

Thermogravimetric characteristics and kinetic study of biomass co-pyrolysis with plastics

Jayeeta Chattopadhyay, Chulho Kim, Raehyun Kim, and Daewon Pak[†]

Graduate School of Energy and Environment, Seoul National University of Technology,
172 Gongneung-2 dong, Nowon-gu, Seoul 139-743, Korea
(Received 30 August 2007 • accepted 29 February 2008)

Abstract—The pyrolysis of pure biomass, high density polyethylene (HDPE), polypropylene (PP) and polyethylene terephthalate (PET), plastic mixtures [HDPE+PP+PET (1 : 1 : 1)], and biomass/plastic mixture (9 : 1, 3 : 1, 1 : 1, 1 : 3 and 1 : 9) were investigated by using a thermogravimetric analyzer under a heating rate at 10 °C/min from room temperature to 800 °C. Paper was selected as the biomass sample. Results obtained from this comprehensive investigation indicated that biomass was decomposed mainly in the temperature range of 290-420 °C, whereas thermal degradation temperature of plastic mixture is 390-550 °C. The percentage weight loss difference (W) between experimental and theoretical ones was calculated, which reached a significantly high value of (–)15 to (–)50% at around 450 °C in various blend materials. These thermogravimetric results indicate the presence of significant interaction and synergistic effect between biomass and plastic mixtures during their co-pyrolysis at the high temperature region. With increase in the amount of plastic mixture in blend material, the char production has diminished at final pyrolysis temperature range. Additionally, a kinetic analysis was performed to fit with TGA data, the entire pyrolysis processes being considered as one or two consecutive first order reactions.

Key words: Solid Waste, Co-Pyrolysis, Biomass/Plastic, Thermogravimetric Analysis, Kinetic Study

INTRODUCTION

Pyrolysis treatment for municipal solid waste (MSW) has been found to provide alternative resources of energy and chemical raw materials. An appropriate method may show the right way to get rid of the problems of waste disposal. Pyrolysis or degradation of pure components of MSW has already been studied extensively. Major components of MSW are cellulose or lignin derived materials, polymer based material and inorganic material [1], followed by putrescible and incombustible [2]. Recycling processes for MSW can be performed in a variety of ways, ranging from mechanical, material or chemical recycling to energy recovery [3]. Two constraints affect the achievement of recycling targets: first, recycled materials are not suitable for the whole range of applications; and secondly, different components of wastes are not easily separated from the post-consumer stream [4]. Nowadays, co-pyrolytic techniques have received much attention because they provide an alternative way of disposal and can easily convert polyolefines and cellulose derived materials into high value feedstock, and the specific benefits of this method potentially include the volume reduction of waste; the recovery of various chemicals, and the replacement of fossil fuels [5].

Biomass fuels are usually composed of various kinds of biopolymers which actually consist of cellulose, hemicellulose and lignin. The degradation of cellulosic materials has already been studied in detail. Shafizadeh and many others [6-14] have examined the pyrolysis of cellulose and especially the mechanisms of pyrolysis reactions. Antal [11] has proposed the latest theory for the mechanism of pyrolysis of cellulose. Plastics in MSW consist of mainly poly-

ethylene (PE), polypropylene (PP), polyethylene terephthalate (PET) and polystyrene (PS) with some poly(vinyl chloride) (PVC) and poly(vinylidene chloride) (PVdC). The mechanisms for the pyrolysis and decomposition rates of PE [14,15], PP [14,16], PET [17-19], PS [14,20], PVC [21-23], PVdC [24] are presented in literature. Basically, thermogravimetric analysis (TGA) is one of the easiest methods for analyzing thermal decompositions and kinetics of pyrolysis process for solid raw materials such as coal, biomass and plastic [25-31]. Many researchers have evaluated the kinetics of pyrolysis processes by calculating separate slopes of mass degradation by applying the Arrhenius equation [27,28].

Pyrolysis of biomass generally provides three types of products: gaseous components, tar or heavy oil fractions containing volatile species, and char fractions. The investigation of pyrolysis of cellulose, the major component of paper biomass provides that liquids are produced through free - radical formation by the thermal cleavage of oxygen-containing chemical bonds [31]. During this process, dehydration of carbohydrate unit can occur, which leads to the formation of char. Pyrolysis of cellulose under hydrogen atmosphere produces a higher yield of liquid products as char formation is suppressed and recondensation or recombination of thermal cracking products is reduced. During the co-pyrolysis of biomass with plastics, this hydrogen is generally provided by polyolefinic plastics (HDPE and PP contains 14 wt% of hydrogen) and also by PET (which contains 4.5 wt% of hydrogen), resulting in the less amount of char production and enhancement of liquid tar formation. Sharypov et al. [32] examined the co-pyrolytic behavior of biomass with synthetic polymer mixtures and reported that biomass was degraded at lower temperature than the polyolefins, and for each component of biomass/plastic mixtures independent thermal behaviors were observed. Similarly, the thermal decomposition of PP in the presence of wood flour, lignin, cellulose and charcoal has also been studied by using

[†]To whom correspondence should be addressed.
E-mail: daewon@snu.ac.kr

the thermogravimetric method [33]. But most of the studies have been done by mixing single plastic material with various biomass resources. The co-pyrolytic behavior of biomass with mixture of various plastic is not so clear in thermogravimetric aspects. Moreover, polyolefinic plastics have mostly been taken into account during the co-pyrolysis process with biomass, but here the effect of PET has also been considered.

In the present work, special attention was directed to clarify the interaction of plastic mixture (HDPE, PP, and PET) with biomass during the pyrolysis under nitrogen atmosphere by using a thermogravimetric analyzer. The thermal events were identified properly during the co-pyrolysis of plastic/biomass blend materials. Also observed was how the co-pyrolytic behavior was changed with the variation in the amount of plastic mixture and biomass in the blend materials. The kinetic data were also obtained to fit thermogravimetric data, the total processes being considered as one to two consecutive first order reactions.

EXPERIMENTAL

1. Materials

In this study, paper used in our daily writing purposes was employed as the biomass feedstock; also, commercially available high density polyethylene (HDPE), polypropylene (PP) and polyethylene terephthalate (PET) beads were used as polymer feedstock. Some characteristics of the used paper biomass and plastic polymers have been written in Table 1. During the preparation of biomass sample, the sample paper was first torn into small pieces (size less than 10 mm×10 mm), followed by soaking in water for some times. The wet paper pieces were smashed properly by using mortar and piston, and were heated up to 100 °C to remove extra water present with the biomass. At the same time, HDPE, PP and PET beads were transformed into powder form by using solvent - non-solvent effect of individual plastic polymer. Toluene (above 80 °C) has been used as solvent in the case of HDPE and PP, whereas PET was dissolved in hot DMSO. In all the cases, ethanol was used as non-solvent. Three kinds of plastics (HDPE, PP and PET) have been mixed up properly in 1 : 1 : 1 (w/w) proportions with shaking them for sufficient time; thereafter, these plastic mixtures were homogenized with appropriate proportions of biomass with the same shaking method. The various biomass/plastics blend materials have the compositions of 9 : 1, 3 : 1, 1 : 1, 1 : 3 and 1 : 9 (w/w). In this paper, biomass, plastic mixtures and biomass/plastics blends materials are indicated as BM, PM, BP1, BP2, BP3, BP4 and BP5, respectively.

2. Thermogravimetric Analysis

Pyrolysis was carried out with a thermogravimetric analysis (Shi-

madzu TGA - 50H, Japan). About 7 mg of sample was pyrolyzed up to 700 °C to 800 °C under 30 ml/min nitrogen flow (99.99 vol% N₂; oxygen in negligible amount) at heating rate of 10 °C/min. This nitrogen flow rate ensures an inert atmosphere during the pyrolysis of sample. At the same time, the small amount of sample and the flow heating rate ensure that the heat transfer limitations can be ignored. From TGA results some other thermogravimetric parameters have been calculated. The definitions of those parameters are written below:

The percentage of weight loss (P) can be calculated by using this equation:

$$P = [(W_o - W_t) / W_o] \times 100 \quad (1)$$

Where W_o and W_t are the weight of the sample initially and at temperature T , respectively. Also, the value of calculated weight of blends ($W_{blend(cal)}$) is defined by this equation:

$$W_{blend(cal)} = a_1 W_1 + a_2 W_2 \quad (2)$$

Where W_i is the weight of each material at same operational conditions. $W_{blend(cal)}$ is the weight of the blend of two materials having mass fraction a_1 and a_2 at any temperature. At the same time, we calculated the percentage weight loss difference (ΔW), which has been defined as,

$$\Delta W = P_{blend(exp)} - P_{blend(cal)} \quad (3)$$

Where $P_{blend(exp)}$ and $P_{blend(cal)}$ are the weight loss percentage of blends derived experimentally and theoretically in the same operational conditions, respectively.

RESULTS AND DISCUSSIONS

1. Thermal Analysis of Individual Materials and their Mixtures

The thermogravimetric curves for pyrolysis of individual materials (BM, HDPE, PP and PET) and their blends are shown in Fig. 1 and Fig. 2, respectively. We further calculated the percentage weight loss (P) (Eq. (1)) of BM, PM and their blends at various temperatures in Table 2, from which we could evaluate the exact amount of degradation for different samples. It can be seen that paper biomass had started decomposing at a lower temperature than plastics, but rapid degradation started at 350 °C. Initial degradation (around 100 °C) of biomass may be due to the physical loss of water from the biomass sample [34]. PP and HDPE begin to decompose at 280 °C and 400 °C, respectively, while PET starts decomposing initially at 200 °C, but rapid degradation starts at 420 °C. Initial narrow degradation of PET may be due to the evaporation of DMSO solvent,

Table 1. Analysis of biomass and plastic samples

Sample	Proximate analysis (wt% dry basis)			Ultimate analysis (wt% dry ash free)					HHV (kJ/g)
	Ash	Volatile matter	Fixed carbon ^a	C	H	N	O ^a	S	
Paper biomass	1.5	81.1	17.4	50.7	6.3	0.3	42.6	0.1	20.45
HDPE	0.5	99.5	-	85.0	14.6	-	-	0.2	46.88
PP	1.1	98.9	-	83.6	14.2	-	-	2.2	46.11
PET	-	87.1	12.9	62.1	4.8	-	33.1	-	23.92

^aBy difference.

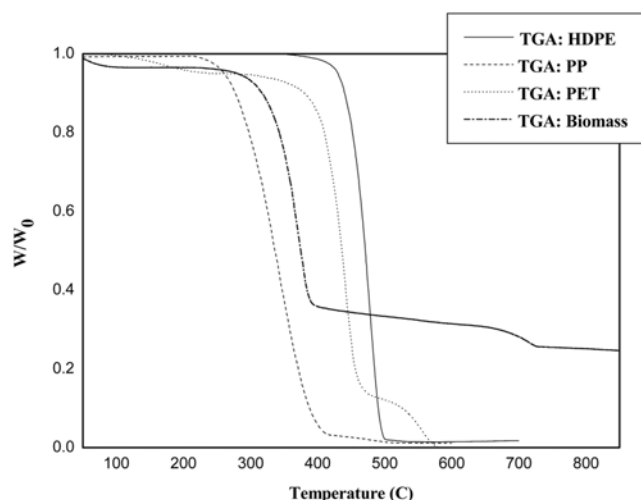


Fig. 1. Thermogravimetric curve for pyrolysis of individual plastic (HDPE, PP and PET) and biomass.

which perhaps was still present in trace amount in the PET pyrolysis sample. At the same time, a small lump was also observed in PET thermogram at around 500–550 °C temperature. Martín-Gullón et al. [35] noticed a similar type of curve during the thermal degradation of PET in mixtures of helium and oxygen atmosphere. In our case, the small amount of oxygen evolved from DMSO solvent during the pyrolysis process might be responsible for this type of result. In the first step (420–490 °C), the main part of the material (88 wt%) is finished, and there is a second step, which leads to the total consumption of the remaining char; the presence of oxygen influences this second step. In all the thermograms, the weight loss increased with increase in the temperature for all samples. Since the chemical bonds in plastic break more easily at higher temperatures, increase of weight loss is observed more rapidly with temperature. It has also been seen that the weight loss curves of HDPE, PP and PET have almost the same trends.

It is seen in Fig. 2 that PM started decomposing at around 250 °C, but rapid degradation was started at 400 °C. Here, initial degradation may be attributed to the decomposition of PP. As we

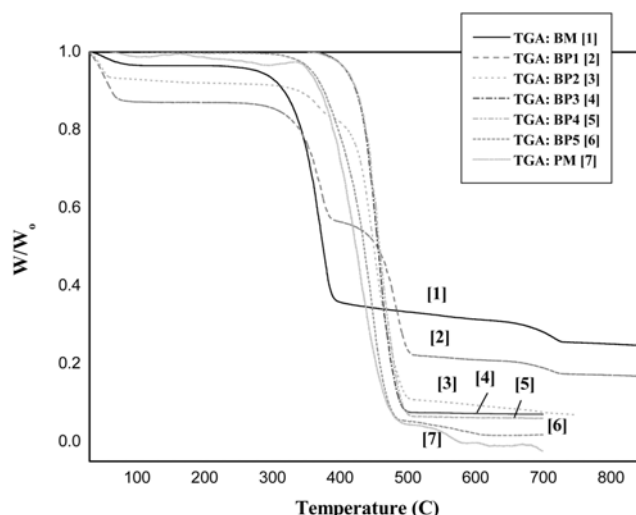


Fig. 2. Thermogravimetric curves for pyrolysis of BM, PM and their various blends.

know, the main reason for the thermal degradation of these kinds of plastics is the radical chain process; therefore, during the co-pyrolysis of plastics PP can start radical formation at lower temperature and can initiate the scission in the other plastic polymer (PP and PET) chain. On the other hand, thermogravimetric curves for blends of BM and PM lie between the ones of the isolated materials at the final temperature range. The weight loss of BM is higher than that of other samples at the temperature range of 300–400 °C; whereas from 400 °C, the weight loss of BM is lower than that of PM and its blends. This might be due to the higher content of ash (1.5%) and fixed carbon (17.4%) in BM sample than that of PM and PM/BM blends, resulting in the lower weight loss at the higher pyrolysis temperature. Another possibility is that BM starts decomposing at lower temperature than plastics; therefore, BM has a higher weight loss at the low temperature region due to the dehydration reaction, while plastic has a higher weight loss at the high temperature region [4]. From Fig. 2 and Table 2, it is worth noticing that the weight loss of the entire blends is higher than that of BM at 500 °C, which is an indication of significant interaction or synergistic effect between

Table 2. Percentage weight loss for pyrolysis of BM, PM and their blends at various temperatures

Temperature	Compositions of the samples						
	BM (Biomass)	PM (HDPE+PP+PET) [1 : 1 : 1]	BP1 (90% BM+ 10 % PM) (9 : 1)	BP2 (75% BM+ 25% PM) (3 : 1)	BP3 (50% BM+ 50% PM) (1 : 1)	BP4 (25% BM+ 75% PM) (1 : 3)	BP5 (10% BM+ 90% PM) (1 : 9)
100 °C	3.4	0.014	12.8	6.9	0.023	0.87	0.18
200 °C	3.5	0.03	12.9	7.9	0.655	0.92	0.22
300 °C	6.8	0.16	14.4	8.5	0.8	0.99	0.53
400 °C	64.2	1.25	43.6	17.9	2.9	2.95	21.4
500 °C	66.7	88.6	76.5	88.7	92.3	92.9	94.7
600 °C	68.5	90.8	78.9	90.6	92.7	93.8	97.8
700 °C	71.8	91.2	81.0	92.4	92.9	93.9	98.15
800 °C	74.9	-	82.9	94.2	-	-	-
850 °C	75.3	-	83.2	-	-	-	-

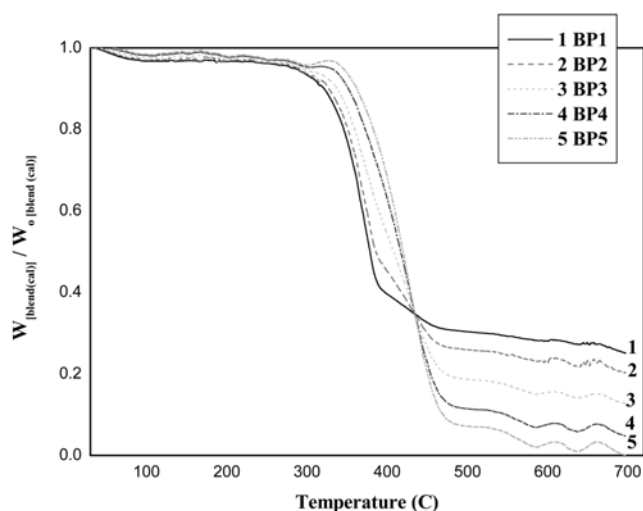


Fig. 3. Thermogravimetric curves obtained by calculation for pyrolysis of various blends of BM and PM.

biomass and plastics during pyrolysis reaction.

To evaluate the interactions between biomass and plastics, the weight of blends at different pyrolysis temperatures has been calculated theoretically and plotted against temperature in Fig. 3. The equation (Eq. (2)) to evaluate the calculated weight of blends ($W_{blend(cal)}$) applies when there is no interaction between the blending materials, for a thermogram of blend identical to the calculated curves based on pure material thermograms [2]. The thermograms of Fig. 1 were used to calculate those of the blend. It is seen from the Fig. 2 and Fig. 3 that there are the clear discrepancies between the experimental and calculated curves. The amount of the char of the experimental cases (Fig. 2) is diminished in comparison to the calculated cases (Fig. 3), which may be due to the enhancement of liquid production during pyrolysis in hydrogen atmosphere. Hydrogen might be supplied from the plastics materials.

For further illumination of the effect between the biomass and plastic samples during co-pyrolysis, the percentage weight loss difference (ΔW) has been calculated by using Eq. (3) for various blend materials. The various extended effects of plastic materials on bio-

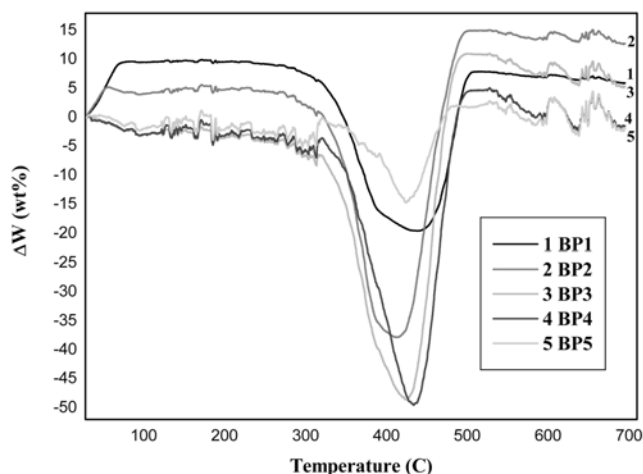


Fig. 4. Variation of ΔW for BM, PM and their various blends.

mass can be evaluated during co-pyrolysis from the weight loss difference value of different blend materials. In Fig. 4 the variation of ΔW with temperature has been described for the different BM and PM blends. It can be seen that, for all the blends, it is less than $\pm 10\%$ before 300°C ; as at this temperature plastics were not started their decomposing, so could not get any chance to interact with biomass sample. However, the ΔW value is not equal to zero at this stage, this may be due to the experimental error such as the different initial weights of the samples. For all the blend samples, ΔW sharply increases in the negative direction with temperature up to 400°C , and then starts inclining. It reaches a value of -15 to -50% at around 450°C for various blend materials. After 500°C , it stops inclination. Actually, this can be explained by the fact that at about 300°C plastic mixtures (PM) are starting degradation initially, and with further increase in the temperature a plastic state was growing to produce and resulting in the inhibition of volatile matter formation. With further heating, PM begins to decompose quickly, resulting in the sharp decrease of ΔW value. After 500°C , the devolatilization processes of the blends have been essentially finished, so ΔW becomes stable at this stage. The difference of weight loss percentage (ΔW) between experimental and theoretical ones is about -3 to 15% at 500°C – 700°C . This value reached the highest level of -50% at around 450°C in the case of BP3 and BP4 samples, in which biomass and plastics were present in 1 : 1 and 1 : 3 proportions, respectively; and has shown the maximum interaction during co-pyrolysis. On the other hand, BP1 and BP5 samples had the least value of -20 and -15% at the same thermal range, respectively. The results indicate that the interactions were diminished for the blend samples in which any one of the components (BM or PM) was present in least amount. It can also be concluded from the results that the synergistic effects of plastic mixtures on biomass are stronger than those of biomass component on plastics. That's why the percentage weight loss difference value is greater negatively in BP4 (-50%) than that of BP2 (-40%). Although the value of W has changed from one sample to the other, all the blend materials have shown significant synergistic effects between biomass and plastic mixtures at the high temperature region during co-pyrolysis process.

The mechanism of the synergistic effect between biomass and plastic during co-pyrolysis is not very clear. According to the literature, a radical chain process is the main reason for the thermal degradation of polyolefines, which actually is the consecutive effect of various steps of radical initiation, chain propagation and radical termination [4]. The mechanisms of this process and composition of products were studied in a number of articles [36,37]. The investigation of pyrolysis of cellulose, the major component of paper biomass sample, has shown that liquids are produced through free radical generation by the thermal cleavage of oxygen-containing chemical bonds [13]. During this process, dehydration of carbohydrate unit can occur, which leads to the formation of char. Pyrolysis of cellulose under hydrogen atmosphere produces a higher yield of liquid products as char formation is suppressed and recondensation or recombination of thermal cracking products is reduced. This hydrogen is generally provided by polyolefinic plastics (HDPE and PP contain 14 wt% of hydrogen) and also by PET (which contains 4.5 wt% of hydrogen) during the co-pyrolysis of biomass and plastics, resulting in the less amount of char production and enhancement of liquid tar formation. In this process, initially biomass com-

ponents can start radical formation initiating the scission of synthetic plastic polymer chain. This possibility has already been discussed by Sharypov et al. [1,5] by taking into account the degradation of biomass components at lower temperature than polyolefines and the additional data regarding the composition of light liquids obtained during the co-pyrolysis process.

2. Kinetic Analysis

By using integral method, the kinetic parameters, activation energy and pre-exponential factor of pyrolysis processes of biomass, plastic and biomass/plastic bled materials were determined [38]. It is assumed that solid pyrolysis of solid fuel is a first order reaction [39-41]. So the equation of pyrolysis reaction of biomass and plastic can simply be expressed by the following formula:

$$dx/dt = A \exp(-E/RT)(1-x) \quad (3)$$

Where A is pre-exponential factor, E is activation energy, T is temperature, t is time, and x is mass fraction or pyrolysis conversion. It is defined as $x = (W_o - W)/(W_o - W_f)$, where W_o is the initial weight of the test sample; W_i is the weight at temperature T and W_f is final weight at the end of the pyrolysis. At a constant heating rate of H ($=dT/dt$) during pyrolysis, Eq. (3) can be rearranged and after integration it will be

$$\ln[-\ln(1-x)/T^2] = \ln[AR/HE(1-2RT/E)] - E/RT \quad (4)$$

For most values of E and for the temperature range of the pyrolysis, it may be shown that the expression $\ln[AR/HE(1-2RT/E)]$ in Eq. (4) is essentially constant. Therefore, if the left side of Eq. (4) is plotted against $1/T$, a straight line should be obtained if the process can be assumed as a first order reaction. From the slope, $-E/R$, the activation energy E can be determined, and by taking the temperature at which $W_i = (W_o + W_f)/2$ in the place of T in the intercept term of Eq. (3), the pre-exponential factor A can also be determined [4].

Fig. 5 and Fig. 6 show typical plots of $\ln[-\ln(1-x)/T^2]$ versus $1/T$, indicating that for isolated pyrolysis of plastics, HDPE, PP and PET, and also for the PM, BP2, BP3, BP4 and BP5, single first order reaction should be used to describe the pyrolysis process, whereas for BM and BP1, two independent first order reactions are suitable. In the case of BM and BP1, Eq. (3) has been applied separately to each of the stages by calculating the value of x separately for each reaction. From the slope of each line, the value of E and A can be obtained for different stages. Table 3 shows the kinetic parameters of all the samples that were determined by this method. The kinetic parameters are calculated from $x=3-15\%$ to $88-92\%$, which repre-

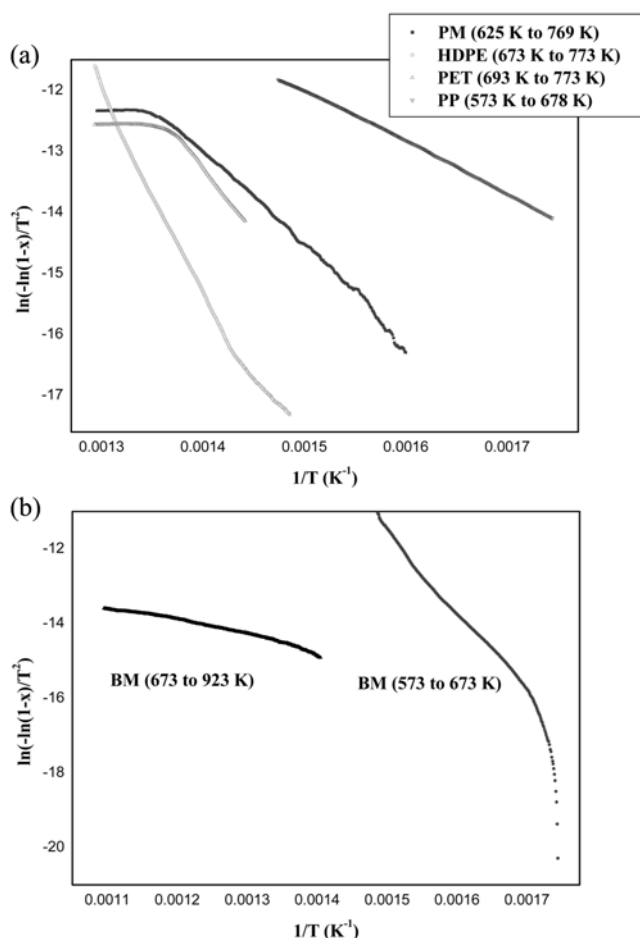


Fig. 5. Plot of $\ln(-\ln(1-x)/T^2)$ vs $1/T$ of (a) HDPE, PP, PET, and Plastic mixture (PM) pyrolysis calculated by one-step integral method and of (b) Biomass (BM) pyrolysis calculated by two-step integral method.

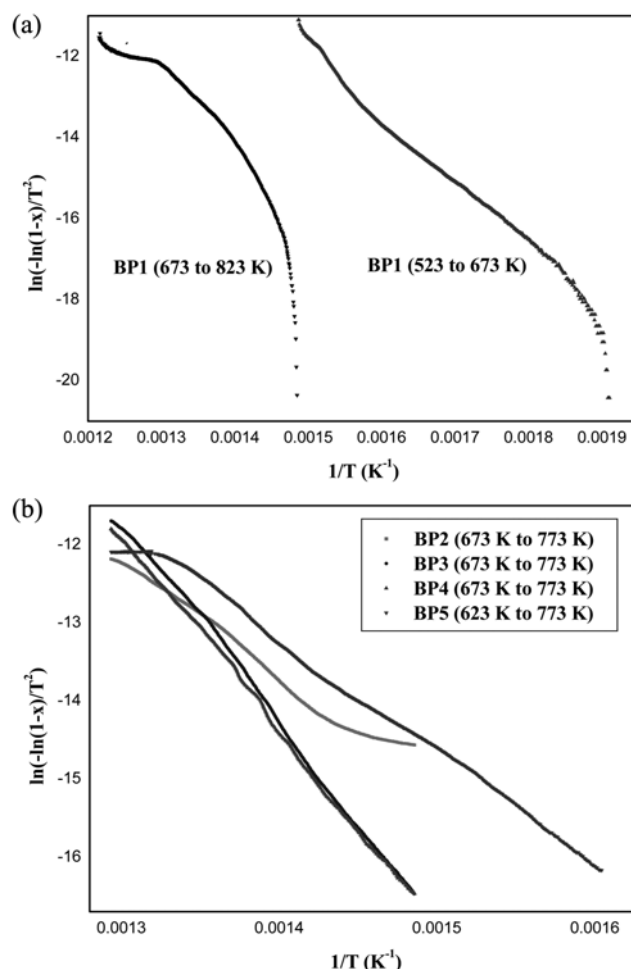


Fig. 6. Plot of $\ln(-\ln(1-x)/T^2)$ vs $1/T$ of (a) BP1 pyrolysis calculated by two-step integral method and (b) BP2, BP3, BP4 and BP5 pyrolysis calculated by one-step integral method.

Table 3. Kinetic parameters and characteristic temperatures for pyrolysis of BM, PM and their blends

Sample	Temp. (K)	Conversion range (%)	E (kJ/mol)	A (min ⁻¹)
BM (1 st Step)	573-673	9-85	177	1.109×10^{10}
BM (2 nd Step)	673-923	85-92	32	6.730×10^{10}
HDPE	673-773	1-99	280	1.282×10^{10}
PP	573-678	15-96	70	9.715×10^9
PET	693-773	15-88	166	1.9198×10^{10}
PM	625-769	3-95	122	4.349×10^{10}
BP1 (1 st Step)	523-673	15-66	140	8.927×10^9
BP1 (2 nd Step)	673-823	66-96	204	4.703×10^9
BP2	673-773	15-88	128	2.758×10^{10}
BP3	673-773	3-92	218	2.742×10^{10}
BP4	673-773	3-93	210	1.6052×10^{10}
BP5	623-773	3-95	121	1.1759×10^{10}

sents the main pyrolysis region of all the samples.

In a wide range of temperatures, the reactivity of isolated plastics follows the order: HDPE<PET<PP. At the same time, reactivity of plastic mixtures (PM) is greater than that of HDPE and PET. Whereas, activation energy values for biomass pyrolysis are 177 kJ/mol for the first stage, and only 32 kJ/mol for the second step. For different blends of biomass and plastics, only for BP1 sample have activation energies been calculated in two different stages: 140 kJ/mol for 1st stage and 204 kJ/mol for 2nd stage; whereas, for all others, kinetic parameters were calculated by using the one-step method. During the comparison of kinetic parameters between the BM and BP1, the activation energy value of BP1 is intermediate between the BM and PM, in the first subinterval of temperatures (523-673 K), whereas in the second subinterval (673-823 K) activation energy value has been increased significantly by mixing only small amount of plastics. All other blend samples (BP2 to BP5) have shown similar pyrolysis behaviors. Activation energy values have shown the trend: BP2≈BP5<BP3≈BP4. The results show that mixing of the PM in the biomass sample up to an optimum amount (75%) has increased the activation energy value of the blend, but then after it diminishes.

Reaction with high activation energy needs a high temperature or a long reaction time [42]. For biomass or plastic pyrolysis, high activation energy means that the reaction needs more energy from the surroundings during the reaction. The change of activation energy of various blends shows that plastics and biomass blends of various compositions have different pyrolysis reactivities at different temperatures.

CONCLUSIONS

From the thermogravimetric analysis of paper biomass, plastic mixtures (HDPE, PP and PET) and their various blends [Biomass : Plastics mixture :: 9 : 1, 3 : 1, 1 : 1, 1 : 3 and 1 : 9], the following conclusions can be drawn: (1) biomass is decomposed at a lower temperature than plastics mixture; (2) the temperature range is wider for organic matter devolatilization from biomass than that of plastics; (3) initial degradation temperature has been shifted to the higher range with greater amount of plastics in the blends; and (4) the amount

of residue has been diminished at the final temperature range with increase of plastics in the blend materials.

In comparison between the theoretically calculated weight of blends ($W_{blend(cal)}$) and the experimental one ($W_{blend(exp)}$) at various temperatures, there are the clear discrepancies between the experimental and calculated curves. The amount of the char of the experimental cases is diminished in comparison to the calculated cases, maybe due to the enhancement of liquid production during pyrolysis in hydrogen atmosphere; hydrogen might be supplied from the plastics materials. For various blends of biomass and plastics, the difference of percentage weight loss (ΔW) between experimental and theoretical ones is about (–)15 to (–)50% at around 450 °C. These experimental results indicate a significant synergistic effect during plastics and biomass co-pyrolysis at the high temperature region.

The kinetic analysis results show that first order reactions together with the Arrhenius law account for the different subintervals of weight loss found quite satisfactorily for individual materials and their blends. For HDPE, PP, PET and biomass/plastic blends having compositions of 3 : 1, 1 : 1, 1 : 3 and 1 : 9, the pyrolysis process can be described by one first order reaction. Whereas, pyrolysis of biomass and 9 : 1 biomass/plastics blend sample can be described by two consecutive first order reactions.

During the comparison of kinetic parameters between the BM and BP1, the activation energy value of BP1 is intermediate between the BM and PM, in the first subinterval of temperatures (523-673 K), whereas in the second subinterval (673-823 K) the activation energy value has been increased significantly by mixing only small amount of plastics. All other blend samples (BP2 to BP5) have shown similar pyrolysis behaviors. Activation energy values have shown the trend: BP2≈BP5<BP3≈BP4. Therefore, mixing of the PM in the biomass sample from 50% to an optimum amount of 75% has increased the activation energy value of the blend, but then after it diminishes.

ACKNOWLEDGMENT

This research project is financially supported by Seoul R & BD Program. The authors are grateful for their financial support.

REFERENCES

1. V. I. Sharypov, N. G. Beregovtsova, B. N. Kuznetsov, L. Membrado, V. L. Cebolla, N. Marin and J. V. Weber, *J. Anal. Appl. Pyrolysis*, **67**, 325 (2003).
2. Y. Matsuzawa, M. Ayabe and J. Nishino, *Polym. Deg. Stab.*, **71**, 435 (2001).
3. L. Vivero, C. Barriocanal, R. Alvarez and M. A. Diez, *J. Anal. Appl. Pyrolysis*, **74**, 327 (2005).
4. L. Zhou, Y. Wang, Q. Huang and J. Cai, *Fuel Process. Tech.*, **87**, 963 (2006).
5. N. Marin, S. Collura, V. I. Sharypov, N. G. Beregovtsova, S. V. Baryshnikov, B. N. Kutnetzov, V. Cebolla and J. V. Weber, *J. Anal. Appl. Pyrolysis*, **65**, 41 (2002).
6. F. Shafizadeh, *Adv. in Carbohydrate Chem.*, **23**, 419 (1968).
7. A. Broido and M. Weensteen, In Proceedings of the 3rd International Conference on Thermal Analysis. Basel: Birkhauser Verlag, 285 (1971).

8. H. . Higgins, *J. Polym. Sci.*, **28**, 645 (1958).
9. A. G. W. Bradbury, Y. Sakai and F. Shafizadeh, *J. Appl. Polym. Sci.*, **23**, 3271 (1979).
10. F. J. Kilzer and A. Broido, *Pyrolytics*, **2**, 151 (1965).
11. Jr. M. J. Antal, *Advances in solar energy*. New York: Solar Energy Society, pp. 61-111 (1983).
12. G. R. Ponder, G. N. Richards and T. T. Stevenson, *J. Anal. Appl. Pyrolysis*, **22**, 217 (1992).
13. B. K. Kandola, A. R. Horrocks, D. Price and G. V. Coleman, *J. Rev. Macromol. Chem. Phys.*, **C36**(4), 721 (1996).
14. S. L. Mardosky, editor. *Thermal degradation of organic polymer*, Interscience Publishers (1964).
15. M. Murata and T. Makino, *Bull. Chem. Soc. Jpn.*, **12**, 2414 (1973).
16. M. Murata and T. Makino, *Bull. Chem. Soc. Jpn.*, **1**, 192 (1975).
17. M. Dziêcio³ and J. Trzecznyński, *J. Appl. Polym. Sci.*, **77**, 1894 (2000).
18. B. Saha and A. K. Ghosal, *Chem. Engg. J.*, **111**, 39 (2005).
19. B. Saha, A. K. Maiti and A. K. Ghosal, *Thermochimic. Acta*, **444**, 46 (2006).
20. M. Murata and T. Makino, *Bull. Chem. Soc. Jpn.*, **7**, 1241 (1975).
21. R. R. Stromberg, S. Straus and B. G. Achhammer, *J. Polym. Sci.*, **35**, 355 (1959).
22. R. Knuemann and H. Bockhorn, *Combust. Sci. Tech.*, **101**, 285 (1994).
23. C. H. Wu, C. Y. Chang, J. L. Hor, S. M. Shin and F. W. Chang, *Canadian J. Chem. Eng.*, **72**, 644 (1994).
24. A. Ballistreri, S. Foti, P. Maravigna, G. Montaudo and E. Scamporrino, *Polymer*, **22**, 131 (1981).
25. C. A. Koufopoulos, G. Maschio and A. Lucchesi, *Canadian J. Chem. Eng.*, **67**, 75 (1989).
26. T. Hatakeyama and F. X. Quinn, *Thermal analysis - fundamentals and applications to polymer science*, Wiley, Chichester (1999).
27. M. N. Nassar, *Energy Sources*, **21**, 131 (1999).
28. K. G. Mansaray and A. E. Ghaly, *Energy Sources*, **21**, 899 (1999).
29. J. A. Caballero, A. Marcilla and J. A. Conesa, *J. Anal. Appl. Pyrolysis*, **44**, 75 (1997).
30. L. Helsen and E. vanden Buick, *J. Anal. Appl. Pyrolysis*, **56**, 51 (2000).
31. E. Kastanaki, D. Vamvuka, P. Grammelis and E. Kakaras, *Fuel Process. Technol.*, **77-78**, 159 (2002).
32. V. I. Sharypov, N. Marin, N. G. Beregovtsova, S. V. Baryshnikov, B. N. Kuznetsov, V. L. Cebolla and J. V. Weber, *J. Anal. Appl. Pyrolysis*, **64**, 15 (2002).
33. E. Jakab, G. Varhegyi and O. Faix, *J. Anal. Appl. Pyrolysis*, **56**, 273 (2000).
34. F. J. Kilzer and A. Broido, *Pyrolytics*, **2**, 151 (1965).
35. I. Martin-Gullón, M. Esperanza and R. Font, *J. Anal. Appl. Pyrolysis*, **58-59**, 635 (2001).
36. N. Horvat and F. T. T. Ng, *Fuel*, **78**, 459 (1999).
37. H. Bockhorn, A. Hornung, U. Hornung and D. Schawaller, *J. Anal. Appl. Pyrolysis*, **48**, 93 (1999).
38. A. W. Coats and J. F. Redfern, *Nature*, **68**, 201 (1964).
39. V. K. Mustafa, O. Esber, K. Ozgen and H. Cahit, *J. Anal. Appl. Pyrolysis*, **45**, 103 (1998).
40. P. R. Solomon, M. A. Serio, R. M. Carangelo and J. R. Markham, *Fuel*, **65**, 82 (1986).
41. G. P. Ying, V. Enrique and P. Luis, *Fuel*, **75**, 412 (1996).
42. M. J. Lazaro, R. Moliner and I. Suelves, *J. Anal. Appl. Pyrolysis*, **47**, 111 (1998).