FINITE ELEMENT MODELLING OF MICROWAVE PYROLYSIS OF 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. The end product of this process is usually referred as biochar and it is considered as an efficient method for sequestering carbon to offset atmospheric carbon-dioxide. Among the different methods available, microwave assisted pyrolysis has proven to be very efficient in terms of energy utilization. In this study, an attempt has been made to develop a finite element model (FEM) in order to couple electromagnetic heating, combustion, and heat and mass transfer phenomena during microwave 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. It can eventually be used to study and optimize the production of biochar from a wide variety of lignocellulosic biomass.

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 the process variables. The process of pyrolysis produces solids (charcoal), liquids (H_2O and organics), and gases (CO, CO_2, CH_4, H_2). Proportions and composition depend on feedstock and process conditions (e.g., heating rate) (O. Masek, 2009). The production of biochar through the process of pyrolysis has come about to be an extremely efficient and popular technology in recent years.

Biochar finds use in the release of energy-rich gases which are then used for producing liquid fuels or directly for power and/or heat generation. It 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.

Recently, there has been a surge on finding alternate methods of efficient pyrolysis techniques for different biomass sources. One of the methods proven to have measured up to good efficiency standards is the use of microwave or microwave assisted pyrolysis methods to form biochar and other useful volatiles. There is a growing interest in the scientific world regarding the research of modeling and simulation studies involved in the production of biochar as well other by products in the process of pyrolysis. Numerical and modeling 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).

There is poor understanding of the mechanisms involved in application of electromagnetic energy for the pyrolysis of biomass and the actual energy distribution inside the biomass when subjecting them to electromagnetic field. The electromagnetic field distribution inside the microwave oven can be traced out by solving the Maxwell's equations (Dev et al., 2008c). Finite Element Method (FEM) is commonly used for solving Maxwell's equations to get the energy distribution in a complex object or within a multimode cavity and it is capable of simulating power density distribution in 3-D space. (Fu and Metaxas, 1994; Zhou, Puri, Anantheswaran et al., 1995).

FEM technique competes very favourably with the other numerical methods, as it is based on reducing the Maxwell's equations to a system of simultaneous algebraic linear equations (Delisile, Wu & Litva, 1991). FEM can readily model heterogeneous and anisotropic materials as well as arbitrarily shaped geometries. It can also provide both time and frequency domain analyses which are important to microwave heating problems like field distribution, scattering parameters and dissipated power distribution for various materials and geometries (Dai, 2006).

Taking into account all the above mentioned facts, in this study, a Finite Element Model (FEM) of the microwave pyrolysis of lignocellulosic biomass was developed and

simulation studies were conducted for biomass subjected to 3 to 15 minutes (with increments of 3 minutes) of heating under 2450 MHz and power densities of 5 W/g, 7.5 W/g and 10 W/g in order to visualize and investigate the energy 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 (m3)
E	Total Electric field intensity (V.m-1)
E_x	Electric field intensity x component (V.m-1)
E_y	Electric field intensity y component (V.m-1)
E_z	Electric field intensity z component (V.m-1)
H	Total Magnetic Field Intensity (A.m-1)
H_x	Magnetic field intensity x component (A.m-1)
H_y	Magnetic field intensity y component (A.m-1)
H_z	Magnetic field intensity z component (A.m-1)
f	Frequency of microwaves (Hz)

MATERIALS AND METHODS

In this study, the mechanisms involved in production of biochar by microwave heating were investigated. A Finite Element Model was made in order to simulate the microwave heating of biomass and to predict the optimal conditions for the maximization of biochar using the process.

Microwave Pyrolysis Set-up

The pyrolysis bioreactor system made of quartz used for the simulation (to be custom built at a later stage) is shown in figure 1. It consisted of three parts: an upper cylinder, a lower cylinder and a sample stand. The upper cylinder has 40 mm inner diameter and a length of 90 mm length. This was connected to the lower cylinder with an inner diameter of 50 mm and 42 mm height by a taper ground joint. The sample stand had a diameter of 35 mm and 25 mm height. A wood sample of 30 mm diameter and 75 mm length was mounted on the sample stand. The air inside the reactor is purged with nitrogen with a flow rate of 0.003 l/s to create an oxygen free inert atmosphere using two quartz tubings 6.3 mm diameter and 25.4 mm length.

The wood sample was subjected to microwave heating at 2.45 GHz frequency with power densities of 5 W/g, 7.5 W/g and 10 W/g at time intervals of 3 mins starting from 3 to 15 min for simulation purposes.
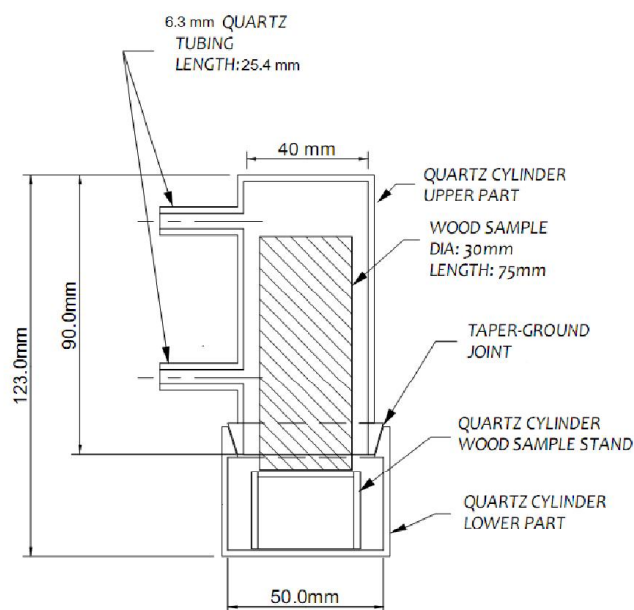

Figure 1: Microwave Pyrolysis Bioreactor Setup

Reaction Kinetics Model for simulation

For this simulation, isothermal conditions are assumed. In case of isothermal methods, a series of evaluations are carried out at different temperatures to determine the reaction rate. Then, Arrhenius equations are used to calculate the activation energies and frequency factors for these reactions. On the other hand, non isothermal methods are dependent on the temperatures at which the reaction rates take place (Willner et. al, 2005).

The three step mechanism described by author Di Blasi in 1998 was used as the kinetics model for modelling and simulation of the microwave 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 (Di Blasi et. al, 2001).The kinetic constants applied to this model were researched by the author through a literature survey from different experimental sources. This simulation work was conducted on the basis of the Scheme C of the three step mechanism model.

Three-step mechanism:

$$WOOD \begin{array}{c} \nearrow^{k_3} CHAR \\ \xrightarrow{k_2} TAR \\ \searrow_{k_1} GAS \end{array}$$
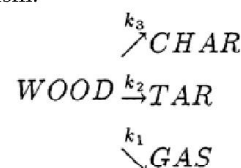
The Kinetic constants for this scheme are:

A1=1.30 x10^8 s^{-1},   E1= 1.40 kJ mol^{-1}
A2=2.00 x10^8 s^{-1},   E2= 1.33 kJ mol^{-1}
A3=1.08 x10^7 s^{-1},   E3= 1.21 kJ mol^{-1}

This mechanism has been applied to model large particle biomass pyrolysis. 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 when coupled with secondary tar reactions and transport phenomena.

Finite element modeling and simulation

A 3D Finite Element Model was developed using COMSOL Multiphysics version 3.5a (COMSOL Inc., USA) software package to simulate the Microwave pyrolysis process for a regular domestic multimode microwave oven configuration. The meshed structure of the microwave cavity along with the bioreactor and wood sample is shown in Figure 2. The cavity dimensions were taken as 267 mm × 270 mm × 188 mm.
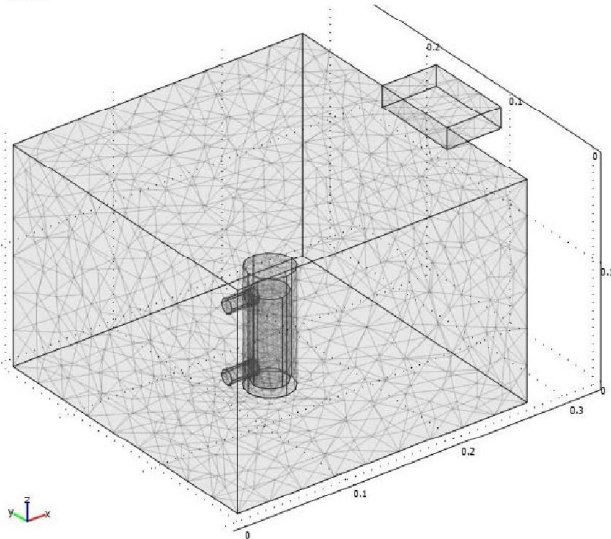
Figure 2: Finite Element Mesh Strucutre

A custom built computer with two AMD Opteron quadcore 2.4 GHz processors and 32 GB primary memory was used to run the simulations.

Mathematics of the Model
Electromagnetics

The Maxwell's equations that govern the electromagnetic phenomena evolving in a given configuration resolved in 3D space were solved for the Electric field intensity (E) (V.m-1) and H Magnetic Field Intensity (A.m-1) (Dai, 2006). The dynamically changing dielectric constant ε' and loss factor ε" were calculated using equations derived from the measurement of dielectric properties.

The time average power dissipated (P_{av}) in each element in a dielectric material was obtained by integrating the poynting vector (P_c) over the closed surface S for each tetrahedral element (eqn. (1)) (Jia and Jolly, 1992).

$$P_{av} = -\frac{1}{2}\int_S P_c \, .dS$$

(1)

Where $P_c = E \times H$

Volumetric heat generation Q can be expressed in terms of power intensity in three orthogonal directions as shown in equation (2) (Lin et al., 1989).

$$Q = \frac{\partial P_{av(x)}}{\partial V} + \frac{\partial P_{av(y)}}{\partial V} + \frac{\partial P_{av(z)}}{\partial V}$$

(2)

Where the suffixes x, y and z indicate time average power dissipated in the corresponding directions and V is the volume in which the heat is generated

Boundary conditions (Fu et al. 2004)

Perfect Electrical Conductor (PEC) boundary condition (n x E = 0) was used for the walls of the cavity and Perfect Magnetic Conductor (PMC) boundary condition (n x H = 0) was used for the symmetry boundaries.

Boundary conditions at the port were taken as follows

Hy = A cos(Πx/α) cos(ωt + βy)   (3)
Ez = (ω μ0 α/ Π) A sin(Π x/α) sin(ωt + βy)   (4)
Hx = (β α/ Π) A sin(Πx/α) sin(ωt + βy)   (5)

Where the x,y and z indicate the corresponding axes and A is the cross sectional area of the waveguide, ω is the phase angle and α & β are arbitrary constants.

Heat transfer

For an incompressible food material heated under constant pressure, the thermal energy equation is given by equation (6) (Zhou et al., 1995)

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

(6)

Where ρ is the density (Kg.m-3), C_p is the specific heat (kJ.kg-1.K-1) and K is the thermal conductivity of the material and T is the absolute temperature in Kelvin.

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.

RESULTS AND DISCUSSION

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 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, Ondrej., 2009, Di Blasi et. al, 2001, Wang et al. 2009)

The weight loss curves are determined taking into account the loss in the weight of the solid residue. It has been observed by researchers, according to these curves, that hemicelluloses decompose at 498–598K, cellulose at 598–648K, whereas lignin decomposes gradually over the temperature range of 523–773K. Considerable degradation rates are concurrently attained by all the components when the temperatures are sufficiently high. (Di Blasi, 2008)

The increase of the biochar yields is based on the minimization of the losses of carbon 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 (<400 °C), high process pressure, long vapour residence time, extended vapour/solid contact, low heating rate, large biomass particle size, optimised heat integration (Masek, Ondrej., 2009).

Another important parameter is the residence time of solids. In case of fast pyrolysis, at low temperatures, it is longer than the residence time of volatiles; particles may be expiated before complete conversion. In such cases, char yields are often higher than the other products. (Di Blasi et. al, 2001)

This simulation study was carried out at a range of temperatures 573K to 773K at 2.45 GHz microwave frequency with power densities of 5 W/g, 7.5 W/g and 10 W/g at time intervals of 3 mins starting from 3 to 15 min. The initial concentration of the wood or biomass sample was taken to be 4000 mol/m³.
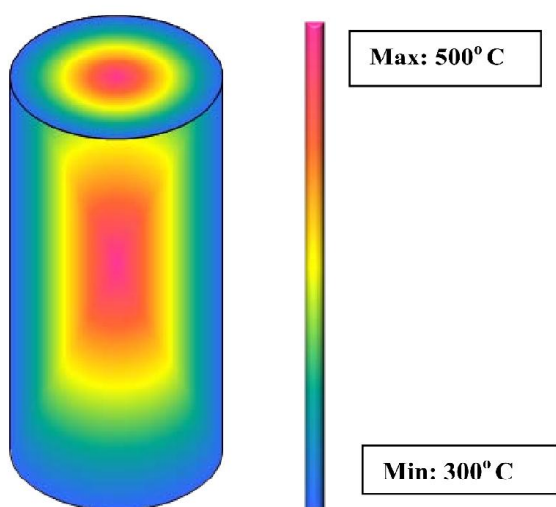
Figure 3: Simulation of Microwave heating of biomass sample with temperature variation profile

Given the kinetic parameters discussed previously, the resulting numerical model for the pyrolysis of the lignocellulosic biomass, at a temperature of 573K, showed minimal amount of products formed in the reaction as shown in Figure 4(a). The wood sample did not show any significant variation from its initial concentration during the pyrolysis process.

When the temperature was raised to 623K, the model showed a visible change in concentration of the biomass, thereby implying the incidence of the pyrolysis reaction. In figure 4(b), it was seen that the wood sample underwent a decrease in concentration till about 0.6 mins of the reaction period and then remained constant. Product formation was observed in this model when compared to the one taking place at 573K. All three phases of products were formed at this temperature although char and syngas formation went only till 0.6 mins while concentration of tar increased till the wood sample completely reacted.

At a higher temperature of 673K, the concentration vs time curve showed an exponential decrease in the concentration of the wood biomass. In turn, the concentrations of tar and char were significant compared to the previous profiles of the model. The concentration of biochar went up to about 1400 mol/mg in a matter of 0.5 mins as seen in figure 4(c) and remained constant with further increase in reaction time. The production of syngases in this reaction remained at bare minimum throughout the pyrolysis of the biomass.

When this model and its kinetics were applied to a temperature of 698K, it was seen as in figure 4(d), that the wood sample got converted to its products in less than 0.5 mins and the highest amount of tar and char formation was observed at this temperature. The yield of biochar was a little more than 1500 mol/mg in the reaction showing about 40% conversion of the biomass, which is a significant degree of conversion of the biomass into char.

An interesting trend was noticed at the temperature of 723K in figure 4(e), though the concentration of tar continued to increase with respect to time, the concentration of char was reduced from that at 698K. In addition to this phenomenon, the complete pyrolysis of the biomass occurred faster (less than 0.2 min) than at the previous temperatures observed in this model.

Finally at an observed temperature of 773K, the complete conversion of the biomass through pyrolysis took place at almost negligible rate of reaction. The char yield at this temperature was less than at 698K while approximately 70% of the biomass was seen to get converted into the liquid product called tar. (Figure 4(f))

This model also considered the effect of different power densities on the process of pyrolysis of the biomass at different ranges of time. At power density of 5W/g, no reaction was observed for 3 mins. The desired temperature of 698K was reached in 6 mins of the reaction and at 9 mins, the entire biomass had converted into the pyrolyzed products. The change in temperature or δT for this time period was observed to be about <50K.

According to the observations made through this model, the temperature of 698K was achieved in 4 mins into the reaction for the power density of 7.5W/g. The entire wood sample was pyrolyzed in 6 mins in this case and δT for this reaction to take place was around 80K.

At the power density of 10W/g, it took the biomass only about 2 mins to reach its desired temperature of 698K and in a further 1 min period, the whole biomass was pyrolyzed to the different products. This rate of reaction was much faster, occurring at a δT of 120K.

CONCLUSION

Simulation results from this study indicated 698K 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. It also showed that the rate of reaction would vary at this temperature for different power densities applied to the microwave set up.

Power density of 5W/g showed negligible reactions in 3 mins and the entire pyrolysis of the biomass sample took place in 9 mins after the desired temperature was reached in 6 mins of the reaction time. A similar trend was observed for 7.5W/g, wherein, 698K temperature was reached in 4 mins of the reaction, and the sample was pyrolysed in 6 mins completely. Though the optimum temperature was attained in less than 2 mins for power density of 10W/g, it was a very unstable reaction with temperature variation of 120K to reach the final products.

This research illustrated the potential for using microwave assisted technology for the higher yield of biochar through pyrolysis of a given biomass. 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 power densities of the reaction is highlighted. This numerical simulation model could be used to further look into designing a microwave assisted bioreactor which aims at higher yields of biochar.

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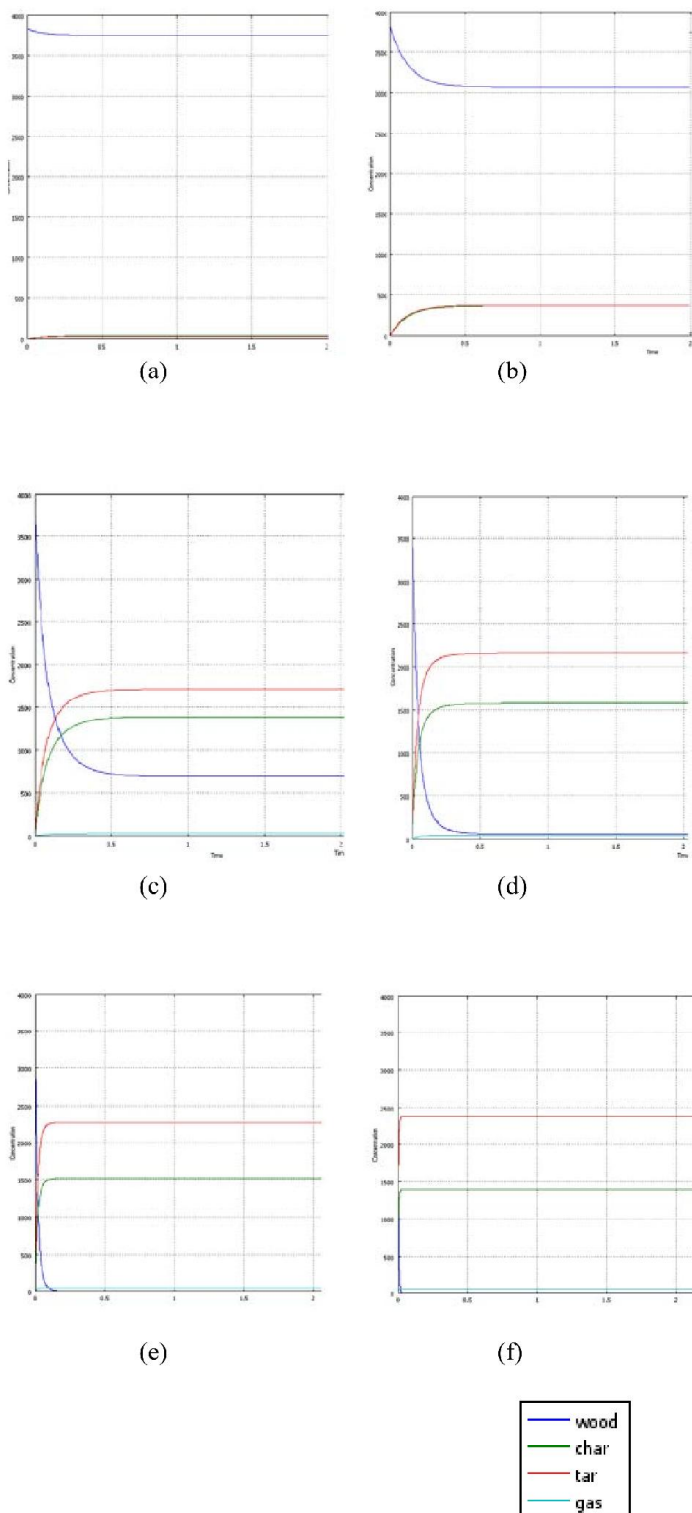
Figure4:
Concentration (mol/mg) vs Time (min) profiles of the different simulation models at temperature range of 573K-773K.
(a) 573K (b) 623K
(c) 673K (d) 698K
(e) 723K and (f) 773K

2 Topics

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