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Pyrolysis kinetic study on homogenized high-density polyethylene with wheat waste using thermogravimetric analysis (TGA)

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Abstract. In this paper, the potential of different ratios of homogenized biomass and plastic wastes blend were investigated. For plastic waste, high-density polyethylene (HDPE) and for biomass, wheat wastes from Iran were selected due to abundance availability of the wastes. Pyrolysis kinetic study were conducted in three different ratios of HDPE (25%, 50% and 75% HDPE) combined with the wheat sample. Parameters used in this study are: heating rate of 10ºC/min, feedstock size less than 250µm, N_2 gas as Gas 1 during pyrolysis, purified O_2 as Gas 2 to complete the combustion and the mass of the blend was kept at 15mg. The activation energy obtained from the Thermogravimetric analysis (TGA) for HDPE:wheat blend of ratio 1:3, 2:2 and 3:1 were 47.3798 kJ/kmol, 39.2978 kJ/kmol and 33.7889 kJ/kmol, respectively for the first decomposition stage and for the second decomposition stage were 17.2758 kJ/kmol, 30.2114 kJ/kmol and 80.8258 kJ/kmol, respectively using the Coats Redfern method. Lower value of activation energy in wheat compare to HDPE reduced the activation energy of homogenized samples. The percentage of carbon in plastic is higher than biomass can affect the emission after combustion. On the other hand, the higher percentage of HDPE in ratio increased the calorific value which is an important matter for a fuel.

1. Introduction

The Energy demands $A = \pi r^2$ continuously increasing due to the population growth and enhanced lifestyle which means sole dependence on fossil fuels alone are not sustainable. This is because fossil fuels are limited and can cause anthropogenic global warming.[1] According to the Science Magazine, a study in 2015 found that Malaysia is ranked 8th worldwide for plastic waste. The study estimated that Malaysia produced 1 million tonnes of mismanaged plastic waste in 2010. [2] On the other hand, improper disposal of biomass such as incineration and open burning has caused a very serious air pollution problem. When these wastes are incinerated, they release their toxic constituents to the atmosphere. This will directly lead to breathing difficulties for people and at the same time cause global warming to the environment. On the bright side, due to the ease in generation and short carbon cycle, biomass and other lignocellulosic waste such as agricultural waste are sustainable and carbon neutral which along with plastic waste can be converted to sustainable clean energy [1,3,4].

As we know Malaysia is a country that is growing rapidly so does its population, it is increasing at a rate of 2.4% every year ever since the year 1994. The rise in population will consequently lead to the

increase of municipal solid waste (MSW) produced. It is predicted by the year 2020, MSW generation will accumulate to 31 tonnes a day due to the yearly rate of population growth. [2,5,6].

Thermochemical conversion techniques such as pyrolysis provide an ideal pathway for fuels production from biomass and plastic waste. Thermogravimetric analysis (TGA) is a well-established technique for studying thermal degradation decomposition of biomass and plastic waste as it proceeds through the steps of pyrolysis. Thermal decomposition behaviour of a solid is predicted by measuring the rate of weight loss as a function of temperature and time. Kinetic parameters of thermal decomposition such as activation energy, E_a and frequency factor, A which essentially characterize the thermal decomposition of biomass can be evaluated from the TGA data. [4,7,8].

In this paper, the focus is more towards the approach of energy recovery to recycle plastic wastes. It is understood that this method, which is energy recovery is most appropriate for plastic wastes and since there is a limited need for pre-treatment, it is labelled as one of the easiest methods as well. This study investigated the potential different ratios of homogenized plastic wastes and biomass blend. For plastic waste, high-density polyethylene (HDPE) and for biomass, wheat wastes from Iran were selected due to abundance availability of the wastes. Pyrolysis kinetic study were conducted in three different ratios of HDPE (25%, 50% and 75% HDPE) combined with the wheat sample.

2. Materials and methods

2.1. Sample Preparation

The biomass and HDPE sample were grinded separately into finer granules by using a Fritsch Pulveriser a, in order to achieve the size of the feedstock that is required to match the parameter of this experiment. Grinding of HDPE will need special attention as the melting point of HDPE is at 180°C, therefore dry ice will be added to the HDPE to cool down the grinding machine to prevent the infusing of HDPE with the grinding blades. Dry ice was chosen to cool down the HDPE as dry ice does not leave behind any residue. The same process is repeated for the biomass excluding the use of dry ice this time [9,10].

The grinded waste HDPE was sieved with a mesh size of 250 μm in order to obtain HDPE samples that are less than 250 μm. The samples were there placed in plastic holder. The wheat sample was undergone the same process to achieve the feedstock size of less than 250 μm. The plastic holders were labelled accordingly as HDPE and Wheat before proceeding to be mixed in the ratios that will be used for the experiemnt.

The HDPE and wheat samples were then mixed into 3 different ratios to be analysed with the Thermogravimetric Analyzer. The samples were mixed into 3 ratios of 1:3, 2:2, and 3:1 with the total mass of mixture to be 15 mg. The HDPE and wheat samples were weighed and measured using an electronic balance before being placed in 3 separate storage envelops with labels of the ratios on each of them [10,11].

2.2. Thermogravimetric Analysis

Thermogravimetric analysis (TGA) of the wheat-high density polyethylene blends were performed by using TGA 2 instrument by Mettler Toledo. The equipment has the capability of achieving a temperature range between 25 to 1000°C. The experiments were conducted in Herriot Watt University, Putrajaya. The temperature range was fixed from an ambient temperature to 1000°C. The kinetic analysis and activation energy were obtained through this analysis.

The experiment was conducted in 3 different ratios of wheat-high density polyethylene blend which were 1:3, 2:2 and 3:1. The experiment was carried out with a constant heating rate of 10°C/min. The decomposition of wheat-high density polyethylene blends occurs between 110°C to 1000°C which were recorded continuously as a temperature function at different conditions to obtain the mass of decomposition. The sample was held for 10 minutes after reaching the temperature of 110°C from ambient temperature in a nitrogen environment. After the 10 minutes, the sample is continuously heated with the constant heating rate of 10°c/min with nitrogen flow until it reaches 900°C and held for another 10 minutes. After 10 minutes, the nitrogen flow was switched to purified oxygen supply until it reaches 1000°C to allow the sample to undergo complete combustion [12,13].

2.3. Experimental design and model development

The kinetic analysis of the wheat-high density polyethylene blend was calculated using modified coats redfern. Generally, the rate of non-isothermal solid decomposition can be described by Equation 1:

$$\frac{d\alpha}{dt} = kf(\alpha) \tag{1}$$

where, α is the conversion of the combustible material and it is defined as Equation 2:

$$\alpha = \frac{m_i - m}{m_i - m_f} \tag{2}$$

where m, m_i and m_f represent the instantaneous, initial (at 383 k) and final mass of the sample, respectively. the reaction rate constant k is expressed in terms of the arrhenius equation as:

$$k = Aexp(\frac{-E}{RT}) \tag{3}$$

the function f (α) can be written as;

$$f(\alpha) = (1 - \alpha)^n \tag{4}$$

substituting into eq. (1) gives

$$\frac{d\alpha}{dt} = Aexp(\frac{-E}{RT})\,(1 - \alpha)^n \tag{5}$$

considering a constant heating rate β = dt/dt, eq. (3) can be rearranged to the following equation.

$$\frac{d\alpha}{dT} = (\frac{1}{\beta})\,Aexp(\frac{-E}{RT})\,(1 - \alpha)^n \tag{6}$$

eq. (4) was integrated using the integral method based on coats redfern equation which was also used recently by [3] and the approximation is given as

$$In\left[\frac{-In(1-\alpha)}{T^2}\right] = In\frac{AR}{\beta E}\left[1 - \frac{2RT}{E}\right] - \frac{E}{RT} \quad IF, \quad N = 1 \tag{7}$$

or

$$In\left[\frac{1-(1-\alpha)^{1-n}}{(1-n)\times T^2}\right] = In\frac{AR}{\beta E}\left[1 - \frac{2RT}{E}\right] - \frac{E}{RT} \quad\quad IF, \quad N \neq 1 \tag{8}$$

in most cases, 2rt/e is very small and therefore the two equations can be approximated by;

$$In\left[\frac{-In(1-\alpha)}{T^2}\right] = In\frac{AR}{\beta E} - \frac{E}{RT} \quad IF, \quad N = 1 \tag{9}$$

or

$$In\left[\frac{1-(1-\alpha)^{1-n}}{(1-n)\times T^2}\right] = In\frac{AR}{\beta E} - \frac{E}{RT} \quad IF, \quad N \neq 1 \tag{10}$$

the plot of $\ln[-\ln(1-\alpha)/t2]$ versus $1/t$ becomes a linear line for $n = 1$; the plot of $\ln[1-(1-\alpha)(1-n)/(1-n) \times t2]$ for $n \neq 1$. the activation energy (e) and the pre-exponential factor (a) can be determined from the slope and intercept of the regression line respectively [13,14].

The coats-redfern is a kind of approximate integral equation. this method is widely used to evaluate kinetic parameters for constant heating rate and it is extensively acknowledged. The calculation process does not involve the reaction mechanism so it can avoid error from the reaction mechanism.

3. Results and discussion

3.1. Decomposition of different ratio of HDPE:Wheat

Thermogravimetric analysis (TGA) and differential Thermogravimetric (DTG) curves of wheat-high density polyethylene blend have been plotted at different ratios of the blend which are 1:3, 2:2 and 3:1 in a nitrogen atmosphere with a flow rate of 25mL/min.

Result in Fig.1 shows that the initial degradation started at 200°C and the degradation completed at 680°C for the HDPE 1:3 Wheat blend. For the blend of HDPE 2:2 Wheat, the initial degradation starts at 220°C and degradation completes at 670°C. For the blend of HDPE 3:1 Wheat, the initial degradation begins at 240°C and the degradation completes at 600°C. Based on the results obtained from the TGA curve, the curves have the same trend of degradation but it is also noticed that as the ratio of HDPE increases in the blend, the final temperature of the degradation decreases.

The pyrolysis processes of the blends are characterized by two decomposition stages unlike the one decomposition stage when the biomass and HDPE are undergone pyrolysis individually. It can be seen that the decomposition intensity changes based on the percentage of each material in the blend. The first decomposition stage is mainly the decomposition of the wheat and slightly influenced by the HDPE due to the reactions being below 350K for the blends. Plastics do not decompose at this temperature and only softens which can affect the mass and heat transfer at this temperature range. The thermal degradation of wheat and high density polyethylene consist of the second decomposition stage. During the second decomposition stage, lignin components of biomass are decomposed. The peaks that can be seen during this stage are a result of the overlap of decomposition of the wheat and HDPE blend which results in a rise of synergistic effect observed.
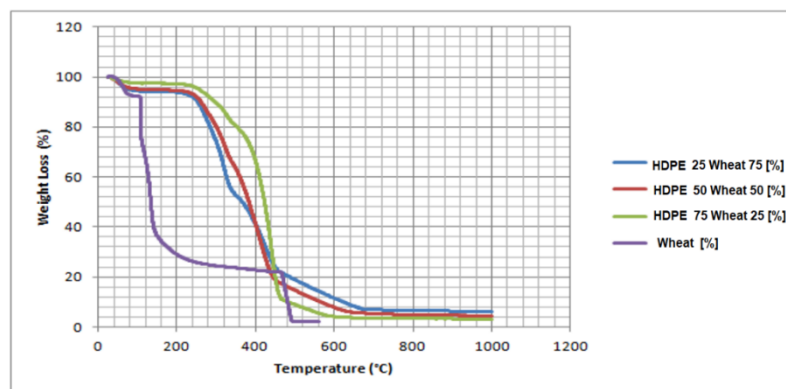

Figure 1. TGA curve of wheat-high density polyethylene blends of different ratios.
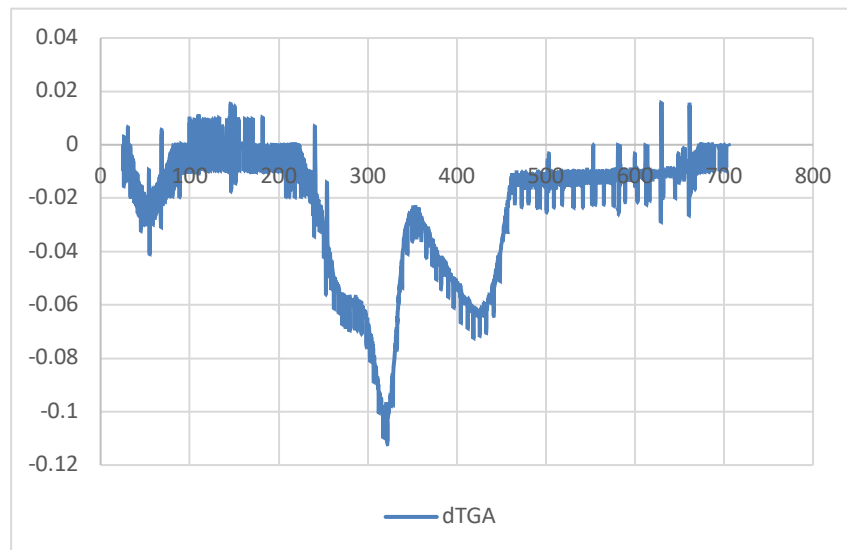
Figure 2. DTG curve of Wheat 3:1 HDPE.

Thermal degradation of the wheat and HDPE contributes to the second decomposition stage. The peak temperature for the Wheat 3:1 HDPE blend is at 315°C, Wheat 2:2 P HDPE is at 410°C and Wheat 1:3 HDPE is at 440°C. This can be seen through the Fig. 2, 3 and 4 below. From these data, it can be seen that the higher the ratio of HDPE in the blends, the higher the peak temperature of each blend. The peak intensity of the first decomposition stage was only higher than the peak intensity of the second decomposition stage when the ratio of HDPE to wheat was 1:3. The peak intensity of the second decomposition stage increased when the percentage of HDPE increased in the ratio which can be seen in the figures below.
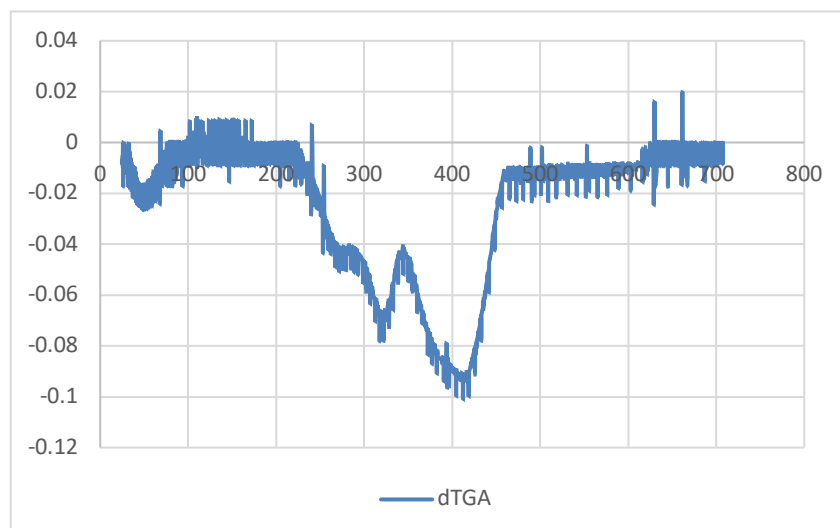

Figure 3. DTG curve of Wheat 2:2 HDPE.

Coats Redfern method is also known as the non-sioconversional method. The pre exponential factor, and activation energy, Ea can be calculated based on the equations. Therefore, the plot of ln [β (da / dt)] as a function of 1/T, the activation energy, pre-exponential factor and R2 can be obtained. It is important to understand the kinetic parameters as it is very important for investigating the wheat-high density polyethylene blend at high temperature and the thermal behaviour stability. The data was denoted by a straight line between the range of (R^2 = 0.9527 to 0.9971) based on the 3 different ratios of wheat-high

density polyethylene blend. The activation energy, pre exponential factor and R^2 of the wheat-high density polyethylene blend can be seen in the Table 1 below. It can be observed that when the HDPE ratio increases, the activation energy for the first decomposition stage decreases and for the second decomposition stage, the activation energy increases when the ratio of HDPE increases. As we can see in Table 1, the obtained value of activation energy for HDPE in conducted experiment is close to the value in other study. As shown in table the activation energy for HDPE 7:3 SW can be compare to the obtain result HDPE 3:1 Wheat in 385-440 ºC range which is slightly different, but it is due to the high value of activation energy of wood sawdust (SW) in that sample. This proves that the results are within the acceptable range.
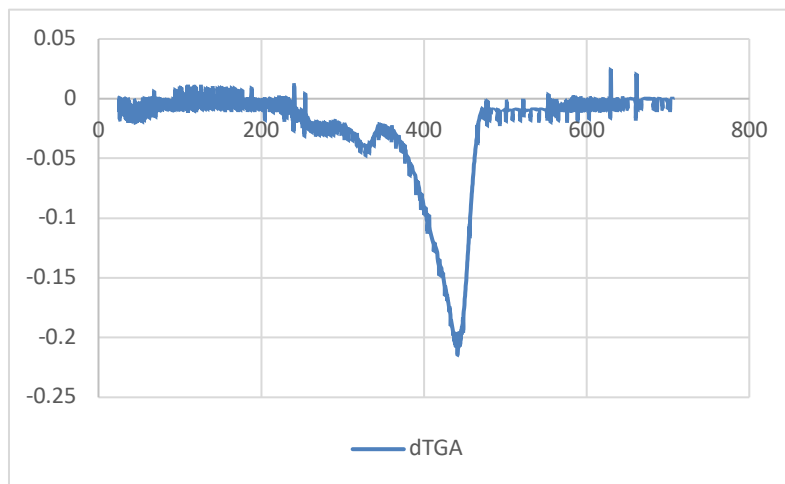

Figure 4. DTG curve of Wheat 1:3 HDPE.

Table 1. Values from kinetic analysis of Coats Redfern.

Sample	Temperature Range (ºC)	Ea (kJ/kmol)	R^2
HDPE	417-490	225.384	0.98
Wheat	240-315	30.5814	0.981
HDPE 1:3 Wheat	295-320	47.3798	0.9971
	350-420	17.2757	0.9527
HDPE 2:2 Wheat	293-322	39.2978	0.9978
	345-380	30.2114	0.9874
HDPE 3:1 Wheat	295-333	33.7889	0.9942
	385-440	80.8258	0.9841
HDPE [15]	440-550	236.2	0.99
HDPE 7:3 SW [15]	286-405	128	0.97
Newspaper [16]	310-370	142.3	0.99

4. Conclusion

In this study, the thermogravimetric and kinetic study of the co-pyrolysis of wheat and high density polyethylene have been examined. The results showed that the thermal decomposition of the wheat-high density polyethylene blend can be categorized by two decomposition stages as shown by the dTGA curve. It is also proven that there exist synergistic effects between the plastic waste which is high density polyethylene and biomass which is wheat. This is proven by the changes that were observed when high density polyethylene was added to the wheat to be pyrolyzed compared to when wheat was pyrolyzed alone.

The examination of the kinetics of the wheat-high density polyethylene blends showed that as the ratio of plastic increased in the wheat-high density polyethylene blend, the activation energy of the first decomposition stage decreased. On the other hand, the activation energy of the second decomposition stage increased when the plastic ratio in the wheat-high density polyethylene blend increased.

The kinetic models of Coats Redfern was used to calculate the activation energy, pre exponential factors and the regression of the wheat-high density polyethylene blends. The results shows that as the ratio of plastic increases in the wheat-high density polyethylene blend, the activation energy of the first decomposition stage decreases. On the other hand, the activation energy of the second decomposition stage increased when the plastic ratio in the wheat-high density polyethylene blend is increased. One way to improve this examination is to mix the wheat and high density polyethylene blend with a homogenizer to obtain homogeneity of the blend to prevent the blend from being pyrolyzed individually. The results obtained will be more accurate and precise if the blend is homogenous and synergistic effect will be more visible.

Acknowledgments

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