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Pyrolysis of Wood for Charcoal Production: A Basic Review of Existing Models

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ABSTRACT

The pyrolysis theory is employed to elucidate the phenomenon occurring within charcoal kilns. Pyrolysis is a thermos-chemical process that involves applying heat in an oxygen-depleted atmosphere to transform organic material into volatile substances (liquids and gasses) and a carbon-rich solid (char). The pyrolysis of wood is a multifaceted phenomenon that encompasses various mathematical equations pertaining to heat transport, drying, fluid dynamics of liquids and gases, anisotropy, surface downturn, numerous chemical reactions, non-linear algebraic partial differential equations which are employed to characterise the process. Researchers across the World have carried out studies on the modelling of the charcoal production process. This paper presents review of existing wood pyrolysis models, contributions and flaws. Basic mathematical models adopted for pyrolysis of wood during charcoal production in the kiln were reviewed. Aspects such as: elemental composition, char and volatiles substances (liquids and gases) were put into considerations. The review of both the physical and chemical processes of pyrolysis was carried out with more emphasis on wood kinetic reaction models and modelling assumptions.

1. Introduction

Wood typically undergoes pyrolysis at temperatures above 200 °C and persists until reaching temperatures between 450-500 °C, with variations observed based on the specific wood species involved. Pyrolysis is a multifaceted phenomenon that encompasses various mathematical equations pertaining to heat transport, drying, fluid dynamics of liquids and gases, anisotropy, surface downturn, and numerous chemical reactions. Additionally, the study of pyrolysis necessitates the utilization of numerous nonlinear algebraic partial differential equations, which are employed to accurately characterize the process. This undertaking requires significant computational resources and labour [1].

1.1 Pyrolysis Process

Pyrolysis comprises both the physical and chemical process. The process involves in pyrolysis are transfer of heat from the source to raise temperature of the inside fuel, release of volatiles and char formation, movement of volatiles as an outcome of heat transfer amongst hot volatiles and colder fuel components for producing tar [2]. The chemistry of the fuel has a substantial

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influence on the chemical processes involved in pyrolysis. The ultimate analysis provides a comprehensive breakdown of the elemental makeup of a given fuel as shown in Table 1. Proximate analysis is a method that can provide a comprehensive understanding of the distribution of major pyrolysis products, namely volatiles and char, in terms of their respective percentages as presented in Table 2 [3].

Table 1 - Ultimate Analysis by Weight (%) of a Typical Dry Wood [3]

Wood Type	H	C	N	O	Ash
Hard Wood	6.5	50.7	0.5	41.7	0.9
Soft Wood	6.2	52.8	0.1	39.6	1.0

Table 2 - Proximate Analysis by Weight (%) of a Typical Dry Wood [3]

Wood Type	Volatile Substance	Fixed Carbon	Ash
Hard Wood	77.4	19.3	3.3
Soft Wood	77.1	22.1	1.5

1.2 Composition of Wood

Three primary substances make up wood which are approximately 50% cellulose, 25% hemicellulose, and 25% lignin. Glucose makes up the polymer known as cellulose. Hemicellulose is a polysaccharide that produces sugars. Lignin, on the other hand, is a complex chemical substance with several rings. The pyrolysis process yields a combination of products that encompasses every anticipated product that was produced upon the separate pyrolysis of every of its three main components. The process of pyrolysis for each distinct component is inherently intricate and influenced by a multitude of factors. The process of combination is characterized by its complexity, as it is influenced by numerous elements that dictate the rate of reactions and result in a vast array of potential products [3].

1.3 Pyrolysis Modelling

The theoretical characterization of pyrolysis involves a set of equations that regulate chemical kinetics, heat transfer, and mass transfer. Several researchers have conducted studies on the design and performance of charcoal kiln [1]. However, there is limited information on the contemporary studies based on modelling of charcoal kiln which functions are to serve as a diagnostic instrument for assessing the significance of different system parameters and to offer system features that are valuable to experimental researchers [3]. The modelling of pyrolysis is highly advantageous as it gives mathematical depiction of the chemical and physical process that occur during pyrolysis characterized by a set of equations, the amalgamation of which can yield significant quantitative insights into the underlying process [3]. Thus, this research aims to review the recent modelling techniques employed in charcoal kiln with a view to obtaining an optimum performance in industries and commercial purposes.

2. Review of Models of Wood Pyrolysis

The chemical processes involved in the pyrolysis of wood are highly intricate, encompassing a multitude of intermediate steps. As a result, several kinetic models have been developed over the course of history to better understand this phenomenon. To date, the development of a comprehensive kinetic model that incorporates all relevant characteristics remains a challenging endeavor. All of the currently available pyrolysis modeling studies are either variations or adaptations of the model proposed by Bamford and Crank [4]. First-order kinetics is used in the proposed model to account for heat generation and conduction in a pyrolyzing solid. However, it neglects to account for the influence of temporal variations in density.

Few decades ago, Fan [5] presented a heat and mass transfer model for biomass particles. This model is characterized by a first-order dependence on the initial particle concentration. However, it does not account for product concentrations due to the omission of secondary reactions in the analysis. Kansa and Perlee [6] introduced a momentum equation to describe the motion of pyrolysis gases within a solid material. The model's efficacy is compromised due to the utilization of arbitrary boundary conditions in formulating the heat and momentum balance equation.

Babu and Chaurisa [7] created a secondary reaction kinetic model for pyrolysis kinetics in response to the limitations of the current models. A computational model was employed to investigate the pyrolysis process of a solitary biomass particle, taking into account the influence of heat transmission phenomena within the particle. The research conducted by Babu and Chaurasia [7] demonstrated a strong alignment with the empirical evidence in contrast to earlier models. Peter and Christian [8] employed one-stop global models to degrade organic fuel down to volatiles and coke, with yield of char. The model's lack of representation of the real situation has resulted in its infrequent inclusion in the literature.

The dynamics of wood's isothermal deterioration within the 528–708 K temperature range were studied by Branca *et al.* [9] in 2003.The researchers developed a semi-global response mechanism based on their findings. The rate of the reaction was hypothesized to be influenced by temperature according to the Arrhenius equation, as well as by the mass of reactants A, B, and C in a linear manner. In 2003, Branca and others devised a unique three-step method for non-isothermal pyrolysis, which encompassed a broad range of heat rates spanning from 3 to 108k/min. The rate at which mass is lost can be expressed as a uniformly pair of individual percentage rates of fractions. Grioui *et al.* [10] created a kinetic model that incorporates many reactions on a semi-global scale. Wood can be split into three pseudo-components, A1, A2, and A3, in the suggested model. Each of these components has a distinct law of kinetics along with global model of mass fraction. The models used the assumption of a consistent ratio between the yield of char and volatiles. The applicability of the model was limited to the specific system upon which it was originally developed.

Prakash and Karunanithi [11] provided an elucidation of the advancement in kinetic modelling pertaining to biomass pyrolysis. The fundamental kinetic constants, kinetic models, and chemical reaction mechanisms required for the pyrolysis process were thoroughly examined and explained.

Lautenberger and Fernandez [12] constructed a Generalized Pyrolysis Model (GPYRO) with the aim of simulating the process of oxidative pyrolysis in white pine slabs, specifically under non-flaming conditions. The applied model utilized a conservative equation to analyze the behavior of gaseous and solid mass, energy species, and gas momentum. This analysis aimed to determine the temperature, mass fractions, and pressure profiles associated with the decomposition process of wood. The model successfully incorporated variables such as mass loss rate, surface temperature, and in-depth temperatures, demonstrating a strong alignment with the experimental data.

The study conducted by Park *et al.* [13] involved both theoretical and experimental investigations into the pyrolysis process of a dry wood sphere with a diameter of 25.4mm. The experiments were conducted in a vertical tube furnace, and the temperature range examined was from 638 to 879 K. The researchers took into consideration the loss of mass and temperature during the process. The proposed model elucidates three concurrent endothermic events that result in the generation of tar, gas, intermediate solids, and the breakdown of tar into char by an exothermic reaction. The model exhibited a high degree of agreement with the empirical data. Grieco and Baldi [14] proposed a kinetic model for dynamic and isothermal pyrolysis test on dried beech and pine woods. The model observed the two different stages during pyrolysis which involves unreacted wood and further reaction of the product not yet escaped from the solid matric. In the pyrolysis study, wood pellets were investigated for kinetics of total weight loss, gas and tar production at heating rate of 0.05 and 1 K/s.

A wet wood pyrolysis model was created by Ding *et al.* [15], accounting for the impacts of moisture, char oxidation, flame radiation, and chemical kinetics. The Arrhenius expression for the moisture drying reaction of dry wood pyrolysis was a single, one-step, nth-order expression. By expressing the mass of gas fluxes as a function of radiation flux and thickness, a fitting correlation between the variables was found. In their investigation of the solar pyrolysis of beech wood pellets, Sorio *et al.* [16] employed the computational fluid dynamics (CFD) tool ANSYS FLUENT 14.0 to model the biomass degrading process of wood. The procedure was run in two temperature ranges: 600–2000 ˚C. The created model is a multi-step, intricate kinetic framework that includes mass (species) transfer, surplus heat, and a secondary tar reaction. The model results agreed well with the experimental data.

A study on the iso-conversional determination of reaction model for pyrolysis of wood, straw, and sewage sludge was conducted by Sobek and Weile [17] in 2020. Although the activation energy for waste biomass was not measured, the profile of the reaction model was established using iso-conversional parameters. In 2023, Flity *et al.* [18] investigated the heat degradation of spruce wood and simulated it in an interior atmosphere at the cone calorimeter size. Using Python, a 3D heat transfer model was created to mimic the degradation of wood at the cone scale. Wood's anisotropic properties were modeled. Mueller*et al.* [19] used a basic CFD model to predict flame spread in quiescent (wind-free) pine needle beds. The model proved that the fuel bed's characteristics affect how quickly flames spread. The summary of the individual authors’ contributions and flaws are as presented in Table 3.

Table 3 - Summary of the Existing Wood Pyrolysis Models

S/N	**Authors**	**Year**	**Contributions**	**Flaws**
1	Bamford *et al.*	[4]	Model for heat conduction and generation assuming first order kinetics	No consideration for change of density as a function of time
2	Fan	[5]	First order heat and mass transfer model in a biomass particle	It cannot analyse product concentrations because secondary reactions were not considered
3	Kansa *et al.*	[6]	Model for momentum equation for the motion of pyrolysis gas within the solid	Suitable kinetic mechanism was not developed and the momentum balance equation was based on arbitrary boundary condition
4	Babu and Chaurisa	[7]	Kinetic model for secondary reactions in pyrolysis kinetics	It considered only one single step first order reaction
5	Peters and Christian	[8]	One step global model of decomposition of organic fuel into volatiles and coke with a fixed char yield	The model does not represent the real situation

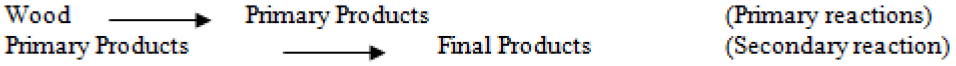
6	Branca *et al.*	[9]	Model for isothermal degradation of wood in temperature range 528-708k, also three step mechanism for non-isothermal pyrolysis heating 3-108k/min	Arrhenius dependence on temperature and mass of the reactants
7	Grioui	[10]	Two-stages, semi-global multi-reaction kinetic model pyrolysis of wood	It assumes constant ration of char to volatiles yield and does not consider varieties of wood
8	Prakash	[11]	Kinetic model of biomass pyrolysis	Experimental result does not conform well with real life situation
9	Lautenberger *et al.*	[12]	Developed a generalised pyrolysis model (GPYRO) for oxidative pyrolysis in white pine slabs under non-flaming condition.	The process only considered pyrolysis under non-flaming conditions.
10	Park *et al.*	[13]	Developed theoretical and experimental investigations into pyrolysis process of a dry wood sphere of 25.4mm diameter	It only considered mass and temperature loss but failed to consider emission of gases.
11	Grieco *et al.*	[14]	Proposed a kinetic model for dynamic and isothermal pyrolysis test on dried beech and pine wood.	There were a lot of heat loss resulting to unreacted wood.
12	Ding *et al.*	[15]	Developed a pyrolysis model of a wet wood taking into considerations effects of moisture, char oxidation, flame radiation and chemical kinetics.	There were a lot of mass and heat loss during the process.
13	Sorio *et al.*	[16]	Studied the solar pyrolysis of beech wood pellets using CFD platform ANSYS FLUENT 14.0 to model the biomass degradation process of wood.	There were excessive heat and mass (species) transport in the particle.
14	Sobek *et al.*	[17]	Studied is conversional determination of reaction model for pyrolysis of wood, straw and sewage sludge	The activation energy for waste biomass was not estimated.
15	Flity *et al.*	[18]	Studied thermal degradation of spruce woo and simulate it at the cone calorimeter scale under inert atmosphere using PYTHON	It only considered heat loss but failed to consider emission of gases.
16	Mueller *et al.*	[19]	Developed a simple CFD model and simulate flame spread in pine needle bed quiescent (no-wind) conditions.	It only considered emission of gases but does not consider mass and heat loss.

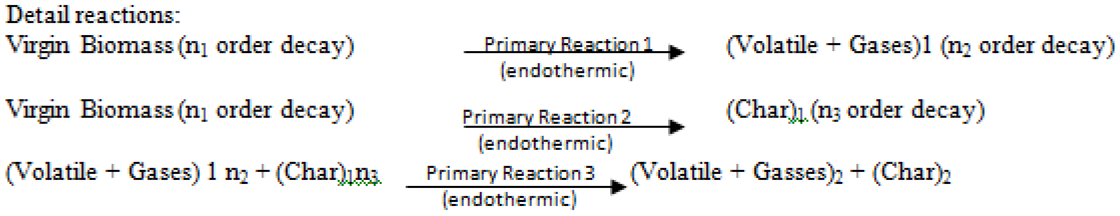
2.1 Wood Kinetic Reaction Models

There are three primary wood kinetic reaction models, namely:

(i) The model is a single-step global reaction model.
(ii) The model is a single-step numerous parallel reactions model.
(iii) The multi-step reactions model is a theoretical framework used to describe chemical reactions that occur through a series of consecutive steps [7].

The authors Babu and Chaurasia [7] provide a description of the kinetic model for multi-step reaction mechanisms.





The presented model illustrates the process of biomass breakdown, wherein reaction 1 represents the conversion of biomass into volatiles and gases, while reaction 2 depicts the formation of char. Reaction 3 results in the production of several forms of volatiles, gases, and char with distinct compositions. The pyrolysis simulation encompasses the major reactions 1, 2, and 3, as well as the secondary reaction [7]

The heat of pyrolysis, also known as the heat of reaction, pertains to the quantity of thermal energy needed to disrupt the molecular bonds inside wood. This parameter holds significant importance in the modeling of pyrolysis processes. In the context of the kinetic scheme of huge wood logs, it is not feasible to use the concepts of positive or negative enthalpy [7]

There is a consensus among researchers that the main pyrolysis reaction of wood and its constituents is characterized by an endothermic process, whereas the secondary charring reaction is known to be exothermic [10].

2.2 Assumptions in Modelling the Pyrolysis of Wood for Charcoal Production

(i) Volatiles, Air and water vapour constitutes the gas phase.
(ii) Raw wood, charcoal and water constitute the solid phase.
(iii) It is assumed that there is free water in solid phase though bound water not modelled.
(iv) The shrinked volume of solid is not modelled.
(v) The initial specific heat capacities are not temperature dependent.
(vi) It is the final model that account for radiation.
(vii) Most of the pyrolysis modelling is assumed to be one-step endothermic reaction forming charcoal and volatiles.
(viii) Pyrolysis does not properly account for formation of liquid tar.

3. Mathematical Modelling Equations

The following are the mathematical formulas that explain mass, momentum, and material balance spanning distinct spatial and temporal elements, like cells or finite volumes, and that illustrate how sources and sinks, as well as time, affect the diffusion of heat through convection and conduction:

3.1 Continuity Equations

Equations 1 and 2 reflect the continuity equations of the gas-solid phases that describe the temperature and concentration gradients inside the isotropic spherical particles [20]:

$$\frac{\partial}{\partial t}(\varepsilon_g \rho_g) + \nabla(\rho_g \cup) = \omega_d + \omega_p \tag{1}$$

$$\frac{\partial}{\partial t}(\varepsilon_s \rho_s) = -\omega_d - \omega_p \tag{2}$$

Where:
U= superficial gas velocity vector
ω_d= mass drying, ω_p = pyrolysis rates,ρ_g= density of gas
ρ_s= density of solid phases, ε_g= volume of porosity of gas
ε_s= volume of porosity of solid phase

3.2 Momentum equation

Equation 3 provides the momentum equation of the gas phase to explain the anisotropic impact that is seen when heating wood either perpendicularly or parallel to the grain direction [20]:

$$\frac{\partial}{\partial t}(\varepsilon_g \rho_g U) + \nabla.(\rho g U U) = \nabla.(\rho_g v_g \nabla U) = \nabla p + (\rho g, a - \rho g) g - \rho g K_v U - \rho g K_i U U \tag{3}$$

Where:
p = ambient perturbation pressure, g = acceleration due to gravity
P_g= atmospheric gas density, while v_g = kinematic viscosity of gas-phase
K_i = inertial resistance coefficient, K_v= viscous flow resistance.

3.3 Energy Equations

The gas- solid phase energy equation translating heat accumulation as a result of heat flow and reactions over time with material balance in the earth kiln were expressed in equations 4 and 5 [21]:

$$\frac{\partial}{\partial t}\left(\varepsilon_g \rho_g C_{pg} T_g\right) + \nabla.\left(\rho_g C_{pg} T_g\right) = \nabla.\left(\rho_g \frac{V_g}{\sigma_t} \nabla T_g\right) - Q_{gs} \tag{4}$$

$$\frac{\partial}{\partial t}\left(\varepsilon_s \rho_s C_{pg} T_s\right) = \nabla.\left(k_s \nabla T_s\right) + Q_{gs} - \omega_p H_p - \omega_d H_d \tag{5}$$

Where:

H_p = Heat of pyrolysis (= 150 kJ/kg)
H_d=Heat of evaporation (= 2.25 MJ/kg)
Q_{gs}= Interphase heat transfer rate

3.4 Equations for Gas-Phase Species

Equations 6, 7, and 8 provide the species equation within the gas phase to express the conservation and concentration of the species in the gas phase for a porous medium [21].

$$\frac{\partial}{\partial t}\left(\varepsilon_g \rho_g Y_v\right) + \nabla.\left(\rho_g U Y_v\right) = \nabla.\left(\rho_g \frac{V_g}{\sigma_v} \nabla Y_g\right) - \omega_p Y_{vs,0} \tag{6}$$

$$\frac{\partial}{\partial t}\left(\varepsilon_g \rho_g Y_h\right) + \nabla.\left(\rho_g U Y_h\right) = \nabla.\left(\rho_g \frac{V_g}{\sigma_v} \nabla Y_h\right) - \omega_d \tag{7}$$

$$Y_a = 1 - Y_v - Y_b \tag{8}$$

Where: the abbreviations Y_a, Y_h, and Y_v represent the mass fractions of air, water vapor, and volatiles, respectively, in gaseous phase.

3.5 Models for Solid-Phase Species

Equations 9, 10, and 11 provide the species equations of the solid phase that characterize the conservation and concentration of the species in the solid phase of the material [21]:

$$\frac{\partial}{\partial t}\left(\varepsilon_s \rho_s Y_w\right) = \nabla.\left(\rho_s D \nabla Y_w\right) - \omega_d \tag{9}$$

$$\frac{\partial}{\partial t}\left(\varepsilon_s \rho_s Y_c\right) = \nabla.\left(\rho_s D \nabla Y_c\right) + \omega_p \frac{1 - Y_{vs,0}}{Y_{vs,0}} \tag{10}$$

$$Y_r = 1 - Y_w - Y_c \tag{11}$$

Where Y_{vs},0 = mass fraction of prospective volatile matter (in solid phase), Y_c is the mass fraction of charcoal (in solid phase), Y_w = mass fraction of water (solid phase) and so on.

3.6 The General Transport Formula

As demonstrated in equation 12, the provided models can be transformed into a generic transport model of θ by utilizing any typical parameter θ of the fluid, like species, momentum, mass, or energy [21].

$$\frac{\partial(\rho \emptyset)}{\partial t} + \frac{\partial}{\partial x_i}\left(\rho \emptyset l_j\right) = \frac{\partial}{\partial x_j}\left(\lceil ø \frac{\partial \emptyset}{\partial x_j}\right) + S\emptyset \tag{12}$$

Where:

⌈=transport coefficient of the general variable ø.

3.7 The System's State Equation

The system's perfect gas state equations are represented by equation 13 [20]:

$$P = \rho RT = \rho \frac{N_{mi}}{i=l^{M_i}} \tag{13}$$

Where:

mi = the species' mass fraction
Mi = species' molecular weight

4. Conclusion

In conclusion, Wood pyrolysis modelling has received tremendous attentions throughout the World. Consequently, it is recognized that biomass is a renewable energy source that is sustainable and has the ability to contribute to a steady supply of energy worldwide. The review shows that thermo-chemical characteristics of wood pyrolysis process are parameters of crucial importance in charcoal production. In addition, the chemistry of the fuel has a substantial influence on the chemical process involved in pyrolysis. Therefore, the determination of whether pyrolysis reaction exhibit endothermic or exothermic behaviour holds a significant importance with the field of modelling. The existing models majorly studied thermal decomposition of wood and the chemical reaction involved but failed to properly investigate heat loss and emission of gases. There is need for development of models with minimum assumptions that will critically address the aspect of heat loss and emission minimization.

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