Asian Journal of
Scientific Research

Advances in Modeling and Simulation of Biomass Pyrolysis

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Abstract: The various aspects of modeling and simulation work carried out so far in biomass pyrolysis since 1946 have been extensively reviewed in the present study. Biomass pyrolysis, one of the few non conventional energy routes, is highly promising and capable of handling the current energy crisis successfully for the present and in the near future. Pyrolysis as a stand alone or as the core of biomass gasification process is complex in nature, the understanding and knowledge of this multifaceted phenomenon can heavily influence the efficiency and effectiveness of the whole gasification process. Even though, the modeling of biomass pyrolysis process was initiated during 1940's gradual changes, improvements and alternates have been carried out throughout these years. All these years, various modeling approaches were adopted, different kinetic schemes were proposed, diverse numerical schemes were followed and range of parameters were implemented, all these have developed a baffling picture over the subject. The complexity of the process, as such the large number of components involved in the intermediates and end products; the dependency of the process over numerous parameters namely the temperature, space and time dependent physical, thermodynamic and transport properties, the particle shape, size, shrinkage factors and moisture content all these justify even today the necessity and requirement of research for further improvement and enrichment in the modeling and simulation fronts of this process. This study sums up the work carried out in literature on modeling and simulation of wood pyrolysis and suggests new research directions and approaches necessarily to be made up in future.

Key words: Biomass pyrolysis, pyrolysis modeling, wood pyrolysis, pyrolysis review, kinetic model, single particle model, pyrolysis bed model

INTRODUCTION

Pyrolysis is the process where, thermal destruction of organics in the absence of oxygen happens. The destructed portion comprise of high energy content and numerous organics content, which leads to the possibility of extraction of energy and chemicals from biomass. Pyrolysis of biomass generates three different products in different quantities: coke, oils and gases.

Primary decomposition of biomass material ($<400°C$) consists of a degradation process, whereas the secondary thermolysis ($>400°C$) involves an aromatization process (Yaman, 2004). The char fraction contains inorganic materials. The pyrolysis liquids are complex mixtures of oxygenated aliphatic and aromatic compounds (Meier and Fiax, 1999). For highly cellulosic biomass feedstocks, the liquid fraction usually contains acids, alcohols, aldehydes, ketones, esters, heterocyclic derivatives and phenolic compounds. At temperatures above $500°C$ the primary tar will crack into low molecular gases. A high gas production can be achieved at high temperatures ($700-900°C$), containing CO_2, CO, CH_4, H_2, C_2H_6, C_2H_4, minor amounts of higher organics and water vapor (Klass, 1998).

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Table 1: Pyrolysis technology variant

Process	Residence time	Heating rate	Temperature (°C)	Products
Carbonation	Days	Very low	400	Charcoal
Conventional	5-30 min	Low	600	Oil, gas, char
Fast	0.5-5 sec	Very high	650	Bio-oil
Flash-liquid	<1 sec	High	<650	Bio-oil
Flash-gas	<1 sec	High	<650	Chemicals, gas
Ultra	<0.5	Very high	1000	Chemicals, gas
Vacuum	2-30 sec	Medium	400	Bio-oil
Hydro-pyrolysis	<10 sec	High	<500	Bio-oil
Methano-pyrolysis	<10 sec	High	>700	Chemicals

The various pyrolysis processes are classified on heating rates and residence times as in Table 1.

The current pyrolysis reactors are fixed beds, augers, ablative processes, rotating cones, fluidized beds and circulating fluidized beds. Apart from fixed beds, the other three from the first have scale-up problems and no large scale commercial implementations found.

In fluidized bed, the challenges lie in scaling up the endothermic pyrolysis reactor, particularly concerning heat transfer and in improving the quality and consistency of the bio-oil. Circulating fluidized bed can be easily scaled up, but, it is rather complex and the products are much diluted, which greatly complicates the recovery of the liquid products.

MODELING

Mathematical modeling, simulation and optimization are the best possible tools for analyzing and developing any complex process. Numerous pyrolysis modeling works have been carried out since, 1946 (Bamford *et al.*, 1946); most of them deal pyrolysis of woody biomass. Pyrolysis modeling can also give greater inputs to biomass gasification, as gasification involves the chemical and physical phenomena constituting pyrolysis, combustion, reduction and drying. Economic and efficient pyrolysis reactors, gasifiers and process schemes can be developed only through better understanding of the phenomena.

Kinetic Modeling

Biomass pyrolysis involves numerous extremely complex reactions with large number of intermediates and end products. Since devising an exact reaction mechanism for biomass pyrolysis is extremely difficult, pyrolysis models are modeled on the basis of visible kinetics.

One Step Global Models

One step global models consider pyrolysis as a single step first order reaction. These one-step models decompose the organic fuel into volatiles and coke with a fixed char yield.
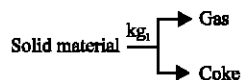
Kung (1972), Lee *et al.* (1976), Kansa *et al.* (1976), Fan *et al.* (1977), Miyanami *et al.* (1977) and Peters and Brueh (2003) are the few, who used one-step reaction mechanism.
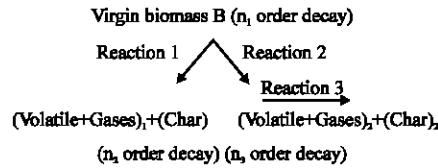
Competing and Parallel Reaction Models
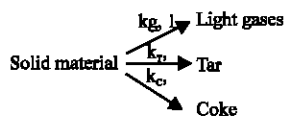
The competing reaction model of Thurner and Man (1981) is the most classical model of wood pyrolysis. It comprises of primary and secondary reactions lumped over a narrow temperature range by means of three competitive reactions and features a varying char yield.

Models with Secondary Tar Cracking

The Broido-Shafizadeh scheme of cellulose pyrolysis (Bradbury *et al.*, 1979) involving the formation of an active solid with a reduced degree of polymerization and two competing reaction pathways is one of the frequently used schemes. Based on this, Koufopanos *et al.* (1991) developed a simple model which can predict the final char yield in different heating conditions. The mechanism includes the secondary reactions between charcoal and volatile pyrolysis products described by first order kinetics

Virgin biomass B (n_1 order decay)

Reaction 1   Reaction 2

Reaction 3

(Volatile+Gases),+(Char)   (Volatile+Gases),+(Char),

(n_2 order decay) (n_3 order decay)

Later, Srivastava *et al.* (1996) extended the Koufopanos mechanism and this was used in many of the latest modeling works (Jalan and Srivastava, 1999; Babu and Chaurasia, 2002a, 2004c; Chaurasia Kulkarni, 2007).

The first two categories of models (one step global models, competing and parallel reaction models) are weak when compared to the third class (secondary tar cracking models), as they assume a constant ratio of the char to volatiles yield. The first two are simple correlation models that cannot be extended to systems different from the one on which they were based. Models with secondary tar cracking are more flexible since they include the description of the primary degradation of the solid and the secondary degradation of primary pyrolysis products and thus can be profitably applied to simulate thermal conversion.

Heat Transfer Models

Recent literature reviews on pyrolysis of biomass can be found in Di Blasi (1993) and Moghtaderi (2006). Moghtaderi (2006) in his study broadly categorized the previous pyrolysis models of solid fuel into thermal and comprehensive models. Thermal models predict the conversion of solid fuel into products or charring rate based on a integrated critical pyrolysis criterion and the energy balance, The comprehensive models describe the degradation of the fuel by chemical kinetic scheme coupled with physical conservation equations for heat and or mass transfer.

The present study, divides pyrolysis models into Single particle models and Particles in bed models. Further, Single particle models are grouped under one dimensional heat conduction models, 2D and 3D models, wet wood models and models with shrinkage factor.

Single Particle Models

As in Fig. 1, when wood is heated it undergoes chemical reactions in which volatile gases are evolved and escape the wood, leaving a porous char behind.

One Dimensional Heat Conduction

The fundamental one-dimensional heat transfer model for wood pyrolysis was first developed by Bamford *et al.* (1946). Many of the pyrolysis models available today are extensions of the one originally formulated by them, who studied the weight loss of wooden slabs, which were exposed to
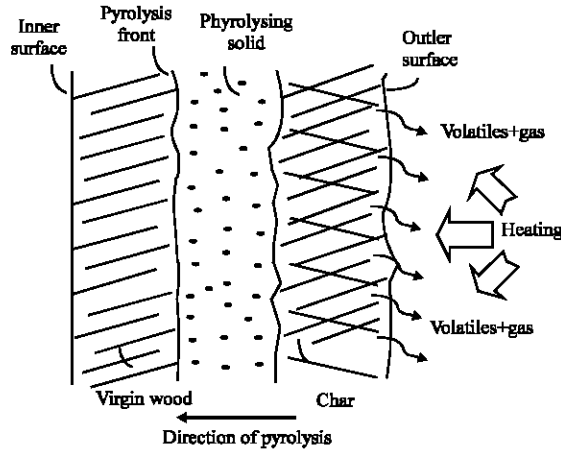
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Fig. 1: Pyrolysis of wood

flame heating. The model consists of a conservation equation for mass and heat inside the decomposing solid, assumes single step reaction and first order kinetics. The equations are:

$$\frac{\partial}{\partial t}(\rho c_p T) = \frac{\partial}{\partial x}\left(K\frac{\partial T}{\partial x}\right) - \frac{\partial}{\partial x}(\rho_g V_g c_g T) - Q_p \frac{\partial \rho}{\partial t} \tag{1}$$

$$\frac{\partial \rho}{\partial t} = -\rho_a A \exp(-E/R_g T) \tag{2}$$

$$\frac{\partial \rho}{\partial t} = \frac{\partial(\rho_g V_g)}{\partial x} \tag{3}$$

The LHS of the Eq. 1 represents the time rate of change of energy content of the wood sample. The RHS contains: the Fourier's law of heat conduction, the heat carried out by the pyrolysing solid by the volatile gases and the energy absorbed or released per unit time.

Equation 2 is the Arrhenius type rate law, where, $\tilde{n}_a$ is the density of the solid which gasifies. Equation 3 is the continuity equation expressing the rate of change of density, in terms of the flow of mass out of the pyrolysing solid. The boundary conditions are:

$$t>0, x = 0, K(\partial T/\partial x) = -Q_p \tag{4}$$

$$t>0, x = s, (\partial T/\partial x) = 0 \tag{5}$$

Bamford Inherited Models

The Bamford's model was used by several researchers (Roberts and Claugh, 1963; Tinney, 1965; Weatherford and Sheppard, 1965; Matsumota *et al.*, 1969). Tinney (1965) has implemented two consecutive reactions scheme in the model and Matsumota *et al.* (1969) have incorporated temperature dependent thermal conductivity and char removal by oxidation.

The assumptions generally retained in many of these models are: (1) local thermal equilibrium between the solid matrix and the flowing gases; (2) no particle shrinkage and surface regression; (3) no condensation of tar through the virgin solid region; (4) negligible kinetic and potential energy and

replacement of internal energy with enthalpy; (5) negligible enthalpy flux due to species diffusion; (6) negligible body forces.

The effects of internal heat convection and variable transport properties were incorporated by Kung (1972). The effect of endothermicity of the decomposition process was considered along with, variable density, specific heat and thermal conductivity. However, inward moisture migration and the possibility of secondary reactions are ignored.

The motion of pyrolysis gases interior to the solid was accounted by incorporating momentum equation (Darcy's law) by Kansa *et al*. (1977). In this manner nonzero pressure gradients in the solid and non uniform convective gas velocities were accounted for.

Pyle and Zaror Models

In one of the many important modeling works in pyrolysis, Pyle and Zaror (1984) have used the model of Bamford and few dimensionless groups to define simplified models. As external and internal heat transfer and intrinsic (first order) pyrolysis kinetics determined from Biot number (hR/K), two pyrolysis numbers (Py, Py') were defined based on the values of Biot number (Bi).

$$P_y = \left(K / k\rho c_p R^2 \right) \tag{6}$$

$$P_y' = \left(h / k\rho c_p R \right) \tag{7}$$

As given in Table 2, the regions of the validity of the various simplified models are defined by the values of the Biot number and the appropriate pyrolysis number.

Model I-Generalized Model

This is Bamford's model, the volatiles leave the solid matrix as soon as they are formed. The enthalpy (q) includes the effect of all phase changes and chemical reactions.

$$\frac{\partial}{\partial t}(c_p \rho T) = K \left(\frac{\partial^2 T}{\partial r^2} + \frac{b-1}{r} \frac{\partial T}{\partial r} \right) + (-q) \left(-\frac{\partial \rho}{\partial t} \right) \tag{8}$$

Assuming First Order Kinetics

$$-\frac{\partial \rho}{\partial t} = A \exp\left(-\frac{E}{R_g T} \right)(\rho - \rho_\infty) \tag{9}$$

where, ρ_∞ is the density of the final char product. The boundary conditions are:

Table 2: Pyle and Zaror (1984) pyrolysis models

Model	Controlling factor	Rang		
		Bi	Py	Py'
I	--	All values		
II	External heat transfer	Small		Small
III	Kinetics	Small		Large
IV	Internal heat transfer	Large	Small	

$$\left. \frac{\partial T}{\partial r} \right|_{r=0} = 0, \text{ all } t; K \left. \frac{\partial T}{\partial r} \right|_{r=R} = h_c(T_f - T) + \varepsilon\sigma(T_f^4 - T^4), \ t > 0 \tag{10}$$

Model II-Uniform Internal Conditions (External Heat Transfer Control)

$$c_p\rho\frac{dT}{dt} = \frac{b}{r}\left\{ h_c(T_f - T) + \sigma\varepsilon(T_f^4 - T^4) + (-q)\left(-\frac{d\rho}{dt} \right) \right\} \tag{11}$$

and the reaction kinetics will be given by

$$\frac{\rho - \rho_\infty}{\rho_0 - \rho_\infty} = \exp\left\{ -\int_0^t A\exp\left(-\frac{E}{R_g T} \right)dt \right\} \tag{12}$$

Model III -Kinetic Control: (Reaction Take Place Isothermally at T = T_f)

$$\frac{\rho - \rho_\infty}{\rho_0 - \rho_\infty} = \exp\left\{ At\exp\left(-\frac{E}{R_g T_f} \right) \right\} \tag{13}$$

Model IV-Internal Heat Transfer Control (Shrinking Core)

Considering, r_c is the radius of the unreacted shrinking core and R is a characteristic dimension of the solid (half thickness for slab, radius for cylinder and sphere) and b is the geometric factor, when pyrolysis is assumed complete at $T = T_p$, then the progress of the reaction front is:

$$\frac{\rho_0 - \rho}{\rho_0 - \rho_\infty} = 1 - \frac{r_c^b}{R^b} \tag{14}$$

Koufopanos *et al.* (1991) have coupled conduction heat transfer with chemical kinetics, used a newly developed kinetic model involving secondary reactions and represented the reactions heat by endothermic or exothermic values according to the conversion rate. The final yield of gaseous and volatile products is not predicted by the kinetic model. The effect of the change in density as a function of time is not considered as in Pyle and Zaror (1984).

In the model of Liliedahl (1998) the thermal conductivity and the specific heat capacity of biomass are assumed to be constant. Similarly, Jalan and Srivastova (1999) have solved the heat transfer equation by neglecting the effect of specific heat and thermal conductivity of char, which are the functions of temperature as reported by Koufopanos *et al.* (1991).

Babu and Chaurasia Models

As discussed above, several of the above models do not include; secondary reactions, thermal conductivity and specific heat capacity of biomass as a function of temperature and convective heat transfer coefficient as a function of Reynolds number and Prandtl number. Further, the kinetic models of Pyle and Zaror (1984) and Koufopanos *et al.* (1991) does not permit the prediction of the concentration and the final yield of gaseous and volatile products.

Keeping these drawbacks in view, Babu and Chaurasia (2004c) have developed improved models for pyrolysis from the earlier models (Bamford, 1946; Koufopanos *et al.*, 1991; Jalan, 1999), used extended Koufopanos kinetic model (Babu and Chaurasia, 2002a) where, the final char yield can be

predicted. The heat transfer equation utilized the boundary conditions developed by Pyle and Zaror (1984) and Koufopanos *et al.* (1991). Introduced a convective heat transfer coefficient and showed its effect on the Reynolds and Prandtl numbers. Properties such as the porosity and permeability are also incorporated, in addition, the Darcy's law and the ideal gas law are also considered to be valid.

The effect of particle size, orders of reaction, thermal and thermodynamic properties, heat of reaction, reactor temperature, etc., have been discussed earlier by Babu and Chaurasia (2002a,b, 2003b, c). The models are:

- Generalized reference model (model I)
- Simplified models (models II and III)

The generalized model incorporates all the possible effects of kinetics, heat transfer, mass transfer and momentum transfer. Few of the assumptions are: The thermal and transport properties vary with the conversion level; Heat transfer occurs by all three modes; Pressure and velocity vary along the sample pores, no moisture content and shrinkage.

The generalized model (Model I) is reported in Table 3 (Eq. 15-27). The first simplified model (Model II) is proposed by assuming convective transport is neglected. In this treatment, the

Table 3: Babu and Chaurasia model

Conservation of biomass, (gases and volatiles)1, (char)1, (gases and volatiles)2 and (char)2

$$\frac{\partial C_B}{\partial t} = -(k_1 + k_2)C_B^{n_1} \tag{15}$$

$$\frac{\partial(C_{G_1}\varepsilon'')}{\partial t} + \frac{\partial(C_{G_1}u)}{\partial r} = D_{eG_1}\left(\frac{b-1}{r}\frac{\partial C_{G_1}}{\partial r} + \frac{\partial^2 C_{G_1}}{\partial r^2}\right) + k_1 C_B^{n_1} - \varepsilon''k_3 C_{G_1}^{n_2} C_{C_1}^{n_3} \tag{16}$$

$$\frac{\partial C_{C1}}{\partial t} = k_2 C_B^{n_1} - k_3 C_{G1}^{n_2} C_{C1}^{n_3} \tag{17}$$

$$\frac{\partial C_{G2}}{\partial t} = k_3 C_{G1}^{n_2} C_{C1}^{n_3} \tag{18}$$

$$\frac{\partial C_{C2}}{\partial t} = k_3 C_{G1}^{n_2} C_{C1}^{n_3} \tag{19}$$

Enthalpy

$$\frac{\partial}{\partial t}(c_p\rho T) = K\left(\frac{b-1}{r}\frac{\partial T}{\partial r} + \frac{\partial^2 T}{\partial r^2}\right) - \left(D_{eG_1}\frac{\partial C_{G_1}}{\partial r}\right)c_{pG_1}\frac{\partial T}{\partial r} + (-\Delta H)\left(\frac{-\partial \rho}{\partial t}\right) \tag{20}$$

Initial conditions

t = 0, CB = CB0, CG1 = CC1 = CG2 = CC2 = 0, T(r, 0) = T0 (21)

Particle boundary conditions

$$t>0; r = 0, \frac{\partial C_{G_1}}{\partial r} = 0 \left(\frac{\partial T}{\partial r}\right)_{r=0} = 0 \tag{22}$$

$$t>0, r = R, D_{eG_1}\left(\frac{\partial C_{G_1}}{\partial r}\right) = k_{mG_1}\left(C_{G_{1}0} - C_{G_1}\right), -K\left(\frac{\partial T}{\partial r}\right) = h_c(T_f - T) + \sigma\varepsilon(T_f^4 - T^4) \tag{23}$$

Dimensionless forms of Eq. (16)-(23) are skipped

Koufopanos *et al.* (1991) correlation : hc = 0.322(k/l)Pr$^{1/3}$ Re$^{0.5}$ (24)

Darcy law and state equation

$$u = -\frac{\phi}{\mu}\frac{\partial p}{\partial x}, p = C_{G_1}R_gT/W_m \tag{25}$$

Other relations

$$\varepsilon'' = \varepsilon_0'' + \gamma(1 - C_B), \phi = \eta\phi_B + (1 - \eta)\phi_{C_1}, \eta = C_B/C_{B0} \tag{26}$$

Conversion of biomass

$$X = \frac{C_{B0} - \left[\left(\sum_{i-1}^{M}C_B\right)/(M+1)\right]}{C_{B0}} \tag{27}$$

conservation equation for the mass concentration of (gases and volatiles)$_1$ (Eq. 16) is modified by neglecting the second term on the left hand side. In effect, the first simplified model (Model II) consists of Eq. 15-24 and 26.

The second simplified model (Model III) neglects the convection and radiation parts in the heat transport of gases within the particle and the effect of the porosity of the solid. Therefore, the mass concentration of (gases and volatiles)$_1$ Eq. 16 and heat transfer model Eq. 20, respectively, become:

$$\frac{\partial C_{G1}}{\partial t} = k_1 C_B^{n1} - k_3 C_{G1}^{n2} C_{C1}^{n3} \tag{28}$$

$$\frac{\partial}{\partial t}(c_p \rho T) = K \left(\frac{b-1}{r} \frac{\partial T}{\partial r} + \frac{\partial^2 T}{\partial r^2} \right) + (-\Delta H) \left(\frac{-\partial \rho}{\partial t} \right) \tag{29}$$

The second simplified model (Model III) consists of Eq. 15, 17, 19, 21, 22, 23, 24, 28 and 29. This model was in excellent agreement with the experimental data (Pyle and Zaror, 1984) as compared to the other developed models (Models I and II).

Volume Reaction Models

Deviating from the fundamental Bamford's concept, Fan *et al.* (1977) proposed a volume reaction model which takes into account simultaneous heat and mass transfer effects in the particle. Assumed first order reaction, the products concentration cannot be analyzed as the secondary reactions are not considered. The reaction was visualized as:

- Conduction and convection of heat from the main body of fluid and radiation from the wall of the vessel to the surface of the particle
- Conduction and convection of heat through the particle
- Thermal degradation of the convertible solid
- Diffusion of the fluid product through pores to the exterior surface of the particle
- Convection and diffusion of the fluid product through fluid film into the main fluid

The general material and heat balances for the solid reactant and fluid product were derived:

$$\frac{\partial C_s}{\partial t} = -\tilde{\gamma}_s \tag{30}$$

$$\frac{\partial(C_A \varepsilon^r)}{\partial t} = \frac{1}{\gamma^{b-1}} \frac{\partial}{\partial \gamma} \left(D_{eG1} \gamma^{b-1} \frac{\partial C_A}{\partial \gamma} \right) + a\tilde{\gamma}_s \tag{31}$$

$$\rho c_p \frac{\partial T}{\partial t} = \frac{1}{\gamma^{b-1}} \frac{\partial}{\partial \gamma} \left(K \gamma^{b-1} \frac{\partial T}{\partial \gamma} \right) + \left(D_{eG1} \frac{\partial C_A}{\partial \gamma} \right) c_g \frac{\partial T}{\partial \gamma} + (-\Delta H)\tilde{\gamma}_s \tag{32}$$

The first term in the right hand side of Eq. 31 represents mass flux. The driving force in the form of grad C_A is identical to that in the Fick's diffusion. The effective diffusivity, D_{eA}, is defined as the overall effect due to the molecular diffusion, eddy diffusion and convective flow. The first term in the right hand side of the Eq. 32 represents the sensible heat transport due to the apparent or effective heat conduction, while the second term stands for the sensible heat transport due to the apparent or effective mass diffusion.

The initial conditions for Eq. 30, 31 and 32 are respectively,

$$T = 0; C_s = C_{s0}, C_A = 0, T = T_0 \tag{33}$$

the boundary conditions for the Eq. 31 and 32 are:

$$r = 0; \frac{\partial C_A}{\partial r} = 0, \frac{\partial T}{\partial r} = 0 \tag{34}$$

$$r = R; D_{eG1}\left(\frac{\partial C_A}{\partial r}\right) = k_{mG1}(C_{A0} - C_A) \tag{35}$$

$$-K\frac{\partial T}{\partial r} = h_c(T - T_s) + h_r(T^4 - T_w^4) \tag{36}$$

Fan, incorporated the effect of the Lewis Number in the above model. Later, the effects of the heat of reaction on the reaction rates have been incorporated by Miyanami *et al.* (1977) in the volume reaction model.

Models Based on Shrinking Core Mechanism

Simplified models of wood pyrolysis are based on the Maa and Bailie developed unreacted shrinking core approximation (Maa and Bailie, 1973; Moghtaderi *et al.*, 1997; Spearpoint and Quintiere, 2001). Maa also accounted temperature dependent property variations and internal convection between solid wood and volatiles.

This model differed from earlier models in the manner in which chemical kinetics is combined with heat transfer. The reaction takes place at an unreacted shrinking core of non-pyrolysed solid which is surrounded by a layer of material that has been pyrolysed. The reaction takes place at the interface between the two solid regions. The thermal energy propagates through the char layer by conduction. The energy that passes to the unreacted core depends upon the temperature gradient and the radius of the unreacted core. This energy initiates pyrolysis. The pyrolysis gases so formed move radially outward.

The solution is highly simplified by the application of integral methods to the heat-transfer problem, owing to change from partial to ordinary differential equations (Galgano, 2003). Maa and Bailie however have assumed a steady-state mass transfer and steady state temperature profile to simplify the scheme for simulation and have neglected the concentration and temperature dependence of various physical parameters.

Taking account of unsteadiness and spatial temperature gradients for virgin and the charred solid, finite-rate kinetics and convective transport Galgano (2003) proposed a shrinking core model and later extended this to include the drying and propagation fronts in wet wood (Galgano and Blasi, 2004). For dry wood zone, the mass conservation of solid is:

$$\frac{dR}{dt} = -A\exp\left(\frac{-E}{R_g T_p}\right), R(0) = R0 \tag{37}$$

The enthalpy conservation for dry wood is obtained from the below equation where, $m_u = 0$.

$$\rho c_p \frac{\partial T}{\partial t} = -\alpha\frac{m_u c_u}{2\pi r L}\frac{\partial T}{\partial r} + \frac{1}{r}\frac{\partial}{\partial r}\left[K_W r\frac{\partial T}{\partial r}\right] \tag{38}$$

The associated boundary conditions are:

$$S_p q_c = S_p q_w + m_p \Delta H (r = R) \tag{39}$$

$$K_w \frac{\partial T}{\partial r}\Big|_{r=0} = 0 \tag{40}$$

where, S_p is the reaction surface area, R is the particle radius, r is the reaction front radius:

$$q_c = K_c \frac{\partial T}{\partial r}\Big|_{R^+}, q_w = K_w \frac{\partial T}{\partial r}\Big|_{R^-} \tag{41}$$

Liliedahl and Sjostrom (1998) have defined a pyrolysis propagation front velocity similar to shrinking core model. The notion of pyrolysis diffusivity is introduced and is assumed to eqnal thermal diffusivity. For small particles the suggested model will equal the simplified Model II of Pyle (1984). Here, the final char yield and reactivity are not predicted.

Other Models

Miller and Bellan (1997) have modeled both micro-particle (kinetically controlled) and macro-particle (diffusion limited) pyrolysis of arbitrary biomass feed stocks; the model incorporates a fully transient momentum equation in contrast to the traditional use of the empirical Darcy's law. Larfeldt *et al.* (2000) have modified the mono-dimensional model of Melaaen (1996) thus accounted the structural changes during pyrolysis of the wood. Janse *et al.* (2000) have developed a model based also on the early work of Bliek *et al.* (1985) for coal pyrolysis. The particle assumed to contain macro (pore diameter > 100 A°) and micro pores (< 100 A°). The flow of vapors is described using the Dusty gas model (Bliek *et al.*, 1985) and structure of wood is incorporated by random pore model (Wakao and Smith, 1962).

2D and 3D Models

The models above discussed are based on one dimensional heat and flow conditions. However, wood is an anisotropic material with different properties (thermal conductivity, permeability) vary along, across and tangential to the grain. Multi dimensional models can give an adequate description of the anisotropic structure of lignocellulosic materials (Di Blasi, 1998) which may lead to accurate predictions when compared to mono-dimensional approach, this point has also been supported by Bounefoy *et al.* (1993). However, Bounefoy (1993) neither considered the moisture content and the anisotropic nature of wood, nor the convective heat transfer as a result of the internal flows of volatile gases.

Freudlund (1993) and Di Blasi (1998) have proposed 2-D models with the consideration of pressure driven internal convection of gases in the pyrolysing wood. The former model considered moisture evaporation in wet wood pyrolysis, while the latter considered dry wood pyrolysis with the primary and secondary reaction schemes.

Di Blasi (1998) model accounted all three modes of heat transport, diffusion and convection of volatile species and pressure and velocity variations. The unsteady 2D model includes equations for virgin solid, active intermediate solid, solid char, total gas phase continuity, enthalpy and momentum (multi dimensional Darcy law) and a linear variation of the solid-phase volume with the conversion level. Enthalpy and momentum are given by:

$$(\rho_c c_c + \rho c_p + \rho_a c_a + \in \rho_g c_g) \frac{\partial T}{\partial t} + \rho_g c_g u_x \frac{\partial T}{\partial x}$$
$$+ \rho_g c_g v_y \frac{\partial T}{\partial y} = \frac{\partial}{\partial x}\left(K_x \frac{\partial T}{\partial x}\right) + \frac{\partial}{\partial y}\left(K_y \frac{\partial T}{\partial y}\right) + q_r \qquad (42)$$

$$u_x = -\frac{B_x}{\mu}\frac{\partial p}{\partial x} \qquad (43)$$

$$v_y = -\frac{B_y}{\mu}\left(\frac{\partial p}{\partial y} + \rho_g\right) \qquad (44)$$

A comparison between the 2D and 1D simulation has shown the multi-dimensional structure of the reaction front affects not only the details of sample conversion dynamics, but also global parameters, such as conversion time and product distribution (Di Blasi, 1998).

Yuen *et al*. (2007a) have presented a 3-D mathematical model for the pyrolysis of wet wood which includes detailed considerations of the evaporation of moisture, anisotropic and variable properties and pressure driven internal convection of gases in wood. The energy conservation equation is expressed in a non-orthogonal curvilinear coordinate system.

Wet Wood Models

Moisture content is an important factor influencing material behaviour; Temperature profiles and pyrolysis rates are modified by moisture content (Bilbao *et al*., 1996). Free water, bound water and constitution water can be found inside the solid each of these requires different temperature and energy for evaporation. Currently, there are four basic ways to model drying of wood (Bryden *et al*., 2002).

The simplest of these is an energy balance in which the drying front is assumed to be infinitely thin and an energy sink at 100°C accounts for the heat of vaporization (Saastamoinen and Richard, 1996), this method cannot be used to model small particles.

A second method (Chan *et al*., 1985) models drying as an additional reaction using Arrhenius expression with different fitting parameters. The disadvantages are: lumped parameters, one-way coupling of drying rate and pressure evolution.

The third method (Alves and Figueiredo, 1989; Bilbao *et al*., 1996) is a non-fitting parameter model, uses an algebraic expression for temperature as a function of moisture content, valid to relatively dry materials of 14 % moisture content.

Fourth method is a diffusion model (Melaaen and Grali, 1997) where, the movement of unbound water and gas within the wood is modelled using a modified Darcy's law and bound water movement is modelled using a diffusion expression. The pressure wave is tightly coupled to drying rate. Cracking and the multi-dimensional water movement not addressed.

An integrated pyrolysis and drying model was developed by Alves (1989). Drying neglects bound water diffusion, pressure gradients inside the solid and free water movement. The enthalpy balance and boundary conditions are:

$$\frac{\partial[(\rho c_p + \rho_l X_M c_{pl})T]}{\partial t}dV = \frac{\partial}{\partial r}\left(K \frac{\partial T}{\partial r} A_p\right)dr$$
$$-\frac{\partial}{\partial r}[(M_g c_{pg} + M_v c_{pv}) A_p T]dr - \left(\sum_i H_n r_{ci} + r_{cp} H_v\right)dV \qquad (45)$$

$$\text{For } t = 0, \forall r \begin{vmatrix} \rho_i = m_i \rho_W \\ \rho_C = \rho_W - \sum_i \rho_i \\ T = T_0; M_g = 0 \\ M_v = 0; X_M = X_{M0} \end{vmatrix} \tag{46}$$

$$\text{For } r = 0, \forall t \begin{vmatrix} \dfrac{\partial T}{\partial r} = 0 \\ M_g = 0 \\ M_v = 0 \end{vmatrix} \text{For } r = R, t > 0 \begin{vmatrix} K\dfrac{\partial T}{\partial r} = h_c(T - T_f) + \sigma\varepsilon(T^4 - T_f^4) \end{vmatrix} \tag{47}$$

Depending on the particle thickness (1 Lm to 50 mm) and pyrolysis temperature (800-2000 K) four pyrolysis regimes were identified (Bryden *et al.*, 2002).

- Thermally thin-kinetically limited (Bi<0.2 and P_y'>5)
- Thermally thin-heat transfer limited (Bi<0.2 and P_y'<5)
- Thermally thick (0.2<Bi<10)
- Thermal wave (Bi>10)

Here, the most practical applications are in regimes 3 or 4.

Bilbao *et al.* (1996) have identified three zones during evaporation, i.e. completely dry solid, drying solid and solid with initial moisture. Galganoand Blasi (2004) have modeled decomposition of moist wood using shrinking un-reacted-core approximation with the assumption of a thermally controlled evaporation of moisture. This treatment could be applied with some approximation only for very thick and moist samples under high level heat fluxes.

Recently, the evaporation of water inside the wet wood has been considered as a chemical reaction (Shen *et al.*, 2007). There is no recondensation of water vapor inside the solid. The energy conservation equation for pyrolysis of wet wood is described as:

$$\frac{\partial}{\partial t}[T(\rho_w c_p + \rho_c c_c + \rho_l c_{pl})] = \frac{\partial}{\partial x}\left(K\frac{\partial T}{\partial x}\right) + Q_r^{"} \tag{48}$$

where, $Q_r^{"}$ is described as the sum of reaction heat of the three pyrolysis reactions at temperature T. The boundary conditions are at $t = 0$, $T = T_0$. When, $t>0$, $x = 0$, a heat balance for the control volume with a height of (Äx) is obtained, similar to the boundary condition for Bilbao's model (Bilbao *et al.*, 1996).

$$\frac{\partial[T(\rho_w c_p + \rho_c c_c + \rho_l c_{pl})]}{\partial t} = \left(\alpha_a q_e^{"} - q_{loss}^{"} - K\frac{\partial T}{\partial x}\right)/\Delta x + Q_r^{"} \tag{49}$$

Where:

$$q_{loss}^{"} = \sigma\varepsilon(T^4 - T_0^4) + h_c(T - T_0) \tag{50}$$

when $t>0$, $x = L$, another heat balance for control volume with a height of (Äx) is established:

$$\frac{\partial[T(\rho_w c_p + \rho_c c_c + \rho_l c_{pl})]}{\partial t} = \left[K \frac{\partial T}{\partial x} - q_b' \right] / \Delta x + Q_r'' \tag{51}$$

where, q_b^* is equal to zero as the bottom of the solid is adiabatic. The model was more precise for wet wood at low heat flux. It was suggested that the effect of gas movement inside the solid, void fraction and volume shrinkage should be taken into account.

Recently, Yuen *et al.* (2007b) have extended a previously developed 3-D model (Yuen *et al.*, 2007a) for the application of the pyrolysis of wet wood coupled with the gas phase combustion to the analysis of a wood sample ignited in a cone calorimeter.

Models with Shrinkage Factor

An important feature of wood pyrolysis is the shrinkage of the particle, which may lose up to 70% of its volume. Most of the models discussed above assumed that the total volume of the particle does not change during thermal degradation. The shrinkage differs in the longitudinal, tangential and radial direction of the wood stem (Bellais *et al.*, 2003).

The shrinking of the solid particle affects pyrolysis in several ways. The medium properties (porosity, permeability, density, mass diffusivity, specific heat capacity and thermal conductivity), the volume occupied by the volatiles (gas and tar), the volume occupied by the solid (wood and char) and consequently the total particle volume change continuously, which affect the temperature profile and product yield (Babu and Chaurasia, 2003e).

So far, shrinkage has been taken into account only in few models. Villermaux *et al.* (1986) described the shrinkage effects assuming that the solid density remains constant as degradation occurs. In the study of Di Blasi (1996) a more advanced version of the previous transport model was extended to include the shrinkage of a degrading particle with variable solid-phase densities.

The modeling considers a conservation equation for tar and the total continuity equation, an enthalpy balance, the Darcy law and the ideal gas law. The volume occupied by the solid is assumed to decrease linearly with the wood mass and increase with the char mass, by a chosen shrinkage factor, α_s:

$$\frac{V_S}{V_{W0}} = \frac{M_W}{M_{W0}} + \frac{\alpha_s M_C}{M_{W0}} \tag{52}$$

where, V_{W0} is the initial effective solid volume. The volume occupied by the volatiles should be made by two contributions, the first due to the initial volume occupied by volatiles, V_{g0} and the second by the fraction, $\hat{a}_s$, of volume left by the solid $(V_{W0}-V_S)$:

$$V_{gP} = V_{g0} + \beta_s (V_{W0} - V_S) \tag{53}$$

In order to account for possible structural changes, V_{g0} may also vary linearly with the composition of the degrading medium, from an initial value V_{gi}, determined by the initial solid porosity, to a final value taken as a fraction, $\tilde{a}$, of the initial one $(V_{gf} = \tilde{a}_s V_{gi})$: $V_{g0} = \varsigma V_{gi} + (1-\varsigma) V_{gf}$. Thus the volatile volume and the total volume are expressed, respectively, as:

$$V_{gP} = \eta V_{gi} + (1 - \eta)\gamma_s V_{gi} + \beta_s (V_{W0} - V_S) \tag{54}$$

$$V = V_{gP} + V_S = \eta V_{gi} + (1 - \eta)\gamma_s V_{gi} + \beta_s (V_{W0} - V_S) + V_S \tag{55}$$

The parameters α_s, β_s and γ_s, which vary from 0 (total disintegration of the particle) to 1 (no shrinkage), should be assigned.

Compared to earlier models, Di Blasi model successfully accounted for heat, momentum and mass transport. Internal gas flow is accounted using Darcy flow with the permeability of the medium expressed as a function of char and wood content. With internal flow and a two-step reaction scheme, Di Blasi was able to predict the products of pyrolysis.

The Di Blasi shrinkage equations are incorporated later in the non shrinking pyrolysis model of Babu and Chaurasia (2004c) which was discussed already. In both cases both primary and secondary reaction paths are affected by the shrinkage of char layer, particularly larger tar yields are predicted for shrinking particles because of the larger temperatures at the primary reaction front and the reduced volatile residence times. Later, Chaurasia and Kulkarni (2007) have studied the same model to analyze the most sensitive parameters in biomass pyrolysis of shrinking and non shrinking particles.

A detailed model of moist wood pyrolysis for non shrinking particles has been presented by Bryden *et al.* (2002), later Hagge and Bryden (2002) expanded this model to include shrinkage of the solid due to pyrolysis for dry wood particles. The derivation starts with an arbitrary differential shrinking element, within this unreacted wood, char and various gas species exist. The inertial terms within the momentum balance equation are negligible, flow can be described using Darcy flow and shrinkage occurs only across the grain.

Bellais *et al.* (2003) have modeled shrinkage in three different ways: Uniform shrinkage, shrinking shell and shrinking cylinder. In uniform shrinkage, the conversion is averaged over the whole particle; this slows down the pyrolysis rate, whereas shrinking shell and shrinking cylinder models enhance the pyrolysis rate. Shrinking shell model is more realistic than uniform shrinkage, but difficult to implement and takes more computing time. Shrinking cylinders model is most complicated to implement as the grid is neither orthogonal nor evenly spaced, so that gradient and divergence calculations are difficult.

Particles in Bed Models

The pyrolysis technologies, fixed beds, fluidized beds and circulating fluidized beds are the practical pyrolysis systems. Apart from developing the single particle models, realistic pyrolysis bed models for the said technologies will the more useful and possibly the ultimate goal of pyrolysis modeling.

Several approaches predicting the solids conversion rate in packed beds have been carried out in the past. To predict the velocity of the burning front in a packed bed, Fatehi and Kavlany (1994) developed a model based on equilibrium assumptions. Goh *et al.* (2000) developed a CFD model based on different zones for virgin, dried, pyrolysed fuel and ash, the conversion requires macro kinetic data. Saastamoinen *et al.* (2000) presented a one dimensional packed bed model, where, drying and pyrolysis are solved on a single particle with vaporization taking place on a shrinking core. Most of these models are restricted to certain part of the conversion process and require empirical information; this limits their application to specific cases.

Even though as according to Di Blasi (1998) reactions by particles in fixed and fluidized gas solid reactors are multi dimensional, comparatively an unsteady, one-dimensional method for spherical particles combines sufficient resolution of particle quantities with reasonable computation time. This is also supported by Man and Byeong (1994), who detected mainly one dimensional behavior in comparison of his results with experiment. Senf (1996) indicate that due to the application to each particle of a packed bed, the complexity of the particle model is limited. Thus, effects like fragmentation, swelling or the description of the boundary layer surrounding a particle are not included.

In the modeling of wood combustion under fixed bed conditions (Peters *et al.*, 2003) the global conversion of the packed bed is represented by the contributions of single particles. For gas phase flow

through the porous bed, the conservation equations for mass, momentum and energy are solved on a Cartesian mesh by Finite Volume method.

Here the whole process, including drying, pyrolysis, char combustion and gasification is incorporated in the authors' model. The governing equations describing the conservation of a scalar ö versus the radius of a solid particle are implemented along with the geometry factor n for an infinite plate, an infinite cylinder and a sphere for n = 0, 1, 2.

$$\frac{\partial}{\partial t}\langle\rho\rangle\langle\phi_s\rangle = \frac{1}{r^{b-1}}\frac{\partial}{\partial r}\left(\Gamma_{eff}r^{b-1}\frac{\partial}{\partial r}\langle\rho\rangle\langle\phi_s\rangle - r^{b-1}\langle\rho\rangle u_{ratio}\langle\phi_s\rangle\right) + \omega \tag{56}$$

The change of the mass fraction Y_i for the species i can be determined by the divergence of the species field and the source term due to the interaction with the solid phase and reactions in the void space of the bed as follows the source term $\dot{\omega}_m$ is the average over the outer integration step which is chosen for the flow field model.

$$\frac{\partial \rho_G Y_i}{\partial t} + \nabla(\rho_G v_G) = \dot{\omega}_m \tag{57}$$

The pressure loss is estimated by Darcy's law, based on the phase averaged velocity. As convective transport is dominant, conduction within the gas is neglected in energy equation.

$$\frac{\partial}{\partial t}(\rho_G c_p T) + \nabla(\rho_G v_G c_p T) = -\nabla p v_G + \dot{\omega}_{con} + \dot{\omega}_{ch} + \dot{\omega}_{th} \tag{58}$$

The sum of convection terms over all n particles in a cell is:

$$\dot{\omega}_{con} = \sum_{k=1}^{n}\alpha_k A_k \frac{1}{\Delta t}\int_0^{\Delta t}(T_{G,k} - T_{G,i})dt \tag{59}$$

The sensible heat with the mass of m species between n solid particles in a volume element:

$$\dot{\omega}_{th} = \sum_{k=1}^{n}\sum_{j=1}^{m}\frac{1}{\Delta t}\int(c_p \dot{m}_{j,k} T_{s,k})dt \tag{60}$$

The heat flux due to conduction between two particles is:

$$\dot{q}_{cond} = \frac{1}{1/K_1 + 1/K_2}\frac{\partial T}{\partial r} = \frac{1}{1/K_1 + 1/K_2}\frac{T_{S,1} - T_{S,2}}{\Delta r_{S,1} - \Delta r_{S,2}} \tag{61}$$

The contact area between two particles is assumed quadratic, is determined by contact angle ã

$$A_c = \frac{1}{2}((R_1 \tan\gamma_a)^2 + (R_2 \tan\gamma_a)^2) \tag{62}$$

The radiative heat loss of each particle according to the surface area weighted ratio,

$$F_{i \to j} = \frac{A_i}{\sum_{j=1}^{n} A_j} \tag{63}$$

The model showed good agreement with experimental results. Pyrolysis of wet wood particles at high heating rates requires further investigation. Also, further research is required to validate the description of the heat transfer with in the bed.

Ravi *et al.* (2004) have developed a semi-empirical model for pyrolysis of sawdust in an annular packed bed. The model assumed heat transfer to occur purely by conduction. The mass loss is assumed to change porosity of the bed and bed thermal conductivity owing to porosity. The model under predicts the values of mass loss and mass loss rates. It was suggested to consider the flow of volatiles in the void space of char bed and by accounting for secondary pyrolysis due to residence of volatiles in the bed.

SIMULATION

As analytical solution of pyrolysis heat transfer model is not possible due to the presence of source term, simulation in biomass pyrolysis has to be carried out using numerical approximation. The advantages of numerical solution are their ability to handle complex geometry and non-linearities in the governing equation and/or boundary conditions.

Finite Difference Method (FDM)

The usual procedure for deriving finite difference equations consists of approximating derivatives in the differential equation via a truncated Taylor series. The variation of the unknown to be computed is somewhat like a polynomial in x, y or z so that higher derivatives are unimportant. Straight-forwardness and simplicity are the advantages of FDM. FDM are weak for problems with high degree of physical complexity like, heat and flow calculations around arbitrarily shaped bodies, strongly time dependent flows, etc., (Ghoshdastidar, 1998).

Most of the pyrolysis models involve solution schemes based on finite differencing (Kung, 1972; Miyanami *et al.*, 1977; Fan *et al.*, 1977; Alves and Figueiredo, 1989; Koufopanos *et al.*, 1991; Bounefoy *et al.*, 1993; Srivastava *et al.*, 1996; Di Blasi, 1996,1998; Jalan and Srivastava, 1999; Janse *et al.*, 2000; Bryden *et al.*, 2002; Bellais *et al.*, 2003; Grioui *et al.*, 2007).

Finite difference method using pure implicit scheme was used by Babu and Chaurasia (2002b). The pure implicit scheme is an unconditionally stable scheme that is there is no restriction on time step, in sharp contrast with the Euler and Crank-Nicholson method (Ghoshdastidar, 1998; Babu and Chaurasia, 2003c). The Tri-Diagonal Matrix Algorithm (TDMA), also known as the Thomas algorithm (Carnahan *et al.*, 1969) was used to solve the discretised form of the heat transfer model (Kansa *et al.*, 1977; Babu and Chaurasia, 2003d, 2004e; Chaurasia and Kulkarni, 2007), the chemical kinetics equations are solved simultaneously with Runge-Kutta fourth order method with both fixed step size (RKFS) and variable step size (RKVS). It is found that the RKVS method is faster than RKFS, but the RKVS method does not give the solution for a particular or fixed time intervals.

Finite Volume Method

In this method, the calculation domain is divided into a number of non-overlapping control volumes. The differential equation is integrated over each control volume. Piecewise profiles expressing the variation of the unknown between the grid points are used to evaluate the required integrals. The major advantage of this method is its physical soundness; the disadvantage is that it is not as straightforward as FDM (Ghoshdastidar, 1998). Only few researchers have adopted finite volume technique (Mousque`s *et al.*, 2001; Peters and Bruch, 2001, 2003; Bellais *et al.*, 2003; Ravi *et al.*, 2004; Yuen *et al.*, 2007a).

Table 4: For single particle pyrolysis

Researcher	Data description
MacLean (1941)	Effective thermal conductivity of wet wood.
Lee *et al.* (1976)	Temperature as a function of particle thickness for t = 5, 10, 15 and 20 min for perpendicular and parallel wood grain heating.
Kansa *et al.* (1977) heat	Temperature and mass loss profile of a 5 cm thick slab of maple with 0.53 cal/cm^{2}sec flux.
Shafizadeh (1982)	Average char yield as a function of temperature.
Pyle and Zaror (1984)	Temperature at the centre and across the radii for cylindrical wood pellet (R = 0.003, 0.009, and 0.011 m) and conversion profile.
Alves and Figueiredo (1989)	Mass loss and conversion profiles of wet wood at 973, 1273 K.
Koufopanos *et al.* (1991)	Residual weight fraction of fine wood particles at 573-873 K.
Tran and White (1992)	Charring rates for different wood species with radiant heat flux.
Bounefoy *et al.* (1993)	Temperature at the centre and distribution across the wood cube.
Bilbao *et al.* (1996)	Temperature at the surface and across the radii of the wood sample for three different heat fluxes.
Home and williams (1996)	Char yield as a function of temperature for 200 µm particle.
Larfeldt *et al.* (2000)	Measured temperatures across the radius of charcoal cylinders.
Di Blasi *et al.* (2001)	Product yields during pyrolysis for five different wood varieties.
Klose (2002)	Pore size distribution data of larch wood and char.
Davidsson and Pettersson (2002)	Shrinkage of wood during pyrolysis as function of temperature
Grioui *et al.* (2006)	Experimental mass loss and mass loss rate curves for olive wood at different temperatures (293-1173 K).
Shen *et al.* (2007)	Thermal decomposition and surface temperature of birch under four different heat fluxes(20,30,40 and 60 kW m^{-2}).
Bellais *et al.* (2003)	Wood particle mass loss rates at 365, 500, 600 and 700°C and comparison with shrinkage models.

Table 5: For pyrolysis of bed of particles

Researcher	Data description
Peters and Bruch (2001)	Measured temperatures across the bed for heat flux of 80, 130 kW m^{-2}.
Peters *et al.* (2003b)	Bed mass and height versus conversion time, mass loss history of beech wood particles and average conversion rate versus primary air flow with heat flux 50 and 100 kW m^{-2} introduced from the top.
Ravi *et al.* (2004)	For annular saw dust bed: Measured temperature profiles along the heater wall, mass loss history of saw dust bed.

Finite Element Method (FEM)

Finite element methods basically seek solutions at discrete spatial regions (called elements) by assuming that the governing differential equations apply to the continuum within each element. It is based on integral minimization principle and provides piecewise (or regional) approximations to the governing equations. The advantage of FEM is with relative ease flow and heat transfer problems with complicated boundary shapes can be modeled, when compared with finite-difference methods. The disadvantage is complicated matrix operations. Not many works found in biomass pyrolysis except Boutin *et al.* (2002).

Data for Model Validation

The following section (Table 4, 5) represents the available literature experimental data, which have been used in model validation so far and also, could be used in future.

INFLUENTIAL PARAMETERS

The pyrolysis process is highly sensitive to property variations; the influential properties can be grouped in general as temperature dependent material properties, spatial properties, time dependent properties, physical properties, thermodynamic properties, transport properties and dimensionless numbers.

Particle Density and Heating Rate

Heating rate conditions influence the chemical pathways and in this way the conversion time and product composition (Besler and Williams, 1996). Experimental observation suggests that char yield is supported at low heating rates because of the larger residence time of primary products within the solid matrix whereas the yield of volatiles increases markedly at fast heating rates, where secondary reactions would be expected to dominate yielding little char. During Simulations Babu (2003e) observed that the final pyrolysis time first decreases at lower values of net heating rate/temperature and increases as net heating rate/temperature increased, which was not reported by earlier investigators. Higher heating rate favors release of hydrocarbon gases like CO, CO_2, CH_4, C_2H_6, etc. (Beseler and Williams, 1996).

Particle density also influences the final product composition and yield. For conversion in the thermally thick regime (intra particle heat transfer control) biomass density mainly affect the activity of secondary reactions of tar vapors and conversion time. They only affect the conversion time in thermally thin regime (external heat transfer control) (Di Blasi, 1997). Interestingly, it was reported that density has no influence on the pyrolysis time (Chaurasia and Babu, 2004).

Reactor Temperature

Pyrolysis at lower temperatures favors the production of char, whereas at higher temperatures results in the fission, dehydration, disproportionation, decarboxylation and decarbonylation reactions, which favors gas production. Di Blasi, (1998) have observed that at high external temperatures the pyrolysis process is heat transfer controlled. Similar to the effect of heating rate, the final pyrolysis time first decreases at lower values of temperature and then increases as temperature is further increased (Babu, 2002b). A sensitivity analysis revealed that, in relation to increase in the concentration of $char_1$, reactor temperature is the most important variable (Babu and Chaurasia, 2004a).

Heat of Reaction

The heat of devolatilization is of importance in modeling thermal effect during pyrolysis. The issue of whether pyrolysis reactions are endothermic or exothermic plays an important role in modeling. The values in literature are highly contradictory; the reason may be due to the size of the particle, the grain orientation (Lee *et al.*, 1976), the heating rate, lignin content (Roberts, 1971), the impurities etc. In principal the thermal degradation (primary reactions) of cellulose is endothermic, while the char formation (secondary reaction) is exothermic (Bellais, 2003).

Considering heat-transfer controlled reaction and self-sustaining reaction (Babu, 2003b, 2004a). The former is characterized by positive value of heat of reaction number Q", e.g. 10 and the latter is characterized by negative value, e.g., -0.5. Here, the production of $(char)_1$ is favored by the endothermic reactions while the production of $(volatile and gases)_1$ is favored by the exothermic reactions.

Thermal Conductivity

Thermal conductivity varies with temperature and conversion of the wood. The study of MacLean (1941) as referred by Leckner and Thunman (2002) is probably the largest single study ever made of thermal conductivity of different woods. A model is derived by Leckner and Thunman (2002) to calculate the effective thermal conductivity applied to different stages of combustion of wood. Also developed two principle models of thermal conductivity and validated by a comparison with direct numerical simulation of the fiber structure. The effective thermal conductivity is estimated from temperature, density and moisture content, shrinkage of wood.

Variations in wood and char thermal conductivity do not significantly affect particle conversion in a thermally thin regime (Di Blasi, 1997). In thermally thick regime pyrolysis largely depends on char thermal conductivity, large variations in conversion time and significant variations in the gas and tar yields were observed.

Specific Heat Capacity

The variations in wood specific heat capacity do not affect the primary product yields, although conversion time shows a linear increase with this parameter (Di Blasi, 1997). Understandably an increase in specific heat gives rise to a solid with a larger thermal capacity, so that the time needed to bring the system to pyrolysis temperature becomes longer and so does the conversion time.

The activity of secondary reactions appears to be significantly influenced by the specific heat capacity of the biomass. As the release of primary volatile products is slowed by successively lower values of wood specific heat, the flow velocity is also reduced. Intra-particle residence times become longer and secondary tar cracking occurs to an even greater extent. Consequently the final tar yield continuously decreases.

Convective Heat Transfer Coefficient and Orders of Reactions

It is possible to get the same extent of conversion of biomass with lesser pyrolysis time under controlled conditions by increasing convective heat transfer at much lower operating temperatures which are much safer than at higher operating temperatures leading to combined convective and radiative heat transfer mechanisms which are not safe (Babu and Chaurasia, 2002a). Pyrolysis is faster for zero order as compared to first order of primary reaction as the rates are independent of initial biomass concentration for zero order (Babu and Chaurasia, 2003e).

Emissivity

It was reported that emissivity has almost no effect on the pyrolysis rate (Davidsson and Pettersson, 2002) whereas initial wood density, specific heat and thermal conductivity affect the heat transfer and the pyrolysis rate as they define thermal diffusivity.

But, It is observed that the effect of emissivity on the concentration of products becomes significant at higher values of emissivity (Babu and Chaurasia, 2004a), where the activities of both the primary and secondary pyrolysis reactions are changing significantly.

Babu and Chaurasia (2004c) found that in thermally thick regime the most dominant properties are emissivity and thermal conductivity and the least sensitive parameter is the convective heat transfer coefficient. The conversion time becomes successively longer as the thermal conductivity of the biomass increases and/or emissivity decreases.

Particle Shrinkage and Moisture Content

Shrinkage impacts the pyrolysis process in several ways. These include thinning the pyrolysis reaction region and increasing the pyrolysis temperatures, reducing secondary reactants, reducing the residence time of the gases within the particle and cooling the char layer due to the higher mass flux rates of pyrolysis products. Within the thermal wave pyrolysis regime these effects significantly reduce the light hydrocarbon yield, increase the tar yield and reduce the pyrolysis time. But at high temperatures, these effects are minimized because more complex conversion of tars to light hydrocarbons takes place.

The presence of moisture content slowed down the surface temperature rise due to the consumption of large portion of energy. Moisture content in the fuel affects solid internal temperature history due to endothermic evaporation. Chan *et al.* (1985) stressed the need to account for the above process in energy balance. In some cases moisture leads to cracking of the surface, while the total heat transfer remains the same, heat is transported more quickly to the interior due to the presence of cracks on the surface. Internal failures result in changed local porosity and permeability, affecting fluid flow inside.

The combined impact of char shrinkage and particle moisture on pyrolysis products and time is a function of pyrolysis regime (Bryden, 2003). Shrinkage has negligible effect in the thermally thin

regime (Bi<0.2), in the thermally thick regime (0.2 = Bi = 10) it reduces the pyrolysis times by 5-30%. In thermal wave regime (Bi>10) it affects both the pyrolysis time and products (Hagge and Bryden, 2002). In general coupling both shrinkage and moisture result in longer pyrolysis times, increased tar yield and decreased light hydro carbon yield than if they were considered separately.

Particle Size, Shape and Orientation

Heat and mass transfer rates are highly affected by particle structure (Di Blasi, 1998). Large particles imply large thermal gradient and also the fluid residence times are sufficiently long to result in secondary reactions (Bamford *et al.*, 1946; Chan *et al.*, 1985). George (1986) has constructed an approximate boundary for particle size (for wood 200 μm; above 500 °C) as a function of temperature; above this boundary, the reaction rate is strongly heat transfer dominated and below this the rate is kinetically controlled.

Particle geometry has certain influence on pyrolysis. The time required for complete conversion of pyrolysis is highest for the slab and lowest for sphere (Chaurasia, 2004). The yield of (volatiles and gases)₁ is a maximum for sphere and is least for slab, while the other yields are more for slab and is least for sphere (Babu and Churasia, 2004d).

Grain orientation is an important parameter in pyrolysis due to the anisotropicity resulted from it. Roberts (1971) mentioned that permeability for flow along the grains is 10^4 times that across the grain. Similarly thermal conductivity along the grains is twice that across the grains. To a large extent, secondary reactions occur as the intensity of the heat flux is increased and for perpendicular grain heating (Di Blasi, 1996).

Wood Varieties

Generally, the successful kinetic models in biomass pyrolysis follow lumped parameter approach. But, still as the true kinetics of biomass depends on the decomposition rates of the main components (Raveendran *et al.*, 1996) which is caused by the biomass type and also with respect to:

- The fractions of the different major components
- The chemical composition of each constituent
- Presence of inorganic components, which can catalyze thermal degradation reactions

Di Blasi *et al.* (2001) found that qualitatively different wood varieties present same behavior and similar process dynamics when internal heat transfer is the controlling mechanism. Quantitatively the differences remain large in terms of temperature profile, product yields and average devolatilization rate. Different thermal diffusivities observed among wood varieties may have influenced in this regard (Shen *et al.*, 2007).

CONCLUSION

From the above review, understandably, biomass pyrolysis has come a long way as far as a practical technology and as the modeling and simulation aspects were concerned. From these observations the following considerations and suggestions can be made.

- Most of the models have limiting assumptions and their applications are limited to definite species and/or operating conditions.
- Least number of works on the integration of the single particle models with realistic pyrolysis reactor models which more or less resemble real world pyrolysis systems.

- Lack of compartmentalized or modular modeling approach, this kind of disintegration and assembly of the problem allows the researcher to modify and improve the individual modules so as to validate and justify the performance of the whole system. This will improve the pyrolysis modeling paradigm in a better way.
- Necessity of more simplified models through elimination of least sensitive parameters. Generalized models in terms of species, particle geometry, application and operation.

Apart from the numerous single particle models, good models are not available to show what is going on with the particles during fixed bed, ablative, fluidized bed and circulating fluidized bed pyrolysis processes such as shape changes and flow through the channels between particles. Design and modelling of pyrolyzers and gasifiers have to be done in close co-operation between manufacturers and universities. However there is confidentiality problem in providing commercial data in supporting modelling studies. As a result many available good models for fluid bed pyrolysis and gasification seem to remain unused. So, even today, modeling the biomass pyrolysis has tremendous scope for further research and improvements for the single particle modeling and more importantly for the modeling of pyrolysis beds.

NOMENCLATURE

a:	Stoichiometric coefficient
A:	Pre-exponential factor
A_p:	Heat transfer area, m^2
b:	Geometry factor (slab = 1, cylinder = 2, sphere = 3)
B_x:	Permeability (x); B_y: permeability (y), m^2
c_p:	Specific heat of pyrolysing solid, c_a: heat capacity of active solid, J/mol K
c_g:	Specific heat of volatiles and gases; c_{pG1} -heat capacity of primary gases and volatiles, J/mol K
c_c:	Specific heat of char, J/mol K ; c_u: specific heat of drying front, J/kg K
c_{pg}:	Specific heat of gases; c_{pl} - specific heat of liquid; c_{pv} - specific heat of vapor, kJ/kg K
C_A:	Molar concentration of fluid product in the solid; C_{A0}: in bulk phase, mol/m^3
C_B:	Concentration of biomass, kg m^{-3}; C_{B0} at initial condition
C_{G1}:	Concentration of primary gases and volatiles, kg m^{-3}; C_{G10} at initial condition
C_{C1}:	Concentration of primary char, kg m^{-3}
C_{G2}:	Concentration of secondary gases and volatiles, kg m^{-3}
C_{C2}:	Concentration of secondary char, kg m^{-3}
C_s:	Molar concentration of solid reactant; C_{s0}: at initial condition, mol m^{-3}
D_{eG1}:	Effective diffusivity of (gases and volatiles)$_1$, D_{eG0} for initial diffusivity, m^2 sec^{-1}
E:	Apparent activation energy
$F_{i?j}$:	View factor
h:	Heat transfer coefficient (overall)
h_c:	Convective heat transfer coefficient; h_r: radiative heat transfer coefficient, W m^{-2} K^3
H_{ri}:	Enthalpy of component i at 0°C; H_v - wood moisture vaporization enthalpy (kJ kg^{-1})
ΔH:	Heat of reaction, J kg^{-1}
k:	Apparent rate constant
k_1, k_2, k_3:	Rate constants, sec^{-1}
k_{mG1}:	Mass transfer coefficient of (gases and volatiles)$_1$ across film, m sec^{-1}
K:	Effective thermal conductivity of pyrolysing solid; K_W: for wood; K_C: for char, W/m K
K_x:	Thermal conductivity (x); K_y: thermal conductivity (y), W/m K

L: Particle length, m

m_p: Mass flux of volatile pyrolysis products; m_v: mass flux of water vapor, kg sec^{-1}

m: Mass flow, kg sec^{-1}

M: Total number of equations used in the simulation model

M_g: Mass flux of the volatile products; M_v - mass flux of water vapor due to drying (kg m^{-2}sec)

M_W: Wood mass; M_{W0}: initial wood mass; M_C: mass of char

n1, n2, n3:   Orders of reactions, dimensionless

p: Gas pressure, N m^{-2}

P_y, P_y':   Pyrolysis numbers

Pr: Prandtl number

q: Apparent enthalpy of pyrolysis reaction; q_r: enthalpy variation due to chemical reaction, kW m^{-3}

q_c: Char heat flux; q_w: dry virgin wood heat flux, W m^{-2}

Q''_e: External heat flux per unit area

Q''_{loss}:   Heat losses per unit area, kW m^{-2}

Q_p: Endothermic energy associated with the generation of unit mass of vapors

R: Particle characteristic radius (half thickness for slab, radius for cylinder and sphere), m

R_0:   Initial radius, m

Re: Reynolds number

R_g: Universal gas constant, J mol^{-1}

r: Radial distance; r_c: radius of the unreacted core, m

r_{ci}:   Rate of reaction of wood component i; r_{ev} evaporation rate (kg m^{-3} sec)

S_p: Reaction surface area, m^2

t: Time, s

T: Particle temperature; T_0 - initial particle temperature; T_f: furnace temperature, K

T_s: Temperature of surrounding fluid; T_w: temperature of wall surrounding solid particle, K

T_p: Pyrolysis front temperature, K

u_{ratio}:   Mass of water/mass of dry fuel

u: Gas velocity; u_x: gas velocity (x); v_x: gas velocity (y), m sec^{-1}

v_G: Gas velocity in the bed; V_g: velocity of volatile gases

V_S: Solid phase (wood and char) volume; V_{W0}: initial wood volume

V_{gp}:   Volume occupied by the pores (total gas and vapor phase volume)

V_{g0}:   Initial volume of volatiles in the pores; V_{gi}: volume corresponding to initial porosity

V_{gf}:   Volume occupied by final gas and vapor phase (gas+tar)

W_m: Mean molecular weight of solid, kg mol^{-1}

X_m: Solid moisture content

Y_i: Species mass fraction

α: Empirical parameter for convective transport

α^a: Average absorptivity

α_s: Shrinkage factor; β_s: shrinkage factor

ρ: Density of the pyrolysing solid

ρ_0:   Initial density; - final density, kg m^{-3}

ρ_w: Dry-wood density

ρ_i: Density of wood component i (kg m^{-3})

ρ_l: Density of liquid; ρ_c: density of char, kg m^{-3}

ρ_g: Density of total volatiles (gases+tar); ρ_a: density of the portion of solid which gasifies, kg m^{-3}

ϵ:	Emissivity coefficient
ϵ'':	Void fraction of particle
ϵ_0'':	At initial condition
ϵ:	Porosity
γ:	Constant for calculating void fraction defined by Eq. 33
$\tilde{\gamma}_s$:	Local solid reaction rate, (mol m^{-3} sec)
γ_a:	Contact angle
γ_s:	Shrinkage factor
Γ_{eff}:	Effective diffusion coefficient
η:	Reaction progress variable
ϕ:	Permeability
ϕ_B:	Permeability of biomass
ϕ_{C1}:	Permeability of char$_1$, m^2
ϕ_s:	Calar value
μ:	Viscosity, kg m^{-1} sec
ω:	Source term
$\dot{\omega}_m$:	Averaged source term
$\dot{\omega}_{th}$:	Averaged thermal source term
$\dot{\omega}_{ch}$:	Averaged chemical reactions source term
$\dot{\omega}_{con}$:	Averaged conduction source term
σ:	Stephan-Boltzmann constant, kW/m^{2}K^4

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