

# Co-pyrolysis of Biomass and Plastics waste: A Modelling Approach

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Thermal co-processing of waste mixtures had gained a lot of attention in the last decade largely due to certain synergistic effects such as higher quantity and better quality of oil, limited supply of certain feedstock and improving the overall pyrolysis process. Many experiments have been done using the TGA analysis and different reactors to achieve the stated synergistic effects in co-pyrolysis of biomass and plastic wastes. The thermal behaviour of plastics during pyrolysis is different from that of biomass because its decomposition happens at a high temperature range (>450 °C) with sudden release of volatile compared to biomass which have a wide range of thermal decomposition. Therefore it is worthwhile to study the possible synergistic effects on the overall energy used during co-pyrolysis process. In this work, two different modelling approaches were used to study the energy related synergistic effect between polystyrene (PS) and bamboo waste. The results show that both modelling approaches give an appreciable synergy effect of reduction in overall energy when PS and bamboo are co-pyrolyzed together. However, the second approach which allows interaction between the two feedstocks gives a more reduction in overall energy usage up to 6.2 % depending on the ratio of PS in the mixed blend.

## 1. Introduction

Pyrolysis has been extensively studied in the past decades because of its potential to convert organic wastes like scrap tyres, sawdust, bamboo, plastic wastes, empty fruit bunch (EFB) and other agricultural waste into carbonaceous residues, liquid hydrocarbon and gases. These products are important fuel substituent and are useful for production of biofuels and bio-chemicals. Pyrolysis is different from combustion because it takes place in the absence of air, therefore no production of hazardous emissions and the recovery of the product is always achieved. Pyrolysis process is considered as a beneficial option in waste treatment largely due to the products generated and the energy recovery when compared to other methods, though the economic issue is still a concern because of the amount of energy used for pyrolysis. Recently thermal co-processing of waste mixtures known as co-pyrolysis had gained an appreciable attention in the literature. There are several reasons for co-pyrolyzing waste samples especially plastics with biomass and one common reason is to obtain high quality and better quantity of oil in comparison with those obtained from biomass pyrolysis alone (Paradela et al., 2009; Vasile and Brebu, 2007). This is because plastics and synthetic polymers have high hydrogen contents and therefore provide hydrogen during the co-pyrolysis process resulting into increase in liquid production (Vasile and Brebu, 2007). Waste are also co-pyrolyzed together to improve the quality of the char produced (Bernardo et al., 2011). Pyrolysis reactors are also built to be able to handle multiple feeds as certain feedstock might be limited by season, supply or availability. From the perspective of pyrolysis reaction, there is a distinct difference in the mass loss and the heat flow profile for plastics and biomass feedstocks. Much energy is needed at the early stage of biomass pyrolysis because of the anhydrous water locked in the biomass structure while plastics on the other hand have low thermal conductivity and a sharp endothermic peak and therefore requires large energy towards the end of the pyrolysis process.

Based on the difference in the pyrolysis behaviour of the two feedstock and the stated synergistic effects of plastics and biomass, it is possible that the co-pyrolysis of two feedstocks can provide certain

processing advantages for energy utilization. Therefore, the main objective of this work is to study the possible overall energy synergistic effect that may exist in the co-pyrolysis of bamboo and polystyrene. Two modelling approaches were used to study the effect of the co-pyrolysis process on the mass loss, volatile evolving rate and the overall energy used for each blends.

## 2. Problem Statement

In the literature, the focus of many works on co-pyrolysis has been on the possible synergetic effects related to quantity and quality of the products. In this modelling study however, we focus on the energy related processing benefits for a proposed co-pyrolysis process using two different modelling approaches. In the first approach, the two feedstocks (Bamboo and PS) were modelled individually while in the second approach, the two feedstocks were pre-mixed at different mixing ratio before the thermogravimetric analysis (TGA) and differential thermal analysis (DTA) experiment and then modelled as a single feedstock.

## 3. Methodology

Before the modelling study, the mixed-waste samples were subjected to experimental study and the results were used to model the pyrolysis progress.

### 3.1 Experimental study

The polystyrene (PS) samples were obtained from analytical grade suppliers while the waste bamboo samples were obtained from a construction site inside the campus of Hong Kong University of Science and Technology. The samples were dried (for bamboo), crushed and sieve to powder form of size less than 400 $\mu$ m. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were performed on the samples using the machine TGA/DTA Setaram II. The samples were heated from 25 °C to 800 °C in a nitrogen purge environment at heating rate of 10 and 30 °C/min. For the mixed-waste approach, the samples were mixed in the ratio 1:3, 1:1 and 3:1 before the TGA/DTA analysis.

### 3.2 Modelling study

A pyrolysis model was developed to describe transiently the progress of the bulk particles using the kinetics obtained from the TGA/DTA experiment. The pyrolysis model proposed in an earlier work (Oyedun et al., 2012) was updated in this work to model the co-pyrolysis model using the bamboo pyrolysis mechanism proposed in another work (Oyedun et al., 2013). The following assumptions were made when constructing the model:

1. The shape of the pyrolyzing particle is spherical.
2. Conduction is the only mode of heat transfer within the particle.
3. The volatiles leaving the particles do not interfere directly with the pyrolysis gas.
4. The only form of inter-particle interaction is heat transfer.

A summary of the model equations used for the co-pyrolysis process is given in Table 1 and the model parameters are listed in Table 2. The model was built on the MATLAB® platform while Crank-Nicolson implicit scheme was used as the finite difference method (FDM) to solve the heat equation (Eq. (4)) numerically. Two modelling approaches were used for this work.

#### 3.2.1 Approach One: Two individual samples modelling approach

In this approach, the pyrolysis model was developed to model the two feedstocks (Bamboo and PS) at the same time at a pre-defined ratio. The only form of inter-particle interaction was the heat transfer and therefore the two particles were assumed not to have any interaction except that they were both heated by the bulk heat from the heating gas as illustrated in Figure 1a. The kinetic parameters for this approach was obtained from the individual experimental TGA/DTA analysis.

#### 3.2.2 Approach Two: Combined sample modelling approach

The particle interaction between the two feedstock was considered in this approach and therefore prior to the TGA/DTA experiments, the two samples were mixed together in pre-defined ratio of 1:3, 1:1 and 3:1 (25 % PS : 75 % Bamboo, 50 % PS : 50 % Bamboo and 75 % PS:25 % Bamboo). The mixed sample was treated as a new single particle and the TGA/DTA results were modelled to obtain the kinetic and the heat flow parameters. In this approach, the particles of the mixed feedstock were heated with the heating gas supplied into the reactor as illustrated in Figure 1b.

The density of the mixtures were estimated from the individual density of bamboo and PS by using the method proposed by Feinstein (Feinstein, 1972) represented by Eq(12) The thermal conductivity of the mixture was calculated using the conductivity-mixture rule proposed by Kasap and Capper (Kasap and Capper, 2006) which was represented by Eq(13). As noted by Günther and Steimle (Günther and Steimle,

1997), the specific heat capacity of the mixed-feed can be directly calculated from the quantities of the individual samples and the correlation was represented by Eq(14).

Table 1: Set of equations for modelling the co-pyrolysis process

Kinetic model equations	
$\frac{d\alpha_i}{dt} = A_i \exp\left(-\frac{E_i}{RT}\right)(1-\alpha_i)^{n_i}$	(1)
$\frac{d\gamma_j}{dt} = A_j \exp\left(-\frac{E_j}{RT}\right)(1-\gamma_j)^{n_j}$	(2)
$\alpha_T = \sum_i \omega_i \alpha_i$	(3)
Heat Transfer model equations	
$\frac{\partial T}{\partial t} = \frac{\lambda}{\rho C_p} \frac{\partial^2 T}{\partial r^2} + \frac{2}{r} \frac{\lambda}{\rho C_p} \frac{\partial T}{\partial r} + \frac{1}{C_p} \sum_i \left( H_i \frac{\partial \alpha_i}{\partial t} \omega_i \right) + \frac{1}{C_p} \sum_j \left( H_j \frac{\partial \gamma_j}{\partial t} \right)$	(4)
$C_{p,p} = \frac{(\alpha_{T,f} - \alpha_T)}{\alpha_{T,f}} C_{p,f} + \frac{\alpha_T}{\alpha_{T,f}} C_{p,c}$	(5)
$\lambda = \frac{(\alpha_{T,f} - \alpha_T)}{\alpha_{T,f}} \lambda_f + \frac{\alpha_T}{\alpha_{T,f}} \lambda_c$	(6)
B.C. 1: $-\lambda \frac{\partial T}{\partial r} \Big _{r=R} = h(T_R - T_{bulk})$	(7)
B.C. 2: $\frac{\partial T}{\partial r} \Big _{r=0} = 0$	(8)
Reactor model equations	
$m_{bulk} = \rho_g \left[ \bar{V}_0 \left( \frac{v}{1-v} \right) + (\bar{V}_0 - \bar{V}) \right]$	(9)
$m_{bulk} C_{\rho,g} \frac{\partial T_{bulk}}{\partial t} = C_{\rho,g} (T_{inlet} m_{inlet} - T_{outlet} m_{outlet})$	(10)
$Q_T = m_{inlet} t_T C_{\rho,g} (T_{inlet} - T_{ambient})$	(11)

Table 2: Model parameters

Model parameters (unit)	Value	Reference
Initial particle diameter (cm)	2.5	-
Inlet temperature of heating gas (°C)	800	-
Reactor void space	0.8	-
Heating gas inlet flow rate (kg/m <sup>2</sup> )	0.5	-
Specific heat capacity of heating gas (J/kg·K)	2400	-
Convective heat transfer coefficient, (W/m <sup>2</sup> ·K)	5.69 + 0.0098T	(Ahuja et al., 1996)
Thermal conductivity of polystyrene	0.16	(Bockhorn et al., 1999)
Thermal conductivity of bamboo (wood)	0.158	(Ahuja et al., 1996)

$$\rho_{mixed} = \frac{1}{[(x_{bam} / \rho_{bam}) + (x_{PS} / \rho_{PS})]} \quad (12)$$

$$\lambda_{mixed} = x_{bam} \lambda_{bam} + x_{PS} \lambda_{PS} \quad (13)$$

$$C_{p, overall}(T) = x_{bam} C_{p, bam}(T) + x_{PS} C_{p, PS}(T) \quad (14)$$

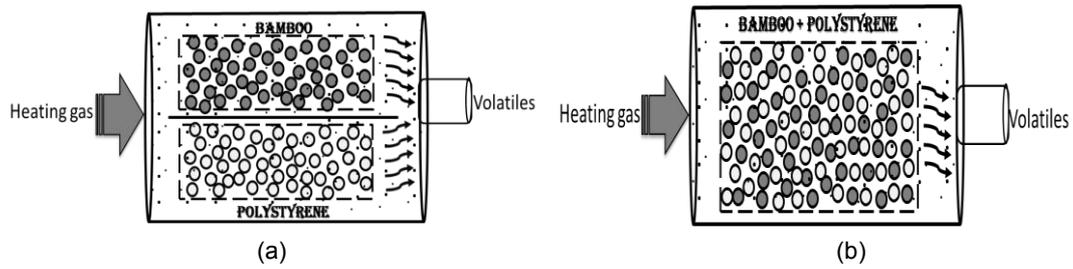


Figure 1: Reactor model illustration for approach one (a) and approach two (b)

## 4. Results and Discussion

The summary of the results of the model analysis are summarised and discussed in this section.

### 4.1 Thermogravimetric analysis (TGA Results)

Thermogravimetric analysis is very essential to study the pyrolysis behaviour and the pyrolysis kinetics of different feedstock. The mass loss profiles in Figure 2 indicate the difference between the pyrolysis behaviour of plastic (PS) and biomass feedstock (bamboo). In Figure 2a, PS has only one decomposition peak at a high temperature range (400 - 470 °C) compared to bamboo that have a broad range of thermal decomposition. The result of the mixed-blends as indicated in Figure 2b shows the curve for the first biomass decomposition shift from the left to right as the ratio of the PS feed increases.

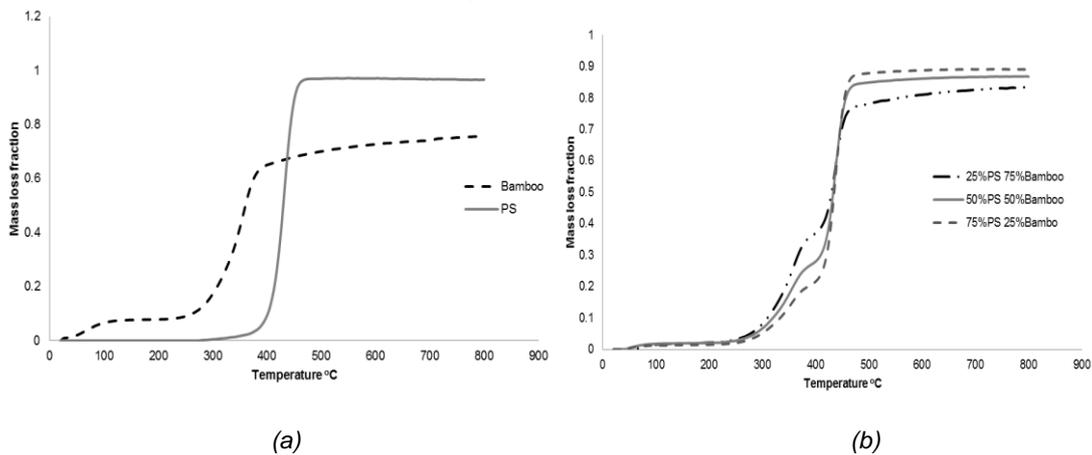


Figure 2: TG Profile for the pyrolysis of pure feedstocks (a) and the mixed blends (b) at 30oC/min

### 4.2 Modelling approach evaluation

#### 4.2.1 Mass loss profile

Figure 3 gives an overview of the simulation results for the mass loss based on the two approaches used as the pyrolysis progresses. In approach one i.e. only heat interaction, the total mass loss fraction depends on the bulk mass. Figure 3a shows that the profile does not show any overlap compared to Figure 3b which shows a distinct overlap between the mixed-blends at the early stage of the pyrolysis process. Only the mass loss profile of approach two agreed with the experimental results as of the TGA in Figure 2b. Therefore approach two gives a clear perspective on the interaction that exists between the thermal decomposition of PS and Bamboo

#### 4.2.2 Volatile generation

The pyrolysis volatile evolving from the reactor as the pyrolysis progresses was studied and the profiles for the two modelling approached are shown in Figure 4. It was observed that for modelling approach one, the volatile generation are distinctive between the two feedstocks (bamboo and PS) as shown in Figure 4a. The peaks for the volatile generation for bamboo comes first while that of the PS feed was at a later stage of the pyrolysis followed by a sudden stop of volatile components. The volatile generation for approach two

as shown in Figure 4b was quite different to what was observed for approach one. The volatile generation was more gradual as the pyrolysis progress. It shows that there exists some interaction between the bamboo and PS feed even at early stage of the pyrolysis. The two peaks for all the mixed-blends for approach two were more closer to each other and at a later stage of the pyrolysis (>0.4 h). As observed, the peak of the relative volatile generation increases as the ratio of the PS feed increases in the mixed-blend at the later stage of the pyrolysis.

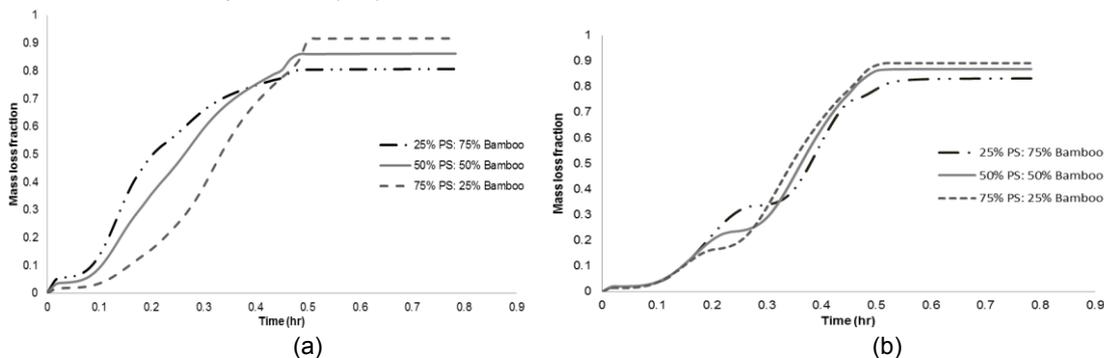


Figure 3: Mass loss profile for approach one (a) and approach two (b)

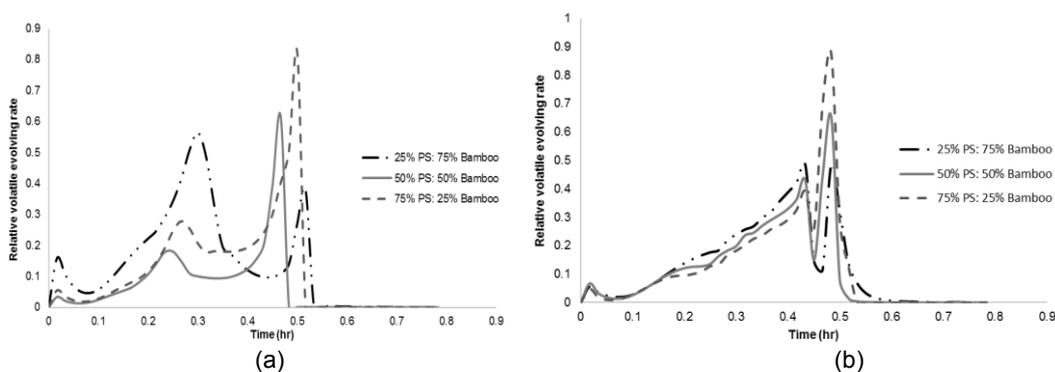


Figure 4: Relative volatile generation rate for approach one (a) and approach two (b)

#### 4.2.2 Energy usage

The focus of this study is to analyse if there is any synergistic interaction between bamboo and PS in terms of the energy relations. The calculated energy of the mixed-blend was determined from the individual pyrolysis of the bamboo and PS samples and then compared with the energy usage determined from the two modelling approaches. From preliminary work, the energy used for pure bamboo and pure PS samples based on 500 kg feed were 12.94 MJ/kg and 20.68 MJ/kg. The energy requirement of PS is quite high because of the high endothermic peak during volatile decomposition.

Table 3 gives a clear comparison between the calculated (expected) energy usage and that of the two approaches. As shown in the energy used for the blends decreases with increase in PS feed. The energy usage determined from the modelling approach two gives the lowest energy compared to approach one and the calculated energy used. It is glaring that the existence of interaction between the bamboo and PS samples aided the reduction in energy usage for the blends.

Table 3: Energy Usage (MJ/kg) Comparison

Blend ratio (wt%)	Calculated	Approach One	Approach Two
25%PS 75%Bamboo	14.875	14.3148	13.9529
50%PS 50%Bamboo	16.810	16.471	15.882
75%PS 25%Bamboo	18.745	18.427	18.069

Besides, up to 6.2 % decrease in overall energy usage was achieved when the PS feed in the mixed-blend was 25 % and the rate reduces as the PS feed increases largely due to the increase in endothermic peak at high PS feed.

## 5. Conclusions

A co-pyrolysis modelling approach is proposed and evaluated in this work. Two different modelling approaches were used to evaluate the possible synergistic effect in terms of energy usage between plastics (PS) and biomass (bamboo) as a case study. The result of the energy usage shows a reduction in energy for the mixed blends for the two approaches. Approach two which allows interaction between the two feedstocks has a more reduction in overall energy up to 6.2 % when the ratio of the PS feed was 25 %.

### Nomenclature

$\alpha$	extent of mass loss reaction	$\gamma$	extent of non-mass loss reaction
$\alpha_T$	overall mass loss fraction	$\omega$	mass loss contribution
$\alpha_{T,f}$	final total mass loss fraction	$T$	temperature (K)
$t$	reaction time (s)	$A$	pre-exponential factor ( $s^{-1}$ )
$n$	order of reaction	$E$	activation energy (J/mol)
$R$	universal gas constant (J/mol-K)	$\rho$	density of feedstock ( $kg/m^3$ )
$\lambda$	thermal conductivity (W/m-K)	$h$	convective heat transfer coefficient ( $W/m^2 \cdot K$ )
$C_p$	specific heat capacity (J/kg K)	$H$	heat of reaction (J/kg)
$v$	void space fraction	$r$	radius of a discrete layer (m)
$m_{bulk}$	mass of bulk environment, kg	$\dot{m}$	mass flow rate, kg/s
$T_R$	particle surface temperature (K)	$T_{bulk}$	bulk temperature (K)
$\bar{V}$	total particle volume ( $m^3$ )	$\bar{V}_0$	initial total particle volume ( $m^3$ )

### Subscript

$i$	mass loss reaction $i$	$j$	non-mass loss reaction $j$
$f$	feedstock	$c$	char
$g$	heating gas	$p$	<i>mixed-particle</i>
<i>inlet</i>	<i>inlet heating gas</i>	<i>outlet</i>	<i>outlet heating gas</i>

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### References

- Ahuja, P., Kumar, S., Singh, P. C. 1996. A model for primary and heterogeneous secondary reactions of wood pyrolysis. *Chemical Engineering & Technology*, 19, 272-282.
- Bernardo, M., Lapa, N., Gonçalves, M., Mendes, B., Pinto, F. 2011. Characterization of chars produced in the co-pyrolysis of different waste: Decontamination and leaching studies. *Chemical Engineering Transactions*, 25, 521-526.
- Bockhorn, H., Hornung, A., Hornung, U. 1999. Mechanisms and kinetics of thermal decomposition of plastics from isothermal and dynamic measurements. *Journal of Analytical and Applied Pyrolysis*, 50, 77-101.
- Feinstein, H. I. 1972. Density of a binary mixture. A classroom or laboratory exercise. *Journal of Chemical Education*, 49, 111.
- Günther, D., Steimle, F. 1997. Mixing rules for the specific heat capacities of several HFC-mixtures. *International Journal of Refrigeration*, 20, 235-243.
- Kasap, S., Capper, P. 2006. *Springer Handbook of Electronic and Photonic Materials*, Springer.
- Oyedun, A., Lam, K.-L., Fittkau, M., Hui, C.-W. 2012. Optimisation of particle size in waste tyre pyrolysis. *Fuel*, 95, 417-424.
- Oyedun, A. O., Gebreegziabher, T., Hui, C. W. 2013. Mechanism and modelling of bamboo pyrolysis. *Fuel Processing Technology*, 106, 595-604.
- Paradela, F., Pinto, F., Gulyurtlu, I., Cabrita, I., Lapa, N. 2009. Study of the co-pyrolysis of biomass and plastic wastes. *Clean Technologies and Environmental Policy*, 11, 115-122.
- Vasile, C., Brebu, M. A. 2007. Thermal valorisation of biomass and of synthetic polymer waste. Upgrading of pyrolysis oils. *Cellulose Chemistry and Technology*, 40, 489-512.