Modelling of Pyrolysis in Wood: A Review

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Abstract

Pyrolysis is an important phenomenon in combustion of wood and the successful modelling of pyrolysis to predict the rate of volatile evolution is central to combustion calculations. This review outlines the various issues pertaining to the understanding and modelling of the complex process of pyrolysis. Both physical and chemical aspects of pyrolysis are discussed with a description of how various parameters like wood composition and structure, heating rate and residence time affect the overall reaction rate and the yield of volatiles. Then, the currently available models are discussed. The present review indicates that a variety of pyrolysis models of varying degrees of complexity are available in the literature. The authors identify that there is a need for greater experimental inputs in the modelling of pyrolysis and closer interaction between modelling and experimental efforts.

Keywords: Kinetics, Modelling, Pyrolysis, Sawdust, Wood.

Introduction

Pyrolysis is essentially the thermal decomposition of organic matter under inert atmospheric conditions or in a limited supply of air, leading to the release of volatiles and formation of char. Pyrolysis in wood is typically initiated at $200^{o}C$ and lasts till $450\text{-}500^{o}C$, depending on the species of wood. Pyrolysis has an important role in the combustion of wood and sawdust since the products of this stage, namely, volatiles and char, subsequently undergo flaming and glowing combustion respectively to release thermal energy. This pivotal role of pyrolysis has prompted many an attempt to model this phenomenon mathematically. The primary objectives of these models are to provide a diagnostic tool for evaluating the importance of the various system parameters and to identify system characteristics useful to experimentalists. However, the inherent complexity of the pyrolysis process has posed formidable challenges to modelling attempts. The pyrolytic decomposition of wood involves a complex series of reactions, and consequently, changes in the experimental heating conditions or sample composition and preparation may affect not only the rate of reaction, but also the actual course of reactions. In this review article, we discuss the chemical and physical aspects of the pyrolysis process and the various issues which complicate the modelling of the pyrolysis process. The focus of the article would be on the modelling of wood pyrolysis, and relevant literature on related topics is presented. A comprehensive review of the basic phenomena of pyrolysis can be found elsewhere [1].

Pyrolysis: the process

The physical and chemical aspects of the pyrolysis process are described in the following sub-sections.

The physical process

The basic phenomena that take place during pyrolysis are: heat transfer from a heat source leading to an increase in temperature inside the fuel; initiation of pyrolysis reactions due to this increased temperature leading to the release of volatiles and the formation of char; flow of volatiles towards the ambient resulting in heat transfer between hot volatiles and cooler unpyrolysed fuel; condensation of some of the volatiles in the cooler parts of the fuel to produce tar; and auto-catalytic secondary pyrolysis reactions due to these interactions. The various issues having a bearing on the pyrolysis process have been discussed in detail in a later section. Although the oxidation of char and the combustion of volatiles are two major processes in combustion, they may be excluded from the stage of pyrolysis.

The chemical process

The chemistry of pyrolysis is strongly influenced by the chemical composition of the fuel. The elemental composition of the fuel may be obtained from ultimate analysis. Table 1 lists the average values obtained from ultimate analysis of two broad classes of wood [2]. A fair idea of the percentage of the major products of pyrolysis (volatiles and char) is obtained from proximate analysis. Table 2 gives the proximate analysis by percentage weight [2]. It is to be noted that volatiles are almost 77% by weight of dry wood. Thus, a weight loss of this order may be expected after pyrolysis is complete and all the volatile matter is released.

Table 1 : Typical Ultimate Analysis of Dry Wood by Weight (%) [2]

Type of wood	H	C	N	O	Ash
Hardwood	6.4	50.8	0.4	41.8	0.9
Softwood	6.3	52.9	0.1	39.7	1.0

Table 2 : Typical Proximate Analysis of Dry Wood by Weight (%) [2]

Type of wood	Volatile matter	Fixed Carbon	Ash
Hardwood	77.3	19.4	3.2
Softwood	77.2	22.0	1.6

The major constituents of wood are cellulose (a polymer glucosan), hemicellulose (a polysaccharide producing wood sugars), and lignin (a multi-ring organic compound). There is some variation in the relative abundance of these constituents in different species of wood but as a rough guideline cellulose is taken to be 50% and the other two 25% each by dry weight [2]. Most fuels of biological origin such as woods of different species of plants and agro-wastes contain the same principal constituents and differ only in their percentage composition [3]. Hence, much of the qualitative discussion in this paper could be extended in applicability to all such fuels, though the quantitative information is valid mainly for wood.

The reaction products of pyrolysis are a combination of the products expected from the separate pyrolysis of each of the three major constituents. Pyrolysis of each individual constituent is itself a complex process depending on many factors. A process with a combination of all the three constituents is even more complex with many more factors governing the rate of the numerous reactions leading to an enormous range of possible products. The pyrolysis characteristics of individual constituents, cellulose, hemicellulose and lignin are described as follows.

Cellulose

Cellulose is a glucon polymer consisting of linear chains of B(1,4) d-glucopyranose units. Its average molecular weight is 100,000. Aggregation of these linear chains within the microfibrils provides a crystalline structure that is highly inert and inaccessible to chemical reagents. Cellulose component normally constitutes 45-50% of the dry wood. Shafizadeh [4] has studied the pyrolysis of cellulose as the temperature is increased. At temperatures less than 300^oC, the dominant process is the reduction in degree of polymerisation. In the second step, at temperatures above 300^oC, there is formation of char, tar and gaseous products. The major component of tar is laevoglucosan that vaporizes and then decomposes with increasing temperature.

Hemicellulose

Hemicellulose is a mixture of polysaccharides mainly composed of glucose, mannose, galactose, xylose, arabinose, 4-0 methylglucuronic acid and galacturonic acid residues. Generally, it is of much lower molecular weight than cellulose and is amorphous in structure unlike cellulose. Its content varies from 20 to 40%. According to Soltes and Elder [5], hemicellulose is thermally most sensitive and decomposes in the temperature range 200^oC to 260^oC. This decomposition may occur in two steps; decomposition of the polymer into soluble fragments and/or conversion into monomer units that further decompose into volatile products. As compared to cellulose, hemicellulose gives rise to more volatiles, less tar and char. The components of tar are organic acids such as acetic acid, formic acid and a few furfural derivatives.

Lignin

Lignin is amorphous in nature and a random polymer of substituted phenyl propane units that can be processed to yield aromatics. It is considered as the main binder for agglomeration of fibrous components. The lignin component in biomass varies between 17 and 30%. According to Soltes and Elder [5], lignin decomposes when heated between 280^oC and 500^oC. Char is the more abundant constituent in the products of lignin pyrolysis with a yield of 55%. A liquid product known as pyroligneous acid consists of 20% aqueous components and 15% tar residue on dry lignin basis. The aqueous portion is composed of methanol, acetic acid, acetone and water. The tar residue consists mainly of homologous phenolic compounds. The gaseous products represent 10% of the lignin and are composed of methane, ethane and carbon monoxide.

Overall Process

The overall process of pyrolysis of wood is believed to proceed as follows [6]. At around 160^oC the removal of all moisture (dehydration) is complete. Over the temperature range 200^oC to 280^oC, all the hemicellulose decomposes, yielding predominantly volatile products such as carbon dioxide, carbon monoxide and condensable vapours. From 280^oC to 500^oC the decomposition of cellulose picks up and reaches a peak around 320^oC. The products are again predominantly volatiles. The decomposition rate of lignin increases rapidly at temperatures beyond 320^oC. This is accompanied by a comparatively rapid increase in the carbon content of the residual solid material.

Thus, thermal decomposition of cellulosic materials such as wood proceeds through a complex series of chemical reactions, coupled with heat and mass transfer processes. Emmons and Atreya [7] estimate that over 200 intermediate products are formed during the pyrolysis of biomass. Roberts [6] puts the number of products at over 100. Since cellulose is the major constituent of wood and pyrolyses over almost the entire range of temperature, several researchers have studied

cellulose pyrolysis in detail, in order to understand the mechanism of pyrolysis of wood. The general set of reactions suggested by Shafizadeh [4] for cellulose pyrolysis are as shown in figure 1:
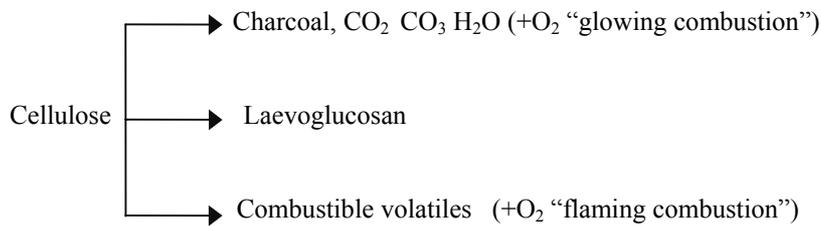

Figure 1 : Set of reactions in the decomposition of cellulose [4].

Lewellen *et al.* [8] provide a more detailed description of possible pathways that may contribute to weight loss during pyrolysis as shown in figure 2.
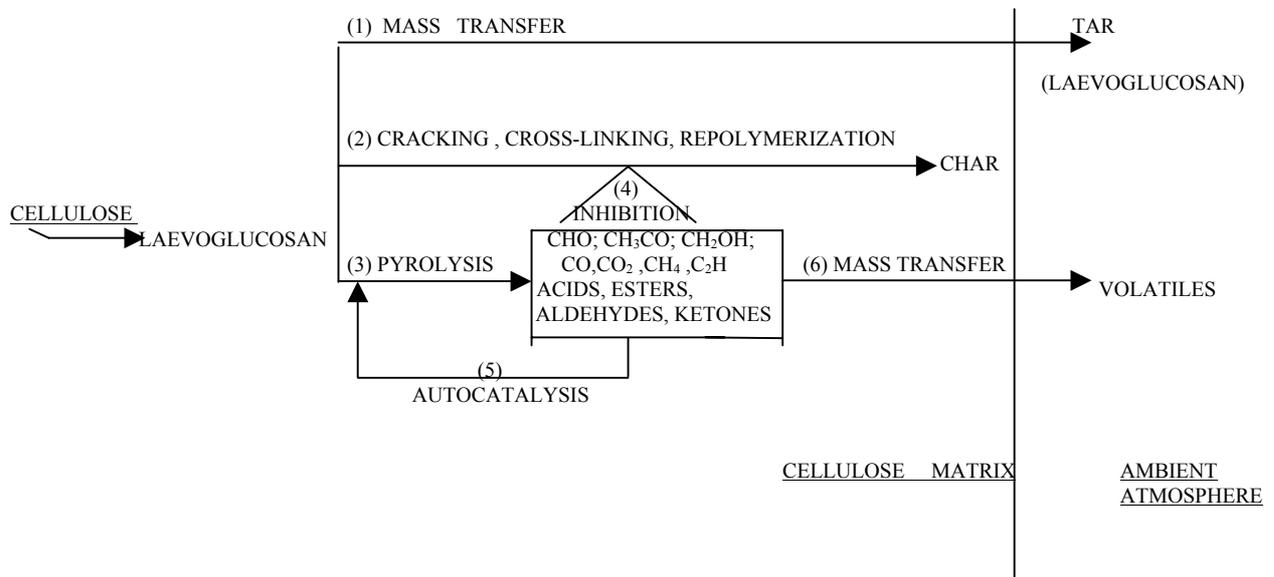

Figure 2 : Pathways of Pyrolysis Reactions [8]

In this scheme cellulose decomposes rapidly to an intermediate product, laevoglucosan. This may then be transported from the cellulose matrix by path 1 to give tar; or may repolymerize, crack, or become cross-linked to give char through path 2; or be pyrolysed through path 3 to lighter volatile products including CO, CO_2, fixed gases, organic acids, ketones, esters, aldehydes, and free radicals, some of which could inhibit char formation through 4, or autocatalyze step 3 through path 5. Lighter stable products would escape the matrix through path 6 to yield volatiles. Thus, there are numerous possible pathways for the pyrolysis of cellulose alone, which reflects the complex mechanism of pyrolysis of wood as a whole.

Di Blasi [9], in her review article, presents the different classes of mechanisms proposed for the pyrolysis of wood and other cellulosic materials. The models are classified into three categories: one step global models; one stage, multi-reaction models; and two-stage, semi-global models. The first category of models consider the pyrolysis as a single step first order reaction given as

$$\text{Solids} \xrightarrow{k} a \text{ Gases} + b \text{ Tars} + c \text{ Char}$$
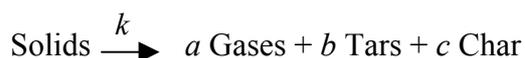
where k is the rate constant of the reaction and a, b and c are the yield coefficients of the different products of pyrolysis. Reaction rate constant k is written in terms of the frequency factor A and the activation energy E according to the Arrhenius equation as $k = A \exp(-E/RT)$. Table 3 gives the values of A and E presented in Di Blasi [9], quoted from different sources in the literature, for different species of wood. It can be observed, that the values span a wide range for different species of wood, and even for a given species, the kinetic constants depend very strongly on the experimental conditions under which the values are obtained..

Table 3. Kinetic Constants for Different Species of Wood [9]

Reference	Sample	Temperature (K)	E (kJ/mol)	A (sec^{-1})
Tran and Rai [10]	Fir Wood	300 - 1100	$101.7 + 142.7X^*$	2.1×10^8
Barooah and Long [11]	Beech sawdust	450 – 700	18 (T < 600) 71 (T > 600)	0.0053 2.3×10^4
Nolan *et al.* [12]	Wood	321 – 720	125.4	1×10^8

* X is the reaction progress variable

The second category of models discusses those mechanisms, which consider simultaneous and competing first order reactions in which virgin wood decomposes into the different constituents of pyrolysis products, *viz.,* tar, char and gases. Such studies have been conducted for small particles of wood by [13-15]. The third class of models consider the pyrolysis to be a two-stage reaction, in which the products of the first stage break up further in the presence of each other to produce secondary pyrolysis products. Such models are presented for cellulose by Bradbury *et al.* [16], for lignin by Antal [17] and for wood by Koufopanos *et al.* [18]. The model by Koufopanos *et al.* [18] was adapted and modified by Srivastava *et al.* [19], and is presented in a later section.

Key issues in modelling pyrolysis

Modelling of pyrolysis implies the representation of the chemical and physical phenomena constituting pyrolysis in a mathematical form. In other words, pyrolysis is to be represented as a system of equations which taken together can provide valuable quantitative information about the process. Pyrolysis, chemically represented, is a huge series of inter-linked reactions. Besides the sheer extent and range of pyrolysis reactions, several other issues complicate the modelling of pyrolysis. More often than not these issues are inter-linked making it extremely difficult to separate the influence of one from another. In the discussion that follows, the major issues are discussed separately. However, at some places it has been found more fruitful to discuss overlapping issues together, to bring out their connection.

Heating rate
The rate of heating influences the reaction pathway and hence, the final products. Pyrolysis is classified into slow pyrolysis, with heating rates of the order of 10$^\text{o}$C/min, and rapid/fast/flash pyrolysis, with heating rates approaching 1000$^\text{o}$C/min. The discussion in this paper generally pertains to the first kind. Experimental observation suggests that char yield is supported at low heating rates whereas the yield of volatiles increases markedly at fast heating rates. It has been proposed by Lewellen et al. [8] that the reaction pathways in the reaction scheme suggested by them differ depending on the heating rate. Under rapid heating rates and thin specimen

conditions, pathways 1 and 3 plus 4 plus 6 (figure 2) would be expected to dominate yielding little char. At low heating rates, particularly those involving large samples, the residence time of all primary products within the pyrolyzing matrix would dominate, accounting for large char yields.

Shafizadeh [4] suggests that intermolecular condensation reactions of cellulose are favoured at low heating rates. With the slower heating rate experienced at the particle interior, any pressure-driven flow rate is reduced, increasing the intra-particle residence time of volatiles and increasing the opportunity for condensation and char formation reaction.

Heat of reaction

The issue of whether pyrolysis reactions are endothermic or exothermic plays an important role in modelling. However, reported values of heat of pyrolysis of wood range from –613 kJ/kg [20] to 1680 kJ/kg [21]. Generally, the reported values pertain to slow heating rates. Fire level fluxes have not been investigated in most cases. In this regard the work of Lee *et al.* [22] seems to be most conclusive. They have calculated the heat of reaction from experimental observation of decomposition rates, solid temperatures and thermal properties, pyrolysis gas compositions and pressures. They have shown that for an incident heat flux of 3.192×10^4 J/m^2-s applied parallel to the grain direction, the pyrolysing region can be divided into three zones: an endothermic primary decomposition zone at T < 250 ^{0}C; an exothermic partial zone at 250 ^{0}C < T < 340 ^{0}C; an endothermic surface char zone at 340 ^{0}C < T < 520 ^{0}C. The overall mass weighted effective heat of reaction is endothermic at -613.2 kJ/kg. It has been observed during experiments that the overall heat of reaction at higher heat fluxes is exothermic, being greater when the heating is perpendicular to the grain orientation than when it is parallel. This may be explained as follows. For heating perpendicular to the grain orientation, pyrolysis gases have a much higher residence time in the solid matrix leading to an increase in secondary pyrolysis reactions, which are believed to be exothermic. Roberts [6] remarks that exothermic behaviour is strongly influenced by lignin content.

Reaction Scheme

The overall reaction mechanism of pyrolysis is yet to be fully understood but several simplifying schemes have been suggested for the purpose of modelling. The pyrolysis of a biomass such as wood consists of two types; namely, primary and secondary. Primary pyrolysis refers to the decomposition of any of the three major constituents of wood. Thus, primary reactions may proceed in parallel with the simultaneous decomposition of lignin, cellulose and hemicellulose in different regions of the fuel depending on the local temperature. The primary reactions depend only on the local solid temperature. Zaror and Pyle [23] suggest that they have a very low enthalpy change. Secondary pyrolysis reactions involve the decompositon products of primary reactions. The products of the primary reactions, mainly char and volatiles, also catalyze the secondary reactions. Such autocatalytic reactions are initiated when the hot volatile products come in physical contact with unpyrolysed sawdust.

Auto-catalytic secondary pyrolysis reactions are difficult to model since experimental information on the mechanism of these reactions and reaction rates is not available. The dependency of such reactions on the residence time of volatiles inside the solid matrix causes further complications in modelling. Even in modelling primary reactions many simplifications have been made. A one-step first order global reaction scheme has been used by most of the earlier models [24-28]. However, based on their experimental work Lee et al. [22] concluded that

such a simple scheme was unlikely to result in an accurate model. They suggested the following multi-step scheme:

$$wood \xrightarrow{\text{heat}} char + tar + gas$$

(1)

$$tar \xrightarrow{\text{char}} char + gas + heat$$
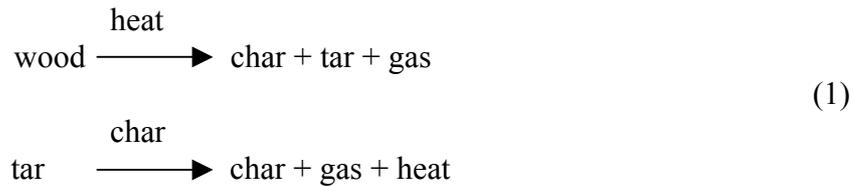
The char catalyzed decomposition reaction would account for the apparent residence time dependency of the exothermic pyrolysis reactions and secondary char formation. Other researchers share this view of the inadequacy of a single-step scheme. Panton and Rittmann [29] have suggested a similar scheme based on their investigation. Similar schemes have also been suggested by Murty and Blackshear [30], Akita [31], and Broido and Nelson [32]. For the special case of flash pyrolysis under rapid heating (400-1000 ^{o}C/min) Lewellen et al. [8] have shown that a single-reaction scheme is adequate. This may be expected since in such cases the residence time is very small and autocatalytic secondary reactions are absent.

Kansa et al. [26] concluded that the modelling of secondary pyrolysis reactions was necessary to narrow down the difference between experimental observations and model predictions. Roberts [6] agrees with this observation. Koufopanos *et al.* [33] proposed a model of two-step mechanism, where an "Intermediate" product is formed in primary pyrolysis, which breaks up into the final pyrolysis products in the secondary stage. Since it was difficult to establish the composition of components of the intermediates experimentally, Koufopanos [18] later modified the mechanism to that shown in figure 3. Jalan and Srivastava [34] have developed a kinetics scheme based on the work of Koufopanos et al. [18] that models multi-step reactions. Theirs is a two-step reaction scheme where the primary decomposition products participate in secondary reactions as shown in figure 3, resulting in a modified final product distribution. However, this does not account for the autocatalytic secondary reactions. The reaction constants used are those proposed by Koufopanos et al. [18]. Srivastava et al. [19] modified the Koufopanos [18] model to allow different orders of reaction for the three reactions shown in figure 3.
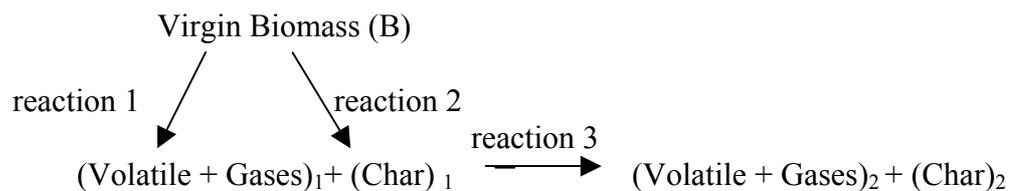
Virgin Biomass (B)

reaction 1   reaction 2

reaction 3

(Volatile + Gases)$_1$+ (Char) $_1$ $\longrightarrow$ (Volatile + Gases)$_2$ + (Char)$_2$

Figure 3 : Two-step reaction scheme [18]

Residence time of volatiles

The results of Lewellen et al. [8] indicate that the residence time of volatile products within the pyrolyzing cellulose matrix is extremely important in determining conversion. Residence time decides the extent of secondary pyrolysis. Competitive pathways such as escape from the matrix, inhibition of char formation and auto-catalysis of secondary pyrolysis, may exist whose rates and extent depend upon residence times of certain products within cellulose.

Particle size

In large particles the fluid residence times are sufficiently long to result in secondary reactions of the volatiles produced by primary reactions [24,35]. Large particle size also implies large thermal gradient. If moisture is present in a fuel particle, it escapes violently resulting in cracking of the surface. Local condensation of volatiles and moisture may also take place in the fuel. This aspect of pyrolysis remains to be investigated experimentally. Though the multi-step reaction scheme models are able to predict the overall tar formation, they do not predict the local condensation of volatiles to produce tar.

Structural effects

Cracking of the wood surface during pyrolysis has been reported by many researchers [6,23,26,36]. Tinney[36], while working on wooden dowels heated in a furnace, reported that the pressure at the center of the dowel rose to several psig and then dropped suddenly to zero before the center temperature reached the furnace temperature. While the pressure was dropping, serious structural failures, such as longitudinal channeling and surface cracking, occur. The effect of surface cracking is to alter the heating characteristics. 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.

Moisture content

Moisture content in the fuel affects solid internal temperature history due to endothermic evaporation [23]. Chan et al [35] further stressed the need to account for the above process in energy balance. Kelbon [37] verified that water evolution has a major effect on the intra-particle energy balance. Chan et al. [35] noted that not accounting for moisture evaporation results in over-prediction of temperature in the numerical solution.

Grain orientation

Grain orientation in wood needs to be taken into account due to anisotropicity resulting from it. Roberts [6] mentions 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. Thus, Roberts notes that secondary pyrolysis becomes important in the case of flow across grains. Kansa et al. [26] used Darcy's law in the momentum equation to model for fluid flow in an anisotropic solid matrix.

Material properties

Material properties are extremely important as parameters in modelling. In particular, thermal conductivity and heat capacity are important properties directly affecting the process of pyrolysis. Since particle density is easily measurable and calculated by most model equations, heat and mass transfer properties are conveniently and typically expressed as functions of density and/or temperature. In most models, the thermal conductivity of the pyrolysing solid has been modeled as a linear function of values for virgin wood and char, depending on the instantaneous value of density. Kung [38] has noted that the temperatures and mass loss predictions are quite sensitive to the value assumed for the thermal conductivity of char. However, accurate measurements of the thermal properties of wood and char at high temperatures have not been made to the best of our knowledge. The problems in this regard are the presence of attendant chemical reactions at high temperatures as well as wide variation in properties based on species and growth patterns of wood.

Approach to modelling

Pyrolysis is mathematically described through a system of coupled equations. The basic equations are those of chemical kinetics, heat transfer and mass transfer. The equations are individually discussed as follows. Table 4 presents a summary of the important contributions to pyrolysis modelling literature.

Chemical kinetics model

The actual reaction scheme of pyrolysis of wood is extremely complex because of the formation of over a hundred intermediate products. Pyrolysis of wood is, therefore, generally modelled on the basis of *apparent* kinetics. Ideally, the chemical kinetics model should account for primary decomposition reactions as well as secondary reactions. The model should take the heating rate into account to determine the scheme of reactions and should consider the possibility of autocatalysis of certain secondary reactions depending on the residence time of volatiles. However, till date models have generally accounted for primary reactions through apparent kinetics and in some cases, some of the secondary reactions through multi-step reaction schemes. Other issues are yet to be accounted for in the existing models.

Table 4 : Important Contributions to Pyrolysis Modelling Literature

Researcher	Important contribution
Bamford et al. [24]	First model of pyrolysis; only conduction , constants k, first order single step reaction
Tinney [36]	Two consecutive reaction schemes
Matsumoto et al. [25]	Temperature dependent k, internal convection char removal by oxidation
Roberts [6]	Compared presence and absence of internal heat transfer, considered k & ρ
Kung [38]	Importance of thermal conductivity of char
Maa & Bailie [28]	Unreacted shrinking core model
Lee et al. [22]	Purely experimental work on sign and value of heat of reaction
Fan et al. [27]	Volume Reaction model for simultaneous heat and mass transfer
Kansa et al. [26]	Momentum equation for motion of pyrolysis gases; modeled anisotropicity
Chan et al. [35]	Multi-step reaction schemes, time -varying global porosity, variable k, fluid flow, contribution of evaporation of inherent moisture to weight loss, volatile properties based on CO, H_2O
Koufopanos et al. [18]	Competing and consecutive reactions to account for both primary and secondary pyrolysis
Bilbao et al. [39]	Work on small samples of sawdust; used TGA to determine A,E values used in the model
Di Blasi [45]	Extended cellulose pyrolysis scheme to wood. Incorporated anisotropic effect by including different properties across and along the wood grain.

Zaror and Pyle [23] suggest a single pseudo-first order reaction scheme

$$\frac{dm}{dt} = -mA\exp\left(\frac{-E}{RT}\right) \tag{2}$$

where A is the apparent frequency factor, E is the apparent activation energy, and m is the mass of reactant.

Bamford et al. [24] have used a single reaction scheme and first order kinetics with a fixed heat of reaction. Matsumoto et al.[25] used Bamford's [24] model but, in addition, considered the rate of char removal by oxidation. Bilbao et al.[39] have achieved good fits between predicted results and experimental data in several studies on pyrolysis of small quantities of powdered wood by employing models using a first order single reaction scheme.

Two or three sets of consecutive or competitive reaction schemes have also been used as the basis of kinetic models. Tinney [36] developed a model based on two consecutive first order reaction schemes with each scheme having its own kinetic constants. While studying pyrolysis of wooden dowels heated in a furnace, he found that the apparent kinetics of the reaction changed abruptly with the structural breakdown, which he observed to occur between $\rho/\rho_o = 1/2$ and $1/3$. Here ρ and ρ_0 are the bulk densities at any time t and at time $t=0$ respectively of the pyrolysing dowels. Thus he proposed

$$\frac{d(\rho/\rho_0)}{dt} = -\frac{\rho}{\rho_0}A\exp\left(\frac{-E}{RT}\right) \tag{3}$$

with A, E and the heat of reaction before and after breakpoint as given in Table 5.

Table 5. Kinetic Data for Wood from Tinney [36]

	A (sec^{-1})	E (kJ/mol)	Heat of reaction (kJ/kg)
Before break point	6 x 10^7 - 7.5 x 10^8	125	125 -210
After break point	4 x 10^8 - 2 x 10^9	152 - 179	840 - 2300

Chan [40] and Koufopanos et al [18] proposed schemes of both consecutive and competing reactions to account for the effect of primary and secondary pyrolytic reactions using apparent kinetics equations. The scheme of reactions of Koufopanos' model, also adapted by Jalan and Srivastava [34] and Srivastava et al [19] is shown in figure 3. Reaction rates for the reactions 1,2 and 3 were determined to be given in the form $k_i = A_i \exp(D_i/T + L_i/T^2)$, with the values of A_i, D_i and L_i as given in Table 6.

Table 6. Kinetic data for wood from Koufopanos et al. [18]

i	Reaction	A_i (sec^{-1})	D_i (K)	L_i(K^2)
1	Biomass → (Volatile gases)$_1$	9.973 x 10^{-5}	17254.4	-9061227
2	Biomass → (Char)$_1$	1.068 x 10^{-3}	10224.4	-6123081
3	(Vol gases)$_1$+ (Char)$_1$ → (Vol Gases)$_2$ + (Char)$_2$	5.7 x 10^5	-9742.6	0

Srivastava et al. [19] and Jalan and Srivastava [34] used $A_3 = 8.3$ x 10^5. The kinetic equations for the mechanism shown in figure 3 can be written as follows:

$$\frac{dm_W}{dt} = -k_1 m_W^{\,n1} - k_2 m_W^{\,n1}$$

$$\frac{dm_{G1}}{dt} = k_1 m_W^{\,n1} - k_2 m_{G1}^{\,n2} m_{C1}^{\,b3}$$

$$\frac{dm_{C1}}{dt} = k_2 m_W^{\,n1} - k_3 m_{G1}^{\,n2} m_{C1}^{\,n3}$$

$$\frac{dm_{G2}}{dt} = k_3 m_{G1}^{\,n2} m_{C1}^{\,n3}$$

$$\frac{dm_{C2}}{dt} = \delta k_3 m_{G}^{\,n2} m_{C1}^{\,n3}$$

where m_W, m_{G1}, m_{G2}, m_{C1} and m_{C2} are the masses of wood, primary and secondary gas and primary and secondary char respectively, n_1, n_2 and n_3 are the orders of the three reactions; k_1, k_2 and k_3 are the rate constants of the three reactions as defined by the kinetic parameters in Table 6, and δ is the yield ratio of secondary char to gas. While Koufopanos [18] found that use of first order assumption for all three reactions led to good agreement with their experimental data, Srivastava *et al.* [19] used $n_2=n_3=1.5$ with two values of n_1: $n_1=0$ and $n_1=1$. They present no comparison with experiments. Jalan and Srivastava [34] have applied this model to simulate pyrolysis in biomass pellets, using $n_1 = 0$ and $n_2=n_3=1.5$. Comparisons with experiments and predictions of Pyle and Zaror [41] show good agreement of spatial and temporal variations of temperature in the pellet.

Chan [40] proposed a mechanism where volatiles and tar formed by primary pyrolysis undergo secondary pyrolysis. The other primary reactions of formation of char and gas from wood are parallel and competing with the tar formation reaction. Evolution of moisture in wood in the form of water vapour was also considered as one of the pyrolysis reactions as shown in figure 4.
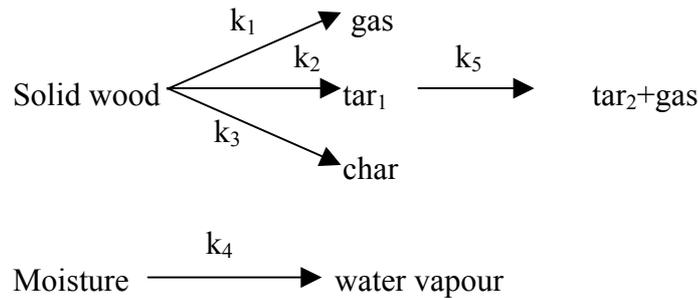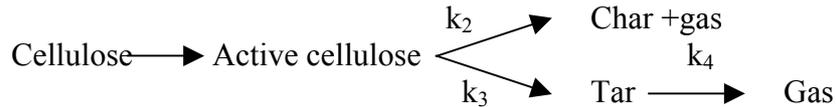

Figure 4. Two-step Mechanism of Chan [40]

If for each reaction, the rate constant is written as $k_i = A_i \exp(-E_i/RT)$, the values of A_i and E_i are tabulated in Table 7.

Table 7. Kinetic Constants used by Chan [40]

i	Reaction	A_i (sec^{-1})	E_i (kJ/mol)

1	Wood $\longrightarrow$ Gas	1.3×10^8	140
2	Wood $\longrightarrow$ (Tar)$_1$	2×10^8	133
3	Wood $\longrightarrow$ Char	1.08×10^7	121
4	Moisture $\longrightarrow$ Water Vapour	5.13×10^6	87.9
5	(Tar)$_1$ $\longrightarrow$ (Tar)$_2$ +Gas	1.48×10^6	144

A similar model was proposed for pyrolysis of pure cellulose by Bradbury et al [16] and used by Di Blasi [42]:

$$\text{Cellulose} \longrightarrow \text{Active cellulose} \overset{k_2}{\underset{k_3}{\lessgtr}} \begin{matrix} \text{Char +gas} \\ \text{Tar} \overset{k_4}{\longrightarrow} \text{Gas} \end{matrix}$$

The overall kinetics of pyrolysis of wood is influenced primarily by the reactivity of cellulose, its major constituent. Roberts [6] provides the experimentally found values of E and A for lignin and purified cellulose respectively. Autocatalysis of the secondary stage by the products of the primary stage may increase the value of A upto 12 times, assuming that autocatalysis has a negligible effect on E [6]. As temperature increases, autocatalysis decreases because the volatiles escape faster from the solid fuel and hence, the reaction rate rises less rapidly.

In view of the importance of kinetics in pyrolysis of a biomass it is necessary to know the values of kinetic parameters of the biomass under a particular set of conditions. However, difficulty arises in studying the thermal behaviour of biomass due to lack of exact knowledge of the course of reactions and their degree of completion. Moreover, the vast number of products resulting from the thermal degradation of biomass hinder a thorough understanding of the process. Thus, several different values of the kinetic reaction constants, the pre-exponential factor and the activation energy, have been used in literature for numerical simulation using the models. Few researchers have used the values of kinetic constants in their simulation that have been estimated from the same wood sample that was used for experimental corroboration. Bilbao et al. [39] have conducted thermo-gravimetric analysis of their experimental sample to obtain the kinetic constants they used. Koufopanos et al [18] have determined both primary and secondary reaction rate constants and heat of pyrolysis by matching models with measured mass loss and temperature profile data. This approach is to be favoured since it enhances the reliability of the model validation.

Heat transfer model
The heat transfer model determines the temperature profiles that serve as input to the kinetics model. Hence, the detail of the heat transfer model often determines the accuracy of prediction of the overall model. The ideal heat transfer model should account for the following phenomena/issues: heat transfer to the surface of the fuel, conduction to the interior, internal convection, effect of surface cracks on heat transfer, effect of internal structural changes on fluid flow, heat of reaction, grain orientation and changes in material properties during the course of pyrolysis. However, the existing models consider only the following aspects: gross surface heat transfer, conduction, internal convection excluding residence time and density governed material properties.

The first model of pyrolysis of wood was developed by Bamford et al. [24]. The model assumes wood to be a continuous solid medium heated by an external source across a well-defined surface. It also assumes thermal diffusivity to be constant. Further assumptions are: heat transfer within the solid is only by conduction; heat can be locally produced or consumed during pyrolysis; volatiles produced during pyrolysis leave the solid as soon as they are produced. Thus, the residence time of volatiles inside the solid is zero. With the above assumptions the model is simplistic at best.

In a later model, Matsumoto et al. [25] used temperature dependent thermal conductivity and included internal convective heat transfer. This model was further enhanced by Kung [38] who studied the effects of slab thickness of wood, char conductivity, and decomposition endothermicity. Roberts'[6] model takes into account convective heat transfer within the solid and considers two extreme cases: namely, rapid internal heat transfer and no internal heat transfer. The solution for each of these two cases differs depending on whether thermal conductivity is assumed to be constant or proportional to density. Their results show that the second approach results in better predictions. However, even this approach appears arbitrary since no experimental evidence has been provided for this simplification. Although the dependency of thermal conductivity on density is well accepted, a direct proportionality is not borne out from the goodness of fit that Roberts [6] has obtained between experimental data and his model. Kansa et al. [26] included momentum equation for the motion of pyrolysing gases within the solid. The model includes porous and permeable structural effects on volatile flow as well as variable properties. Darcy law has been used to account for permeability, thereby considering the anisotropic behaviour of wood. Refinements to this model to include variable properties and more complex reaction schemes are yet to be made.

Fan et al.[27] have used a volume reaction model which accounts for simultaneous heat and mass transfer in the particle. Maa and Bailie [28] have developed the unreacted shrinking core model for high temperatures. 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. In a recent model, Chan et al [35] have added several interesting details. The unsteady rise of temperature in the particle interior is described by using a time-varying global porosity to characterize the internal energy change of the gas and solid. A variable thermal conductivity, dependent on wood density and temperature has been used. Conduction is opposed by the flux of volatile reaction products as they leave the reaction front. Water vapour from evaporation and dehydration has been considered. Volatiles are assumed to have the properties of CO and water, and are assumed to be in thermal equilibrium with the solid as they flow outward in one direction only. According to Chan et al. [35] gas-solid thermal equilibrium may be validated for the slow fluid velocity calculated from measured pressure gradients. In fact, Koh and del Casal [43] have shown that if the Peclet number is large, as in the case of many pyrolysis experiments, the fluid and solid matrix are in "local thermal equilibrium", i.e., $T_s = T_g$. The latent heat of water is treated as one heat of reaction.

Chan et al.[35] used 1-cm-diameter cylinder of wood, compressed sawdust, cellulose or lignin and radiatively heated one face of it. Their energy equation is:

$$[\phi \rho_g c_{p_g} + (1-\phi) \rho_s c_{p_s}] \frac{\partial T}{\partial t} - \frac{\partial}{\partial x}(k \frac{\partial T}{\partial x}) + \rho_g u c_{p_g} \frac{\partial T}{\partial x} + \Delta H_R = 0$$

Where ϕ is the porosity, ρ_g and ρ_s are the bulk densities of the gases and solid respectively, T the temperature, k the effective thermal conductivity (including radiation contribution) and ΔH_R is the total heat of reaction of the pyrolysis processes. At the boundary $x=0$, q_s is the impressed radiant heat flux. The boundary condition is a surface energy balance taking into account convective heat loss, radiative loss and the conductive heat transfer to the interior of the sample. The velocity u is accounted for by lowering the effective conductivity in the computation of heat flux leaving the domain. Di Blasi [44, 45] model the momemtum conservation in the domain using Darcy law, in order to relate pressure gradients to velocities, and they use the ideal gas equation of state to relate the gas phase density, pressure and temperature.
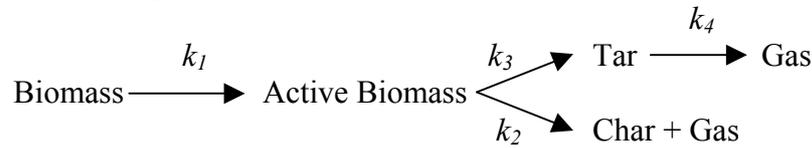
Mass transfer model

The ideal mass transfer model should consider the effect of particle size, grain orientation and internal structure as well as packing on the residence time of pyrolysis gases. The mass transfer model is heavily dependent on the extent of detailing in the chemical kinetics model. This is so because it is the kinetics model that identifies the various species that the mass transfer model must work with. Single step reaction models predict only the lumped gas species and hence, the

$$\frac{\partial(\varepsilon \rho_T)}{\partial t} + \frac{\partial(\rho_T u)}{\partial x} = \frac{\partial}{\partial x}\left(D^* \rho_g \frac{\partial Y_T}{\partial x} \right) + k_3 \rho_A - \varepsilon k_4 \rho_T$$

$$\frac{\partial \rho_g}{\partial t} + \frac{\partial \rho_g u}{\partial x} = (\nu_G k_2 + k_3) \rho_A$$

product distribution is unaffected by a finite mass transfer rate. However, for more complex multi-step reaction schemes, mass transfer does affect the secondary pyrolysis. Di Blasi [42, 44] presents such a model for mass transfer, solving the equations of convection and diffusion for the tar and gases formed by pyrolysis:

where ρ_g, ρ_T and ρ_A are the bulk densities of the gaseous products (tar+gases), tar and active species of the biomass respectively, D^* is the effective diffusivity of the gaseous products, Y_T is the mass fraction of tar in the gaseous products and ν_G is the stoichiometric yield of gas in the decomposition of active biomass and the rate constants k_1, k_2, k_3 and k_4 are schematically illustrated in the following mechanism:

$$\text{Biomass} \xrightarrow{k_1} \text{Active Biomass} \begin{array}{c} \xrightarrow{k_3} \text{Tar} \xrightarrow{k_4} \text{Gas} \\ \xrightarrow{k_2} \text{Char + Gas} \end{array}$$

Experimental studies on this aspect show that mass transfer effects may be neglected for the case of heating parallel to the grain orientation since the residence time is low in this case [40]. This approach of assuming a zero residence time of volatiles is to be found in all the models mentioned in this paper. Although Di Blasi [42,44] does present a semblance of a mass transfer model, effectively the mass transfer model is yet to be developed since residence time is yet to be modeled. One of the reasons that a good mass transfer model has not been developed is the lack of information on secondary pyrolysis reactions.

Conclusions

Understanding and modelling of pyrolysis process is central to wood combustion. The complexity of wood pyrolysis phenomena are primarily due to (a) *complexities of composition*, which include the presence of long and complex organic molecules and their characteristic decomposition reactions, the presence of moisture, and the type of wood considered; (b) *structural effects*, which include the porosity of the wood and the effects like internal and surface cracking during the process of pyrolysis; (c) *heating rate effects*, classifying pyrolysis into slow and fast regimes, and (d) *residence time effects*, which result in auto-catalysis of secondary reactions. The existing literature on pyrolysis modelling suggests that great strides have been made in understanding and modelling pyrolysis in the last three decades. Predictive models of practical utility are now available for various sizes and kinds of wood samples and under a variety of physical conditions.

The present review also indicates that secondary reactions are now being included in recent work on pyrolysis modelling. For sufficiently large particle sizes, the effect of volatile condensation also becomes important. To the best of our knowledge, suitable experimental studies for the above have not been carried out. The mass transfer models exclude the effect of the residence time of volatiles. The heat transfer models so far also excluded the influence of surface cracks, changes in some material properties during the course of pyrolysis and of grain orientation on heat transfer.

It was also found that most researchers did not estimate the kinetic parameters for modelling from the same sample of wood that they used for their experiments. Thus, even good agreement with experimental data may be, at least to some extent, fortuitous.

The authors conclude that in the present state of pyrolysis modelling a lot of clarity has emerged on the physical and chemical factors influencing pyrolysis and various predictive models are available for the designer to estimate the volatile yield under a variety of conditions. However, for further improvement in pyrolysis modeling the authors recommend a greater synergy between the experiments and the process of modelling. It is also expected that more detailed models taking into account autocatalysis, residence time effects, volatile condensation and structural effects, among others, will emerge in the next few years, paving the way for improved simulation of actual processes.

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