

# Multisteps Global Kinetic Analysis of MSW Slow Pyrolysis

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**Abstract**—The goal of this research is to find relationships between single component slow pyrolysis characteristics and mixed components slow pyrolysis characteristics of segregated Municipal Solid Wastes (MSW). The material of this research consists of organic wastes (bamboo wastes and banana leaf wastes) and inorganic wastes (styrofoam wastes and snack wrapping wastes). The materials which used to study were the unprocessed waste. The samples were collected, dried and crushed until passing 20 mesh sieves. Afterwards, pyrolysis was done in a self manufactured macro balance to find the MSW slow pyrolysis characteristics using the thermogravimetry analysis. The 20 gram sample was placed in the furnace whose temperature is increased with 10 °C/min heating rate until reached 400 °C final temperature and held for 30 minutes before the sample is cooled into room temperature. The results of the research show that the global kinetic method could be used to predict the MSW single component activation energy but it should be modified to calculate the mixed sample activation energy. The predictive activation energy values which calculated based on weighed sum of single component have 18.5 % deviations if compared with experimental result.

**Keywords**—Global kinetic, slow pyrolysis, municipal solid wastes

**Abstract**—Tujuan penelitian ini adalah untuk mendapatkan keterkaitan karakteristik slow pyrolysis antara komponen tunggal dan komponen campuran dari sampah kota terseleksi. Bahan yang digunakan dalam penelitian ini terdiri atas sampah organik (sampah bambu dan daun pisang) dan sampah anorganik (sampah styrofoam dan pembungkus kemasan). Dasar pemilihan bahan yang digunakan dalam penelitian ini adalah sampah yang tidak terolah. Pengambilan data diawali dengan pengumpulan bahan baku untuk kemudian dikeringkan dan dihaluskan dan diayak hingga lolos ukuran 20 mesh. Selanjutnya, pirolisis dilakukan dalam sebuah macrobalance untuk mencari karakteristik proses slow pyrolysis bahan dengan menggunakan metoda thermogravimetry. Proses pirolisis dilakukan dengan meletakkan 20 gram bahan baku dalam macrobalance yang suhunya dinaikkan dengan heating rate 10 °C/menit hingga mencapai temperatur akhir pirolisis 400 °C untuk kemudian dipertahankan selama 30 menit sebelum didinginkan hingga suhu kamar. Hasil pengambilan dan pengolahan data mengenai perhitungan energi aktivasi menunjukkan bahwa metode global kinetic dapat digunakan untuk menentukan besarnya energi aktivasi komponen tunggal, namun untuk komponen campuran perlu disempurnakan. Pendekatan penghitungan energi aktivasi proses pirolisis sampel campuran dapat didekati dengan weighed sum dari komponen-komponen tunggal penyusunnya, meskipun simpangan yang didapatkan sebesar 18,5 %.

**Kata Kunci**—kinetika global, pirolisis lambat, sampah kota

## I. INTRODUCTION

The alternative solution to solve energy provision is to find the abundant energy source reserves. Municipal Solid Wastes (MSW) can be one alternative of energy sources, although the conversion technology from wastes to energy is still intensively studied. The prospective technology to convert MSW to energy is pyrolysis, which can convert MSW into gaseous fuel, solid fuel and liquid fuel. The problems which to be faced when pyrolysing MSW are their quantity and their varied components.

The definition of pyrolysis is the solid thermal degradation in a limited oxygen condition, which produce permanent gas, pyrolytic liquid and char [1]. Many researchers have studied the MSW pyrolysis. Pyrolysis of 12 kg MSW within 400 °C-650 °C temperature range for 4 hours could produce 52.2 % pyrolytic liquid, 25.2 % char and 22.6 % permanent gas [2].

The packed bed pyrolyzer could increase char production 30 %-100 % compared with the TGA (Thermo Gravimetry Analysis) processes [3]. The study about municipal solid waste slow pyrolysis in a packed bed pyrolyzer have done by [4] and continue with the study of product characterization which resulting from the MSW slow pyrolysis [5]. The study of pyrolysis which continued with char combustion

characteristics of municipal solid waste carried out [6]. Pyrolysis and combustion characteristics of two RDF (Refused Derived Fuel) samples, 6 plastic based samples and 5 wood based samples conducted [7].

One problem in MSW pyrolysis is how to calculate the pyrolysis energy activation because of their multi components condition. This study tried to find the MSW pyrolysis energy activation based on its component decomposition temperature range.

## II. MATERIAL AND METHODS

### A. Materials

The materials which used as samples in this study had been collected from final dump site Piyungan Yogyakarta. The samples were bamboo wastes and banana leaf wastes represented organic wastes and inorganic wastes which consisted of styrofoam wastes and snack wrap wastes.

### B. Experimental Method

The first experimental step was collecting the samples and dried samples until the moisture content less than 12 %. Afterwards, all of raw materials were crushing and sizing until the particles sizes of samples passed 20 mesh. The main experimental apparatus was macro balance which adopted from [3] and modified by [9], the schematic configuration of the experimental apparatus can be seen in Figure 1. Pyrolysis was done on 20 grams sample with 100 ml/min N<sub>2</sub> as a swept gas. Heating rate which used in this study was 10 °C/min which increased until the sample temperature reached 400 °C and kept constant for 30 min.

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Thermo Gravimetry Analysis were done to obtain the sample pyrolysis graph. The weight losses data were recorded with A&D GF-300 Digital Scale while the sample temperatures obtained from the K type thermocouple which located 2 cm from the center of sample basket and 1 cm above the base of sample basket and recorded with ADAM 4018 data acquisitions system. Energy activation calculated based on Arrhenius formulae with first reaction order, which called global kinetics. Table 1 shows the sample composition variations which used in this research.

### III. RESULTS AND DISCUSSION

The activation energy calculation of single samples pyrolysis process has been carried out by [8]. The calculations showed that the activation energy of the pyrolysis of bamboo was 52.6 kJ/mol, the banana leaves pyrolysis activation energy was 49.1, snack wrap wastes need a minimum energy of 124.2 kJ/mol to pyrolyze and styrofoam waste had activation energy of 118.2 kJ/mol. The summary of single sample pyrolysis activation energies can be seen in Table 2.

The results of calculations using the one-step global kinetic analysis can not describe the process of mixed samples thermal decomposition, therefore the mixed samples pyrolysis activation energy calculations using a multi step global kinetic method carried out to link the activation energy of the decomposition with the decomposition temperature of sample main components. Multistep approach has also been done by [1] and [10].

The process of thermal decomposition of samples based biomass cannot be separated from the process of thermal decomposition of their main components, namely hemicellulose, cellulose and lignin. Hemicellulose degraded over a temperature range 498-598 K (225°C-325°C) with an activation energy varied between 80-116 kJ/mol, while cellulose will pyrolysed decomposed gradually in the range 523-773 K (250°C-500°C) with activation energy of 18-65 kJ/mol and lignin be decomposed with an activation energy in the temperature range 598-648 K (325°C - 375°C) which had an activation energy of 195-286 kJ/mol [1]. For the pyrolysis process of plastic-based samples, it was found that polystyrene will pyrolysed with activation energies 251.2 kJ/mol while low density polyethylene requires activation energy 206.4 kJ/mol [10].

In this study, it appears that the pyrolysis thermal decomposition temperature of the sample followed its main components which can be seen in Figure 2 and summarized in Table 3.

The results of activation energy calculation of the mixture samples (i.e 50 % wt organic-50 % wt inorganic) can be seen in Figure 3 and summarized in Table 4. In the table, it can be seen that the mixed samples pyrolysis temperature range was followed the pyrolysis temperature range of a single sample, but the samples pyrolysis had an over-lapping pyrolysis temperature. It might be caused of the sample mixing process gave the synergetic effect or intercomponents reaction which affect the calculation of activation energy pyrolysis. The synergistic effect which occurred at overlapping pyrolysis temperatures must be considered when pyrolyse the mixture materials. Inorganic wastes gave special

effect to the mixture material because of the effect of styrofoam component which have nearly 100 % volatile. Greater volatile components in styrofoam wastes make the pyrolysis process occurred in lower activation energy. On the contrary, the snack wrap needs the higher activation energy to pyrolyse if compared with the lignocellulosic and styrofoam samples. These different behavior can be explained by the fact that polypropylene soften at about 440°C [10] which can be inhibit the evolution of lignocellulosic volatile matter components.

This study performed a calculations which can be use to predict the activation energy of samples pyrolysis. The predictive calculations were based on [7] which stated that the weight lost of the sample mixture during the study is the weighed sum of single component samples and the result could be seen in Figure 4.

The result of calculation showed that the difference between the predicted results with experimental results is 18.5%, where the experimental results gave activation energy of 55.1 kJ/mol while the predicted results gave activation energy of 45.1 kJ/mol (Figure 5). The difference was presumably because of the intermolecular reactions. In Figures 5, it appears that the predicted results approach the experimental results both in terms of magnitude and temperature range that occurred. On the other hand, the predicted results are not able to estimate the relationship between the experimental results of the single components making up the mixture components. This proves that there is a synergetic effect in the sample pyrolysis mixtures that are difficult to predict.

### IV. CONCLUSIONS

From the research conducted, it could be concluded that the calculation results of pyrolysis activation energy showed that the global kinetic methods can be used to determine the activation energy of single components, but for the mixture components need to be modified by using the shifting method based on single components pyrolysis temperature. Calculation results of the mixed samples pyrolysis activation energy based on weighed sum of the components of a single constituent gave the deviations of 18.5% if compared with experimental results.

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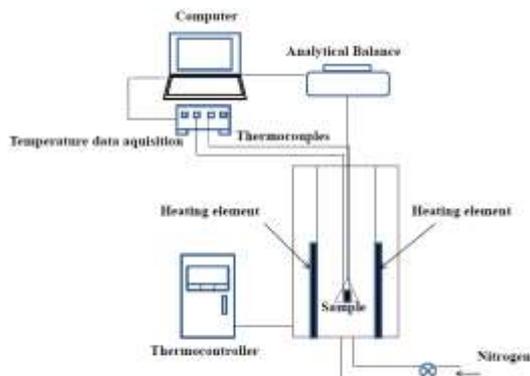


Figure 1. Experimental apparatus

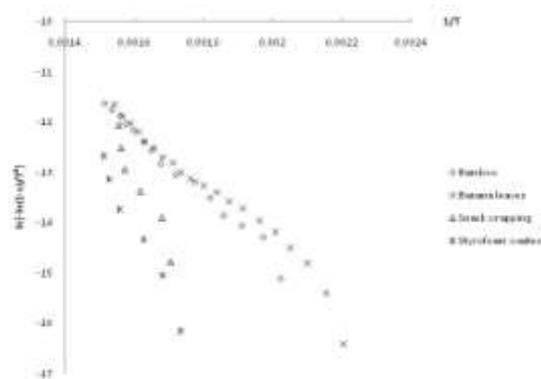


Figure 2. Sample pyrolysis activation energy

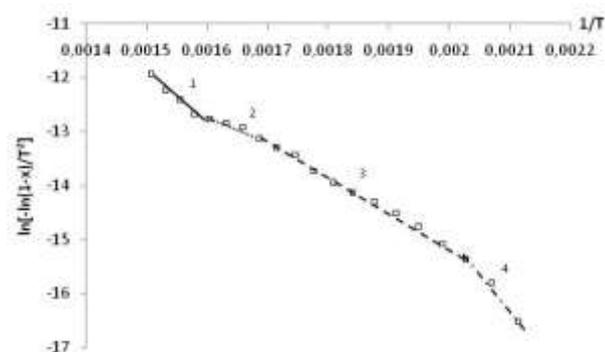


Figure 3. Activation energy of 50 % organic sample based on pyrolysis temperature zone

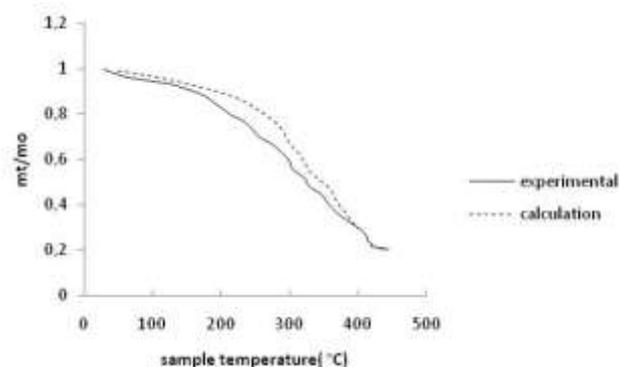


Figure 4. Comparison mt/mo graph between experimental result and calculation result for 50 % organic sample pyrolysis

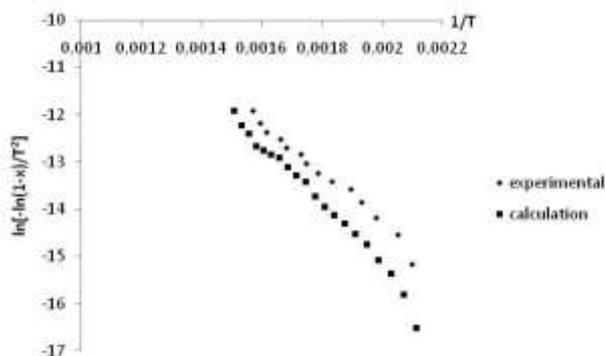


Figure 5. Comparison activation energy between experimental result and calculation result for 50 % organic sample pyrolysis

TABLE 1  
MIXED COMPOSITION VARIATIONS

No.	Variations	Components (%)			
		Bamboo wastes	Banana leaves wastes	Snack wrap wastes	Styrofoam Wrap wastes
1.	RDF 1	100	0	0	0
2.	RDF 2	0	100	0	0
3.	RDF 3	0	0	100	0
4.	RDF 4	0	0	0	100
5.	RDF 5	25	25	25	25

TABLE 2  
SUMMARY OF KINETIC PARAMETERS FOR SINGLE SAMPLE PYROLYSIS\*

Samples	Activation Energy, E (kJ/mol)	Pre-exponential Factor, A (min <sup>-1</sup> )
Bamboo wastes	52.598	3.00 x 10 <sup>7</sup>
Banana wastes	49.063	2.79 x 10 <sup>7</sup>
Snack wrapping wastes	124.186	8.36 x 10 <sup>7</sup>
Styrofoam wastes	118.208	8.37 x 10 <sup>7</sup>

\*Source : [8]

TABLE 3  
SINGLE COMPONENT PYROLYSIS ACTIVATION ENERGY BASED ON PYROLYSIS TEMPERATURE ZONE

Samples	Zone	Temperature range (°C)	Activation energy E (kJ/mol)
Bamboo	1	308.0 – 395.6	60.2
	2	289.5 – 308.0	22.1
	3	264.6 – 289.5	67.2
	4	233.5 – 264.6	31.2
	5	220.9 – 235.5	136.7
Banana leaves	1	321.1 – 383.8	61.0
	2	224.7 – 321.1	36.9
	3	190.8 – 224.7	67.6
	4	180.4 – 190.8	170.5
Snack wrap	1	362.5 – 369.5	416.7
	2	322.2 – 362.5	74.7
Styrofoam	1	368.6 – 387.7	192.2
	2	321.3 – 368.6	86.9
	3	303.4 – 321.3	175.5

TABLE 4  
MIXED SAMPLE PYROLYSIS ACTIVATION ENERGY BASED ON PYROLYSIS TEMPERATURE ZONE

Zone	Temperature range (°C)	Activation energy E (kJ/mol)
1	360 – 390	83.2
2	330 – 360	27.2
3	220 – 330	53.2
4	200 – 220	111.6

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