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The kinetic study of pyrolysis of lignite and polyethylene plastic bag waste using the thermogravimetric analysis

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Abstract. Lignite or low rank coal has a great potential to be utilized as an alternative energy. In this study, the pyrolysis of lignite and polyethylene plastic bag waste with different compositions (0, 25, 50 and 75 wt.% of polyethylene) had been investigated using a thermogravimetric analyzer. The results showed that the decomposition temperature of lignite was in the range of 250-600°C, while the decomposition temperature of lignite-polyethylene plastic bag waste mixtures was around 280-600°C. The addition of polyethylene to the lignite during pyrolysis reaction contributed to the increasing mass decomposition from 32.16 wt.% (lignite only or 0 wt.% of polyethylene) to 72.70 wt.% (75 wt.% of polyethylene). Furthermore, the thermogravimetric data were used to perform the kinetic study. The obtained kinetic parameters (activation energy and pre-exponential factor) for both lignite and lignite-polyethylene plastic bag waste mixtures were in the range of 16.16-28.95 kJ/mol and 0.014-0.212 min⁻¹.

1. Introduction

Indonesia has considerable coal potential. Based on the data from Indonesia Investments [1], Indonesia was the fifth rank of the countries that has the largest coal reserves in the world. Indonesian coal deposit is 0.5% of all coal reserves in the world [2]. South Kalimantan is the second largest area that has coal resources in Indonesia with a total amount of 4.7 billion tons [3]. The coals from this area include the types of lignite and sub-bituminous coals. Lignite is a low grade coal (low rank coal) which is caused by the low energy density and its high moisture content so that it is less efficiently used in direct combustion to produce energy [5].

Plenty of research has been conducted to optimize the use of lignite as an efficient energy source such as by increasing the grade of lignite or by converting it into liquid fuels. There are many methods of converting coal such as gasification, hydrothermal liquefaction [6], or pyrolysis [7]. Pyrolysis is one of the best coal upgrading methods for a clean and efficient utilization of lignite. Lignite contains high adequate-oxygen content, so it is less profitable in the pyrolysis process. The addition of hydrogen in the pyrolysis can improve product quality. However, pure gas hydrogen is still expensive.

Plastic waste still becomes a big problem for the environment. Besides being unable to be decomposed by nature, waste plastic will also cause air pollution if burned. The plastic waste recycling processes cause a major problem in the environment. The plastic waste that is often found in Indonesia is polyethylene in the form of plastic bags. According to Baofeng et al. [6], elements of C



and H contained in the plastic are very high, even higher than coal, and can interact during the pyrolysis process with lignite. It is hoped that plastic waste will help as the hydrogen “donor” during the lignite pyrolysis process.

The coal pyrolysis with polyethylene (PE) and polypropylene (PP) at various conditions demonstrates the enhancement of the liquid yields and the conversion of coals. The synergistic effects have been observed from the previous studies in the mixtures of PE and PP with low rank coal and lignite using hydrogen gas even though at low-set temperature [8]. All studies agree that the plastic contents have a contribution as the hydrogen supplier during coal pyrolysis[8].

In general, a thermogravimetric analysis (TGA) is used to study mass decomposition and kinetics over the pyrolysis of the solid materials including coal and plastic [11]. It plays a role in the determination of mass decomposition of the material linear to time and temperature. The kinetic parameters of this reaction are obtained by applying the Arrhenius law equation [11]. The knowledge of the kinetics of the thermal decomposition of the fuel feedstock is essential for further design of the pyrolysis systems and their conversion mechanisms.

In this research, the thermogravimetric analysis is conducted to investigate the mechanisms of pyrolysis of lignite/polyethylene plastic bag waste mixtures under the nitrogen atmosphere. By considering the overall processes as a one-step first order reaction, the kinetic model is determined to fit the thermogravimetric data.

2. Materials and methods

2.1 Materials

The raw materials utilized in this work included the low rank coal (lignite) from PT Adaro at Tabalong district and the polyethylene plastic bag waste obtained from PT Trijaya Abadi Banjarbaru, South Kalimantan. The particle size of lignite was less than 2 mm and the size of polyethylene plastic bag waste pelletized was less than 3 mm.

2.2 Pyrolysis

The pyrolysis reaction was conducted using a thermogravimetric analyzer Linseis STA PT 1600 with a heating rate of 10°C/min up to 600°C under 50 mL/min of nitrogen. The nitrogen flow was used to ensure an inert atmosphere condition. The mixture of lignite and pellet of PE were homogeneously mixed. Approximately 15 mg of samples and the PE pellets with the ratios of 0, 25, 50, and 75% from the total sample mixture were used for every run that were further labelled by PE, 25PE, 50PE, and 75PE.

2.3 Kinetic study

From the TGA results, the sample decomposition corresponding to the temperature of weight loss (TG) and the weight loss rate (DTG) was gained for the pyrolysis reaction [9, 11]. The weight loss rate (DTG) was calculated by the following equation 1

$$\frac{dW}{dt} = -\frac{1}{W_o} \left(\frac{dWt}{dt} \right) \quad (1)$$

The fraction of weight loss can be determined as the pyrolysis conversion x and can be computed by the following equation 2

$$x = \frac{W_o - W_t}{W_o - W_f} \quad (2)$$

where W_o is the initial mass of the sample; W_t is the mass at certain time t and W_f is the final mass that left at the end of pyrolysis [11].

By using the TGA data, the integral method was used to obtain the kinetic constants, such as the activation energy and the pre-exponential factor during pyrolysis of lignite and polyethylene plastic

bag waste [10, 11]. Many previous studies have made an assumption that a solid material pyrolysis mechanism includes first order reaction, and the heating rate is considered constant during pyrolysis [9, 11]. Following the Arrhenius law equation, thus the calculation for the kinetics of lignite and polyethylene plastic bag waste pyrolysis reaction can be explained by the equation below:

$$\frac{dx}{dt} = A \exp\left(-\frac{E}{RT}\right) (1 - x) \quad (3)$$

where A is pre-exponential factor, E is activation energy, T is temperature, t is time and x is obtained from Eq. (2).

Rewrite Eq. (3) at the heating rate H set at the constant value, H=dT/dt, and then integrating results:

$$\ln\left[\frac{-\ln(1-x)}{T^2}\right] = \ln\left[\frac{AR}{HE}\left(1 - \frac{2RT}{E}\right)\right] - \frac{E}{RT} \quad (4)$$

The expression $\ln [AR/HE(1-2RT/E)]$ in Eq. (4) is essentially constant for the most values of E at the temperature range of the pyrolysis [9, 11]. Then, if the left side of Eq. (4) as the function of y is plotted versus 1/T as the x function, a straight line will be gained if it is assumed that the pyrolysis reaction as a first order reaction. The slope and intercept of the resulted line should be used to determine the activation energy (E) and the pre-exponential factor (A).

3. Results and discussion

3.1. The proximate analysis

The proximate analysis was conducted to determine the raw material (lignite and PE) condition prior to the pyrolysis reaction. This consisted of water content, ash content, volatile matter and fixed carbon analysis.

3.1.1 Water content analysis

The water content was analyzed using a crucible that had been dried in an oven at 105°C for an hour and cooled in a desiccator for 15 minutes. Then 0.5 gram of the sample (lignite and PE) was put into the crucible then heated at 105°C for 180 minutes and cooled in the closed crucible for 15 minutes in the desiccator and then weighed. Afterward, the crucible that contained the sample was heated again at 105°C for 60 minutes and cooled again for 15 minutes in a desiccator then weighed. Then the third step was repeated until the difference between the last and the previous water content results was 0.0003 grams.

3.1.2 Ash content analysis

The ash content was analyzed by calcining a crucible using a furnace with a temperature of 575°C for 120 minutes, then it was cooled in a desiccator for 15 minutes. Next, 0.5 grams of the sample from the previous water content analysis was heated at 105°C for 180 minutes until the weight was stable, then it was weighed. The next step was 2-stage calcination, which was done by calcining it at a temperature of 250°C (the heating rate was 10°C/min.) for 30 minutes, followed by the calcination from 250–575°C for 150 minutes. After that, the sample was cooled in a desiccator and weighed then calcined again at 575°C for 60 minutes. This step was repeated until the weight was stable.

3.1.3 Volatile Matter Analysis

This volatile matter analysis was carried out by calcining the crucible using a furnace at a temperature of 950°C for 30 minutes then cooled and weighed. Next, about 0.5 grams of the sample was put into the crucible and closed then weighed. The calcination was repeated at 950°C for 7 minutes then cooled and weighed again.

3.1.4 Fixed carbon analysis

The fixed carbon value was calculated from the values of water content, ash content and volatile matter by using the equation as follows:

$$\% \text{ Fixed Carbon} = 100 - (\% \text{ Water Content} + \% \text{ Ash Content} + \% \text{ Volatile Matter}) \quad (5)$$

The results of proximate analysis of the lignite and PE are presented in table 1.

Table 1. Proximate analysis for the samples of lignite and PE plastic bag waste.

Samples	Proximate Analysis			
	Water (%)	Ash (%)	Volatile Matter (%)	Fixed Carbon (%)
Lignite	17.10	6.51	59.15	17.24
PE	0.34	3.37	95.61	0.68

3.2. Thermal decomposition of the lignite and the lignite-PE plastic bag waste mixtures

The thermogravimetric analysis (TGA) plotted the weight decomposition of the samples due to the increasing pyrolysis temperature. The TGA results for the lignite and the lignite-PE plastic bag waste mixtures with various compositions are shown in figure 1.

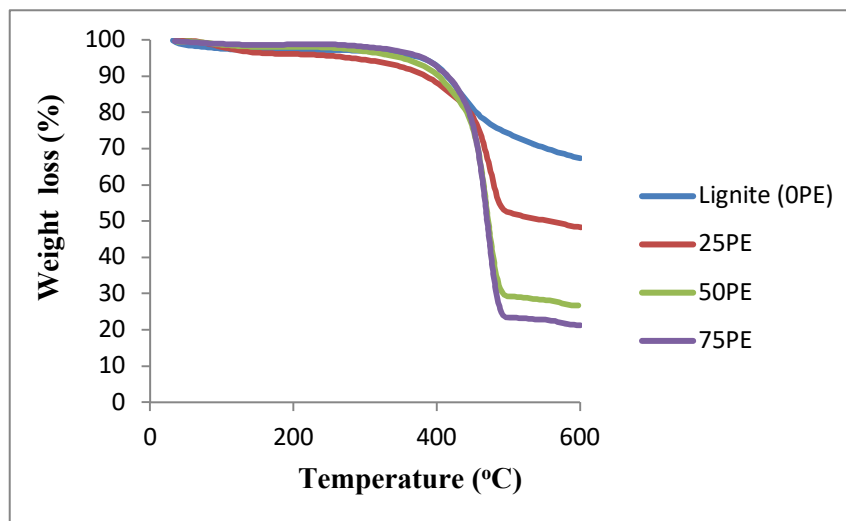


Figure 1. Thermogravimetry curves of lignite and polyethylene (PE) plastic waste pyrolysis.

Based on figure 1, it is obvious that the weight loss of all samples enlarge with the enhancement of temperature. In comparison, the curves of lignite and PE plastic bag waste have different trends in their thermal behavior possibly due to the difference in their structures [9].

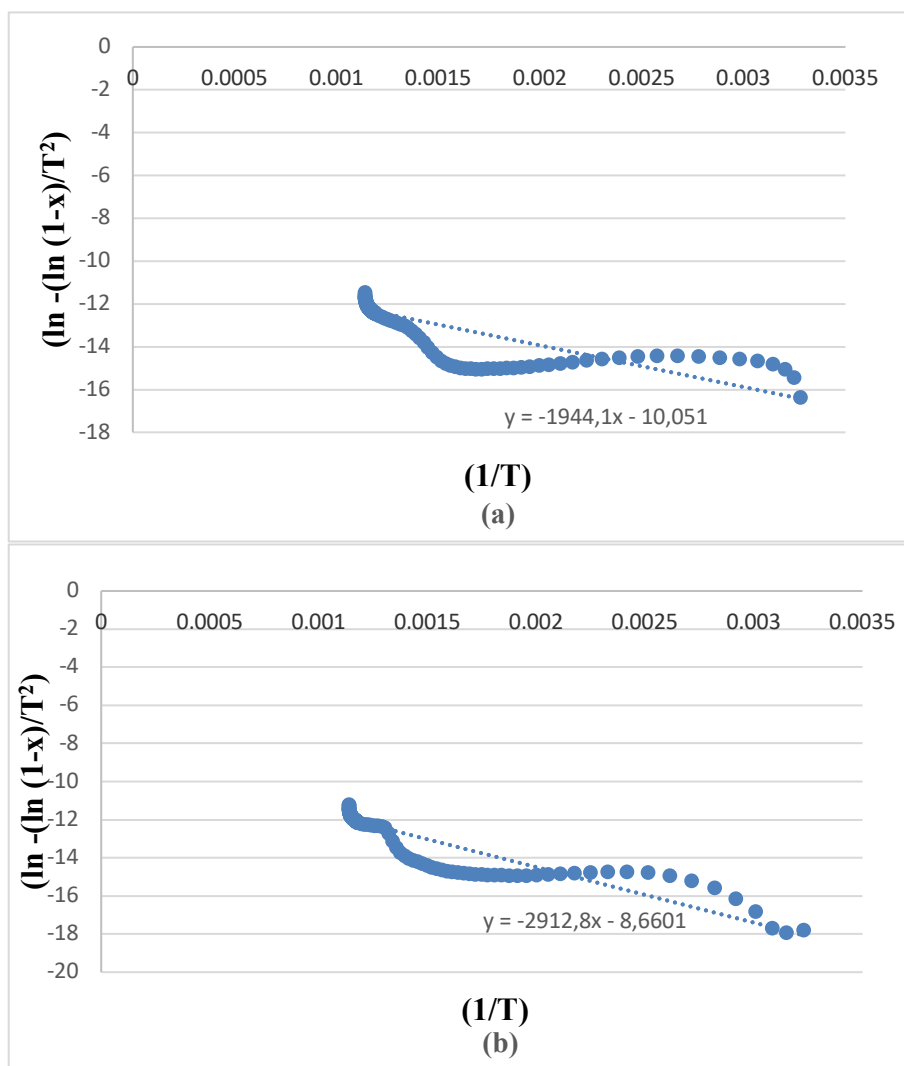
In general, biomass pyrolysis consists of three main steps [9], so does lignite pyrolysis. The first step, which was almost the same for all samples (below 200°C), was water removal. Next, the second step that resulted in the main weight decomposition occurred at different temperature ranges. The lignite itself mainly decomposed at 250-600°C. The addition of PE slightly shifted the main decomposition temperature to 280-500°C. Zhou et al. [8] point out that the second step of lignite pyrolysis is called an active thermal decomposition. This can be the most complicated step because the chemical bonds of the materials start to decompose at high temperatures [9]. The final step is the continuous devolatilization step that occurred at over 600 and 500°C for the lignite and the lignite-PE

mixtures, respectively. In the final pyrolysis reaction, the overall weight loss of lignite pyrolysis was 32.16 %, whereas the overall weight losses for co-pyrolysis of the lignite-PE plastic waste mixtures were 49.93%, 65.06%, and 72.20% due to the addition of 25PE, 50PE, and 75PE, respectively. The lower weight loss of the lignite compared to that of the mixtures possibly due to higher ash and fixed carbon contents [9, 11] as seen in table 1.

To conclude, the addition of PE plastic waste into the lignite pyrolysis through the thermogravimetry analysis (TGA) caused the final decomposition to occur with a lower temperature and the sample decomposition to increase.

3.3. Kinetic study

In order to determine the kinetic parameters of the pyrolysis reaction, namely activation energy and pre-exponential factor, equation 4 was applied. The linear model is established by plotting $\ln[-\ln(1-x)/T^2]$ versus $1/T$ for pyrolysis of the lignite and that of the lignite-PE plastic waste mixtures as shown in figure 2.



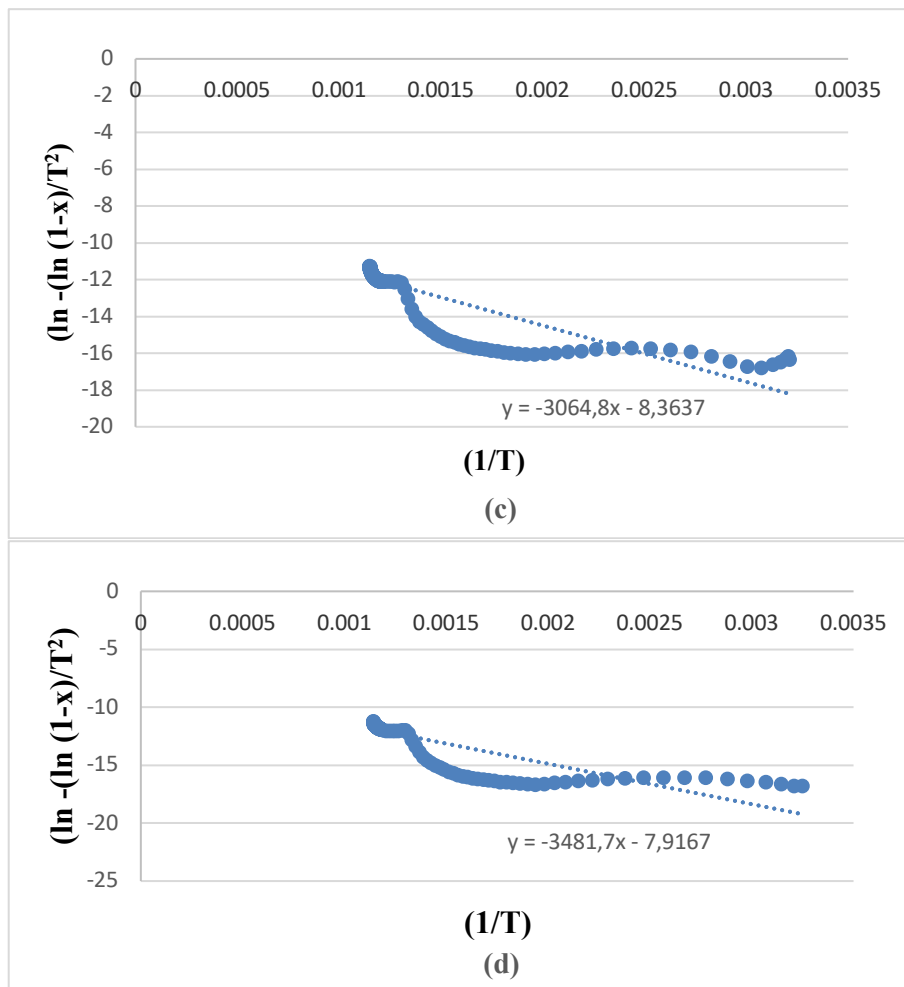


Figure 2. Plots of $\ln(-\ln(1-x)/T^2)$ vs $1/T$ of Lignite (OPE) (a), 25PE (b), 50PE (c), and 75PE (d) from the TGA data.

The results in figure 2 indicate that the data considerably fit the linear regression models with the R^2 values in the range of 0.69 to 0.86. Furthermore, the slope and intercept of each line can be used to compute the activation energy (E) and pre-exponential factor (A) as displayed in table 2.

Table 2. Kinetic parameters for pyrolysis of lignite and PE plastic bag waste.

Samples	E (kJ/mol)	A (min^{-1})	R^2
Lignite (OPE)	16.16	0.014	0.69
25PE	24.22	0.084	0.86
50PE	25.48	0.119	0.77
75PE	28.95	0.212	0.73

Data in table 2 confirm that the activation energy of lignite pyrolysis is 16.16 kJ/mol. During pyrolysis, the activation energy gets increasing to 24.22, 25.48, and 28.95 simultaneously with the increased PE compositions from 25, 50, to 75%, respectively. This result suggested that the energy

required to break the matrix of the lignite-PE plastic waste mixtures was higher than that of the lignite itself. It was because of the strong bonds in the matrix of the polymers in PE plastic waste. Hence, to destroy the bonds, it needed higher temperature and activation energy [9] than that of biomass, including lignite. Thus, the more PE used in the lignite pyrolysis, the more was the activation energy needed. The increase of activation energy as the PE compositions raised shows that the different pyrolysis reactivity is the result of different PE compositions.

4. Conclusion

This study investigated the thermal behaviors of lignite and polyethylene (PE) plastic bag waste using the thermogravimetric analyzer. The lignite started to decompose at a lower temperature than PE. The addition of PE plastic bag waste into the lignite caused the final decomposition to occur with a lower temperature while the sample decomposition got higher. The results from this kinetic study indicate that the first-order reactions of Arrhenius law equation satisfactorily fit for describing the pyrolysis mechanism of lignite and polyethylene (PE) plastic bag waste.

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