

Thermogravimetric Analysis and Global Kinetics of Segregated MSW Pyrolysis

Dwi Aries Himawanto

Department of Mechanical Engineering, Sebelas Maret University

Jalan Ir. Sutami no. 36A, Kentingan, Surakarta, Republic of Indonesia

Ph.D student in Department of Mechanical and Industrial Engineering, Gadjah Mada University

Tel: 62-271-632163 E-mail: dwi_ah@uns.ac.id

Indarto, Harwin Saptoadi & Tri Agung Rohmat

Department of Mechanical and Industrial Engineering, Gadjah Mada University

Jalan Grafika no. 2 Bulaksumur, Yogyakarta, Republic of Indonesia

Received: October 26, 2011

Accepted: November 28, 2011

Published: January 1, 2012

doi:10.5539/mas.v6n1p120

URL: <http://dx.doi.org/10.5539/mas.v6n1p120>

The research is financed by the Directorate General of Higher Education, Ministry of National Education RoI under Disertasion Research Grant in 2010 and Competitive Research Grant in 2009-2010 research program

Abstract

Municipal Solid Wastes (MSW) has great potential as a clean, renewable feedstock for producing modern energy carriers through thermochemical process, called pyrolysis. However, despite their enormous potential as energy sources, their thermal characteristics are still not well known. Moreover many researches just pay a little attention on MSW from developing countries, for example Indonesia MSW contains some indigenous wastes such as bamboo and banana leaves wastes, therefore this paper tries to show the slow pyrolysis characteristics of Indonesian MSW.

Investigations on behaviors of segregated MSW slow pyrolysis have been conducted using macro balance apparatus. Four components of segregated MSW (bamboo wastes, banana leaves wastes, snack wrap wastes and styrofoam wastes) and their blends were pyrolysed and then thermogravimetry analysis has been done and their characteristics such as pyrolysis profiles and activation energies, were analysed and calculated. About 20 grams of samples were pyrolysed under 100 ml/min N₂ at constant heating rate of 10 °C /min from room temperature to 400 °C final pyrolysis temperature and then the temperature of samples were kept constant for 30 minutes. The nitrogen flow serve swept gas which ensures an inert atmosphere during the pyrolysis test. In order to indentify pyrolysis characteristics of the samples, thermogravimetry analysis was performed. The recorded data were weight losses and sample temperatures during the pyrolysis process.

The results of the research showed that bamboo wastes and banana leaves wastes could be categorized as low stability organics, while snack wrap wastes could be categorized as polymer mixture materials and styrofoam wastes could be classified as plastic materials. Meanwhile profiles of blends materials pyrolysis followed the characteristics of their single components which is indicated by peak temperature. This study also found that global kinetic method could calculate the pyrolysis activation energy.

Keywords: MSW, Pyrolysis, Thermogravimetry, Global kinetics

1. Introduction

Municipal Solid Waste (MSW) management become important because of public awareness towards cleaner environment, due to the increase of their quantities and complex components. In Indonesia, the annual MSW production in 2008 were 36.5 billion tons which consists of 58% organic wastes, 14% plastic based wastes, 9% paper based wastes and wood based wastes. The limitations and impact of existing MSW treatments technology forced researchers to develop alternative waste treatments technology and the one alternative is to convert MSW to energy. On the other side, the depletion of fossil fuel reserves and the increasing of energy need makes researches about alternative energy sources with abundant reserves more important.

Slow pyrolysis of MSW can be a prospective technology to treat MSW if compared with other alternatives which can solve environmental and energy problems. Pyrolysis is defined as thermal degradation of solids in a limited oxygen condition that can produce permanent gas, pyrolytic liquid and char (Di Blasi, 2008). A research of the MSW pyrolysis using 12 kg MSW with a temperature range 400 °C – 650 °C for 4 hours could produce 52.2% tar, 25.2% char and 22.6% gas (Ojolo and Bamgboye, 2005). A study about segregated MSW slow pyrolysis in a packed bed pyrolyzer showed that packed bed pyrolysis system could increase char production 30% - 100% compared with the TGA processes (Swithenbank, et al., 2005). A research which carbonized MSW as an artificial coal showed that the heating value of MSW char could reach a half of coal heating value (Matsuzawa, et al., 2007). An optimum slow pyrolysis condition which could produce the balance pyrolysis product was conducted by Phan et al. (2008) and found the optimum pyrolysis temperature should be below 500 °C. Grammelis et al. (2009) conducted a research about pyrolysis kinetics and combustion characteristics of waste recovered fuels, and found that the thermal degradation of the refuse derived fuel samples was modeled assuming four parallel reactions corresponding to the devolatilisation of cellulose, hemicellulose, lignin and plastics.

Moreover many researches pay only a little attention on MSW from developing countries, for example Indonesia MSW contains some indigenous wastes such as bamboo and banana leaves wastes, therefore this paper tries to show the slow pyrolysis characteristics of Indonesian MSW.

2. Materials and Methods

2.1 Samples

Materials tested in this research were unprocessed MSW components which were taken from Final Waste Dipsal Site Piyungan Yogyakarta, and consist of organic wastes and unorganic wastes, which could be seen on Figure 1.

The organic wastes consists of bamboo wastes (from Javanese traditional basket) and banana leaves wastes (from Javanese traditional food wrap). These wastes come from Indonesian traditional market. The anorganic wastes, especially plastic based wastes, consists of snack wrap wastes and styrofoam wastes. All of samples were crushed until the particles sizes of samples passed 20 mesh.

2.2 Methods

Pyrolysis was carried out with macro balance which was adopted from Swithenbank et al. (2005). About 20 grams of sample was pyrolysed under 100 ml/min N₂ at constant heating rate of 10 °C /min from room temperature to 400 °C final pyrolysis temperature which is kept constant for 30 minutes. The nitrogen flow serve swept gas which ensures an inert atmosphere during the pyrolysis test.

In order to indentify pyrolysis characteristics of the samples, thermogravimetry analysis was performed. The recorded datas were weight losses and sample temperatures during the pyrolysis process. A K-type thermocouple was inserted into the sample which located 2 cm from the center of sample basket and 1 cm above the base of sample basket. The sample temperatures were recorded with ADAM 4018 data acquisitions system, while the weight losses recorded with A&D GF-300 Digital Scale. The scheme of experimental apparatus is described in Figure 2.

3. Results and Discussion

3.1 Single Component Pyrolysis

Pyrolysis temperature ranges of each samples could be seen on Table 1, the table shows that bamboo was pyrolysed starting from around 241.6 °C and continuing until 410 °C, where the highest mass loss occurred at about 277.9 °C, while the banana leaves wastes was pyrolysed from 199 °C to 414.7 °C with the highest decomposition rate at 321.8 °C. Snack wrap wastes were thermally degraded at temperatures between 262.5 °C and 410 °C with the highest mass losses occurred at 362.5 °C. Styrofoam wastes were pyrolysed at 316.3 °C – 417 °C with two peak temperatures which occurred at 370.6 °C and 407.5 °C. From the experimental results, it could be concluded that bamboo wastes was starting pyrolysed at of hemicellulose decomposition temperature. Heikkinen et al. (2004) explained that the maximum decomposition rates of xylan, the one of hemicellulose type, occurred at 298 °C. The same results also occurred on banana leaves wastes pyrolysis. Based on the peak temperature, i.e. the temperature which highest devolatilisation rates occurred which defined by Heikkinen et al. (2004), bamboo wastes and banana leaves wastes categorized as low stability organic component (LSOC), i.e. materials which have the peak temperature around 300 °C. The peak temperature of snack wrap wastes occurred at 362.5 °C, which is close to the peak temperature of milk carton (Heikkinen et al. (2004)), i.e. 368 °C, although the main material of snack wrap wastes is polypropylene which has peak temperature around 472 °C. This result gave prediction that snack wrap

wastes were laminated materials which consisted of several materials and one of those material had the lower peak temperature than polypropylene. Styrofoam wastes pyrolysis had two peak temperatures, i.e. 370.6 °C and 407.5 °C which could be categorised as plastic materials which have high thermal stability and have peak temperature above of 400 °C. The styrofoam wastes pyrolysis which is used in this research followed the thermal decomposition of GS and polystyrene, which have peak temperature 394 °C and 467 °C. GS is the real plastic wastes from Germany and the exact composition is unknown (Heikkinen, et al., 2004).

3.2 Pyrolysis of Blends Materials

Table 2 shows the pyrolysis temperature ranges and the peak temperature of mixed components samples. It could be seen that the mixed component samples initial pyrolysis temperature located between the initial pyrolysis temperature of each component with exception in organic mixed component.

The initial pyrolysis temperature of organic mixed component higher than the single component pyrolysis initial temperature. It caused of synergetic reactions which occurred between the component.

Banana wastes – bamboo wastes mixed samples begin to decompose at 176.3 °C and finished at 418.8 °C and signed with one maximum mass loss rate at 322.7 °C and one shoulder located at 273.4 °C. According to Di Blasi (2008) biomass started to be decomped at 227 °C, while Kalita et al. (2009) found that bamboo dust pyrolysed at 190 °C to 365 °C. Shoulder which located at left side of maximum loss rate temperature indicated that the sample was lignocellulosic material which maximum mass loss rate just occurred at one sample while the other sample would be signed with little peak (shoulder). Snack wrapping – styrofoam mixed wastes pyrolysis occurred at 284.4 °C – 396.8 °C with two maximum mass losses temperature.

Meanwhile for the unorganic-organic blends gave the same results i.e there were some peak which represented their main component as seen in Figure 3 –Figure 6. From those figures, could be seen that bamboo wastes – snack wrap wastes mixtures started pyrolyse at 183.3 °C and continuing until 416.3°C with three peak temperatures which occurred at 276.5 °C, 316.3 °C and 394.3 °C. The first peak temperature referred to bamboo peak temperature, the third peak temperature near to the snack wrap temperature, while the second peak temperature occurred as the effect of synergetic reactions between the components. The phenomena could be seen in banana wastes – snack wrap wastes mixtures.

A different phenomena could be seen in the styrofoam based mixtures pyrolysis. It could be observed that the first peak temperature, which represented biomass component temperature, were lower than its component peak temperatures. These conditions predicted caused of the styrofoam physical characteristics i.e melt and hardened while pyrolysed.

3.3 Global Kinetic Analysis

Energy activation is calculated based on Arrhenius formulae with first reaction order, which called global kinetics, and expressed as the following formulae

$$\frac{dx}{dt} = Ae^{-\frac{E}{RT}}(1-x) \quad (1)$$

where A is pre-exponential factor, E is activation energy, T is temperature, t is time, x is pyrolysis conversion which calculated as

$$x = \frac{w_0 - w}{w_0 - w_f} \quad (2)$$

if β is a constant heating rate which defined as

$$\beta = \frac{dT}{dt} \quad (3)$$

Rearranging equation (1) gives

$$\frac{dx}{dT} = \frac{A}{\beta} e^{-\frac{E}{RT}}(1-x) \quad (4)$$

$$\frac{dx}{(1-x)} = \frac{A}{\beta} e^{-\frac{E}{RT}} dT \quad (5)$$

Integrating equation (5), the following equation can be obtained

$$-\ln(1-x) = \frac{A}{\beta} \int e^{-\frac{E}{RT}} dT \quad (6)$$

Since $\int e^{-\frac{E}{RT}} dT$ has no exact integral, $\int e^{-\frac{E}{RT}} dT$ can be expressed as an asymptotic series and integrated, with the higher order terms ignored, and equation (6) becomes

$$-\ln(1-x) = \frac{ART^2}{\beta E} \left[1 - \frac{2RT}{E}\right] e^{-\frac{E}{RT}} \quad (7)$$

Rearranging equation (7) gives the following equation

$$-\frac{\ln(1-x)}{T^2} = \frac{AR}{\beta E} \left[1 - \frac{2RT}{E}\right] e^{-\frac{E}{RT}} \quad (8)$$

Expressing equation (8) into logarithmic form gives

$$\ln\left[-\frac{\ln(1-x)}{T^2}\right] = \ln\left[\frac{AR}{\beta E} \left[1 - \frac{2RT}{E}\right]\right] - \frac{E}{RT} \quad (9)$$

Since $\frac{2RT}{E} \ll 1$ is assumed,

$$\ln\left[-\frac{\ln(1-x)}{T^2}\right] = \ln\left[\frac{AR}{\beta E}\right] - \frac{E}{RT} \quad (10)$$

And by make a plot the relation between $\ln\left[-\frac{\ln(1-x)}{T^2}\right]$ and $1/T$, give straight line with $-E/R$ slope thus the

activation energy can be defined, and by taking the temperature at which $W_t = (W_o + W_f)/2$ in the place of T in the intercept term of Eq. (10), the pre-exponential factor A can also be determined.

Figure 7 – Figure 13 displayed the plot between $\ln\left[-\frac{\ln(1-x)}{T^2}\right]$ and $1/T$ for the samples both singles and mixed,

and the results of all samples summarized in Tables 3.

The results showed that bamboo pyrolysis activation energy is 52.598 kJ/mol, the previous study about *bamboo dust* pyrolysis had been done by Kalita et al. (2009) and found that the pyrolysis activation energy was 98.22 kJ/mol with reaction order 3.55 at temperature range 190 °C – 365 °C. Meanwhile PS and LDPE had activation energy were 251.2 kJ/mol and 206.4 kJ/mol (Sorum (2001)), while the activation energy of styrofoam wastes and snack wrap wastes which found from this study were 118.208 kJ/mol and 124.186 kJ/mol. From this study also found the pyrolysis activation energy of banana leaves was 49.063 kJ/mol.

For biomass based materials, the pyrolysis activation energy influenced by thermal decomposition process of their main component i.e hemicellulose, lignin and cellulose. Hemicellulose decomposed at temperature range 225 °C – 325 °C with activation energy varied between 80 – 116 kJ/mol, lignin pyrolysed at 325 °C – 375 °C and have higher activation energy 195 – 286 kJ/mol, while cellulose thermally decomposed gradually at 250 °C – 500 °C and had the lowest activation energy 18 – 65 kJ/mol (Di Blasi, 2008).

Meanwhile blend materials pyrolysis activation energy values gave several results. The lignocellulosic blends samples pyrolysis gave the lower activation energy if compared with their component, it caused of the synergistic effect which occurred at overlapping pyrolysis temperatures. Unorganic wastes blends pyrolysis also

occured at the lower activation energy than their components. These phenomenon is predicted caused by the efect of styrofoam component which have nearly 100% of volatile matter. The greater volatile components in styrofoam wastes make the pyrolysis process could done with lower activation energy, these occured in styrofoam wastes based blends.

On the contrary, the snack wrap wastes based blends need a higher activation energy if it is compared their lignocellulosic component and if compared with styrofoam based blend pyrolysis, these different behaviour can be explained by the fact that polypropylene soften at about 440 °C (Cai, et al., 2008) which could be inhibit the volatile matter evolution of lignocellulosic component so that to increase the activation energy.

4. Conclusions

The results of this research showed that the organic components wastes could be catogorized as low stability organics, while the snack wrapping could be categorised as mixed polymer material. Styrofoam wastes could be categorised as plastic material which have high thermal stablity. This study also found that global kinetic method could to calculate the pyrolysis activation energy. The lignocellulosic blends pyrolysis gave the lower activation energy if compared with their component. Anorganic wastes blends pyrolysis also occured at the lower activation energy than their components. On the contrary, the snack wrap wastes based blends need the higher activation energy if compared their lignocellulosic component and if compared with styrofoam based blend pyrolysis.

References

- Cai, J., Wang, Y., Zhou, L., & Huang, Q. (2008). Thermogravimetric Analysis and Kinetic of Coal/Plastic Blends during Co-Pyrolysis in Nitrogen Atmosphere. *Fuel Processing Technology*, 89, 21-27. <http://dx.doi.org/10.1016/j.fuproc.2007.06.006>
- Di-Blasi, C. (2008). Modeling Chemical and Physical Processes of Wood and Biomass Pyrolysis. *Progress in Energy and Combustion Science*, 34, 47-99. <http://dx.doi.org/10.1016/j.pecs.2006.12.001>
- Grammelis, P., Basinas, P., Malliopoulou, A., & Sakellariopoulos, G. (2009). Pyrolysis Kinetics and Combustion Characteristics of Waste Recovered Fuels. *Fuel*, 88, 195-205. <http://dx.doi.org/10.1016/j.fuel.2008.02.002>
- Heikkinen, J. M., Hordijk, J. C., de Jong, W., Spliethoff, H.(2004). Thermogravimetry as a tool to clasify waste components to be used for energy generation. *J.Anal.Appl.Pyrolysis*, 71, 883-900. <http://dx.doi.org/10.1016/j.jaap.2003.12.001>
- Himawanto, D. A., Indarto, Saptoadi, H., & Rohmat,T. A.(2011). Characteristics and Global Kinetics Approaches of Segregated MSW Slow Pyrolysis (in Indonesian language). *Jurnal Reaktor*, 13(3), 140-147.
- Kalita, P., Mohan, G., Pradeep, K., & Mahanta, P. (2009). Determination and Comparasion of Kinetic Parameter of Low Density Biomass Fuels. *Journals of Renewable and Sustainable Energy*, 1, 023109. <http://dx.doi.org/10.1063/1.3126936>
- Matsuzawa, Y., Mae, K., Hasegawa, I., Suzuki, K., Fujiyoshi, H., Ito, M., & Ayabe, M. (2007). Characterization of Carbonized Municipal Waste as Substitute for Coal Fuel. *Fuel*, 86, 264–272. <http://dx.doi.org/10.1016/j.fuel.2006.06.008>
- Ojolo, S. J., & Bamgboye, A. I. (2005).Thermochemical Conversion of Municipal Solid Waste to Produce Fuel and Reduce Waste. *Agricultural Engineering International: the CIGR Ejournal*, Vol. VII, Manuscript EE 05 006.
- Phan, A. N., Ryu, C., Sharifi, V. N., & Swithenbank, J. (2008). Characterisation of Slow Pyrolysis Products from Segregated Wastes for Energy Production. *J.Anal.Appl.Pyrolysis*, 81, 65-71. <http://dx.doi.org/10.1016/j.jaap.2007.09.001>
- Sørum, L. (2001). Characteristics of MSW for Combustion System, Technical Report, SINTEF Energy Research.
- Swithenbank, J., Sharifi, V. N., & Ryu, C. (2005).Waste Pyrolysis and Generation of Storable Fuel. SUWIC Department of Chemical and Process Engineering, The University of Sheffield.
- Yang, Y. B., Phan, A. N., Ryu, C., Sharifi, V., Swithenbank, J. (2007). Mathematical Modelling of Slow Pyrolysis of Segregated Solid Waste in A Packed-Bed Pyrolyser. *Fuel*, 86, 169-180. <http://dx.doi.org/10.1016/j.fuel.2006.07.012>

Table 1. Singles component samples pyrolysis temperature ranges

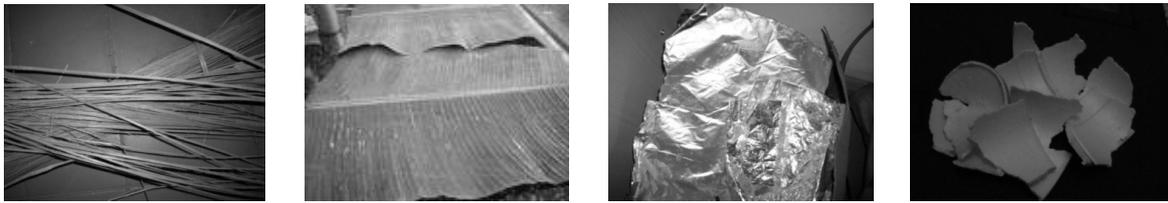
Sample	Pyrolysis Temperature (°C)	Peak Temperature (°C)
Bamboo wastes	143.1 – 426.5	277.9
Banana leaves wastes	130 - 414.7	321.8
Snack wrap wastes	222.8 – 422.7	362.5
Styrofoam wastes	316.3 - 417	370.6; 407.5

Table 2. Mixed samples pyrolysis temperature ranges

Sample	Pyrolysis Temperature (°C)	Peak Temperature (°C)
50 % banana wastes – 50 % bamboo wastes	176.3 – 418.8	322.7
50 % snack wrap wastes– 50 % styrofoam wastes	284.4 – 396.8	390.9; 415
50 % bamboo wastes – 50 % snack wrap wastes	183.3 – 416.3	276.5; 316.3; 394.3
50 % bamboo wastes – 50 % styrofoam wastes	143.3 – 462.3	232.8; 357.0
50 % banana leaves wastes – 50 % snack wrap wastes	166.9 – 425.9	312.1; 409.5
50 % banana leaves wastes – 50 % styrofoam wastes	173.7 – 405.0	276.2; 338.1; 401.5

Table 3. Summary of kinetic parameters for samples pyrolysis

Samples	E (kJ/mol)	A (min ⁻¹)	R ²
Bamboo wastes	52.598	3.00 x 10 ⁷	0.9869
Banana wastes	49.063	2.79 x 10 ⁷	0.9649
Snack wrapping wastes	124.186	8.36 x 10 ⁷	0.9292
Styrofoam wastes	118.208	8.37 x 10 ⁷	0.9776
50 % banana leaves– 50 % bamboo wastes	35.014	1.97 x 10 ⁷	0,9543
50 % snack wrapping– 50 % styrofoam wastes	84.005	4.44 x 10 ⁷	0.9715
50 % bamboo wastes – 50 % snack wrapping wastes	78.04	4.87 x 10 ⁷	0.9745
50 % bamboo wastes – 50 % styrofoam wastes	33.46	1.59 x 10 ⁷	0.9759
50 % banana leaves wastes – 50 % snack wrapping wastes	65.615	4.00 x 10 ⁷	0.9866
50 % banana leaves wastes – 50 % styrofoam wastes	56.771	3.39 x 10 ⁷	0.9769



(a) (b) (c) (d)
 Figure 1. Materials
 (a) Bamboo wastes; (b) Banana leaves wastes; (c) Snack wrap wastes; (d) Styrofoam wastes

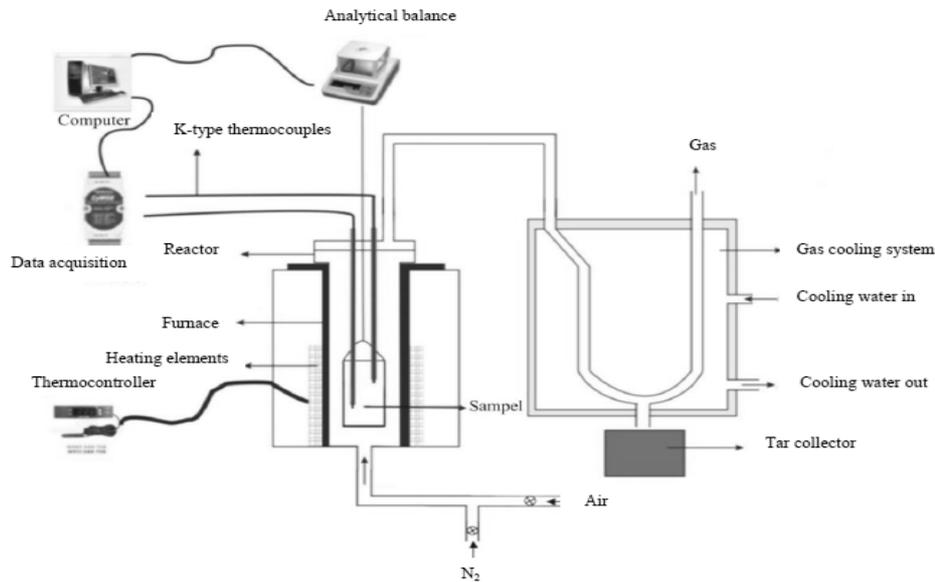


Figure 2. Experimental apparatus schematic

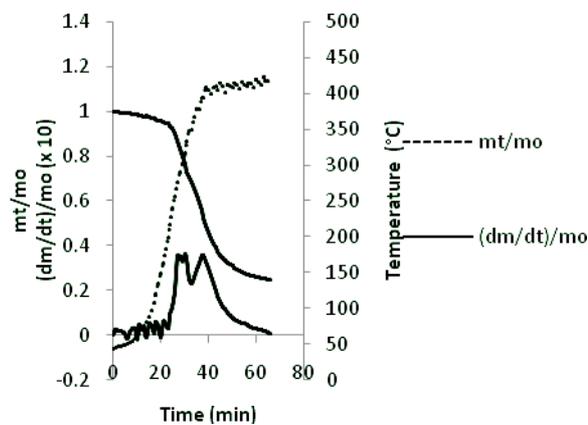


Figure 3. Bamboo – snack wrap wastes pyrolysis characteristics

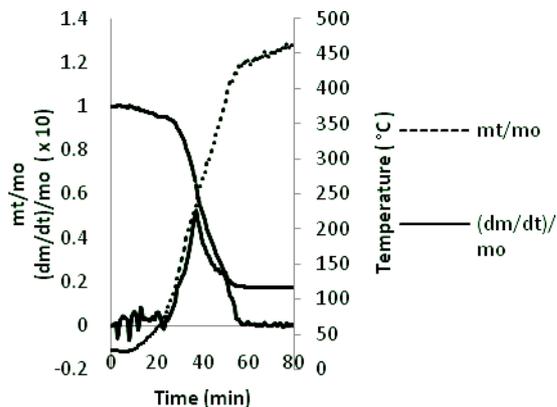


Figure 4. Bamboo – styrofoam wastes pyrolysis characteristics

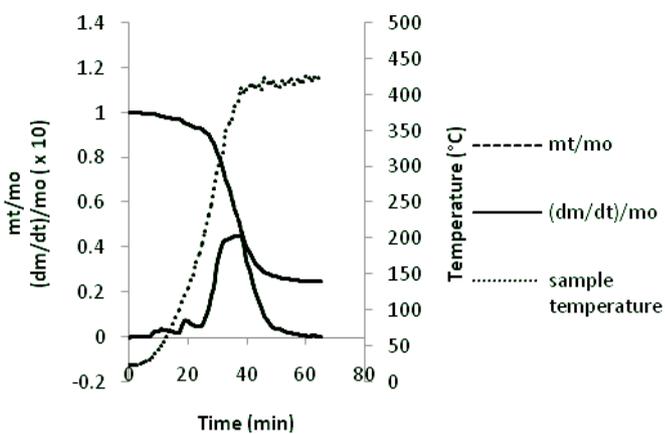


Figure 5. Banana leaves – snack wrap wastes pyrolysis characteristics

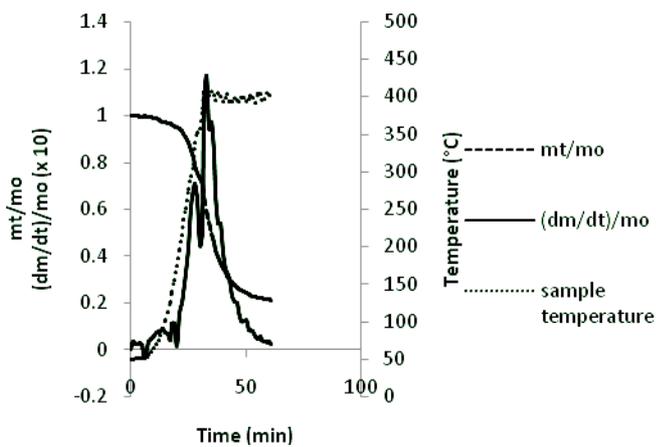


Figure 6. Banana leaves – styrofoam wastes pyrolysis characteristics

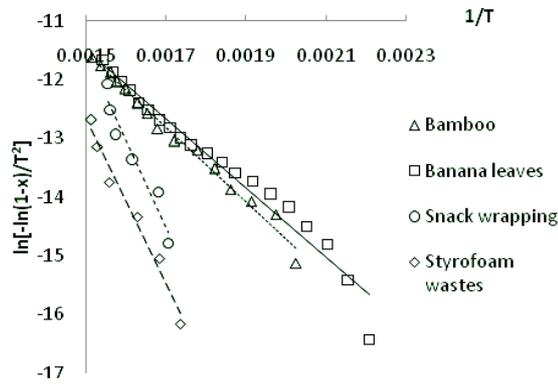


Figure 7. Plot of $\ln\left[-\frac{\ln(1-x)}{T^2}\right]$ vs $1/T$ of single component samples pyrolysis

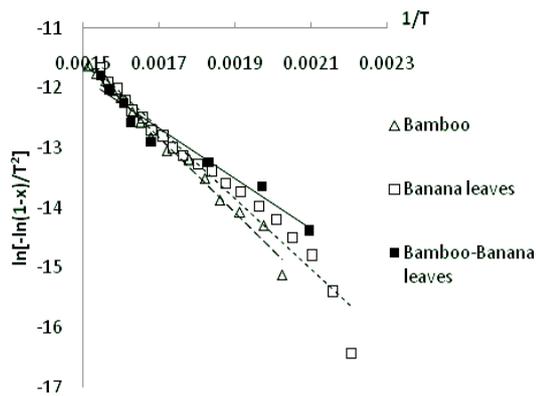


Figure 8. Plot of $\ln\left[-\frac{\ln(1-x)}{T^2}\right]$ vs $1/T$ of banana leaves wastes, bamboo wastes and their blends pyrolysis

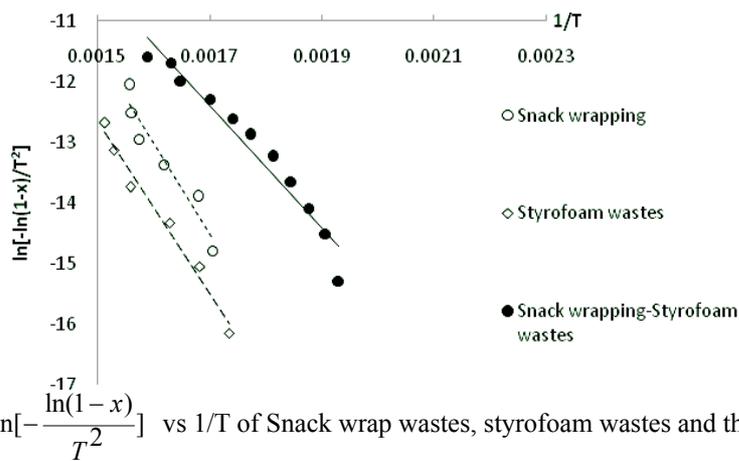


Figure 9. Plot of $\ln\left[-\frac{\ln(1-x)}{T^2}\right]$ vs $1/T$ of Snack wrap wastes, styrofoam wastes and their blends pyrolysis

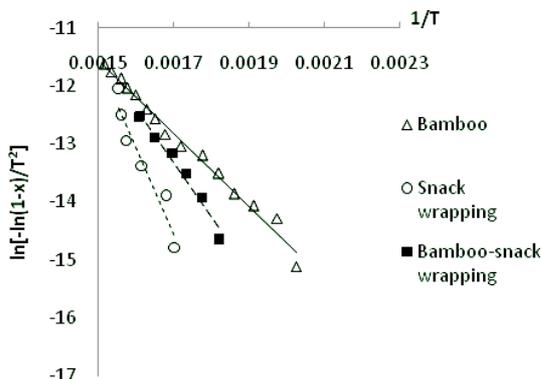


Figure 10. Plot of $\ln\left[-\frac{\ln(1-x)}{T^2}\right]$ vs $1/T$ of bamboo wastes, snack wrap wastes and their blends pyrolysis

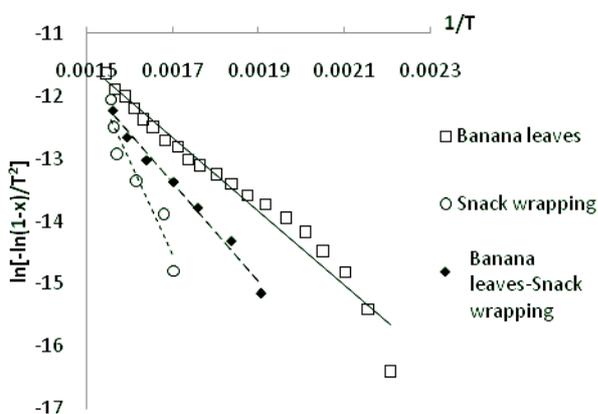


Figure 11. Plot of $\ln\left[-\frac{\ln(1-x)}{T^2}\right]$ vs $1/T$ of banana leaves wastes, snack wrap wastes and their blends pyrolysis

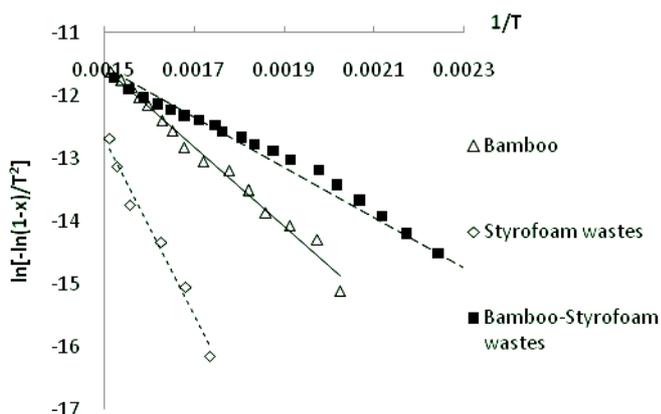


Figure 12. Plot of $\ln\left[-\frac{\ln(1-x)}{T^2}\right]$ vs $1/T$ of bamboo wastes, styrofoam wastes and their blends pyrolysis

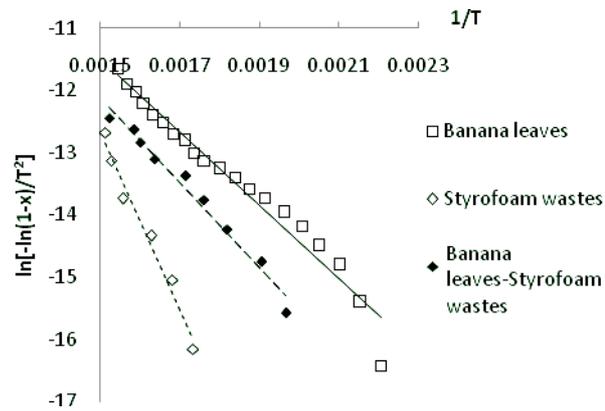


Figure 13. Plot of $\ln\left[-\frac{\ln(1-x)}{T^2}\right]$ vs $1/T$ of Banana leaves wastes, styrofoam wastes and their blends pyrolysis