Finite Element Modelling and Experimental Validation of Rapid Pyrolysis

of Lignocellulosic Biomass

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ABSTRACT

Considerable research has been devoted towards determining the kinetics of the pyrolysis of lignocellulosic biomass such as wood residues and agricultural waste. In this study, we have developed a finite element model (FEM) in order to simulate the coupled heat and mass transfer phenomena during pyrolysis. The resulting sets of partial differential equations were then solved simultaneously using the COMSOL Multiphisics software package. This numerical modelling and simulation approach helped the visualization of the process. In this work, cylindrical sections of birch wood biomass were pyrolysed in a laboratory-scale thermal desorption unit. The influences of final pyrolysis temperature, and pyrolysis holding time on the biochar yields were investigated. Results showed that with increase in time and temperature, the yield of total pyrolysis products decreased. On the other hand, higher pyrolysis temperatures and holding times resulted in the increase of char content in the wood for fast pyrolysis. A technique to maximize the amount of char in the product was also identified through by optimizing the parameters within the temperature range of this study

INTRODUCTION

One of the important thermochemical conversion techniques of biomass is known as pyrolysis. It is the thermal decomposition of biomass at low or absence of oxygen. Pyrolysis converts organics to solid, liquid and gas by heating in the absence of oxygen. The amounts of solid, liquid, and gaseous fractions formed and the distribution of their products are dependent distinctly on feedstock and the process variables (e.g., heating rate). The process of pyrolysis produces solids (charcoal), liquids (H_2O and organics), and gases (CO, CO_2, CH_4, H_2). (Masek, 2009). The end product of this process is usually referred as biochar. Biochar is highly useful in the mopping up of excess Green House Gases (GHGs) from fossil fuels. It is used in sequestration of carbon in soil and thereby reduces carbon dioxide levels in the atmosphere through uptake by plants. The production of biochar through the process of pyrolysis has come about to be an extremely efficient and popular technology in recent years.

The quantitative nature of the pyrolysis products is largely dependent on the reactor configuration, the chemical and physical properties of the biomass as well as on the heating rate and holding time of the process. For a lignocellulosic biomass, e.g. wood, the yield depends on the wood structure and particle size. In a conventional pyrolysis process, a classical hardwood produces lower char yields with respect to the initial dry mass than classical softwoods. Moreover, as the particle size of the wood block increases, liquid production becomes successively less favoured. Many researchers have attributed differences in heating rates to be an important factor for varying quantitative yields of the lignocellulosic pyrolysis products. (Masek, 2009, Di Blasi et. al, 2001, Wang et al. 2009).

The weight loss curves are determined by taking into account the loss in the weight of the solid residue. It has been observed by Di Blasi (2008), through these curves, that hemicelluloses decompose at 225–325ºC, cellulose at 325–375ºC, whereas lignin decomposes gradually over the temperature range of 250–500ºC. Considerable degradation rates are concurrently attained by all the components when the temperatures are sufficiently high.

The increase in the biochar yield is based on the minimization of the carbon losses in the form of gases and liquids. Biochar is a product of both primary (char) and secondary (coke) reactions. There are number of methods employed to improve the yields of biochar with factors like low

pyrolysis temperature, high process pressure, long vapour residence time, extended vapour/solid contact, low heating rate, large biomass particle size, optimised heat integration (Masek, 2009).

Another important parameter is the residence time of solids. In case of fast pyrolysis, at low temperatures, the residence time of char is longer than that of volatiles. As a result, volatile matter may be expelled before complete conversion. In such cases, char yields are often higher than the other products. (Di Blasi et. al, 2001)

There is a growing interest in the scientific world regarding the research of modelling and simulation studies involved in the production of biochar as well as other by-products in the process of pyrolysis. One of the earliest research work done in this area was carried out to model and verify experimentally the physical and chemical processes involved during the pyrolysis of a large biomass particle (Chan et al., 1985). It emphasized the need for more information regarding the char deposition rates and its thermal properties over a wide range of temperatures. Numerical and modelling studies have been conducted which focus on estimation of optimum parameters in pyrolysis of biomass (Babu et al., 2004). Different approaches used in the transport models have also been presented at both the single particle and reactor levels, together with the main achievements of numerical simulations (Di Blasi., 2008).

FEM technique competes very favourably with the other numerical methods due to the Partial Differential Equations (PDE's) discretization and solution procedure applied in the analysis of the model (Baggio et al., 2009). The advantage of FEM is that it allows modelling of complicated boundary shapes with relative ease for flow and heat transfer problems (Prakash & Karunanithi, 2009).

Taking into account all the above mentioned facts, in this study, a Finite Element Model (FEM) of the pyrolysis of lignocellulosic biomass was developed and simulation studies were conducted for biomass subjected to 10, 15 and 20 minutes of heating at 300°C, 350°C and 400°C in order to visualize and investigate the temperature distribution within the biomass. The objective was to maximize the production of biochar.

NOMENCLATURE

k	Kinetic reaction constant (s^{-1})
A_x	Arrhenius constant (s^{-1})
E_a	Activation energy of reaction (kJ mol^{-1})
Pav	Time average power dissipated (W)
Pc	Poynting Vector -power dissipated over unit area (W.m^{-2})
ρ	Density of the material (kg.m^{-3})
Cp	Specific heat capacity of the material (kJ.kg^{-1}.K^{-1})
T	Temperature (K)
K	Thermal conductivity (W.m^{-2}.K^{-1})
Q	Power Source Term (W.m^{-3})
V	Volume (m^{3})

MATERIALS AND METHODS

### 2.1. Reaction Kinetics Model for simulation

For this simulation, isothermal conditions were assumed. In case of isothermal methods, a series of evaluations must be carried out at different temperatures to determine the reaction rate. Then, Arrhenius equations can used to calculate the activation energies and frequency factors for these reactions.

The three step mechanism described by Di Blasi (1998) was used as the kinetics model for modelling and simulation of the pyrolysis of wood. The advantage of this mechanism lies in the comparable activation energies of reactions which do not allow the selectivity to be displaced toward only one of the products. This simulation work was conducted on the basis of the Scheme C of the three step mechanism model of Di Blasi et. al. (2001).

2.2. Three-step mechanism:

The three step mechanism (equation (1)) and the reaction kinetic constants for this scheme were:

$$WOOD \begin{array}{c} \overset{k_3}{\nearrow} CHAR \\ \overset{k_2}{\rightarrow} TAR \\ \underset{k_1}{\searrow} GAS \end{array} \qquad (1)$$
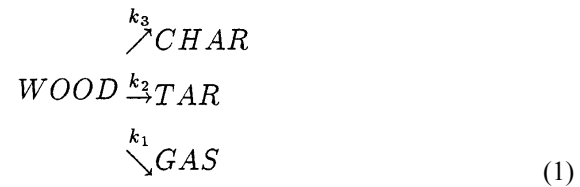
A_1=1.30 x10^8 s^{-1}, E_1= 1.40 kJ mol^{-1}
A_2=2.00 x10^8 s^{-1}, E_2= 1.33 kJ mol^{-1}
A_3=1.08 x10^7 s^{-1}, E_3= 1.21 kJ mol^{-1}

Where A_1, A_2, A_3 are the Arrhenius constants, E_1, E_2, E_3 are the activation energies. k_1, k_2 and k_3 are the reaction rate constants for the formation of gas, tar and char respectively calculated using the Arrhenius equation from the corresponding Arrhenius constants and activation energies (equation 2).

$$E=Ae^{(-k/RT)} \qquad (2)$$

This mechanism has been applied to model large particle biomass pyrolysis (Di Blasi et al, 2001). This scheme is taken into account in this study because it can predict the qualitative correct behaviour of wood pyrolysis along with the dependence of product yields on temperature.

2.3. Mathematics of the Model

The temperature distribution inside the lignocellulosic biomass sample was obtained by solving the conductive heat transfer equations.

2.3.1. Heat transfer

For an incompressible material heated under constant pressure, the thermal energy equation is given by equation (1) (Zhou et al., 1995)

$$\rho C_p \frac{\partial T}{\partial t} = \nabla.(K\nabla T) + Q \qquad (3)$$

Where ρ is the density (kg.m^{-3}), Cp is the specific heat (kJ.kg^{-1}.K^{-1}) and K is the thermal conductivity of the material ((W·K^{-1}·m^{-1}) and T is the absolute temperature in Kelvin (K). Different mesh element sizes were used for different sub-domains based on the dielectric properties of the sub-domain and the precision required in the sub-domain of interest.

Although heating rate of the pyrolysis reaction plays a major role in obtaining the desirable yields of the product, this simulation technique could only be limited to rapid or fast pyrolysis of 1000°C/min as isothermal conditions were assumed.

2.3.2. Boundary conditions

Temperature boundary conditions were used for all the boundaries except the circular ends of the cylindrical wood sample. Surface to ambient boundary conditions were applied for the circular ends in order to simulate the heating mechanism inside the quartz sleeve of the Thermal Desorption Unit.

2.4. Finite element modelling and simulation

A 3D Finite Element Model was developed using COMSOL Multiphysics version 4.0 (COMSOL Inc., USA) software package to simulate the pyrolysis process for the Chinese birch wood sample. The meshed structure of the quartz tube with the wood sample is shown in Figure 1.

The dimensions of the cylindrical wood sample were and the quartz sleeve were taken as 3 mm ϕ X 70 mm h and 6mm outer ϕ and 4 mm inner ϕ X 100 mm h respectively. A custom built computer with two AMD Opteron dualcore 2.4 GHz processors and 16 GB primary memory was used to run the simulations.


Figure 1: Finite Element Mesh Structure of the glass tube reactor with the wood sample

2.5. Experimental set up for validation of the simulation

Longitudinal pieces of Birch wood obtained from the local market were cut into pieces of 3mm diameter and 70mm length. In this study, the pyrolysis experiments were conducted in a Thermal Desorption Unit (Supelco, Inc.) (Figure 2) with the sample wood pieces insulated inside quartz tubes of 6mm outside diameter and 100mm in length. The objective of this investigation was to determine the effect of the pyrolysis temperature on pyrolysis yields. Thus a quantity of 0.3-0.5 g of the sample was placed in the reactor and the temperature was raised to a fast pyrolysis rate of 1000°C/min to final test

temperatures of 300, 350, and 400°C and held for 10, 15 and 20 min respectively. Due to the constraints of the equipment, the temperature of pyrolysis could be raised only to 400°C and hence the model was validated till this temperature.
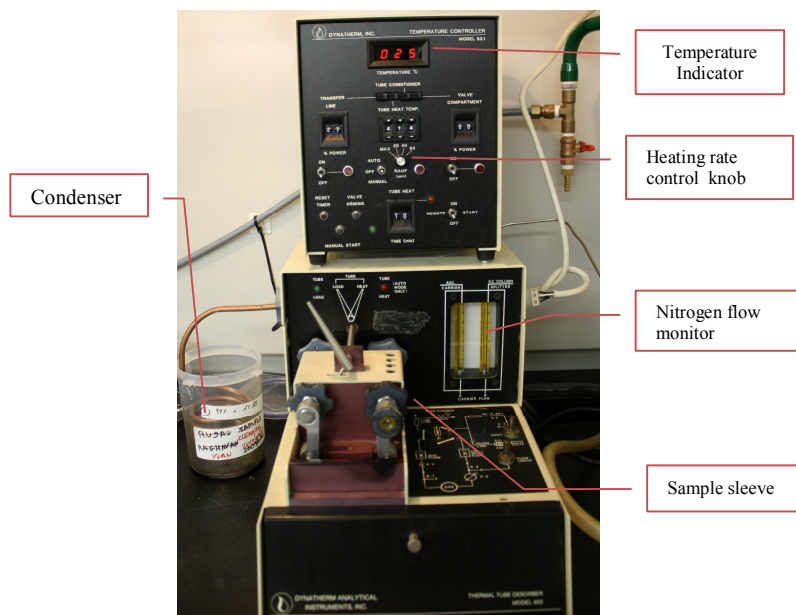
Figure 2 Experimental set up for validation: Thermal Desorption Unit (Supelco, Inc.)

The volatiles produced during the process were constantly displaced with nitrogen gas purged into the system and then condensed in a water- bath. After pyrolysis, the solid char was removed and weighed to analyze the total yield.

RESULTS AND DISCUSSION

3.1. Simulation results

This simulation study was carried out at a range of temperatures of 300°C, 350°C and 400°C for 0 to 75 minutes of heating. The initial concentration of the wood or biomass sample was taken to be 3800 mol.m^{-3}, based on the molecular weight and density of birch wood (Paper on Web, 2010).

The temperature profiles obtained as a result of the simulation of the heating of biomass sample at 400°C is shown in Figures 3, 4 and 5. At 0 min, the whole birch wood sample was around the temperature of 20°C except the surface which was at 400°C. With the progress of the pyrolyses reactions, due to the conductive nature of the heating, the surface of the wood sample reached higher temperatures before the interiors of the biomass. As the conductive heating of the wood sample continued, the whole sample was heated within 10 min of the commencement of the pyrolysis and the wood reached 400°C (Figures 3, 4 and 5).

These findings of the simulations corroborate with other studies which have also shown that in the conventional method, the surface of the wood is heated by convective heat transfer from high-temperature gas and by conduction from the surface to the wood core. The poor thermal conductivity of wood leads

to the temperature at the wood surface being higher than that at the wood core and it takes relatively a long time to attain thermal equilibrium (Masek, O., 2009, Miura et al., 2004).

Given the kinetic parameters discussed previously, the resulting numerical model for the pyrolysis of the lignocellulosic biomass, at a temperature of 300°C, showed minimal amount of products formed in the reaction as shown in Figure 6 (a). The wood sample did not show any significant variation from its initial concentration during the pyrolysis process.

When the temperature was raised to 350°C, the model showed a visible change in concentration of the biomass, thereby implying the incidence of the pyrolysis reactions. In Figure 6(b), it was seen that the wood sample underwent a decrease in concentration till about 0.6 hours (36 min) of the reaction period while the quantity of char increased. Hence product formation was observed in this at this temperature when compared to the one taking place at 300°C. All three phases of products were formed at this temperature although char and syngas formation went only till 18 min while concentration of tar was higher. Both quantities remained constant beyond this time period for 350°C.

At a higher temperature of 400°C, the concentration vs. time curve showed an exponential decrease in the concentration of the wood biomass. In turn, the quantities of tar and char were significantly higher compared to the previous profiles of the model. The concentration of biochar went up to about 1400 mol.m^{-3} in a matter of 0.4 hours (24 min) as seen in Figure 6(c) and remained constant with further increase in reaction time. The production of syngases in this reaction was negligible throughout the pyrolysis of the biomass. This may be attributed to the small sample size of the woody biomass.
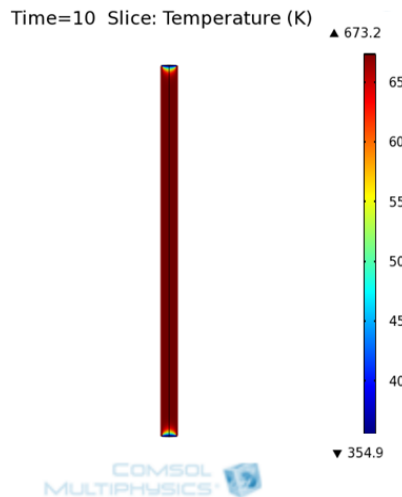
The desired temperature of 400°C was equilibrated in 10 min of the reaction and by 20 min; the entire biomass had converted into the pyrolyzed products (Figure 6).
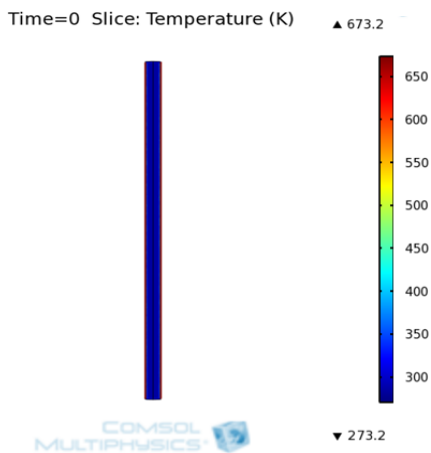
Figure 3: Simulated temperature profile of biomass at 0 min for heating at 400°C
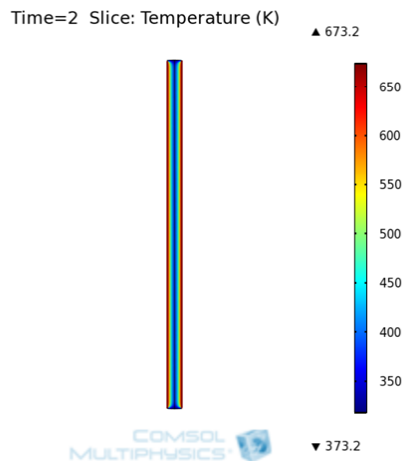
Figure 4: Simulated temperature profile of biomass at 2 min for heating at 400°C

Figure 5: Simulated temperature profile of biomass at 10 min for heating at 400°C

3.2. Experimental validation

The experimental validation of the simulation results was carried out in a Thermal Desorption Unit (Supelco, Inc.) (Figure 2) with the sample wood pieces heated inside quartz tubes of 6mm outside diameter and 100mm in length. The simulation results led to the configuration of an experimental design for the experiment to be conducted for 10, 15 and 20 min at the heating rate of 1000°C/min.

In this investigation, temperature and time were taken as the two factors and a face centered cubic design matrix was formed with eight central levels of the design as shown in Table 1. Based on the experimental results, the following biochar yields were obtained from fast pyrolysis of the Chinese birch wood samples as shown in Figure 7.

A response surface plot was drawn from the data with a coefficient of regression as $R^2 = 0.83$. The model is given as equation (4).
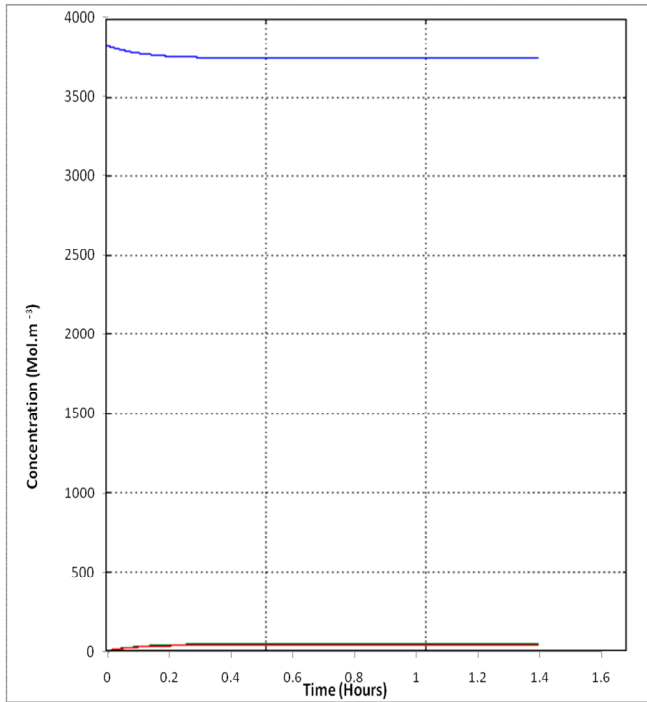
$$Yield = -80.67 + 0.38*Temp - 0.27*Time \qquad (4)$$

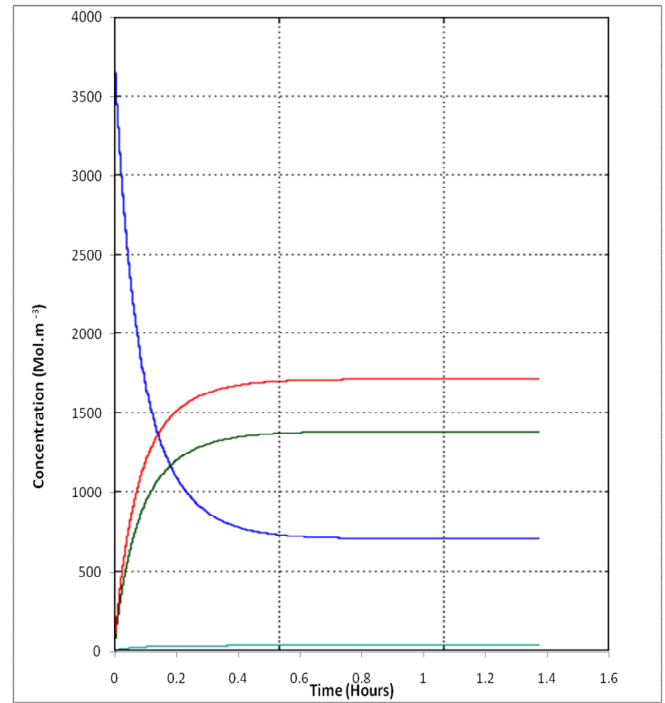**Table 1.** Experimental conditions with a two factorial face centered design

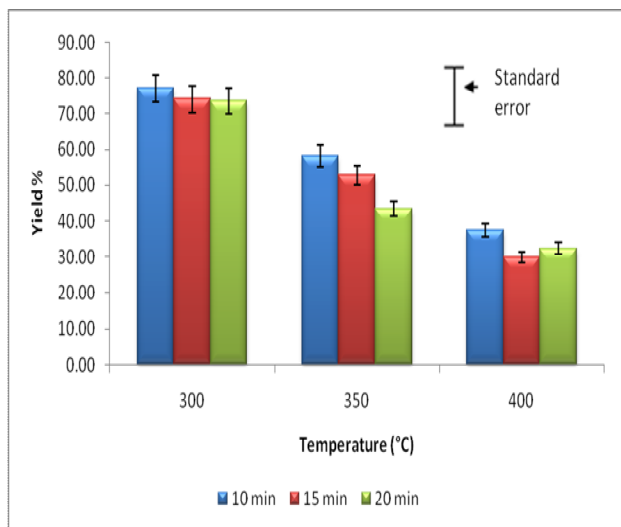| Test	Temperature (°C)	Time (min)
1	300	10
2	300	20
3	400	10
4	400	20
5	300	15
6	400	15
7	350	10
8	350	20
9	350	15
10	350	15
11	350	15
12	350	15
13	350	15
14	350	15
15	350	15
16	350	15

(b)

(a)

(c)

wood
char
tar
gas
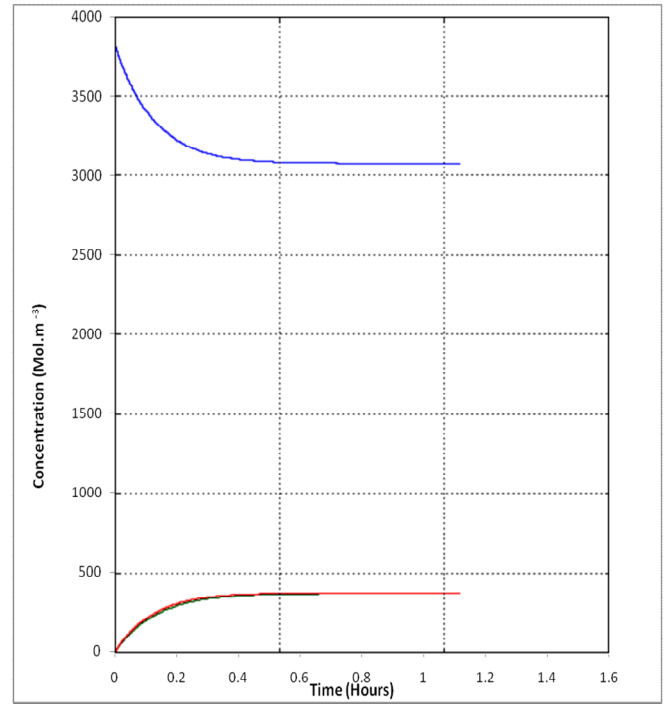
Figure 6: Concentration vs Time profiles of the different simulation models at temperature range of 300°C-400°C. (a) 300°C (b) 350°C (c) 400°C

Figure 7 The comparison of pyrolysis yields on varying pyrolysis temperatures & time at 1000°C/min

With the increase in temperature of pyrolysis, the total product yield after the process reduced from approximately 77% at 300°C (10 min) to 32% at 400° C (20 min) as illustrated in Figure 7. Many researchers have attributed this decrease in the char yield with increasing temperature, either to greater primary decomposition of the wood at higher temperatures or to secondary decomposition of the char.

This conclusion is consistent with previous studies of cellulose and lignocellulosics (Sensoz and Can, 2002, Valenzuela-Calahorra et al., 1987). On the contrary, the simulation results confirm that the yield is higher at lower temperatures mainly due to the retention on un-pyrolysed wood and not due to complete pyrolysis of the sample. This is supported by Boetang (2007) in the study on the characterization of char from switchgrass produced at <500°C.

Another important result of this study was the effect of the continuous disposition of secondary gases from the reactor. This possibly resulted in higher yield of biochar as the secondary reactions were prevented.

CONCLUSIONS

Simulation results from this study indicated 400°C to be the optimum temperature at which highest yield of biochar is found by the process of pyrolysis based on the kinetics of the model taken into consideration under the specified temperature range. It also showed that the amount of char formed would vary based on the pyrolysis holding time.

Though the thermal equilibrium was attained in approximately 10 mins the pyrolysis process continued for a maximum of only 20 mins. Through this simulation and modelling study, the kinetics of the different pyrolysis parameters as well as further attempts of optimizing char yield through variation of time, temperature and heating rate of the reaction is highlighted. This numerical simulation model could be used to further look into designing a reactor for pyrolysis which aims at higher yields of biochar. The results showed that with increase in pyrolysis temperature and duration of reaction

at the same temperature, the yields of biomass decreased. On the contrary, the quantity of biochar in them increased and continuous disposition of the secondary pyrolytic products will result in increased char yield.

REFERENCES

[1] Masek, Ondrej. Biochar- production technologies. , 2009. www.geos.ed.ac.uk/sccs/biochar/ documents/ BiocharLaunch-OMasek.pdf. Accessed on 26-09-2009.

[2] Chan, W.R., M. Kelbon and B.B. Krieger. Modelling and experimental verification of physical and chemical processes during pyrolysis of large biomass particle. Fuel, 1985; 64: 1505-1513.

[3] Babu, B.V., Chaurasia, A.S, 2004. Pyrolysis of biomass: improved models for simultaneous kinetics and transport of heat, mass and momentum. Energy Conversion and Management 45:1297–1327.

[4] Di Blasi, 2008. Comparison of semi-global mechanisms for primary pyrolysis of lignocellulosic fuels. Journal of Analytical and Applied Pyrolysis 47: 43–64.

[5] Baggio, P., Baratieri, M., Fiori, L., Grigiante, M., Avi, D., Tosi, P., 2009. Experimental and modelling analysis of a batch gasification/pyrolysis reactor. Energy Conversion and Management, 50 (6): 1426-1435

[6] Prakash, N and Karunanithi, T. Advances in modelling and simulation of Biomass Pyrolysis. Asian Journal of Scientific Research, 2, 2009; 1: 1-27.

[7] Wilner, T. and Brunner, G, 2005. Pyrolysis Kinetics of wood and wood components. Chem. Eng. Tech, 28 (10).

[8] Di Blasi and Branca, C. Kinetics of Primary Product Formation from Wood Pyrolysis. Ind. Eng. Chem. Res., 40, 2001; 5547-5556.

[9] Zhou, L.; Puri, V.M.; Anantheswaran, R.C. and Yeh, G. Finite element modelling of heat and mass transfer in food materials during microwave heating – model development and validation. J. Food Engineering. 25, 1995; 509-529.

[10] Wang, Xian-Hua., Chen, Han-Ping., Ding, Xue-Jun., Yang, Hai-Ping., Zhang, Shi-Hong., and Shen, Ying-Qiang. Properties of gas and char from microwave pyrolysis of pine sawdust. BioResources 4, 2009; 3: 946-959.

[11] McClaughlin, H., Anderson, P. S., Shields, F. E., and Reed, T. B. All Biochars are Not Created Equal, and How to Tell Them Apart. A digital reprint issued at the North American Biochar Conference, Boulder, CO – August 2009.

[12] Paper on web, 2010. Properties of wood. www.paperonweb.com/wood.htm. Accessed on 21-01-2010.

[13] Miura, M. et al., 2004. Rapid pyrolysis of wood block by microwave heating. J. Anal. Appl. Pyrolysis 71: 187–199.

[14] Şensöz, Sevgi and Can, Mukaddes. Pyrolysis of Pine (Pinus Brutia Ten.) Chips: 1. Effect of Pyrolysis Temperature and Heating Rate on the Product Yields', Energy Sources, Part A: Recovery, Utilization, and Environmental Effects, 24: 4, 347 — 355

[15] Valenzuela-Calahorro, C., A. Bernalte-García, V. Gómez-Serrano, and J. Bernalte-García. 1987. Influence of particle size and pyrolysis conditions on yield, density and some textural parameters of chars prepared from holm-oak wood. J. Anal. Appl. Pyrolysis 12:61–70.

[16] Boateng A. A., 2007. Characterization and Thermal Conversion of Charcoal Derived from Fluidized-Bed Fast Pyrolysis Oil Production of Switchgrass. Ind. Eng. Chem. Res, 46, 8857-8862.