Analysis of Biomass Pyrolysis Product Yield Distribution in Thermally Thin Regime at Different Heating Rates

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Abstract
A better understanding of biomass pyrolysis process at various thermal regimes is fundamental to the optimization of biomass thermochemical conversion processes. In this research work, the behaviour of biomass pyrolysis in thermally thin regime was numerically investigated at different heating rates (1, 5, 10 and 20 K/s). A kinetic model, consisting of five ordinary differential equations, was used to simulate the pyrolysis process. The model equations were coupled and simultaneously solved by using fourth-order Runge-Kutta method. The concentrations of the biomass sample (Maple wood) and product species per time were simulated. Findings revealed that tar yield increased with increase in heating rate. Char yield, however, decreased with increase in heating rate. Results also showed that the extent of secondary reactions, which influenced gas yield concentration, is a function of residence time and temperature. This model can be adopted for any biomass material when the kinetic parameters of the material are known.
Keywords: Biomass, pyrolysis, kinetic model, thermally thin regime

1. Introduction
Ever increasing energy demand and the problem of greenhouse gases emissions from combustion of fossil fuels have resulted in seeking alternative, environmentally friendly and renewable energy sources [1]. For quite some decades, biomass energy has been attracting attention as one of the possible alternatives for fossils. Biomass is a versatile renewable source of energy that can be readily stored and transformed into electricity and heat. Developing countries have a greater interest in biomass because their economies are largely based on agriculture and forestry [2]. Although there are several methods of converting biomass into energy, thermochemical processes are often used due to the possibility of converting the feedstock into three constituents; solid (char or carbon), liquid (tar and other heavy hydrocarbons) and gas (CO_2, CO, H_2, C_2H_4 and H_2O et c.) through these processes. Pyrolysis, being a precursor of other thermochemical processes (gasification and combustion) plays a vital role in determining the eventual product yield distribution. Many research works have been done on pyrolysis process [3-7] but little attention is paid to results interpretations relative to the thermal regimes under study. This, in turn, has led to some misconceptions about the effect of various process parameters on pyrolysis. This work is therefore set out to numerically investigate the effect of different heating rates on biomass pyrolysis product distribution in thermally thin regime. In this regime, the rate of heat transfer to and within the particle is very fast compared to the reaction rate. Therefore, the solid temperature will be essentially the same as that of the reactor environment and the overall controlling factor is the intrinsic kinetics [22]. Hence, biomass decomposition reaction takes place isothermally and the process progresses under conditions of pure kinetic control. In other words, pyrolysis occurs throughout the particle and there is no char insulating the unreacted core [23]. Over the years, many reaction mechanisms have been devised for the study of biomass pyrolysis. These are either one-step global models [8-12] or one- or two-stage multiple reaction models [13-19]. Prakash and Karunanithi [20] have reviewed some advances in modeling and simulation of biomass pyrolysis. In this study, a two-stage multiple reaction model was used. This is because models as such consider intra-particle secondary reactions of primary products of pyrolysis.

2. Modeling
2.1 Pyrolysis mechanism
The pyrolysis mechanism adopted for this study was proposed by Park *et al.* [21]. As shown in Figure 1, the virgin biomass (wood) primarily decomposes by three competitive endothermic reactions to yield gas, tar and intermediate solid. The tar generated from primary pyrolysis participates in secondary reactions yielding more gas and char. The intermediate solid, however, further decomposes through exothermic secondary reactions into char. A detailed description of this model has been given by Park *et al.* [21].
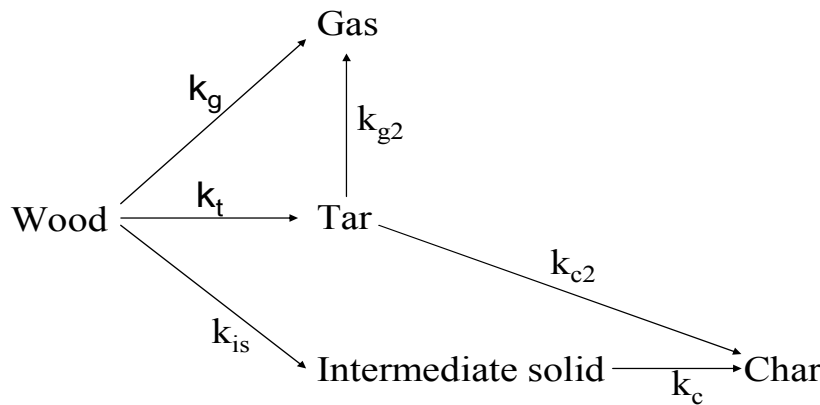
Figure 1. Pyrolysis mechanism [21]

2.2 Model equations

2.2.1 Solid mass conservation equation

The virgin biomass instantaneous mass balance equation (equation (1)) contains three competitive consumption terms, each for the reaction yielding gas, tar and intermediate solid, given as

$$\frac{\partial \rho_w}{\partial t} = -(k_g + k_t + k_{is})\rho_w \tag{1}$$

The intermediate solid instantaneous mass balance equation (equation (2)) contains two terms, one for the conversion of the intermediate solid to char and the other from tar to yield char, given as

$$\frac{\partial \rho_{is}}{\partial t} = k_{is}\rho_w - k_c\rho_{is} \tag{2}$$

Similarly, the char instantaneous mass balance equation (equation (3)) contains two terms, one for the conversion of intermediate solid to char and the other from tar transformation to char, given as

$$\frac{\partial \rho_c}{\partial t} = k_c\rho_{is} + k_{c2}\rho_t \tag{3}$$

2.2.2 Gas mass balance equation

The gas instantaneous mass balance equation (equation (4)) has two terms, one for the conversion of the virgin biomass solid (wood) to gas and the other from tar secondary reaction to yield gas.

$$\frac{\partial \rho_g}{\partial t} = k_g\rho_w + k_{g2}\rho_t \tag{4}$$

2.2.3 Tar mass balance equation

The tar instantaneous mass balance equation (equation (5)) contains three terms, the first for the conversion of virgin biomass to tar, the others for the conversion of tar to gas and char.

$$\frac{\partial \rho_w}{\partial t} = k_t\rho_w - k_{g2}\rho_t - k_{c2}\rho_t$$

$$\frac{\partial \rho_w}{\partial t} = k_t\rho_w - (k_{g2} + k_{c2})\rho_t \tag{5}$$

Equations (1) to (5) are the ordinary differential equations describing the mass change of biomass and its products based on the pyrolysis kinetic mechanism shown in Figure 1.

The reaction rates were assumed to follow Arrhenius rate expression of the form

$$k_i = A_i \, exp(E_i/RT) \tag{6}$$

Arrhenius kinetic parameters were obtained from Park *et al.* [21]. Table 1 gives the details of the kinetic parameters. As in virtually all thermo gravimetric analysis, temperature and time have linear relationship and therefore, the process takes place under temperature-time relationship given by

$$T_i = T_o + (hr) \times t_i \tag{7}$$

where t_i is given by

$$t_i = t_0 + i \times \Delta t \tag{8}$$

3. Numerical solution

Equations (1) to (7) were simultaneously and numerically solved by using fourth order Runge-Kutta method. This method is adequate for this case because the model equations are coupled ordinary differential equations. A total of five subroutines were written, one for each of the ordinary differential equations, in order to obtain a complete set of solution. The process was terminated when the concentration of the virgin biomass (Maple wood) reduced to 0.0003. Beyond this point, pyrolysis was considered too slow and of no practical significance. The data for four different heating rates (1, 5, 10 and 20 K/s) were obtained for the various species and were analyzed.

Table 1: Kinetic parameters for Arrhenius equation

Reaction (i)	A_i (s^{-1})	E_i (J/mol)
t	1.08×10^{10}	148,000
g	4.38×10^{9}	152,700
is	3.75×10^{6}	111,700
c	1.38×10^{10}	161,000
c_2	1.0×10^{5}	108,000
g_2	4.28×10^{6}	108,000

4. Result and discussion

Considering the quantity of data generated from the numerical study, it is very important to carefully present the characteristic features of the concentration profiles of various species resulting from the pyrolysis process. Figure 2 shows the species concentration profiles for wood pyrolysis process at 1 K/s. As shown in the figure, the initial temperature being high enough to initiate the process (673 K), biomass decomposition began almost immediately.
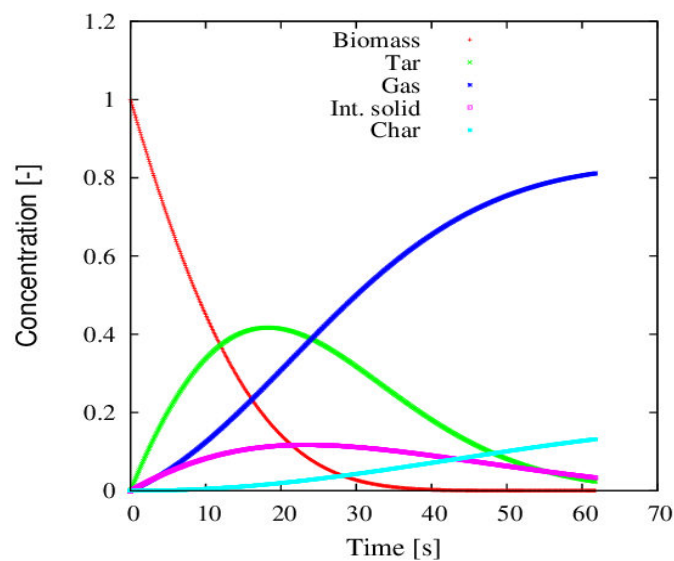

Figure 2: Biomass and product species concentration profiles with time at 1 K/s

This decomposition reaction resulted in the formation of gas, tar and intermediate solid. As the temperature increased, the tar and intermediate solid formed further participated in some secondary reactions, characterized by decrease in the concentration of the two species, resulting in the production of more gas and char. The details of these secondary reactions have been given somewhere else [21]. The process was terminated when biomass concentration had become so low (0.0003) that no significant decomposition reaction took place any more. At 1 K/s, the final pyrolysis time was about 62 s as shown in Figure 2.

Figures 3, 4 and 5 respectively show the concentration profiles of both the biomass sample and the product species at 5, 10 and 20 K/s. Although the profiles were similar for all heating rates considered, the peaks and the final values of the product species concentration profiles, the extent of secondary reactions and the time required for the completion of the pyrolysis process were different for each heating rate.
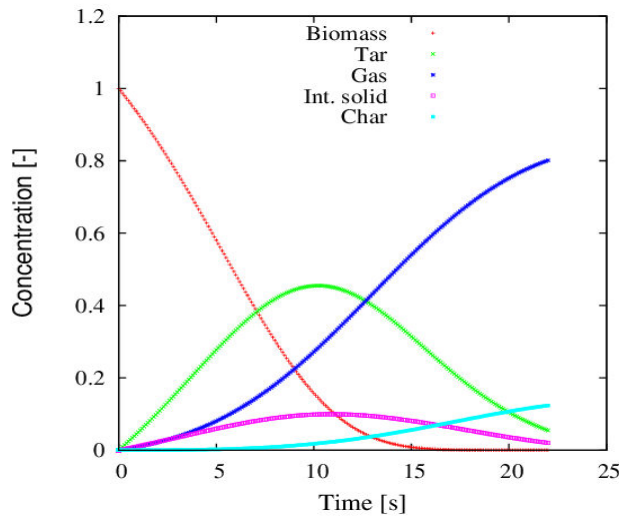
Figure 3: Biomass and product species concentration profiles with time at 5 K/s
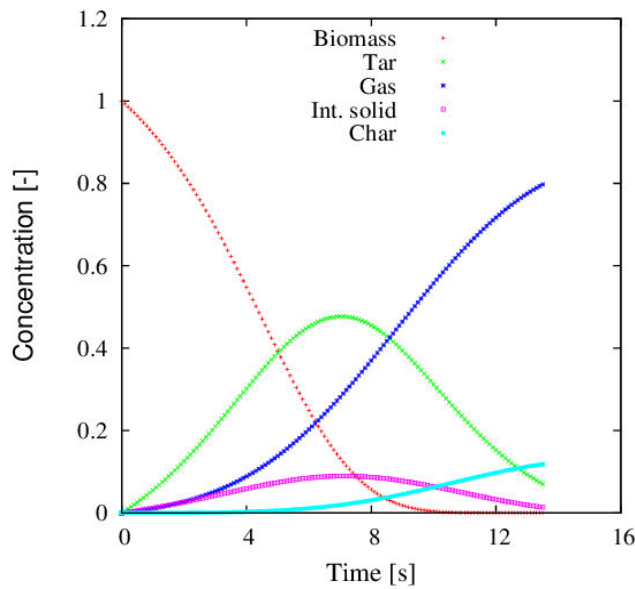

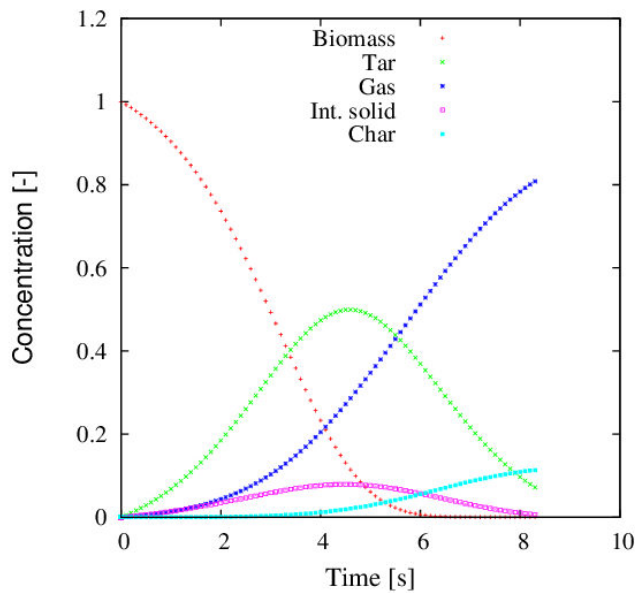Figure 4: Biomass and product species concentration profiles with time at 10 K/s

Figure 5: Biomass and product species concentration profiles with time at 20 K/s

Table 2 shows the final pyrolysis time, temperature and concentration of the product species at 1, 5, 10 and 20 K/s.

Table 2: Final pyrolysis time, temperature and concentration of initial biomass sample and product species.

Heating rate (K/s)	1	5	10	20
Final pyrolysis time (s)	61.8	22.0	13.5	8.3
Final pyrolysis temperature (K)	734.8	783.0	808.0	839.0
Final concentration of initial biomass (-)	0.00026	0.00025	0.00024	0.00024
Final concentration of tar (-)	0.0233	0.0547	0.0702	0.0717
Final concentration of gas (-)	0.8114	0.8012	0.7976	0.8083
Final concentration of intermediate solid (-)	0.0335	0.0203	0.0139	0.0065
Final concentration of char (-)	0.1318	0.1238	0.1183	0.1135
*Material balance	1.000	1.000	1.000	1.000

*This is an application of conservation of mass concept to physical systems. In this case, it is the summation of the final concentration of initial biomass, tar, gas, intermediate solid and char.

From Table 2, it is seen that as the heating rate increased, the final pyrolysis temperature also increased. This was because the rate of heat transfer to the sample increased with heating rate. It is also observed from the table that the final pyrolysis time decreased with increasing heating rate. This was due to the fact that as the heating rate increased, the rate of chemical reaction was accelerated, resulting in a speedy completion of the pyrolysis process. These results are in agreement with findings made by Srivastava *et al.* [24]. In the same vein, the final concentration of char decreased as the heating rate increased. This was because increase in heating rate favoured the yield of non-solid (tar and gas) products during primary pyrolysis and also facilitated secondary reactions. The decrease in the final concentration of the intermediate solid with increasing heating rate is also attributable to this reason. The final concentration of gas appeared to be inconsistent as heating rate increased because secondary reactions, which led to more gas yield, depend on both residence time and temperature, and the extent of these reactions is a compromise between the two factors.

5. Conclusion

Product yield distribution during biomass pyrolysis process in thermally thin regime at different heating rate has been investigated. A kinetic model, consisting of five ordinary differential equations, was developed. Results showed consistent trend in the yield distribution of tar and char while there was a variation in gas yield due to the influence of tar secondary reactions. This model can be used to predict product yield distribution of pyrolysis process in thermally thin regime.

Nomenclature

A: pre-exponential factor   (1/s)

E: activation energy   (J/mol)

k: reaction rate constant   (1/s)

R: universal gas constant   (J/(mol K))

T: temperature   (K)

t : time   (s)

ρ: density   (kg/m^3)

Subscripts

c: char, primary char formation reaction

c_2: secondary char formation reaction

g: gas, primary gas formation reaction

g_2: secondary gas formation reaction

is: intermediate solid, intermediate solid formation reaction

t: tar, tar formation reaction

w: initial virgin biomass

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