

## Kinetic Modeling in Biomass Pyrolysis – A Review

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**Abstract:** Biomass pyrolysis is one of the efficient and economic non conventional energy routes for human kind over the years. The process as a supplement for fossil fuels receives more attention under the current energy crisis. It has wide scope for further improvements in the reactor design, process design and as a part of gasifier design. The design problems can be conveniently handled through precise process models. Pyrolysis modeling requires inputs from kinetic model in order to analyze and solve heat transfer models of single particle and pyrolysis bed; the chemistry and complication of the process which involves hundreds of intermediates have paved the way for development of numerous kinetic models in the past. The models and parameters on the whole imply a perplexing portrait to the end user. This work discusses the progress made in the kinetic modeling front as far as biomass pyrolysis is concerned. It examines the chemistry, reaction mechanisms, kinetic models and kinetic parameters involved in the pyrolysis process.

**Key words:** Biomass, Pyrolysis, Modeling, Review, Kinetic Parameters

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### INTRODUCTION

The socio economic development of any country mainly relies on independence and self sufficiency in the energy fronts. In enhancing the energy options the current research and exploration in non conventional energy technology involuntarily leads to efficient and regulated utilization of the abundantly available natural renewable resource, the biomass.

Biomass provides a clean, renewable energy source that could dramatically improve our environment, economy and energy security. Few of the advantages and benefits of biomass for energy usage are<sup>[1]</sup>:

**Abundance:** availability of biomass is worldwide, which assures uninterrupted supply of raw material to the energy unit.

**Secure:** a significant contributor to the national energy supply and will ensure economical benefits along with greater autonomy and freedom from external resources.

**Domestic Resource:** not sensitive to world price fluctuations or the supply uncertainties of imported fuels.

**Socio-economic Development:** creation of employment opportunities in rural areas

**Environmental Benefits:** when used sustainably and allowed regrowth, reduces CO<sub>2</sub> and SO<sub>2</sub> accumulation in the environment.

**Properties and Composition of Biomass:** The contents of biomass are complex mixture of numerous organic compounds and polymers. Lignin, cellulose and hemicellulose are the major compounds, their ratios and properties depend on the species. The composition of different biomass are shown in Table 1.

The elemental composition of biomass (Table 2) is rich in oxygen and carbon and has a low heating value. It has extremely high reactivity, after devolatilization a large volatile fraction and a highly reactive char is obtained. Dry wood has about 50 weight% carbon, 6 weight% hydrogen and 44 weight% oxygen<sup>[1]</sup>. Biomass has low ash, nitrogen and sulfur contents. However, straws and grasses have substantially higher amounts<sup>[3]</sup>.

**Pyrolysis:** Pyrolysis is one of the thermochemical biomass conversion processes (Fig.1) 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 generates three different products in different quantities: coke, oils and gases. The chemistry and products of biomass pyrolysis are given in Table 3.

**Kinetic Modeling:** Biomass pyrolysis involves numerous extremely complex reactions and end up with large number of intermediates and end products, devising an exact reaction mechanism and kinetic modeling for biomass pyrolysis is extremely difficult, hence, pyrolysis models are modeled on the basis of

**Table 1:** Composition of Different Biomass Type (wt% on dry basis)<sup>[2]</sup>

Type	Cellulose	Hemicellulose	Lignin	Others	Ash
Soft wood	41	24	28	2	0.4
Hard wood	39	35	20	3	0.3
Pine bark	34	16	34	14	2
Straw (wheat)	40	28	17	11	7
Rice husks	30	25	12	18	16
Peat	10	32	44	11	6

**Table 2:** Elemental compositions, ash content and calorific heating value (dry basis)<sup>[1]</sup>

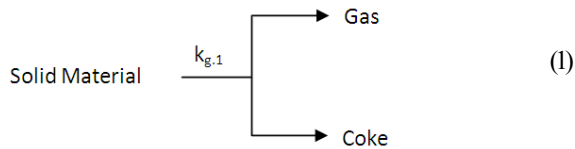
Fuel	C % wt	H % wt	O % wt	N % wt	S % wt	Ash % wt	Heating Value kJ/g
Birch wood	48.8	6.0	44.2	0.5	0.01	0.5	20.0
Pine wood	49.3	6.0	44.2	0.5	0.01	0.5	20.1
Bark	47.2	5.6	46.9	0.3	0.07	3.9	20.9
Wheat straw	49.6	6.2	43.6	0.6	n.a	4.7	18.6
Miscanthus	49.5	6.2	43.7	0.6	n.a	3.3	18.5
Sugar cane	49.5	6.2	43.8	0.5	n.a	3.7	18.5
Reed grass	49.4	6.3	42.7	1.6	n.a	8.8	18.8
Peat	53.1	5.5	38.1	1.3	0.2	5.6	20.5
Coal	80.4	5.0	6.7	1.3	0.53	7.0	30.4

**Table 3:** Characterization of chemistry and products of biomass pyrolysis<sup>[4]</sup>

Type	Feature and Process	Products and their characterizations
Pyrolysis of holocellulose	<p>General effects: Colour changes from brown to black, flexibility and mechanical strength are lost, size reduced, weight reduced</p> <p>Processes: Dehydration – also known as char forming reactions produces volatile products and char. Depolymerization – produces tar</p> <p>Effect of temperature: At low temperatures dehydration predominates, at 630K depolymerization with production of levoglucosan dominates. Between 550 and 675K products formed are independent of temperature</p>	<p>Volatile products: Readily escape during pyrolysis process, 59 compounds are produced out of which 37 have been identified CO, CO<sub>2</sub>, H<sub>2</sub>O, acetal, furfural, aldehydes, ketones.</p> <p>Tar: Levoglucosan is principal component.</p> <p>Char: As heating continues there is 80% loss of weight and remaining cellulose is converted to char, prolonged heating or exposure to higher temperature (900K) reduces charformation to 9 %.</p>
Pyrolysis of lignin	<p>Conventional (Carbonization): At 375-450 K endothermic reaction From 675 K exothermic reaction Maximum rate occurring between 625 and 725 K</p> <p>Fast and Flash pyrolysis: High temperature of 750K, rapid heating rate, finely ground material, less than 10% moisture content, rapid cooling and condensation of gases, yields in 80% range, char and gas used for fuel</p>	<p>Char: approximately 55%</p> <p>Distillates: 20%, methanol, methoxyl groups, acetone, acetic acid</p> <p>Tar: 15%, phenolic compounds and carboxylic acid</p> <p>Gases: CO, methane, CO<sub>2</sub>, ethane</p> <p>Bio-oil: will not mix with hydrocarbon liquids, cannot be distilled, substitute for fuel oil and diesel in boilers, furnaces, engines, turbines, etc.</p> <p>Phenols: utilizes a solvent extraction process to recover phenolics and neutrals, 18-20% of wood weight, secondary processing of phenol pharmlaldehyde resins, adhesives, injection molded plastics.</p> <p>Other chemicals, extraction process: chemical for stabilizing the brightness regression of thermochemical pulp (TMP) when exposed to light , food flavorings, resins, fertilizers, etc.</p>

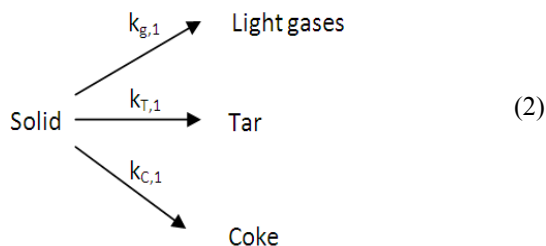
visible kinetics. Thus, pyrolysis kinetic modeling paved the way for researchers to propose different reaction schemes in different times; in due course this has developed a long history. Hence even today it is difficult to develop a precise kinetic model taking into account all the parameters concerned. Revisiting the mechanisms for pyrolysis of biomass so far developed reveals a general approach: virgin biomass as the raw material and with gas / volatiles, tar, char as the end products.

**One Step Global Models:** One step global models were used during the initial stages of the modeling of pyrolysis process; these 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 [5].



Miyunami *et al* [6] and Fan *et al* [7] have used one step global kinetic scheme in their Volume Reaction Model. Wichman *et al* [8] applied the global one-step reaction mechanism together with a one dimensional formulation to the energy equation. This model lacks the effects of moisture and char oxidation. Laraqui *et al* [9] extended the model by adding convective heat transfer to the one step reaction mechanism. Kung [10], Kansa *et al* [11], Kanury [12] and Lee *et al* [13] have also used one step global mechanism. One step global models do not represent the real situation, hence, their use was sparingly found in literature.

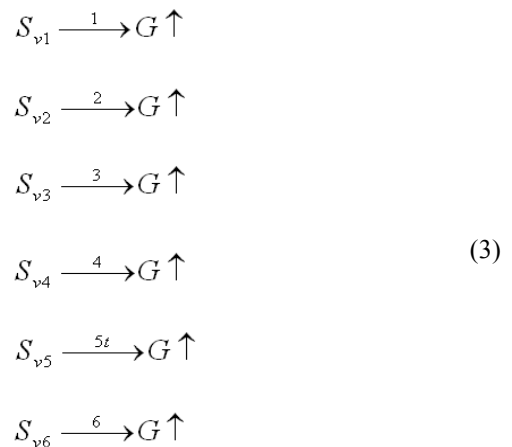
**Competing Models:** The competing reaction model of Thurner *et al* [14] is the most classical model for wood pyrolysis. It features a varying char yield. The model comprise of secondary reactions lumped with primary reactions over a narrow temperature range by means of three competitive reactions, their investigation was restricted to the determination of the kinetic data of the primary reactions.



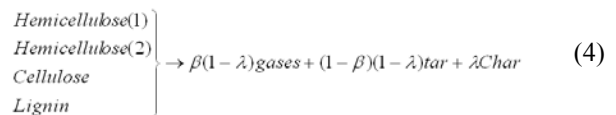
It was assumed that the activation energies for the char-formation reaction (reaction 3) is about the same as that for the weight-loss reactions. This led to a final residual weight which is independent of the pyrolysis temperature. Recently Shen *et al* [15] in their modeling of pyrolysis of wet wood under external heat flux used the Thurner *et al* [14] one-step, multi-global reaction scheme.

This model is empirical and therefore was kept as simple as possible. As there was no means to measure secondary reactions, the cracking reactions are lumped into the primary reactions. This scheme has a varying char yield.

**Parallel Reaction Models:** Alves *et al* [16] have assumed a new reaction scheme and corresponding kinetics were experimentally determined for very small samples of dry pine wood sawdust, with negligible internal temperature gradients. Six independent reactions were identified



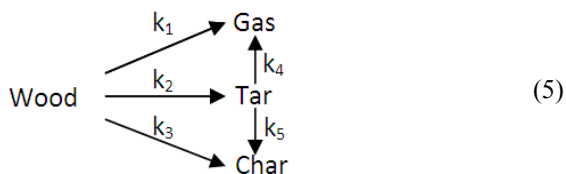
where,  $S_{vi}$  is the volatile part of component  $i$  of wood. Gronli [17] developed a model assuming birch wood comprising of four constituents and estimated the kinetic parameters. It was later implemented by Larfeldt *et al* [18] in a comprehensive model for drying and pyrolysis of wood. This scheme has a fixed char yield and does not feature secondary reactions.



On the same lines Svenson *et al* [19] have pyrolysed small particles of cellulose, xylan and lignin and calculated kinetic parameters. The decomposition of each constituent was expressed by first order kinetics or by two exponential functions if the first order model as not satisfactory. This scheme has a fixed char yield and does not feature secondary reactions.

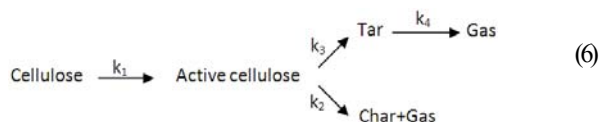
**Models with Secondary Tar Cracking:** Chemical processes of biomass pyrolysis are described through a primary and secondary stage<sup>[14,20,21,22,23]</sup> as follows:

The competing reaction model of Thurner *et al*<sup>[14]</sup> was added with tar cracking and repolymerization, here, the tar decomposes into lighter gases or polymerized into coke in exothermic reactions.



Here, primary reactions are assumed to be adequately represented as first order in the mass of pyrolyzable material and having an Arrhenius type of temperature dependence. Secondary reactions are assumed to occur only in the gas/vapor phase within the pores of the solid matrix and their rates are proportional to the concentration of tar vapors<sup>[24,25]</sup>. Chan *et al*<sup>[21]</sup> have also included dehydration reactions along with the tar cracking to the competing reaction model. Recently Janse *et al*<sup>[26]</sup> and Mousque's *et al*<sup>[27]</sup> have followed the above reaction scheme for wood pyrolysis.

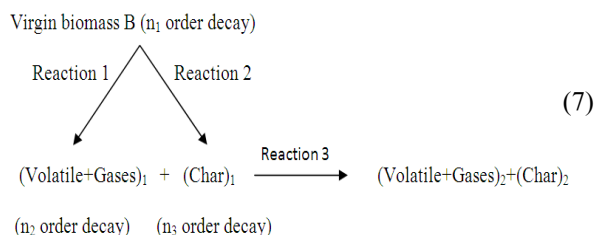
Broido *et al*<sup>[28]</sup> have showed that cellulose decomposes by a multistep mechanism at low temperatures. Later Bradbury, Sakai and Shafizadeh<sup>[29]</sup> have simplified Broido's reaction work. This simplified reaction scheme, called the 'Broido-Shafizadeh model', is generally accepted today with the kinetic parameters are frequently quoted and used in simulations. This mechanism accounts for the formation of an active solid with a reduced degree of polymerization and two competing reaction pathways: (a) intermolecular dehydration, predominating at low temperatures, leading to char and gas and, in air to smoldering combustion; and (b) depolymerization reaction, predominating at high temperatures, leading to tar and, in air, to flaming combustion. The reactions are endothermic and their rates are represented as first order in the mass of pyrolyzable material and with an Arrhenius type of temperature dependence.



The Broido-Shafizadeh scheme of cellulose pyrolysis (with kinetic constants  $k_1$ ,  $k_2$  and  $k_3$  in Bradbury *et al*<sup>[29]</sup> was extended to include secondary reaction with kinetic constant  $k_4$ <sup>[24]</sup>. Di Blasi<sup>[30]</sup> as in his previous study<sup>[31]</sup> used the above Broido-Shafizadeh scheme of cellulose pyrolysis, extended to include secondary tar cracking.

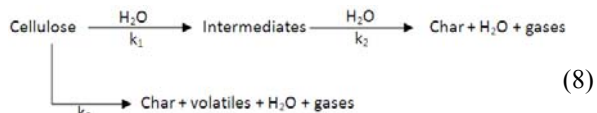
Koufopoulos *et al*<sup>[32]</sup>, attempted to correlate the pyrolysis rate of the biomass with its composition. The pyrolysis rate of the biomass was considered to be the sum of the rates of the main biomass components: cellulose, hemicelluloses and lignin. The model provides an initial reaction (reaction 1) which describes the overall results of the reactions prevailing at lower pyrolysis temperatures (below 473 K). This first step is considered to be of zero-order and is not associated with any weight loss. The intermediate formed further decomposes through two competitive reactions, to char (reaction 3) and to gaseous/volatile products (reaction 2). It is assumed that the reactions follow the Arrhenius law. This model is relatively simple and can predict the final char yield in different heating conditions.

Koufopoulos in his further revelations<sup>[33]</sup> included the secondary reactions between charcoal and volatile pyrolysis products described by first order kinetics. Later, Srivastava *et al*<sup>[34]</sup> have extended the Koufopoulos *et al*<sup>[33]</sup> mechanism, and this was used in many of the later modeling works Jalan<sup>[35]</sup>, Babu *et al*<sup>[36,37,38]</sup> and Chaurasia *et al*<sup>[39]</sup>.



Here, the primary pyrolysis products participate in secondary interactions (reaction 3) causing a modified final product distribution.

Varhegyi *et al*<sup>[40]</sup> tried to eliminate the over simplicity of 'Broido-Shafizadeh model, stating that a partial reaction in the scheme may correspond in reality to a group of reactions and proved the validity of the following reaction kinetic scheme under the given experimental conditions



Here,  $k_0$ ,  $k_1$  and  $k_2$  are rate constants for reactions 0, 1 and 2 respectively. Reaction 0 is the non-catalyzed decomposition observed in open pan thermogravimetric experiments. Reaction 1 is the hydrolysis of cellulose in the presence of water. Reaction 2 is the secondary reaction of the intermediates in the sealed sample holder. The rates of reactions 1 and 2 depend on the amount of water vapors in the system.

**Table 4:** Kinetic modes and parameters collected from literature

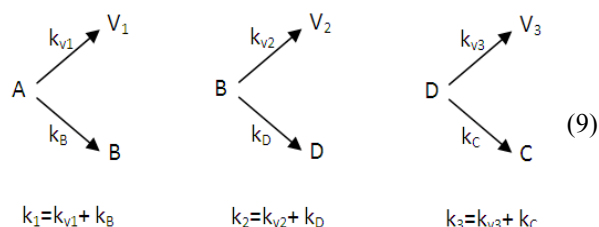
Author & Scheme of Reaction	Kinetic Model	Kinetic Parameters	
		Activation energy E or E <sub>i</sub> (kJ/mol)	Pre-exponential factor A or A <sub>i</sub> (s <sup>-1</sup> )
Kung <sup>[10]</sup> - One step global mechanism	$\frac{\partial \rho}{\partial t} = -a_p \frac{(\rho - \rho_f) e^{-E_p / RT(t)}}{(1 - \frac{\rho_f}{\rho_w})}$	30 kcal/mole <sup>[45]</sup>	5.25 × 10 <sup>7</sup> <sup>[45]</sup>
Thurner <i>et al</i> <sup>[14]</sup> - Three Competing reactions model with primary reactions only	$\frac{dY_i}{dt} = -k_i Y_i; \quad k_i = A_i \exp(-E_i / RT)$	84 112.7 106.5	5.16 × 10 <sup>6</sup> 1.48 × 10 <sup>10</sup> 2.66 × 10 <sup>10</sup>
Alves <i>et al</i> <sup>[16]</sup> - Six independent first order reactions	$-\frac{\partial \rho_i}{\partial t} = \rho_i k_i \exp(-E_i / RT)$	83, 146, 77, 60, 139, 130	0.70 × 10 <sup>5</sup> , 0.20 × 10 <sup>10</sup> , 0.43 × 10 <sup>4</sup> , 0.29 × 10 <sup>2</sup> , 0.51 × 10 <sup>7</sup> , 0.32 × 10 <sup>6</sup>
Koufopoulos <i>et al</i> <sup>[33]</sup> - Mechanism with secondary interactions between charcoal and volatiles, described by first order kinetics	$\frac{dC_B}{dt} = -k_1 C_B^{n_1} - k_2 C_B^{n_2}$ $\frac{dC_{G_1}}{dt} = k_1 C_B^{n_1} - k_3 C_{G_1}^{n_2} C_{C_1}^{n_3}$ $\frac{dC_{C_1}}{dt} = k_2 C_B^{n_2} - k_3 C_{G_1}^{n_2} C_{C_1}^{n_3}$ $\frac{dC_{G_2}}{dt} = k_3 C_{G_1}^{n_2} C_{C_1}^{n_3}$ $\frac{dC_{C_2}}{dt} = k_3 C_{G_1}^{n_2} C_{C_1}^{n_3}$ $k_1 = A_1 \exp[(D_1 / T) + (L_1 / T^2)]$ $k_2 = A_2 \exp[(D_2 / T) + (L_2 / T^2)]$ $k_3 = A_3 \exp[-E_3 / R_c T]$	Constants for E <sub>1</sub> and E <sub>2</sub> D <sub>1</sub> =17254 K D <sub>2</sub> =10224K L <sub>1</sub> =-9061227K <sup>2</sup> L <sub>2</sub> =-6123081K <sup>2</sup> and E <sub>3</sub> =81	A <sub>1</sub> =9.973 × 10 <sup>-5</sup> A <sub>2</sub> =1.068 × 10 <sup>-3</sup> A <sub>3</sub> =5.7 × 10 <sup>5</sup>
Bonnefoy <i>et al</i> <sup>[46]</sup> - One step endothermic devolatilization kinetic model	$\frac{\partial \rho}{\partial t} = -A \rho \exp(-E / RT)$	120	5 × 10 <sup>6</sup>
Janse <i>et al</i> <sup>[26]</sup> - Lumped consecutive reaction scheme similar to Di Blasi <sup>[47]</sup>	For reactions (1)-(3) $r_i = A_i e^{(-E_i / R_g T)} (1 - \varepsilon_m - \varepsilon_M) \rho_w$ For reactions (4),(5) $r_i = A_i e^{(-E_i / R_g T)} \frac{y_t P M_t}{RT}$	177.0 <sup>[48]</sup> 149.0 <sup>[48]</sup> 9.28 × 10 <sup>9</sup> <sup>[48]</sup> 125.0 <sup>[48]</sup> 87.8 <sup>[24]</sup> 87.8 <sup>[24]</sup>	1.11 × 10 <sup>11</sup> <sup>[48]</sup> 3.05 × 10 <sup>7</sup> <sup>[48]</sup> 8.60 × 10 <sup>4</sup> <sup>[24]</sup> 7.70 × 10 <sup>4</sup> <sup>[24]</sup>
Hagge <i>et al</i> <sup>[49]</sup> , Bryden <i>et al</i> <sup>[50]</sup> - one step multi reactions kinetic model	Rate of production of wood: $\dot{\omega}_w = -(k_1 + k_2 + k_3) \rho_w f$ Rate of production of char: $\dot{\omega}_c = k_3 \rho_w f + \varepsilon k_5 \rho_T f$	88.6 <sup>[14]</sup> 112.7 <sup>[14]</sup>	1.44 × 10 <sup>4</sup> <sup>[14]</sup> 4.13 × 10 <sup>6</sup> <sup>[14]</sup>

Table 4: Continued

	Rate of production of moisture: $\dot{\omega}_T = k_1 \rho_w f - \varepsilon f (k_4 + k_5) y_T \rho_g$	106.5 <sup>[14]</sup>	7.38 × 10 <sup>5</sup> <sup>[14]</sup>
		107.5 <sup>[24]</sup> 107.5 <sup>[51]</sup> 88 <sup>[52]</sup>	4.28 × 10 <sup>6</sup> <sup>[24]</sup> 1 × 10 <sup>5</sup> <sup>[51]</sup>
	Rate of production of tar: $\dot{\omega}_V = k_6 \rho_M f - k_7 G_V$		
	Rate of production of vapor: $\dot{\omega}_g = (k_1 + k_2) \rho_w f - \varepsilon f k_5 \rho_T + k_6 \rho_M - k_7 G_V$		
	Rate of production of gas:	(k <sub>7</sub> =125cm <sup>-1</sup> ) <sup>[52]</sup>	5.13 × 10 <sup>10</sup> <sup>[52]</sup>
Peters <i>et al</i> <sup>[53]</sup> - Single step pyrolysis model	For beech wood: 123.1 $r_i = k_0 \exp\left(\frac{-E_a}{RT}\right) \prod_{k=1}^3 c_{i,k}$	For beech wood: 1.35 × 10 <sup>9</sup> For wood char: 149.38	For wood char: 3.01 × 10 <sup>2</sup>
Bellais <i>et al</i> <sup>[54]</sup> - Two parallel reactions of wood decomposition into volatiles and char	w <sub>i</sub> = k <sub>i</sub> m <sub>wood</sub> i = char or volatiles	E <sub>1</sub> =74.13; E <sub>2</sub> =54.919	A <sub>1</sub> =10.356; A <sub>2</sub> =114
Branca <i>et al</i> <sup>[43]</sup> - Proposed a three step mechanism involving m independent parallel reactions	$\frac{\partial Y_i}{\partial t} = -k_i c_i$	E <sub>1</sub> =147 ; E <sub>2</sub> =193; E <sub>3</sub> =181;	A <sub>1</sub> =2.527×1011; A <sub>2</sub> =1.379×1014; A <sub>3</sub> =2.202×1012
Grioui <i>et al</i> <sup>[44]</sup> - Developed a two-stage, semi-global multi-reaction kinetic model, involving three primary pseudo components and an intermediate solid	$\frac{dm_{A_1}}{dt} = -k_1 m_{A_1}$ $\frac{dm_{A_2}}{dt} = -k_2 m_{A_2}$ $\frac{dm_{A_3}}{dt} = -k_3 m_{A_3}$ $\frac{dm_{C_2}}{dt} = \gamma_2 k_2 m_{A_2}$ $\frac{dm_B}{dt} = \beta k_3 m_{A_3} - k_4 m_B$ $\frac{dm_{C_3}}{dt} = \gamma_3 k_4 m_B$	105.89, 106.78, 169.56, 51.04	3.5 × 10 <sup>7</sup> , 3.72 × 10 <sup>6</sup> , 7.23 × 10 <sup>11</sup> , 3.4 × 10 <sup>11</sup>
Shen <i>et al</i> <sup>[15]</sup> - Used Thurner <i>et al</i> <sup>[14]</sup> one-step, multi reactions kinetic model	$\frac{\partial \rho_w}{\partial t} = -(k_1 + k_2) \rho_w$ $\frac{\partial \rho_c}{\partial t} = k_1 \rho_w$ $\frac{\partial \rho_g}{\partial t} = k_2 \rho_w$ $\frac{\partial \rho_l}{\partial t} = -k_3 \rho_l$ $\frac{\partial \rho_v}{\partial t} = k_3 \rho_l$	106.5 <sup>[14]</sup> 88.6 <sup>[14]</sup> 88 <sup>[21]</sup>	7.38 × 10 <sup>5</sup> <sup>[14]</sup> 1.44 × 10 <sup>4</sup> <sup>[14]</sup> 5.13 × 10 <sup>10</sup> <sup>[21]</sup>

Boutin *et al*<sup>[41]</sup> in his recent work on flash pyrolysis of cellulose pellets, developed kinetic pathways derived from the Varhegyi *et al*<sup>[40]</sup> (Eq. 8) model. This simplified pathway implies only the phenomena occurring inside the solid and liquid phases and does not include the process occurring in the gas phase.

**Other Models:** Branca *et al*<sup>[42]</sup> have studied the kinetics of the isothermal degradation of wood in the temperature range 528–708 K, suggested the following semi-global reaction mechanism:



Where, A is wood, B and D are intermediate solid-phase reaction products.  $V_1$ ,  $V_2$  and  $V_3$  are product classes which lump the volatiles generated in the three stages and C the final charred solid residue. The reaction rates are assumed to be present in the usual Arrhenius dependence on temperature and to be linearly dependent on the mass of the reactant, A, B and D. Recently, Branca *et al*<sup>[43]</sup> also proposed a three step mechanism for non isothermal pyrolysis with wider heating rate (3-108 K/min) here the overall mass loss rate is a linear combination of the single fraction rates.

Grioui *et al*<sup>[44]</sup> developed a two-stage, semi-global multi-reaction kinetic model where wood is subdivided into three pseudo-components  $A_1$ ,  $A_2$ ,  $A_3$ ; each of them corresponds to specific kinetic law and a mass fraction.

The proposed kinetic scheme is

- $A_1$  (1<sup>st</sup> pseudo component of olive wood)  $\rightarrow G_1$  (gas)
- $A_2$  (2<sup>nd</sup> pseudo component of olive wood)  $\rightarrow \gamma_2 C_2$  (charcoal) +  $G_2$  (gas)
- $A_3$  (3<sup>rd</sup> pseudo component of olive wood)  $\rightarrow \beta B$  (intermediate solid) +  $G_3$  (gas)
- B (intermediate solid)  $\rightarrow \gamma_3 C_3$  (charcoal) +  $G_4$  (gas)

The mass fractions ( $\beta$ ) of the intermediate product (B) and those of the non-degradable solid “charcoal” ( $\gamma_2$  and  $\gamma_3$ ) depend on temperature.

One step global models, competing and parallel reaction models are weak when compared to models

with secondary tar cracking, as they assume a constant ratio of the char to volatiles yield. The above simple correlation models 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. In order to account wood variety and shrinkage factors, it is necessary to formulate semi-global kinetic mechanisms to estimate reliable kinetic data and investigate the dependence of physical properties on temperature and solid composition. The different kinetic model equations and the parameter values collected from literature are given in Table 4.

**Kinetic Parameters:** Table 4. Kinetic modes and parameters collected from literature

**Conclusions:** Among the reaction mechanisms, the secondary tar cracking schemes, particularly the extended Koufopoulos kinetic mechanism<sup>[34]</sup> is the most widely used schemes which cover most of the possible aspects of pyrolysis reactions. The scheme along with Koufopoulos kinetic parameters<sup>[33]</sup> can predict reasonably accurate primary and secondary product distributions along with wide heating rates and temperature range.

Experimental works to produce reliable kinetic data are very limited in biomass pyrolysis kinetic modeling; more of this will strengthen the existing models. The overall kinetics of the bed of particles has to be considered where, the effect of the size and shape of the particle and the effect of the neighboring particles should be accounted for. Preferably it is necessary to develop generalized kinetic models which can be applied to any size and shape of the particle. Most of the models reported here are based on single particle and the kinetic parameters proposed cannot be used directly for the modeling of the pyrolysis of zone of the biomass gasifier. Also, development of kinetic models along with semi global kinetic mechanisms accounting generalization of wood variety is necessary.

**Nomenclature:**

- $a_p, A_i$  Pre-exponential factor ( $s^{-1}$ )
- $E_p, E_i$  Activation energy (kJ/mol)
- $R, R_g$  Universal gas constant (J/mol K)
- $T$  temperature (K);  $T_0$  - initial temperature(K);  $T_f$  - final temperature, K
- $\rho_f$  Final density of solid ( $kg/m^3$ );  $\rho_w$  Virgin wood density ( $kg/m^3$ );  $\rho_T$  - Density of tar ( $kg/m^3$ )
- $\rho_C$  Density of char ( $kg/m^3$ );  $\rho_g$  - Density of

- volatiles (kg/m<sup>3</sup>);  $\rho_l$  - Density of liquid (kg/m<sup>3</sup>)
- $\rho_v$  Density of vapor (kg/m<sup>3</sup>);  $\rho_M$  - Density of moisture (kg/m<sup>3</sup>)
- CB concentration of virgin biomass, kg/m<sup>3</sup>
- CG1 concentration of gases and volatiles1, kg/m<sup>3</sup>
- CC1 concentration of char1, kg/m<sup>3</sup>
- CG2 concentration of gases and volatiles2, kg/m<sup>3</sup>
- CC2 concentration of char2, kg/m<sup>3</sup>
- $k_i$  rate constants, s<sup>-1</sup>
- n1, n2, n3 orders of reactions
- $\epsilon_m$  micro pore porosity;  $\epsilon_M$  macro pore porosity
- P pressure (pascal)
- $M_t$  Tar molar mass (kg/mol)
- $y_t$  Tar fraction
- f Shrinkage factor
- $\epsilon$  Void fraction
- $G_v$  mass flux of water vapor
- $\beta$  mass fraction of intermediate product ;  $\gamma_2$ ,  $\gamma_3$  mass fractions of charcoal
- $m_{A1}$ ,  $m_{A2}$ ,  $m_{A3}$ ,  $m_{C2}$ ,  $m_B$  mass of the constituents  $A_1$ ,  $A_2$ ,  $A_3$ ,  $C_2$ , B. (kg)

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