Parametric Studies of Wood Pyrolysis Particles

W. Afef, A. Mohamed Ammar, G. Kamel, O. Ahmed

Abstract—In the present study, a numerical approach to describe the pyrolysis of a single solid particle of wood is used to study the influence of various conditions such as particle size, heat transfer coefficient, reactor temperature and heating rate. The influence of these parameters in the change of the duration of the pyrolysis cycle was studied. Mathematical modeling was employed to simulate the heat, mass transfer, and kinetic processes inside the reactor. The evolutions of the mass loss as well as the evolution of temperature inside the thick piece are investigated numerically. The elaborated model was also employed to study the effect of the reactor temperature and the rate of heating on the change of the temperature and the local loss of the mass inside the piece of wood. The obtained results are in good agreement with the experimental data available in the literature.

Keywords—Wood, Pyrolysis, Modeling, Convective heat transfer, Kinetic.

I. INTRODUCTION

THERMAL conversion of the biomass offers effective and economic process to provide the solid fuels, liquid and gas and or to produce chemical derived from biomass [1]. The pyrolysis process consists of the thermal degradation of biomass feedstock, in the absence of oxygen/air, driving behind the full products (charcoal), liquids (tar) and formation of gas (H_2, CO_2, CO…). In fact, the study of pyrolysis gains the increasing importance, because it is implied in any heat treatment of the biomass particles. However, pyrolysis is a complex process which can be prone to the influence of several factors such as the types of raw materials used, the heating rate and the pyrolysis temperature and the type of reactor, driving with a complex mixture of components [2].

Many models in the literature aim at representing the pyrolysis of one wood particle [3]-[10]. Calling upon two disciplines, the heat and mass transfer in porous environment and the chemical kinetics, the majority of the authors developed models with the aim of studying the behavior of wood and more generally of the biomass according to the temperature. The modeling of the thermal degradation of wood is complex because of the close coupling between the chemicals and the processes of heat and the mass transfer. To study the decomposition of wood several models are presented in the literature. The first mathematical model for the wood pyrolysis was proposed by [11]. According to this model, the equation for heat conduction in a pyrolyzing solid is combined with those for heat generation, assuming first order kinetics. Thereafter, [12] developed a model which demonstrates that the pyrolysis reaction comprises endothermic and exothermic phases. Pyle and Zaror [13] defined models of the kinetics of the primary pyrolysis of wood particle. These models predict the evolution of the density and the temperature of the solid residues. However, [14] defined a model of the pyrolysis of a wood particle based on two primary and secondary reactions. Using this model, it is possible to predict the change of the temperature and the solid state of conversion wood. Di Blasi et al. [15] carried out experiments on pyrolysis of wood cylinder to investigate the role of wood variety on the characteristics of mass loss and temperature dynamics, yield of char, gas and liquid products and gas composition. Also, [16], [17] presented a more refined model considering the contracting of a particle of biomass during pyrolysis based on the coupling of the heat transfers with the chemical kinetics of pyrolysis. Babu et al. [4] developed a model of pyrolysis based on the coupling of the transfers of heat with the chemical kinetics of pyrolysis. They introduced into their model the coefficient of convective heat transfer and they showed its effect on Reynolds and Prandtl numbers. Grioui et al. [18] proposed a kinetic model comprising four stoechiometric stages. This model is used to study the pyrolysis of a cylindrical wood piece and the operational influence of the parameters on the mass loss and the profiles of temperatures within the particle. This model appears to be a rather simple and reliable numerical tool to test the validity of the different hypothesis concerning kinetic parameters, thermophysical properties and heat and mass transfer during wood carbonization in comparison with experiments. Abbassi et al. [19] investigated pyrolysis of biomass both experimentally and numerically. The reactor was divided into three zones that were treated as perfectly stirred reactors. Tar as a major product of pyrolysis was assumed to crack into methane CH4, carbon monoxide CO, carbon dioxide CO2 and hydrogen H2, determined by an Arrhenius expression. The model was validated with measurement and was used to control plant operation.

In the present work, the influence of various conditions such as particle size, heat transfer coefficient, reactor temperature, and heating rate of biomass particle have been studied. The work carried out in the present study is important and useful for optimal design of the biomass gasifiers, reactors, etc. It is very useful in the design of industrial pyrolysis units also.

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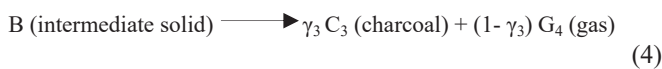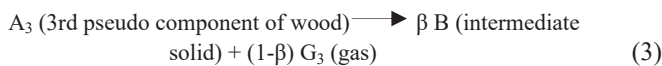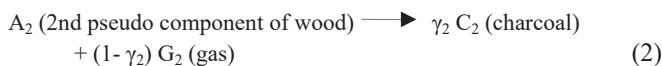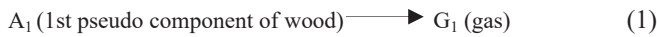
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II. THE PYROLYSIS MODEL

A. Kinetic Scheme

Pyrolysis is the thermal degradation that occurs in the solid phase of a material when it is heated. The bonds between the molecules start to break at elevated temperatures, leading to release of volatile compounds and changes from the original structure of the material. This is seen as mass loss. Technically, 'pyrolysis' refers only to thermal degradation without oxygen; in general, (regardless of the oxygen concentration) the mechanism is called thermolysis. In this work, the kinetic model of [18] for the description of the degradation of the wood particle is adopted. This model is limited to the three following stages: wood is divided into three fractions A_1, A_2 and A_3. The A_1 fraction gives only one gas component G_1; the A_2 fraction gave a gas component G_2 and a solid component C_2 not degradable (compared to coal); the S_3 fraction gives a one gas component G_3 and a solid component B, the B fraction gives a one gas component G_4 and a solid component C_3.

$$A_1 \text{ (1st pseudo component of wood)} \longrightarrow G_1 \text{ (gas)} \quad (1)$$

$$A_2 \text{ (2nd pseudo component of wood)} \longrightarrow \gamma_2 C_2 \text{ (charcoal)} + (1-\gamma_2) G_2 \text{ (gas)} \quad (2)$$

$$A_3 \text{ (3rd pseudo component of wood)} \longrightarrow \beta B \text{ (intermediate solid)} + (1-\beta) G_3 \text{ (gas)} \quad (3)$$

$$B \text{ (intermediate solid)} \longrightarrow \gamma_3 C_3 \text{ (charcoal)} + (1-\gamma_3) G_4 \text{ (gas)} \quad (4)$$

The differential equations describing the kinetic scheme are:

$$\frac{d\rho_{A_1}}{dt} = -k_1 \rho_{A_1} \quad (5)$$

$$\frac{d\rho_{A_2}}{dt} = -k_2 \rho_{A_2} \quad (6)$$

$$\frac{d\rho_{A_3}}{dt} = -k_3 \rho_{A_3} \quad (7)$$

$$\frac{d\rho_{C_2}}{dt} = \gamma_2 k_2 \rho_{A_2}$$

$$\frac{d\rho_B}{dt} = \beta k_3 \rho_3 - k_4 \rho_B \quad (9)$$

$$\frac{d\rho_{C_3}}{dt} = \gamma_3 k_4 \rho_B \quad (10)$$

where

$$k_i = k_{0i} \left(\frac{-E_{ai}}{RT} \right) \quad (11)$$

for i =1; 2; 3 and 4

The activation energies E_{ai}, pre-exponential coefficients k_{0i}, γ_2, β and γ_3 are defined by experimental correlations in [20].

B. Energy Balance

The physical model considered in this study is represented by a one dimensional wood particle is which is placed in a reactor at constant temperature. The heat transfer at the particle surface takes place essentially by convection and radiation. Fourier's law was usually used to describe heat transfer inside material [21]. Thermal conductivity was also considered independent of the temperature. Similar with the development of the experimental conditions, the thermal properties are dependent on the temperature such as thermal conductivity and the specific heat capacity were obtained and used in modeling [22], [23]. Some typical models showed the progress of the description of the process, which will be provided as:

$$\rho C_{pw} \frac{\partial T}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} \left(\lambda_w \frac{\partial T}{\partial r} \right) + S \quad (12)$$

$$S = \left(k_1 \rho_{A1} + k_2 \rho_{A2} + k_3 \rho_{A3} \right) + \Delta H + k_4 \rho_B \Delta H_4 \quad (13)$$

$$\rho = \nu_1 \rho_{A1} + \nu_2 \left(\rho_{A2} + \rho_{C2} \right) + \nu_3 \left(\rho_{A3} + \rho_B + \rho_{C3} \right) \quad (14)$$

where $\nu_{i=1,2,3}$ are the mass fraction, their values are reported in in [20].

The initial and boundary conditions are

$$\text{At } t=0, \text{ and } 0 \leq r \leq r_0, T = T_0 \quad (15)$$

$$\text{for } t > 0, \text{ at } r=0, \frac{\partial T}{\partial r} = 0, \text{ due to symmetry} \quad (16)$$

$$\text{for } t > 0, \text{ at } r=r_0, -\lambda \frac{\partial T}{\partial r} = h(T - T_f) \quad (17)$$

where h represents the global heat transfer coefficient (convective and radiative).

TABLE I
CORRELATION OF PROPERTIES IN THE MODEL

Property	Correlation/value	Source
Thermal conductivity of wood (W/ m K)	$\lambda_w = 0.13 + 3.10^4 \times (T - 273)$	[24]
Specific heat of wood (J /kg K)	$c_{pw} = 1112 + 4.85 \times (T - 273)$	[24]
Heat of reaction (1,2,3) (J/ kg)	$\Delta H = 100 \cdot 10^3$	[14]
Heat of reaction (4) (J/ kg)	$\Delta H_4 = 42 \cdot 10^3$	[14]
Wood emissivity	$\varepsilon_w = 0.85$	[25]

III. NUMERICAL SOLUTION

Equation (12) along with initial and boundary condition given by (15)-(17) are solved by Finite Volume Method (FVM) [26]. This Method was successfully employed by [27]-[31] to solve highly nonlinear sets of coupled partial differential equations along with nonlinear boundary

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conditions due to fluid solid non-catalytic reactions. Equations (5)-(10) are solved by Runge-Kutta fourth order method. The values of various parameters employed in the present study are listed in Table I.

IV. Results and Discussion

A. Model Validation

To validate the obtained results by the model during the pyrolysis of a cylindrical wood particle, the experimental results of [14] were employed in Table II. Fig. 1 shows that the model describes correctly the temperature profiles at the axis of the particle and the experimental data of [14] corresponding to a reactor temperature T_f=623 K. The result of the elaborated model correctly describes the change of the temperature to the axis of the particle while revealing the peak of temperature characteristic of the exothermic phenomenon to a value which is of the same order of magnitude as that proposed in literature [32], [33]. According to the diagram one can note that the computed values starting from the model are qualitatively and quantitatively in good agreement with the measured values of the experiments. In fact, the relative variation defined by the following relations is with the order of 3%.

$$e = \left(\frac{1}{N} \sum_{i}^{N} 2 \frac{\left| T_{cal} - T_{exp} \right|}{T_{cal} + T_{exp}} \right) \times 100 \qquad (18)$$

TABLE II
EXPERIMENTAL DATA OF [25]

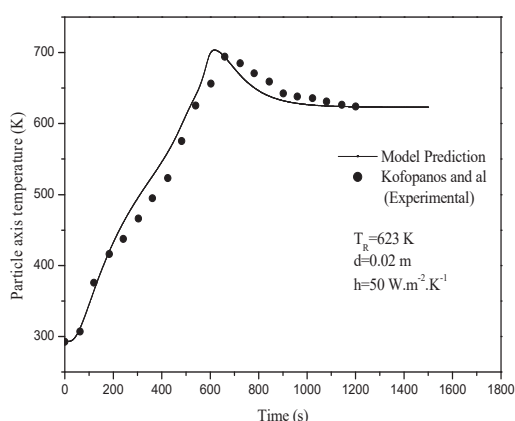| Materiel	TYPE	Measurements
Reactor	Cylindrical shape	d_R=38 mm
		Q_{vg}=1667 cm^3.min^{-1}
		T_0=293 K
		P=101.3 KPa
		h= 60 W.m^{-2}.k^{-1}
Sample	Pine wood particle	d=20 mm
		L=80 mm
		ρ_w=650 kg.m^{-3}

Fig. 1 Temperature profile at the axis of the wood particle: Comparison between model prediction and experimental data of [14]

Fig. 2 shows the variations in mass between the experimental results of [14] and the computed values of the mass loss obtained during the heat treatment of the pine

sample. By qualitative analysis, the first observation is that the evolution of the residual density of the wood particle is correctly simulated. The relative variation with experimental measurements does not exceed 6%. A, one can observe that the variations in mass presented in Fig. 2 break up into three phases. During the drying phase (105°C), the sample wood mass does not vary because the sample was dried beforehand out of drying oven. During the thermal phase of stabilization (170°C) we observe the light ones lower mass always lower than 1,2% which can be due to the vaporization of boiler feed water and/or degradation or the volatilization of the natural extracts present in wood. These variations of mass are observed at several types of wood and more particularly in the case of the pine [34].
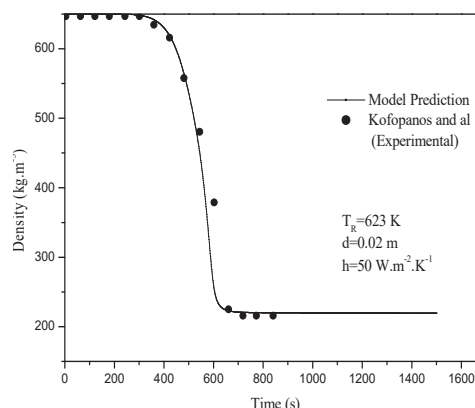

Fig. 2 Variation of mass profile of cylindrical particle: Comparison between model prediction and experimental data of [14]

B. Parametric Study

The model is used to predict the pyrolysis characteristics under different process conditions. The effects of various process parameters are assessed from the simulation studies. We study in this paragraph the effect of evolution of temperature, the variations of mass and loss of density of a piece of wood. The wood used is of cylindrical shape and have the following characteristics with diameters d=20.10^{-3} m and initial density ρ_w=650 kg.m^{-3}. The pyrolysis of the piece of wood is carried out at a temperature of furnace T_f=623 K and the coefficient of heat exchange is h=50 W.m^{-2}.K^{-1} in different operating conditions.

1. Effect of Wood Particle Diameter

Fig. 3 shows the evolution of the temperature at the surface and inside of the wood particle at different positions according to time. The temperature profiles show the existence of two main regions: the most external is essentially ($d/2 \leq r \leq d$) determined by heat transfer effects, and the second ($0 \leq r \leq d/2$) by reaction energetics. For the first region, heating rates become slower as the distance from the external surface increases because of the increasing internal heat transfer resistance, but the degradation of the main wood components takes place at about the same time. For the inner core of the sample, due to the slower heating rates of the final conversion stage, the endothermic degradation of the low-temperature

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components is completed before the high-temperature and exothermic degradation [35], [36]. As a result, a peak is obtained for the center temperature. Indeed, the temperature dynamics remain qualitatively the same, but the size of the second region becomes successively smaller as the externally applied radiation intensity is increased [37]. In other words, as the spatial temperature gradients increase, endothermic and exothermic processes become more coupled given that they take place at the same time for a successively larger portion of the sample. The simultaneous degradation of all the wood components results in a local process nearly isothermal, dominated by transport phenomena.

Fig. 3 Predicted temperature profile at various locations of wood cylinder

Fig. 4 shows the evolution of the density at different positions of the piece of wood. One can interpret that the density starts to decrease on the surface of the sample. In fact, diffuse heat inside the piece of wood, the reduction in the density inside the particle becomes closer to that of surface towards the axis. This is due to the exothermic effects. These results are explained by the increase of the thermal resistance of the charcoal layer that develops as the front of the reaction progresses from the surface towards the axis of the particle [38].
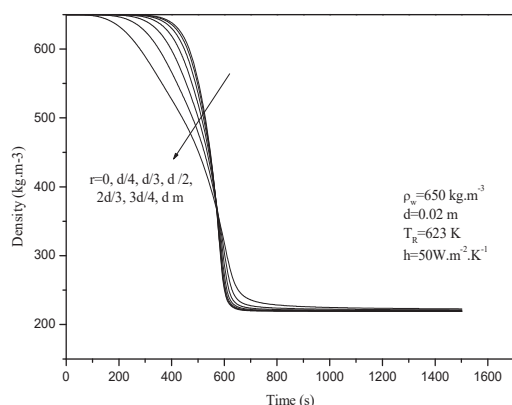

Fig. 4 Predicted of the density at various locations of wood cylinder

Fig. 5 shows the loss rate of density loss rate at different positions of the piece of wood. The density loss rate of becomes more important inside and with the axis of the sample that on its surface. Indeed, the heat released by the

reactions of pyrolysis confined in an increasingly weak wood zone thickness causes the very fast increase in the temperature and the rate of loss of density per contribution with that on the level of the surface of the wood particle.
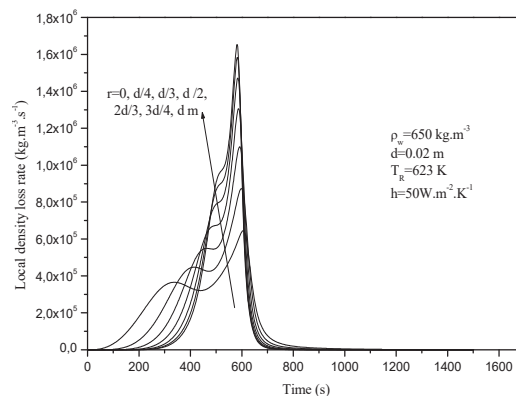

Fig. 5 Predicted of the density loss rate at various locations of wood cylinder

2. Effect of a Total Heat Transfer Coefficient

To study the influence of the heat transfer total coefficient on the evolution of various sizes characterizing the mechanism of pyrolysis we will assign to the coefficient of transfer of heat the following values h= 50,60,70,80 and 90 $W.m^{-2}.K^{-1}$. Figs. 6, 7 and 8 respectively illustrate the temporal evolution of the temperature profile, the variations of the mass and the loss of density of a piece of wood. It is noticed that if the value of h increases, the slope of the curve of variation of mass believes and consequently the thermal decomposition of the biomass becomes faster than for the case or the coefficient of transfer of heat is low. This is can be explained by the fact that if the value of h increases the transfer of energy towards the particle becomes more intense. It follows indeed the increase in the temperature to the axis of the particle. To better explain the influence of the increase of heat transfer coefficient we introduced the change of the duration of the pyrolysis cycle. It is observed that the duration of the pyrolysis cycle decreases if the overall heat exchange coefficient increases (Fig. 9) reflecting an increase in the slope of the weight loss curves.
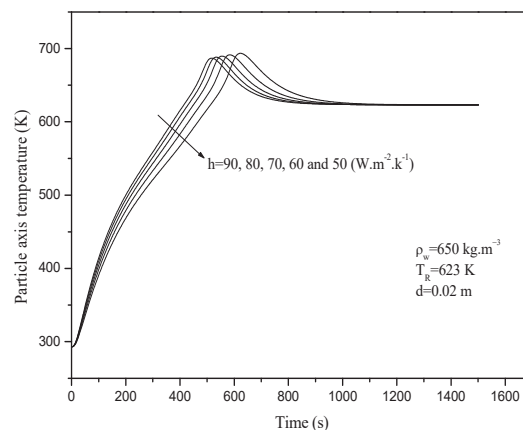

Fig. 6 Effect of total heat transfer coefficient on temperature profile

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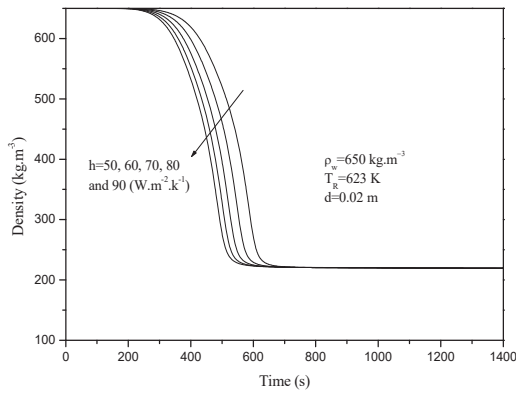Vol:9, No:10, 2015

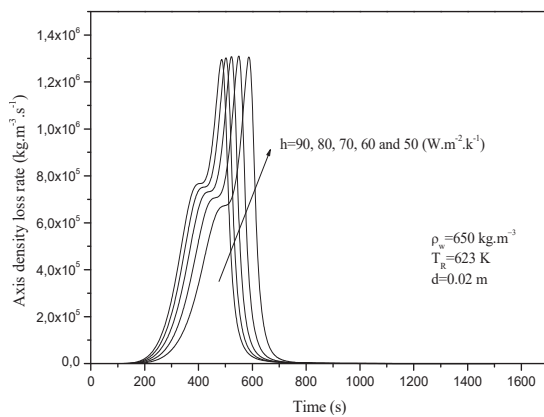Fig. 7 Effect of total heat transfer coefficient on variation density profile

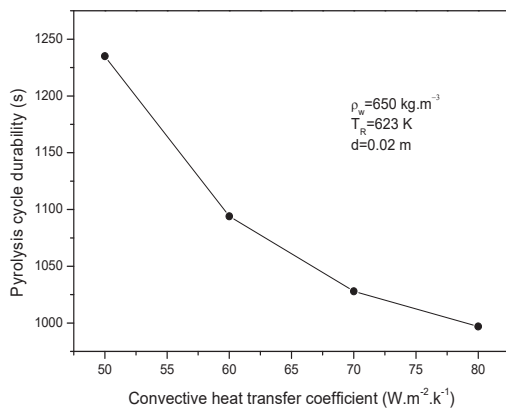Fig. 8 Effect of total heat transfer coefficient on density loss rate

Fig. 9 Variation the duration of the pyrolysis cycle in function of the heat transfer coefficient

3. Effect of the Final Reactor Temperature on the Pyrolysis Mechanism

To study the influence of the temperature of the furnace on the evolution of various sizes characterizing the process of pyrolysis, we will assign to the temperature of the furnace the following values T_f=600, 650,700 K. Figs. 10, 11 and 12 respectively illustrate the evolution of the temperature, the evolution of the density and the evolution the loss rate of density to the axis of the piece of wood. These results show that when the temperature of the furnace is increased, the time

of pyrolysis becomes shorter. In fact, the duration of the exothermic peak inside the particle decreases when the temperature of the furnace increases. This increase is explained by the speed of the secondary reactions and the convective and radiative transfer important.

One can also observe that a reduction in the temperature of the furnace generates a reduction the speed of loss of density which is in conformity with the experimental results [13].
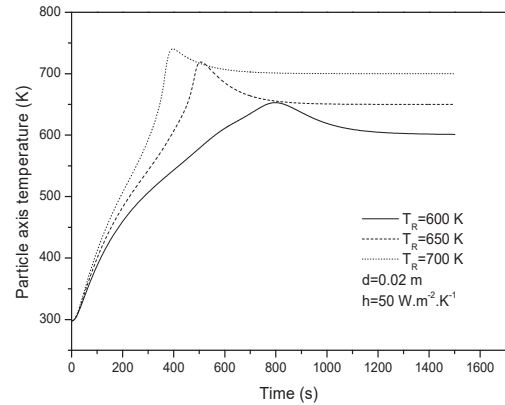

Fig. 10 Effect of the reactor temperature on temperature profile

Figs. 11 and 12 represent the effect of the reactor temperature, respectively, on the density evolution and the density loss rate at the axis of the pine wood particle ($d = 2 \cdot 10^{-2}$m). As the final reactor temperature increases, the particle gets heated up faster leading to an increased pyrolysis rate, a steeper fractional residue profile, and lower pyrolyzing time. Higher final reactor temperature also leads to a lower final residue.

To better explain the influence of the increase of reactor temperature we introduced the change of the duration of the pyrolysis cycle. It is observed that the duration of the pyrolysis cycle decreases if the overall reactor temperature increases (Fig. 13) reflecting an increase in the slope of the weight loss curves.
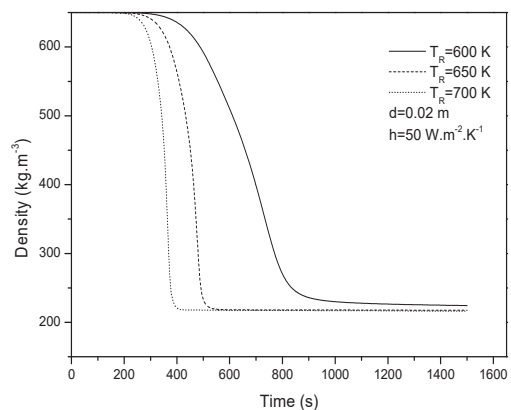

Fig. 11 Effect of the reactor temperature on variation density profile

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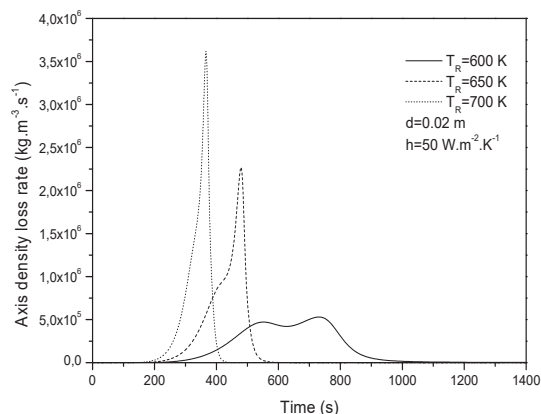International Journal of Chemical and Molecular Engineering
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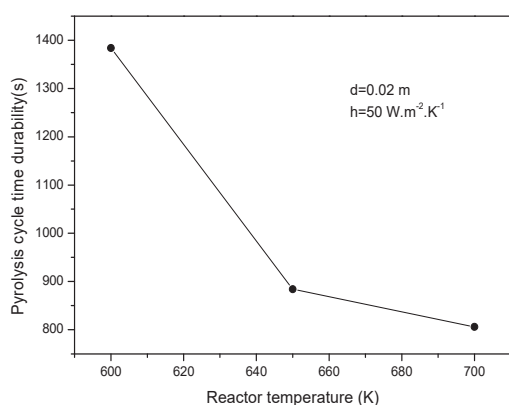Fig. 12 Effect of the reactor temperature on density loss rate

Fig. 13 Variation the duration of the pyrolysis cycle in function of the reactor temperature
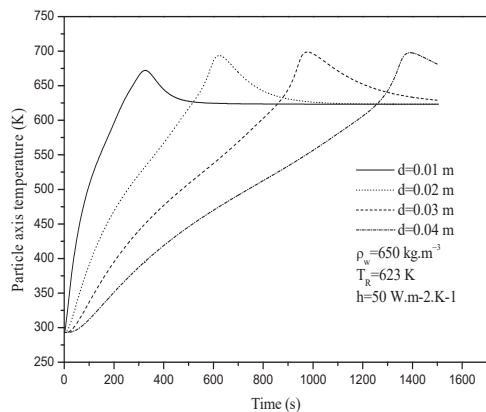

Fig. 14 Effect of particle size on temperature profile

4. Effect of the Particle Size on the Pyrolysis Mechanism

To study the influence of the size of the wood particle on the evolution of various sizes characterizing the process of pyrolysis, we will assign to the temperature of the furnace the following values d=0.01, 0.02, 0.03 and 0.04 m. Figs. 14, 15 and 16 respectively illustrate the evolution of the profile of the temperature, the evolution of the density and the evolution the speed of loss of density to the axis of the piece of wood. Fig. 14 shows that the time of pyrolysis believes the diameter of the particle as increases. In fact, this time lag is with the

increase in the thermal resistance of the coal seams which are formed when the front of the reactions of pyrolysis advances surface towards the axis of the particle.

As, Fig. 15 shows as the warming-up time becomes more important because of the thermal resistance which increases with the thickness. One can also observe that an increase in the diameter of the particle generates a longer time of pyrolysis and the loss rate of more important density. However, the fractional residue profiles are different for different particle size with initial and final residue remaining constant.
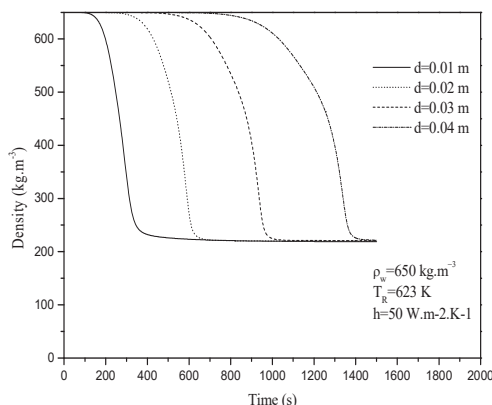

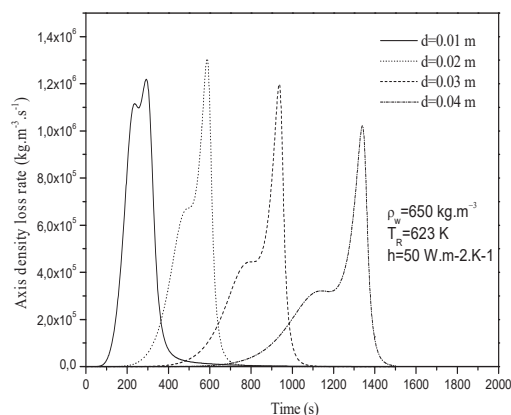Fig. 15 Effect of particle size on density profile

Fig. 16 Effect of particle size on density loss rate

Thermal information obtained by TG-DTA analysis in the literature [39] shows that the first step frequently corresponding to dehydration, merging into a second stage thermal degradation which is exothermic in the case of wood. This last step is displayed clearly in wood degradation curves Fig. 14. One can also observe that an increase in the diameter of the particle generates a longer time of pyrolysis and the loss rate of more important density.

To better explain the influence of the increase of the particle size we introduced the change of the duration of the pyrolysis cycle. It is observed that the duration of the pyrolysis cycle increases if the overall diameter of wood particle increases (Fig. 17) reflecting a decrease in the slope of the weight loss curves.
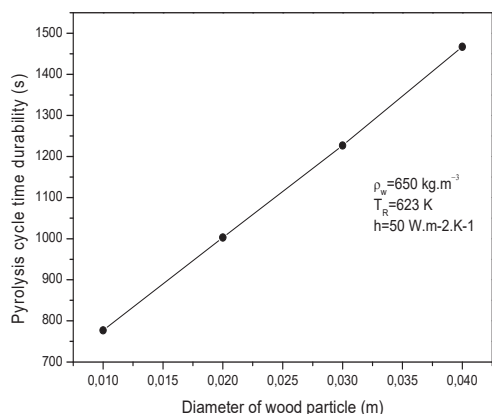
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Fig. 17 Variation the duration of the pyrolysis cycle in function of the diameter of wood particle

V. CONCLUSION

In this work, a kinetic-heat transfer model for pyrolysis of a single wood particle has been presented. The model has been found to predict the pyrolysis characteristics of wood particles. The simplified model, considering the exothermic reaction only, is found to explain the pyrolysis behavior well. The center temperature reaches a peak during pyrolysis. The simulated temperature profiles show that the surface temperature attains the bulk temperature after a significantly long period, thus emphasizing the importance of considering the external film heat transfer resistance in the model.

NOMENCLATURE

C_{pw}	Heat capacity of solid at constant pressure (J kg^{-1}K^{-1})
d	Cylindrical diameter of wood particle (m)
D	Reactor tube diameter (m)
e	Average absolute deviation (%)
E_{ai}	Activation energy (J mole^{-1})
h	Global heat transfer coefficient (W m^{-2}K^{-1})
k_i	Pre-exponential factor (s^{-1})
k_{i0}	Reaction rate constant (s^{-1})
L	Length of wood particle (m)
r	Radial distance (m)
R	Gas constant (J mole^{-1}K^{-1})
S	Source term (J m^{-3})
T	Temperature (K)
T_0	Initial temperature (K)
T_f	Final temperature (K)
T	Time (s)

Greek Letters

α	Thermal diffusivity (m^2 s^{-1})
ε	Emissivity
λ	Thermal conductivity(W m^{-1}K^{-1})
μ	Dynamic viscosity (kg m^{-1} s^{-1})
ρ	Fluid density (kg m^{-3})
σ	Stefan–Boltzmann constant(W m^{-2}K^{-4})
ΔH	Heat of reaction (J kg^{-1})

Subscript

f	final
g	gas
i	reaction index
R	reactor
s	surface of wood particle
w	wood
0	initial

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