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Kinetic Study on the Pyrolysis and Gasification of Plastic Waste

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With the large volume of consumer plastic waste generated worldwide, one common problem in the Philippines involves the disposal and treatment of solid wastes. Current processes in the disposal of post-consumer plastic wastes such as incineration or landfill are not fully acceptable based on international standards. As such, there is an urgent need for a practical, safe and efficient disposal method which can also convert waste into useful energy. Pyrolysis and gasification are very well-known thermal degradation processes that convert carbonaceous materials into useful gaseous products that still contain significant amount of energy. The parameters obtained from the kinetic study of these processes are very essential in the design of useful conversion technologies such as reactors and gasifiers. In this study, the pyrolysis and gasification of plastic waste samples were investigated in a thermogravimetric analyser (TGA).

The kinetic parameters for the pyrolysis of the samples were obtained at heating rates ranging from 10 - 30 K/min. The mean activation energies for the pyrolysis reaction were found to be 124.1 kJ/mol and 107.3 kJ/mol, for samples X and Y. In terms of the temperature at which maximum degradation occurs, the differential thermogravimetric (DTG) curve of the plastic waste sample resembles that of a ternary mixture containing polypropylene (PP), polyethylene (PE) and polyethylene terephthalate (PET). For the gasification of the plastic waste samples with CO_2, a temperature higher than 600 °C is required to attain significant conversion. The activation energies for the gasification of the waste plastic samples were found to be 144.7 and 147.8 kJ/mol for samples X and Y.

1. Introduction

Current technologies that involve disposal of post-consumer plastic wastes such as incineration or landfill are known to have many disadvantages with respect to international standards which focus on recovery of energy and raw material (Encinar and Gonzalez, 2008). The packaging industry is considered as one of the major plastic consumers with about 52 % of the total consumption (Hujuri et al, 2008). A significant increase in the consumption of plastics resulted to increased generation of plastic wastes. Plastic wastes consist primarily of mixture of polyethylene (PE), polypropylene (PP), and polyethylene terephthalate (PET), low-density polyethylene (LDPE), polyvinyl chloride (PVC), and polystyrene (PS). These wastes are known to be non-biodegradable and add to the problems of solid waste management in many areas.

Most studies are focused on the conversion of these plastic wastes to valuable chemical products using various thermal degradation processes such as pyrolysis and gasification. Pyrolysis is a thermal degradation of a material in the absence of oxygen and involves the removal of volatile components such as hydrocarbon gases, tars and phenols. Gasification, on the other hand, involves reaction of a carbonaceous material with either steam or CO_2 producing carbon monoxide, hydrogen and light hydrocarbons. The most common device to carry out these reactions is the thermogravimetric analyser (TGA) due to its simplicity and the valuable information obtained from it is enough to derive kinetic information from the reactions.

In this study, two plastic waste samples obtained from different sources underwent pyrolysis and gasification in a TGA. Kinetic information obtained from this reaction includes activation energies and reaction rate constants.

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2. Methodology

2.1 Samples and Materials

Two types of plastic wastes were obtained from two different damp sites and labelled as Sample X and Sample Y. Only the plastic components of the wastes were isolated, crushed and grinded to yield particle sizes ranging from 1 - 2 mm. The proximate and ultimate analyses of the plastic samples are shown in Table 1. Gasification and pyrolysis of the plastic samples were done using ultra-high purity N_2 and CO_2 gas along with air to oxidise the remaining char and combustibles in the sample.

Table 1: Analysis of the plastic samples

Sample	Proximate analysis (wt% wet basis)				Ultimate analysis (wt% dry, ash-free)			
	Moisture	Volatile Matter	Fixed Carbon	Ash	C	H	O	N
X	0.6	90.5	3.7	5.2	65.3	13.9	20.7	0.3
Y	0.9	92.1	3.1	3.9	73.1	22.4	4.4	0.1

2.2 Pyrolysis and gasification experiments

Plastic wastes were crushed to yield particle sizes ranging from 1 - 2 mm. Plastic samples weighing 15 ± 1 mg was used in the thermogravimetric analyser (TA Q50) and heated under N_2 environment to 600 °C at a heating rate ranging from 10 - 30 °C/min. Nitrogen gas used in the TGA flowed at a flow rate of approximately 80 mL/min. Mass, time and temperature data were recorded every 2 s to yield weight loss (TG) and differential weight loss (DTG) curves.

Gasification with CO_2 was performed in the same TGA using 15 ± 1 mg of plastic sample. Gasification of the sample initially involved heating of the sample at 110 °C to remove the moisture under N_2 environment. The temperature of the sample was then elevated at a rate of 90 °C min^{-1} to the desired gasification temperature, which was varied from 600 to 900 °C. At this point, the volatile matter was removed. When the mass of the sample became constant, CO_2 was introduced to the reactor to gasify the resulting char. After a definite period of gasification, the gas mixture was then switched to an air/N_2 mixture for the combustion of the remaining char.

2.3 Modelling of the pyrolysis reaction

In this study, the single reaction model was used. The extent of conversion (X) or the fraction of the pyrolysed material is calculated as Eq(1):

$$X = \frac{m_i - m}{m_i - m_f} \tag{1}$$

where m_i = initial mass of the sample after removal of moisture (mg), m = mass of the sample at any time, t (min) and m_f = mass at the end of the pyrolysis process (mg). The reactivity or the reaction rate of pyrolysis is given by Eq(2):

$$\frac{dX}{dt} = k(T)f(X) \tag{2}$$

where k(T) = rate constant (min^{-1}) and f(X) = kinetic model-dependent function. The temperature dependence of the rate constant is further defined as Eq(3):

$$k(T) = A \exp\left(-\frac{E}{RT}\right) \tag{3}$$

where A, E, R and T are the frequency factor (min^{-1}), the activation energy (kJ mol^{-1}), the universal gas constant (kJ mol^{-1} K^{-1}) and the gas temperature (K). With f(X) = 1 – X and defining $\beta = dT/dt$, the Coats and Redfern (1964) method was used to calculate the pre-exponential factor and the activation energy. The resulting equation after ignoring the higher order terms will give Eq(4):

$$\ln\left[-\frac{\ln(1-X)}{T^2}\right] = -\frac{E}{RT} + \ln\left[\frac{AR}{\beta E}\left(1-\frac{2RT}{E}\right)\right] \tag{4}$$

In the plot of the left-hand side of the equation versus 1/T, the slope will be -E/R and the y-intercept can readily evaluate the frequency factor at the given heating rate β. The activation energy of the pyrolysis reaction is then reported as the average of the activation energies obtained from each runs with a specific heating rate.

2.4 Modelling of the gasification reaction

For the gasification reaction, the char conversion (x) was calculated as Eq(5):

$$x = \frac{W_0 - W}{W_0 - W_{ash}} \tag{5}$$

where W_0 = sample mass at the start of the gasification (mg), W = sample mass (mg) at gasification time, t (min) and W_{ash} = mass of the ash that remained after complete combustion with air/N_2 mixture (mg). The modified volumetric model proposed by Kasaoka et al (1985) is given by the Eq(6):

$$x = 1 - \exp\left(-\alpha t^{\beta}\right) \tag{6}$$

where α and β are empirical constants obtained from the conversion data by the least-square method. Differentiation of this equation leads to the determination of a specific reaction rate constant as follows

$$k(x) = \frac{1}{1 - X}\frac{dx}{dt} = \alpha^{\frac{1}{\beta}} \beta[-\ln(1 - x)]^{\frac{\beta - 1}{\beta}} \tag{7}$$

For consistency, all models were evaluated at char conversion range of 0 to 0.5 to unify all gasification curves. Previous investigation also used *x* = 0.50 to evaluate the rate constant for gasification reactions of various carbonaceous materials at gasification temperatures ranging from 700 °C to 900 °C (Kim et al., 2014). The capability of the model to represent the experimental data was assessed using the squared value of correlation index, R^2.

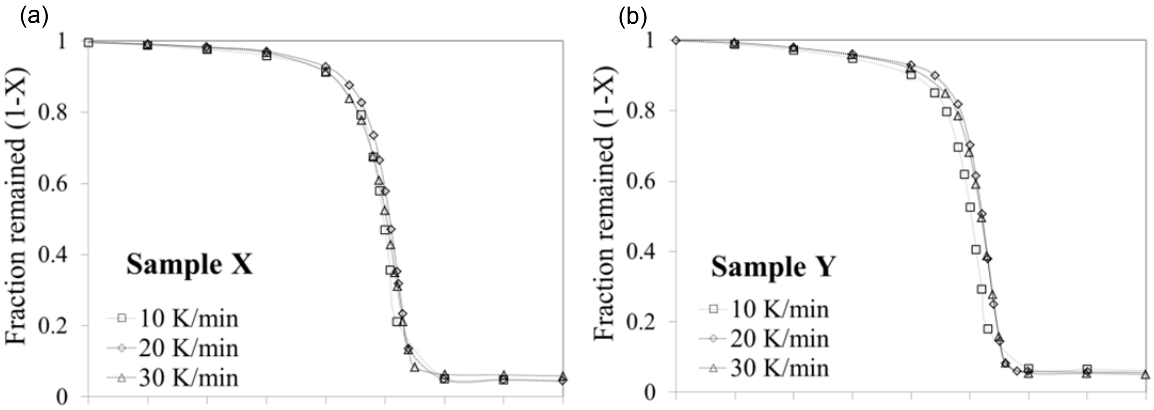

Figure 1: Thermograms of (a) sample X and (b) sample Y at different heating rates during pyrolysis

3. Results and discussion

This sections discusses variation of activation energies and frequency factors at different heating (pyrolysis) rates of plastic samples, and the impact of CO_2 gasification on the plastic wastes samples.

3.1 Pyrolysis of plastic samples

Figure 1 shows the TGA curves of the waste plastic samples at various heating rates. It can be seen from these plots that the mass of Samples X and Y started to decrease at about 240 °C. Sample Y appears to have greater initial pyrolysis rate than Sample X which can be explained from the lower activation energy of the pyrolysis reaction of Sample Y. The faster pyrolysis rate of Sample Y can also be attributed to its slightly higher volatile component compared to Sample X. The presence of higher amounts of volatile matter of Sample Y will influence faster pyrolysis reaction rate. For both plastic samples, the mass became nearly constant at about 5 % of the initial mass at approximately 500 °C.

The activation energies (E_A) of the reaction were obtained using Eq(4) and tabulated in Table 2. The variation of the activation energies with the heating rate can be explained by the heat transfer limitation within the sample. The values of the activation energies obtained were found to be similar to that of PS and PP (Encinar and Gonzalez, 2008) at heating rates between 10 - 30 K/min.

To compare the rate of pyrolysis of both plastic samples, Figure 2 shows the variation of pyrolysis rate with the heating rate. From this plot, Sample Y shows higher pyrolysis rate compared to Sample X as determined from the lower activation energy of pyrolysis of Sample Y compared to that of Sample X. Sample X shows an approximate linear relationship between the heating rate and maximum pyrolysis rate compared to sample Y which may indicate that Sample X has more uniform composition than Sample Y.

Table 2: Activation energies and frequency factors at various (pyrolysis) heating rates

Heating	Sample X			Sample Y		
Rate, β	E_A (kJ/mol)	A (h^{-1})	R^2	E_A (kJ/mol)	A (h^{-1})	R^2
10	124.17	9.12×10^{14}	0.9897	109.34	2.27×10^{13}	0.9705
20	120.94	6.03×10^{14}	0.9893	110.04	3.10×10^{13}	0.9963
30	127.24	9.88×10^{14}	0.9880	102.78	8.68×10^{13}	0.9883
Mean	124.11	8.34×10^{14}		107.39	2.08×10^{13}	

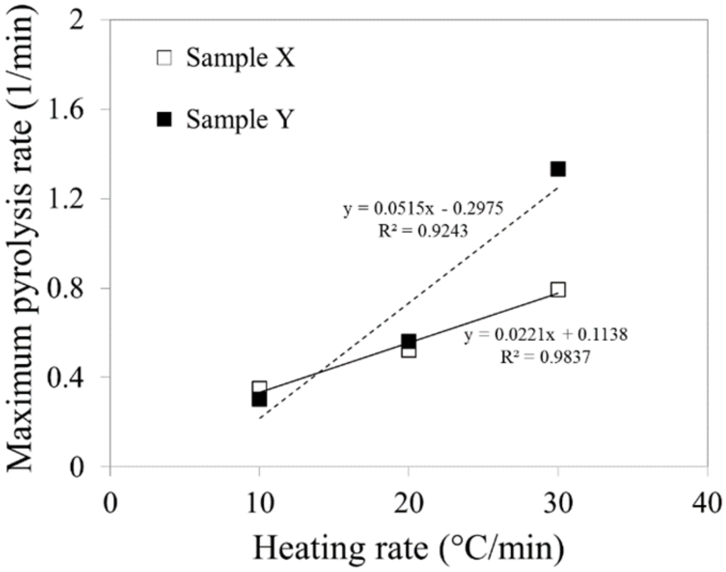

Figure 2: Variation of maximum pyrolysis rate with heating rate

3.2 Gasification of plastic waste samples with CO_2

For Sample X, an increase from 600 °C to 700 °C resulted to about 7.5 times increase in gasification rate while about 5 times for Sample Y. The increase in gasification temperature from 700 °C and 800 °C resulted to almost the same increase in gasification rate for both Samples X and Y. When temperature was increased to 900 °C, the increase in gasification rate was found to be 3 times and 7 times, for Samples X and Y. At higher temperatures, it can be deduced that some of the inorganic constituents of the plastic waste samples responsible for its catalysis may have been volatilised and the enhancement of the gasification rate is mainly due to the increase in the temperature.

In a related study which involved co-gasification of rubber seed shell and high-density polyethylene mixtures, high conversions at higher temperatures was also due to promotion of secondary cracking and other endothermic gasification reactions such as the water gas shift reaction (Chin et al., 2014). At 600 °C, the two samples behaved similarly in terms of the extent of char conversion as shown in Figure 3. Such low conversion can be attributed to the complex nature of the polymeric materials present in the waste plastic samples which requires higher temperature for its thermal degradation. Using the modified volumetric model, the Arrhenius parameters can be obtained and showed in Table 3.

Table 3: Activation energies and frequency factors of gasification of plastic samples with CO_2

Sample	E_A (kJ/mol)	A (h^{-1})	R^2
X	144.77	9.12×10^{14}	0.9897
Y	147.78	6.03×10^{14}	0.9893

From these constants, lower activation energy for Sample X is a clear manifestation of the catalytic effect from the inorganic components present in its ash. This trend in the rate is a complete reverse of what was observed from the rate of the pyrolysis reaction. It is therefore evident that the ash component in the plastic samples possesses catalytic activity and enhances the rate of gasification. Numerous investigations support this result since ash contains inorganic species that catalyses gasification reactions. In pyrolysis, the volatile matter in the samples is being removed until char is produced. The rate of pyrolysis can therefore be influenced by the volatile components of the samples.

Unlike gasification, the char produced was practically free from volatile matter and reacts directly to CO_2 with the inorganic species present in the ash acting as a catalytic agent. Although this study did not quantify the component of the ash, it is believed that the enhancement of the gasification reactions at lower temperatures is greatly influenced by these components. The modified volumetric model was found to best correlate the gasification of the plastic waste samples.

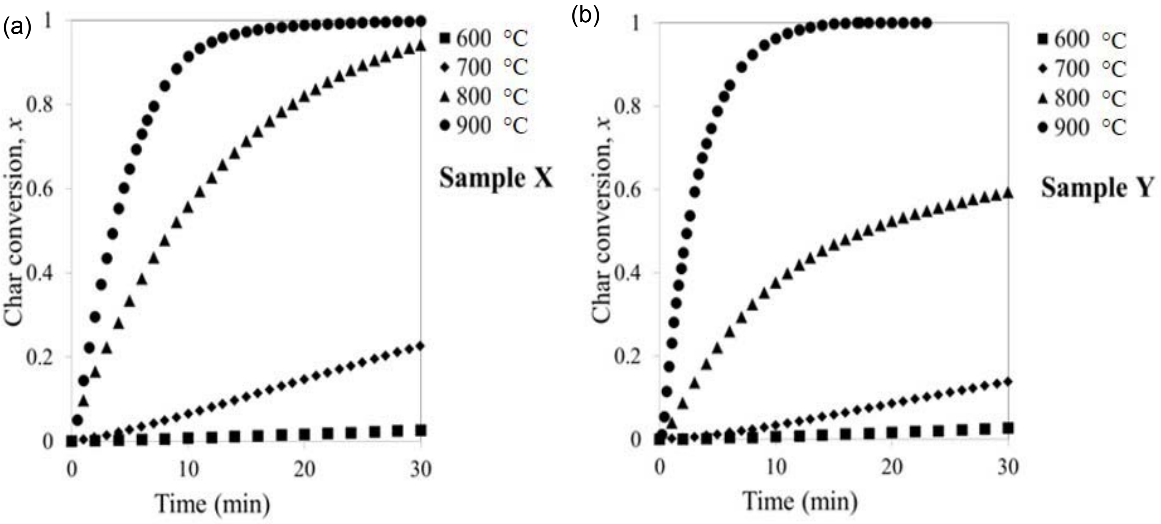

Figure 3: Time-conversion plots for the CO_2 gasification of plastic waste samples, (a) sample X, (b) sample Y

4. Conclusions

In this study, the kinetics of pyrolysis and gasification of plastic waste samples was investigated in terms of kinetic parameters such as activation energy and relative reaction rates. Initial decomposition of both plastic wastes was observed at 240 °C and terminated at 500 °C. Nearly 5 % of the samples remained at 500 °C and the activation energies of both samples was similar to a mixture of polystyrene and polypropylene. Sample Y was observed to react faster compared to Sample X during pyrolysis which may be due to a slightly higher amount of volatile matter in Sample Y. Sample X was found to be more reactive to gasification compared to Sample Y. This is due to the relatively higher amount of ash in Sample X compared to Sample Y. Highly reactive ash components may account for the high reactivity towards gasification of plastic samples. Increase in the gasification rate was found to range from 5 - 7 times at lower temperatures and negligible effect at higher temperatures. Both the single-reaction and modified volumetric models were sufficient to correlate pyrolysis and gasification reactions of plastic waste samples.

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