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Research paper



Characterization Studies on Waste Plastics as a Feedstock for Energy Recovery in Malaysia

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Abstract

Increase in the energy usage and declining of non-renewable fossil fuels has changed the perceptions to energy recovery methods to satisfy the need of the energy. Through extensive research and innovation of technology, especially to recover the plastic waste to energy feedstock has been developed. The chosen plastic waste samples are polyethylene terephthalate (PET), high-density polyethylene (HDPE), and polypropylene (PP). This sample is collected from daily household waste and was characterized according to the resin types or plastic types. In this research the determination of the moisture content and ash analysis has been carried out using proximate analysis and also determination of the carbon, hydrogen, nitrogen, and sulphur content has been carried out by using the ultimate analysis. In addition, the calorific value of the samples has been determined and activation energy is obtained based on thermogravimetric analysis (TGA) data. The chosen kinetic modelling is modified Arrhenius equation. According to the results, HDPE was the best choice for energy recovery from waste plastics in Malaysia due to high calorific value, low activation energy, low moisture content and ash content and it has low sulphur content among all the plastic samples experimented.

Keywords: *waste plastics, kinetic, pyrolysis, activation energy.*

1. Introduction

Plastic waste is one of the biggest environmental problems as it affects the sustainability of the environment. It is also influenced by the population growth, social behavior, and demographic aspects [1]. In such developing country like Japan, recycling centre are well developed in order to cater the conversion of waste into useful products, including recycling of plastic wastes [2]. Mainly there are more than 100 types of plastic but usually only 6 types of plastic are most common and these are distinguished with a number to enable to categorize and recognize it [3]. The continuous disposing plastic in the landfills will cause serious environmental problems as plastics takes up to billion years to degrade naturally. The energy conversion is a sustainable way to fully utilize the waste in order to meet the energy demand.

A review study by [1] suggested that Malaysia as one of the developing country with average GDP growth of 4.6%, currently focusing on the development of sustainable and energy generation. They suggested that 3.3% growth rate has been anticipated for municipal solid waste (MSW) production throughout the country due to the lack of proper waste management network and over 80% of the collected MSW are landfilled with inert and unsanitary sites throughout the country. Based on their study, MSW production is increasing 3% annually, due to the increment of population also the growth of cities formation. The same influencing factors is applied for all developing countries like Indonesia, Philiphines and Nigeria. The total daily MSW generated from 2012 and 2013 are 29,711 t/day and 30,518 t/day, respectively, which varies for different cities; 45 t/day in Klang to 3000 t/day in Kuala Lumpur. Annual report from Ministry of Housing and Local Government (MHLG) in 2002 showed that 13,069 t/day in 1996 and 16,248 t/day in 2001 of MSW were generated in line with population increase from 15,146,236 to 17,136,575. On the other hand, 20% increase of total MSW generated causes the 3.3% growth rate annually. Currently, Malaysia shows a progressive increase in population from 2000 to 2015 from 23.9 to 30.65 million with a growth of 30.5% [4].

It is found that more than 40% of waste in Malaysia is organic waste as discussed by [5] dominating other types of wastes e.g. paper, plastics, glass, metal, textiles and wood wastes. The generation of plastics waste increased with population expansion. From 1990 to 1999 plastic consumption is decreased lightly due to economic crisis, but the usage of plastic increased in 2000 with the introduction of plastic packaging materials into the market [6,7].

Therefore, conversion of plastic waste to potential energy is possible as it from petrochemical source, especially having high calorific value [1]. Several studies has proposed the potential of waste plastics in producing usable fuel such as gasoline and hydrogen [8,9]. The abundant biomass waste in Malaysia is potential to be added to waste plastics as a feedstock in co-pyrolysis process for producing bio-fuel [10].

In this study, three different types of waste plastics namely HDPE (high density polyethylene), PET (polyethylene terephthalate) and PP (polypropylene) from municipal solid waste treatment plant in Malaysia have been investigated. The characteristics of waste plastics also have been evaluated by proximate and ultimate analysis and calorific value determination. This analysis is use to determine the moisture, ash content, C, H, N, O and S content and also to determine the quantity of heat produced by combustion under standard conditions by calorific value determination. Furthermore, the activation energy of different types of waste plastics is calculated using modified Arrhenius equation based on thermogravimetric analysis.

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2. Methodology

2.1. Sample Preparation

Sample that needed in this study is different type plastics with resin code labelled form Number 1, 2, and 5 which is PET, HDPE, and PP. The samples were cleaned and cut into small pieces and placed in separate beakers. Finally, to obtain homogenous particle the samples undergoes gradation analysis using sieves. Gradation process or testing is also called as sieve analysis; it is basic but important to measure the gradation to find and define that is compliant for the experiment. For this experiment, the sieves were used to obtain a homogenous particle size after the sample is cut down into small pieces. Obtained homogenous particle is stored into a container according to sample and labelled. For each sample of plastic, the same method repeated to obtain the homogenous size in the range of 0.5 mm to 1 mm in size [11].

2.2. Thermogravimetric Analysis

The plastic samples are analysed to determined physical and chemical properties. To determine the weight percent of carbon, hydrogen, nitrogen, and sulphur of plastic samples, ELEMENTAR Vario MICRO cube was used. The sample of plastic is weighted using a small tin capsule with the amount of 2 to 3 mg. Next, the capsule is folded or wrapped with tin foil without any air in it and placed it into the auto sampler. The closed tin capsule will fall into the reactor chamber where excess oxygen is supplied to mineralized the plastic sample at 990°C.
Additionally, some specified analysis was conducted such as calorific value analysis and TGA. This method covers the method of determination the heat of combustion of hydrocarbons in the plastic samples. The sample is weighted to approximately 1.0 g and burned in the oxygen bomb calorimeter under the controlled conditions and the temperature reading is observed before, during, and after combustion for thermochemical and heat transfer calculations using Parr 6300 EF Bomb Calorimeter. TGA analysis was used in the determination of kinetic energy, Arrhenius activation energy and the moisture loss and ash residue from temperature of 120°C to 1000°C. In this experiment the heating rate was set at 10°C/min and the mass of decomposition was recorded as function of temperature continuously. The results are plotted in a mass of loss curve, based on it Arrhenius activation energy is calculated from the heating rate versus constant absolute temperature. The activation energy values have been found using modified Arrhenius equation and DTGA curve was plotted as in the following equations (1) to (4) [4]:

$$\alpha = \frac{m_o - m}{m_o - m_f} \tag{1}$$

Where α is considered as the conversion of the waste plastics, m_o is the initial sample weight, m is the sample weight at time t, and m_f is the final sample weight.
The kinetics is simplified to first order by assuming the reaction order is close to unity. The well-known rate expression can then be written as:

$$\frac{dx}{dt} = k(1-x)$$
$$k = k_o \exp(-E_a / RT) \tag{2}$$

Where R is the universal gas constant (8.314 J/Kmol), k_o is the pre-exponential factor (min^{-1}) and E_a (kJ/mol) is the activation energy. With a linear heating rate of a ($K\ min^{-1}$),

$$a = \frac{dT}{dt} \tag{3}$$

The integration shows as follows:

$$In\left[-In(1-x)\right] = In\left[\frac{k_o RT^2}{aE_a}\left(1-\frac{2RT}{E_a}\right)\right] - \frac{E_a}{RT} \tag{4}$$

The graph of In[-In(1-x)] against 1/T was plotted corresponding to a straight line with a slope which is activation energy (E_a/R) by using the pre-exponential factor.

3. Results and Discussion

3.1. Ultimate Analysis

Ultimate analysis provides information of the percentage of carbon (C), hydrogen (H), nitrogen (N), and sulphur (S) in plastic waste.

Table 1: Ultimate analyses of different plastic materials.

Type of Plastics	C (%)	H (%)	N (%)	S (%)
PET	63.12	4.50	0.03	0.05
HDPE	85.96	12.03	0.20	0.02
PP	85.16	12.47	0.20	0.04

Table 1 shows that the ultimate analysis in the entire plastic sample and the obtain results almost similar as the percentage of carbon in PET (63.94%), HDPE (86.99 %) and PP (86.88%) acquired by [5]. Therefore, the obtain results are within the acceptable tolerance range, and the difference is usually caused by the mixture of different composition that used by the manufacturer when producing the plastic.
Based on Figure 1, all the plastic waste, PET, HDPE and PP have C and H as the main elements. Basically the high content of carbon (C) includes the combustible carbon and incombustible carbon carbonate contents. However, nitrogen (N) and sulphur (S) contents determine the undesirable emissions amount such as NOx and SOx, two critical emissions from combustion process for a fuel feedstock. Figure 1 also shows that plastics have none or very small amount of sulphur and nitrogen content compared to coal. This proves that plastic is cleaner and more environmental friendly.

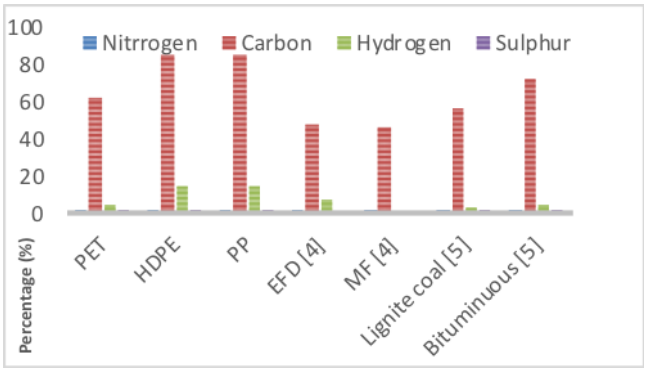


Fig. 1: Comparison of CHNS of plastic with biomass and coal

3.2. Calorific Value Analysis

Calorific value (CV) is the energy or heat released when the plastic sample is burnt. The correlation of the obtain results based on Figure 2 HDPE (43.77 MJ/kg), PET (22.75 MJ/kg), and PP (45.61 MJ/kg) almost similar to the findings such that HDPE (44 ± 0.36 MJ/kg), PET (22.96 ± 0.03 MJ/kg) and PP (46.50 ± 0.11 MJ/kg)

[12]. Therefore, it shows the maximum amount of energy can be theoretically recovered from the plastic sample source. However, there are drawbacks the actual energy that recovered its depending on the conversion energy. Typically, diesel and gasoline fuel have the higher CV, but Figure 2 shows that PP plastic sample has the highest CV value along with HDPE. [13]

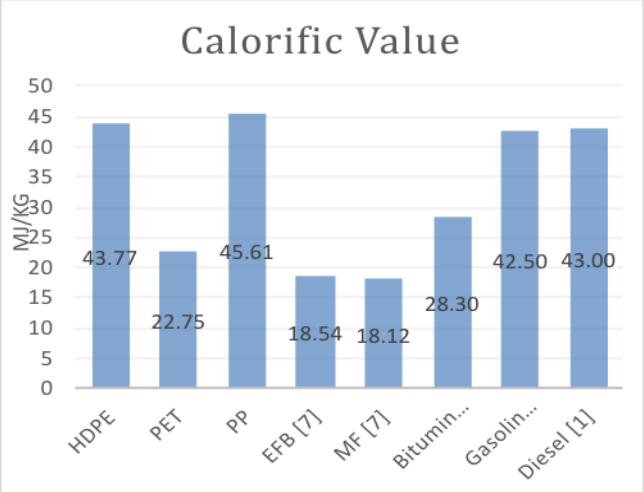


Fig. 2: Comparison of plastic sample with biomass, coal and liquid fuel

3.3. TGA Analysis and Activation Energy

Weight-loss curves based on thermogravimetric analysis of HDPE, PP and PET are discussed in Figure 3a, 3b, and 3c, which show the typical TG curves. In all the experiments the final temperature is 978.2 °C and the decomposition curve for the heating rate is at 10 °C/min. Based on the figures, HDPE sample decomposed faster than PP, followed by PET. The decomposition of the samples is based on first-order reaction. The results show that all plastics start to degrade at 300 °C and complete the degradation at around 500 °C except PET sample which completely degraded at 900 °C.

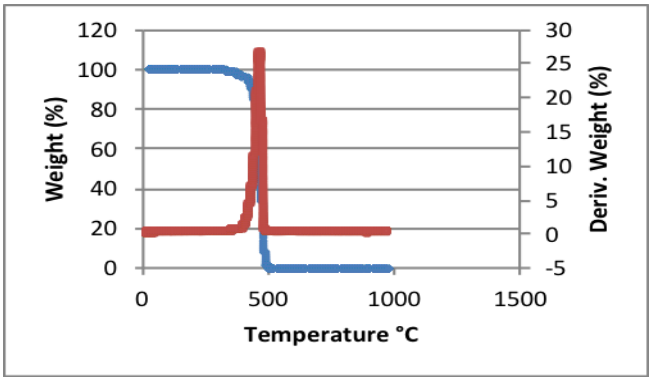


Fig. 3a: Decomposition curve of HDPE

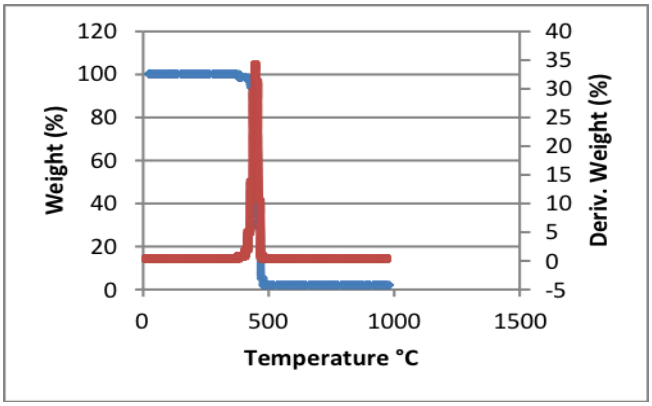


Fig. 3b: Decomposition curve of PP

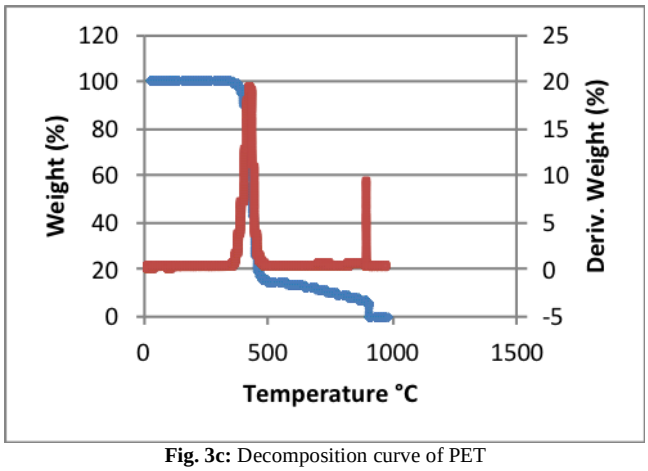


Fig. 3c: Decomposition curve of PET

Based on the plotted graph the moisture loss of the tree samples is very minimal and based on [3], PET have (0.4 ± 0.3 wt %), HDPE have (0.1 ± 0.1 wt%), and PP have (0.1 ± 0.1 wt%). This shows that experimented plastic sample have very limited moisture content.

The value ash residue obtain by percentage of weight loss for PET is 7.24 wt%, PP is 2.35 wt% and HDPE is 0.74 wt%. Usually the ash residue for PET is 8.3 ± 0.1 wt%, [14] which is slightly higher compare to this study, for PP is usually range from 1.99 to 3.55 wt% [5], therefore the experimented value within the range and for HDPE usually ranges from 0.18 to 1.40 wt% [5], were the results obtain is within the range.

The activation energy values have been investigated using modified Arrhenius equation and DTGA curve were plotted. The graph of In[-In(1-x)] against 1/T was plotted the corresponding to a straight line with a slope which is activation energy (E_a/R) by using the pre-exponential factor. The activation energy values for the HDPE, PP and PET has been tabulated as shown in Table 2.

Table 2: Activation energy of plastics samples

Type of plastics	Ea (kJ/mol)	R^2
PET	262.58	0.9518
HDPE	225.36	0.9724
PP	310.96	0.9972

The activation energy that had been found PP has the highest among all, due to the corresponding DTGA curve peak. Apparent the activation energy of HDPE range 233–326 kJ/mol, 184–336.7 kJ/mol, for PP and PET range from 162.15–338.98 kJ/mol which all the results obtained from the Arrhenius equation are within the range [7, 14-15].

Basically high activation energy will not react without any input of energy. For instance, combustion of coal will release energy, but the rate of reaction is zero in room temperature. To be exact, it would not be good if the coal combust spontaneously because the loss of energy due to fast reactions. There for once there is input of energy such as ignition, it's enough energy to provide the molecules to overcome the barrier releasing energy.

4. Conclusion

The resulting conclusions based on this research which to study the potential type of plastic waste as feedstock for energy recovery form waste treatment plant in Malaysia and compare different type of plastic properties and structures from municipal solid waste treatment plant in Malaysia.

According the proximate and ultimate analysis, PP has the lowest amount of moisture and ash content as well as highest percentage of carbon and lowest percentage of sulphur compared to biomass such as EFD and MF and coal samples.

Furthermore, the calorific values were calculated. It is found that PP and HDPE samples have calorific value of 45.61 MJ/kg and 43.77 respectively, which is higher compared to common diesel and gasoline.

Moreover, to justify the plastic as good feedstock for energy recovery, the activation energy of different types of plastic using Thermogravimetric analysis (TGA) has been found based on the degradation curve and DTGA curve. According to the results, HDPE has lowest activation energy among the entire plastic sample experimented which PP is 310.96 kJ/mol, PET is 263.58 kJ/mol, and HPDE is 225.36 kJ/mol.

In conclusion, the conducted experiment proves that the potential plastic waste sample as feedstock for energy recovery is high density polyethylene (HDPE). This because HDPE has the lowest activation energy, moisture and ash content, also higher in calorific value.

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