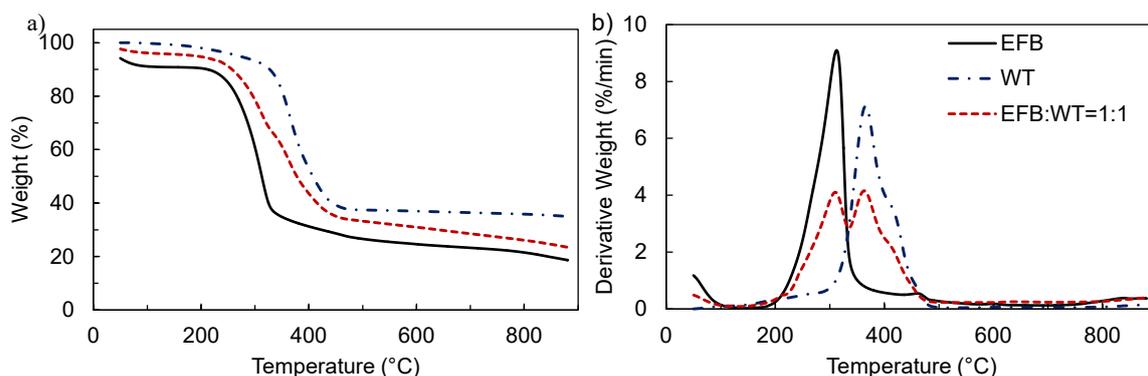

Figure 1: The decomposition curve of EFB, WT and their blends at 10 °C/min in (a) TG and (b) DTG format

3.3 Synergistic analysis

Figure 2 depicts the theoretical and experimental TG and DTG curves of EFB-WT blends pyrolysed at 10 °C/min in a N_2 atmosphere. The reactivity of the blend during pyrolysis can be studied from the peak position and height of DTG curve as an indicator for reactivity (Chong et al., 2017). To investigate the synergistic interaction between EFB and WT, the theoretical and experimental values of the blends are presented in Figure 2. The same TG and DTG curve indicate that the reactivity of feedstock blend is merely following the trend of feedstock proportion (measured through Eq(1)). The difference shows some form of synergism interaction that either promote or inhibit the behavior of mass loss.
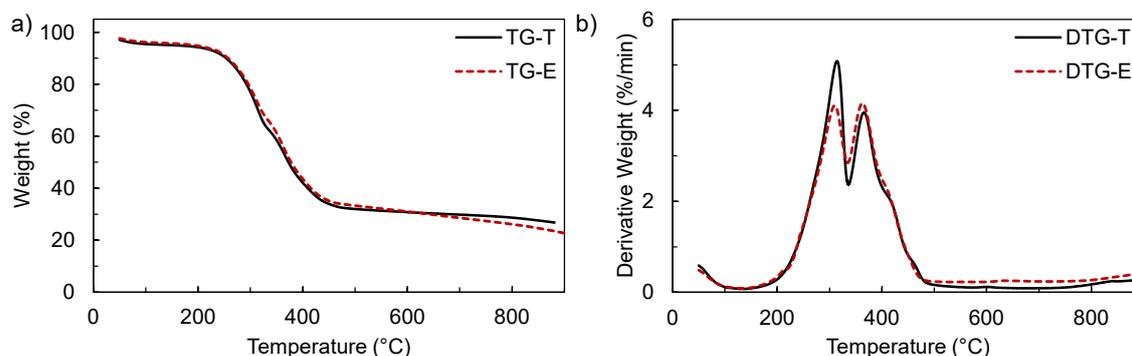

Figure 2: (a) TG and (b) DTG curves of the blend EFB:WT=1:1 at 10 °C/min. T represents the theoretical value and E represents the experimental values.

From the TG curve, the experimental value (depicted in Figure 2a – red dotted line) shows higher mass loss towards the end of experiment (600-800 °C) indicating that a larger portion (~3 wt%) of feedstock has been decomposed. In the DTG curve (Figure 2b), an inhibitive effect is observed in the first peak, where the red line (experimental) appears below the black line (theoretical). This portrays a reduced in reactivity intensity of the feedstock in the temperature region of ~316 °C. In the second peak (~371 °C), the intensity of decomposition rate has been promoted (red line is higher than the black line), where more components within the blend are being degraded at a higher rate. The existence of synergism might be due to several factors, such as the interaction between different composition in the blend or the presence of metals in trace amount, which requires

further studies. As an example, it has been reported in the co-pyrolysis study of sewage sludge and oil shale that the presence of minerals in oil shale might inhibit the degradation of organic matter leading to a lower reactivity (Lin et al., 2016).

3.4 Activation energy, E_α

The activation energy is obtained by implementing the model-free, FWO method. The displayed results in Figure 3 comes with an average linear correlation of at least 0.955, indicating the reliability of data. Overall, the activation energy of all three cases changes with the conversional level, representing the occurrence of complex multi-step reaction mechanism during pyrolysis (Mong et al., 2019). This further affirms that the FWO method implemented to evaluate the activation energy of the process is able to determine the apparent activation energy at different conversion degree with high accuracy (Lu et al., 2020). The conversion fraction of 0.15-0.7 has been selected for analysis due to avoidance of inaccuracy of data due to DTG peak tails during the start and end of experiment.
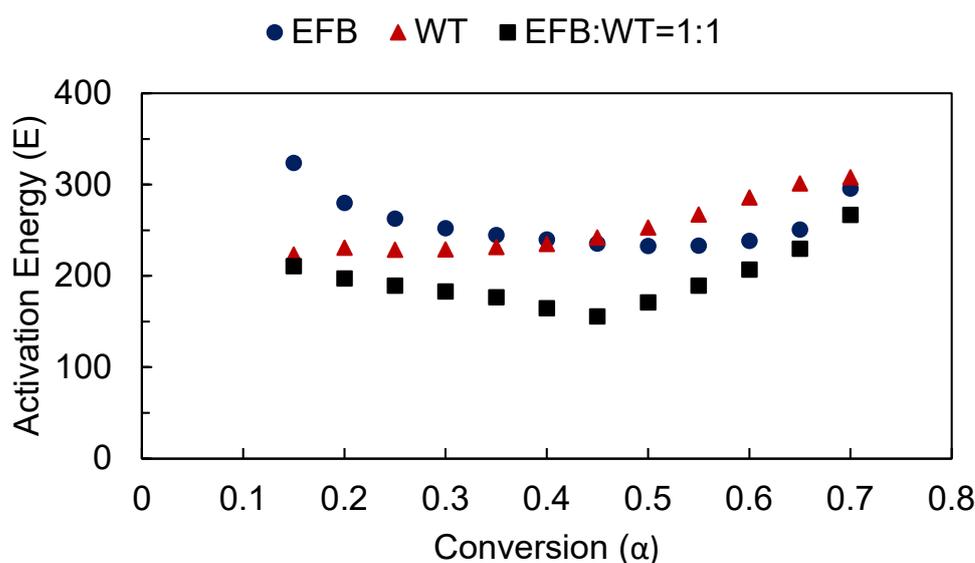

Figure 3: Activation energy of EFB, WT and the blend at various conversional level

The activation energy of EFB shows a decreasing trend (from 210.7 kJ/mol at α=0.15 to 155.7 kJ/mol at α=0.45), follow by an increasing trend (from 155.7 kJ/mol at α=0.45 to 266.7 kJ/mol at α=0.7). E_α is high initially as more energy is required to overcome the energy barrier for chemical reaction to commence. The E_α reduces gradually as the cellulosic components in EFB is broken down. The increase of E_α towards the end of experiment shows the decomposition of lignin component which is harder to decompose (Chong et al., 2017). The activation energy of WT is relatively constant during the initial conversion (223.1-234.9 kJ/mol for α=0.15-0.4) but increases during the latter part of conversion (from 242.1 kJ/mol at α=0.45 to 307.8 kJ/mol at α=0.7). This can be due to the decomposition of oil and lubricant at the initial stage of pyrolysis, followed by the natural rubber. Cherbański et al. (2017) reported a lower activation energy of oil (33.1 kJ/mol) and natural rubber (124.1 kJ/mol) when compared with styrene-butadiene and styrene-butadiene rubber (161.6 kJ/mol). This explanation fits perfectly with the changes of E_α for WT obtained in this work, where an increase in E_α at a higher conversion shows that styrene-butadiene and styrene-butadiene rubber are being degraded.

Overall, the feedstock blend has a lower activation energy as compared to the pure feedstocks, which indicates some form of synergism between the blend that reduces the energy required to undergo decomposition. From the change of E_α with conversional level, the initial conversion follows the pathway of EFB and the latter conversion period follows WT. This portrays the benefits of blending the biomass waste (EFB) and rubber waste (WT) for co-pyrolysis as it requires a lesser amount of energy. In the work of Chen et al. (2019) that investigated the co-pyrolysis benefits of tobacco stalk (TB) and scrap tyre (SC), a blending at specific ratio (8 : 2 = TB : ST) is shown to be able to achieve a lower average activation energy (29.24 kJ/mol) when compared with the pure feedstock pyrolysis (TB = 31.1 kJ/mol; SC = 70.66 kJ/mol). Other benefits, for instance, the potential of obtaining higher bio-product yield or higher quality of bio-products can also be further investigated in future studies.

4. Conclusions

Synergism interaction during co-pyrolysis of EFB and WT is investigated in this work. Although each of the feedstocks has high volatile content, the mass loss behaviour is entirely different due to different composition that decomposes at varying temperature. Reactivity of the blend (EFB : WT = 1 : 1) is shown to be lower as compared to the pure feedstock (EFB and WT) as the composition is diluted due to mixing effect of two feedstock. Synergism of the blend is found to be present in the blend co-pyrolysis as the process leaves behind a lower amount of leftover, indicating more components have been decomposed. The blend is also found to promote the decomposition rate at 371 °C but inhibits the reaction rate at 316 °C. From the kinetics analysis on the present pyrolysis study, a lower activation energy is found for the blend between EFB and WT. This further shows proof of synergism as the interaction between EFB and WT has been found to reduce the required energy for decomposition, which is beneficial for the entire thermal-conversion process. Thus, it can be surmised that co-pyrolysis of EFB and WT at 1 : 1 mass ratio is potentially capable of overcoming the energy intensive process of pyrolysis while generating a lower amount of leftover.

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