

## COMPUTATIONAL INVESTIGATIONS OF PYROLYSIS IN POROUS MEDIA: IMPACT OF HEAT AND MASS TRANSFER

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### ABSTRACT

The present paper deals with impact of heat and mass transfer on pyrolysis mechanisms in a porous media. Importance of porous medium anisotropy is addressed by using a two-dimensional simulation of the problem. To do so, the energy equation is discretized in space by a central differencing while modeling of mass transfer is based on pressure instead of velocity formulation. The kinetics is assumed to follow the lumped-parameter model which is mainly described by a three competitive reactions scheme. Results shed light on the role of grain over the pyrolytic behavior. The grain structure is found to strongly affect heat conduction as well as flows of volatile products through the pores.

### KEYWORDS

Porous media, Pyrolysis, multi-dimensional approach, Numerical

### NOMENCLATURE

$A$	preexponential factor in the pyrolysis model ( $s^{-1}$ )
$c_p$	specific heat capacity at constant pressure ( $J.kg^{-1}K^{-1}$ )
$d_{por}$	characteristic pore diameter (m)
$K$	intrinsic permeability ( $m^2$ )
$E$	activation energy ( $J.mol^{-1}$ )
$M$	molecular weight ( $kg.mol^{-1}$ )
$P$	pressure (Pa)
$R$	universal gas constant ( $=8.3144 J.mol^{-1}K^{-1}$ )
$t$	time (s)
$T$	temperature (K)
$\vec{V}$	velocity vector ( $m.s^{-1}$ )
$u$	velocity component in $x$ direction ( $m.s^{-1}$ )

$v$	velocity component in $y$ direction ( $m.s^{-1}$ )
$x, y$	Cartesian coordinates (m)
$\Delta h$	heat of pyrolysis ( $J.kg^{-1}$ )
$\varepsilon$	porosity
$\varphi$	incident heat flux density ( $W.m^{-2}$ )
$\lambda$	conductivity ( $W.m^{-1}K^{-1}$ )
$\eta$	converted fraction
$\sigma$	Stefan-Boltzmann constant ( $=5.67 \times 10^{-8} W.m^{-2}K^{-4}$ )
$\tau$	production rate ( $kg.m^{-3}.s^{-1}$ )
$\mu$	viscosity ( $kg.m^{-1}.s^{-1}$ )
$\omega$	emissivity

### Subscript

AMB	ambient
COND	conduction
C	char
G	gas
RAD	radiation
T	tar
W	virgin wood

### INTRODUCTION

Thermal degradation of materials subjected to high thermal flux is still today a challenge that scientists face. It involves many complex mechanisms as drying, pyrolysis, char and external gas phase processes. Moreover, such mechanisms are even more complex when the involved material is a porous, heterogeneous and insulating one like wood. The development of thermo-chemical processes for biomass conversion requires a better understanding of the mechanisms and rates involved in thermal degradation processes. Such a task comes also within the

framework of knowledge improvement in fires as well; pyrolysis is always the first step in the gasification and combustion process.

A large number of studies [1-4] have been dedicated to chemical reactions involved in pyrolysis. To do so and in order to reduce the complexity of the problem, thermal degradations of a wood sample are generally conducted under kinetic regime, i.e. experiments are carried out on wood powder and under inert atmosphere. Thus, thermo-gravitational analyses are conducted in order to link mass losses to kinetic reaction models. Even if no consensus concerning the kinetics of wood and cellulose pyrolysis has been put forward, lumped-parameter models are now currently used. These models distinguish three main classes of products: char (the solid residual), gas (low molecular weight gaseous species, mainly CO, CO<sub>2</sub>, H<sub>2</sub> and C<sub>1</sub>-C<sub>2</sub> hydrocarbons) and tars (condensable, high molecular weight, organic components) and propose then a network of competitive and consecutive reactions between each others. Each reaction is assumed to follow an Arrhenius type expression; its activation energy and preexponential factor may be estimated through thermo-gravimetric analysis.

As previously explained, such chemical studies are generally conducted under kinetic regime. However, some recent numerical studies [5-7] focus on mathematical model for thermally thick pyrolysis of wood: heat and mass transfer in the porous structure are modeled in addition to pyrolysis reaction. Temperature profiles, product yield distributions and converted fraction agree well with experimental results. Nevertheless, these numerical results have been conducted in a one-dimensional way, i.e. an infinite width wood sample is heated by a constant and uniform heat flux. Thus, such analyses implicitly do not take into account anisotropic structure of wood and its influence on the development of pyrolysis process.

Di Blasi [8] is the only one who proposed a two-dimensional analysis of pyrolysis in a square lignocellulosic particle, exposed to a high temperature environment. She emphasized a strongly different behavior between heat and mass transfer along and across the solid grain, which affects the dynamics of material degradation. To do so, the well-known Broido-Shafizadeh reaction scheme was used. Nevertheless, the latter was found to be [9] just relevant when thermal pretreatments of *ca* 15h are applied, which is not the case in the most applications: design of biomass combustors, flash pyrolysis reactors, wood fires.

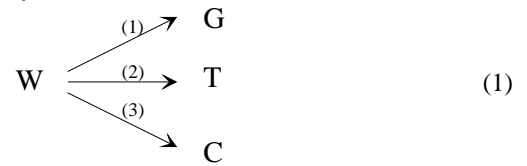
The aim of this study is to use a two-dimensional numerical approach to characterize redwood pyrolysis. The specificity of redwood is that the ratios between longitudinal and tangential properties are not so high than the one used by Di Blasi for lignocellulosic particle, which may affect the specific anisotropic heat and mass transfer behavior. Then, a more adapted three parallel reaction scheme has been chosen to model pyrolysis of wood.

## MATHEMATICAL MODEL

### Pyrolysis model

One of the most difficult tasks in such a modeling is to choose a reaction model that satisfactorily describes pyrolysis under thermal regime. A kinetic scheme with three parallel reactions has been chosen to take into account production of

primary gas, tar and char. Indeed, a both experimental and numerical study, made by Grønli [10] on thermally thick pyrolysis of wood, showed a competition between char, tar and gas formation, which is dependent on the wood pellet's temperature history.



In addition to closely describe kinetics of pyrolysis, the particular structure of wood material has to be taken into account. Indeed, wood is a porous material which, because of its natural feature, shows strong heterogeneities in its structure. For instance, Redwood is mainly composed of fibers, which leads that physical properties between parallel and perpendicular direction to the fibers are not of the same order of magnitude. Anisotropy of wood structure has been addressed in integrating in the numerical approach characteristic parameters with regard to fibers orientation. To best describe thermal degradation, the model must characterize transfers according to two directions and as a result, two dimensional simulations have been undertaken.

Heat and mass transfer are described through a representative volume technique. The investigated area is divided into several small areas in which it is assumed that transfers occur homogeneously. A spatial average on microscopic scale is then implicitly assumed to obtain transfer at a macroscopic level. The formulation of the mathematical model is based on the following main assumptions:

- local thermal equilibrium between the solid matrix and gas is assumed,
- sample are considered free of water,
- convection into the solid structure is assumed to follow the Darcy's law,
- change of thermodynamic characteristics of wood is a direct function of the conversion rate,
- the secondary reactions (such as tars decomposition) are negligible,
- shrinkage and thermal swelling phenomena are not taken into account.

The model takes into account radiative, convective and conductive heat transfer in the solid matrix as well as momentum transfer through the pores of both virgin and charred regions. Thus, the two-dimensional model resolved the set of equations listed below.

### Conservation equation for Pyrolysis

The mathematical model is based on the chosen kinetics and the change from virgin wood to char is controlled by:

$$\frac{\partial \rho_W}{\partial t} = -(\tau_G + \tau_T + \tau_C) \quad (2)$$

$$\frac{\partial \rho_C}{\partial t} = \tau_C \quad (3)$$

in which  $\tau_G$ ,  $\tau_T$  and  $\tau_C$  are linked to the density of virgin wood according to:

$$\tau = Ae^{-E/RT} \quad (4)$$

with  $A$ ,  $E$  and  $T$  as the frequency factor, activation energy and temperature respectively (see Table 1).

### Momentum equation

The mass equation in the gas phase and tar is written:

$$\left. \begin{aligned} \frac{\partial \rho_G}{\partial t} + \vec{\nabla} \cdot (\rho_G \cdot \vec{V}) &= \tau_G \\ \frac{\partial \rho_T}{\partial t} + \vec{\nabla} \cdot (\rho_T \cdot \vec{V}) &= \tau_T \end{aligned} \right\} \quad (5)$$

Instead of solving the complete momentum equation, Darcy's law is used for finding the velocities:

$$\vec{V} = -\frac{K}{\mu} \cdot \vec{\nabla} P \quad (6)$$

The Darcy or creeping – flow regime is justified when the viscous forces dominate over the inertia forces, i.e. when the Reynolds number that is based on the characteristic length scale is smaller than 1 which is the case in our problem.

Assuming that the density in the gas phase follows the ideal gas law as :

$$P = \frac{(\rho_G + \rho_T)RT}{M} \quad (7)$$

an equation for determining  $P$  is obtained by combining equations (5)-(6)-(7). Then pressure equation is written:

$$\frac{\varepsilon M}{R} \frac{\partial}{\partial t} \left( \frac{P}{T} \right) + \frac{M}{R} \vec{\nabla} \cdot \left( \frac{K}{\mu} \frac{P}{T} \cdot \vec{\nabla} P \right) = \tau_G \quad (8)$$

### Conservation equation of energy:

The energy equation for the porous media implicitly assumes that temperature of solid and gas phase are equal in time.

$$\begin{aligned} \varepsilon (\rho c_p)_{eq} \frac{\partial T}{\partial t} - \vec{\nabla} \cdot \left( \frac{c_{p_g} K_{eff}}{R \mu_{eff}} P \cdot \vec{\nabla} P \right) \\ - \varepsilon \vec{\nabla} \cdot (\lambda_{eff} \vec{\nabla} T) = \tau_G \Delta H_G + \tau_T \Delta H_T + \tau_C \Delta H_C \end{aligned} \quad (9)$$

Wood density, pressure and temperature are calculated by solving equations (2)-(8)-(9) respectively. Nevertheless, to do so, assumptions have to be addressed for estimating conductivities and wood properties during pyrolysis. For instance, the locally varying effective transport coefficient  $\lambda_{eff}$  due to averaging is approximated by the following expression:

$$\lambda_{eff} = \varepsilon \lambda_G + \lambda_{COND} + \lambda_{RAD} \quad (10)$$

which takes into account heat transfer by conduction in the gas, virgin wood and char and radiation in the pores. The latter is believed to be significant at high temperature [11]. Both of the convective and radiative transfers are direct functions of the reaction rate coefficient.

$$\begin{aligned} \lambda_{COND} &= \eta \cdot \lambda_w + \eta \cdot (1 - \lambda_c) \\ \lambda_{RAD} &= \frac{4\varepsilon \sigma \omega_{por} T^4}{1 - \varepsilon} \left( \eta \cdot d_{por_w} + \eta \cdot (1 - d_{por_c}) \right) \end{aligned} \quad (11)$$

Reaction	$A$ ( $s^{-1}$ )	$E$ (kJ/mol)	$\Delta H$ (kJ/kg)
gas	$1.3 \times 10^8$	$1.403 \times 10^5$	$-1.5 \times 10^5$
tar	$2 \times 10^8$	$1.331 \times 10^5$	$-1.5 \times 10^5$
char	$1.1 \times 10^7$	$1.213 \times 10^5$	$-1.5 \times 10^5$

Table 1: Kinetic data, heat of pyrolysis for redwood [10]

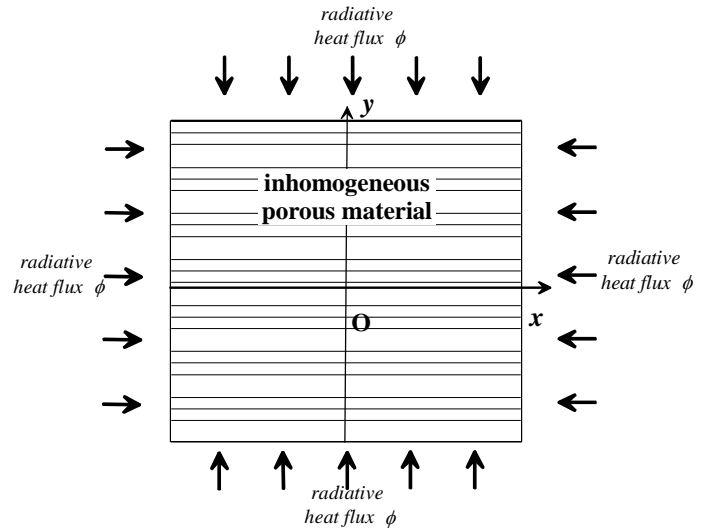


Figure 1: Sketch of the numerical case

### Numerical scheme

The set of equations are solved on a two-dimensional fixed Cartesian grid in space. The mesh contains 50x50 nodes and discretization in the  $x$  and  $y$  directions are similar, i.e.  $2 \times 10^{-4}$  m. A test grid was performed in order to characterize the influence of spatial resolution on the results obtained. Table 2 gives details on two different mesh sizes and the maximum of production rate  $\tau$  obtained for each case. Taking into account that pyrolysis is almost depicted in the same way for the two meshes; we mainly worked with the coarser grid because of the CPU time difference. For instance, 600 seconds of simulation time require approximately 86 hours of CPU time on a 2.8 GHz Xeon processor while only 48 hours are necessary for the coarsest grid. Moreover, it is important to stress out that an even coarser grid was inconclusively tested:  $\Delta x$  and  $\Delta y$  were equal to  $2.5 \times 10^{-4}$  m and such a resolution leads the results to such significant errors that the simulation diverges.

mesh	$\Delta x = \Delta y$ ( $m^2$ )	$\tau_g$ ( $kg \cdot m^{-3} \cdot s^{-1}$ )
50x50	$2.0 \times 10^{-4}$	1.485
60x60	$1.5 \times 10^{-4}$	1.476

Table 2: Test of mesh size

The convective and diffusive terms are discretized by first-order central differencing. Note that the coefficients (convective and diffusive terms) are obtained through an harmonic average in order to guaranty continuity of flux at the interface between each nodes. Because of a strong coupling between the variables, the scheme is implicit and a procedure of convergence is applied at each time step. The set of equations are solved by a classical conjugate gradient method, specially developed for sparse matrix. A relative error must be specified to advance in time. The

results presented hereinafter were obtained  $10^{-5}$  relative error level.

### Boundary Conditions

The boundary conditions applied assume that a  $\varphi$  incident heat flux occurs at the surface but heat losses are assumed to be directly linked to radiant transfers only. Therefore, the net flux heating the porous material is equal to:

$$\varphi_n = \varphi - \omega \sigma (T^4 - T_{amb}^4) \quad (12)$$

The boundary conditions for momentum transfer at the material surface are assumed to arise in a close environment in which no pressure change occurs.

### RESULTS

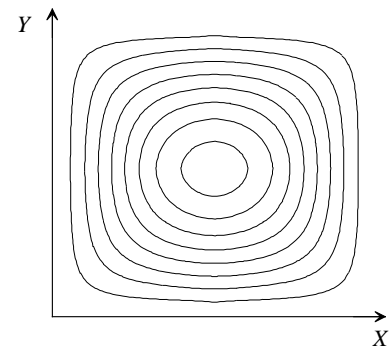
Pyrolysis of a 2-cm-square sample of redwood free of water has been studied and the  $\varphi$  incident heat flux to the surface is fixed to  $50 \text{ kW.m}^{-2}$ . Figure 1 presents a sketch of the numerical configuration. As we consider a square shape, simulations were only performed on a quarter of the whole domain and symmetry conditions were applied along the  $Ox$  and  $Oy$  axis. As already mentioned, the purpose of our investigation is to simulate pyrolysis of a realistic wood material by taking into account its heterogeneous properties. To do so, the convective and diffusive coefficients were estimated in connection with the direction of the considered fluxes. Redwood is mainly organized in fibers and properties of such a wood material differ along and across the solid grain [12,13]. The permeability and the conductivity coefficients are the main parameters which vary significantly in the two directions. Table 3 lists both the parallel and

perpendicular parameters for redwood.

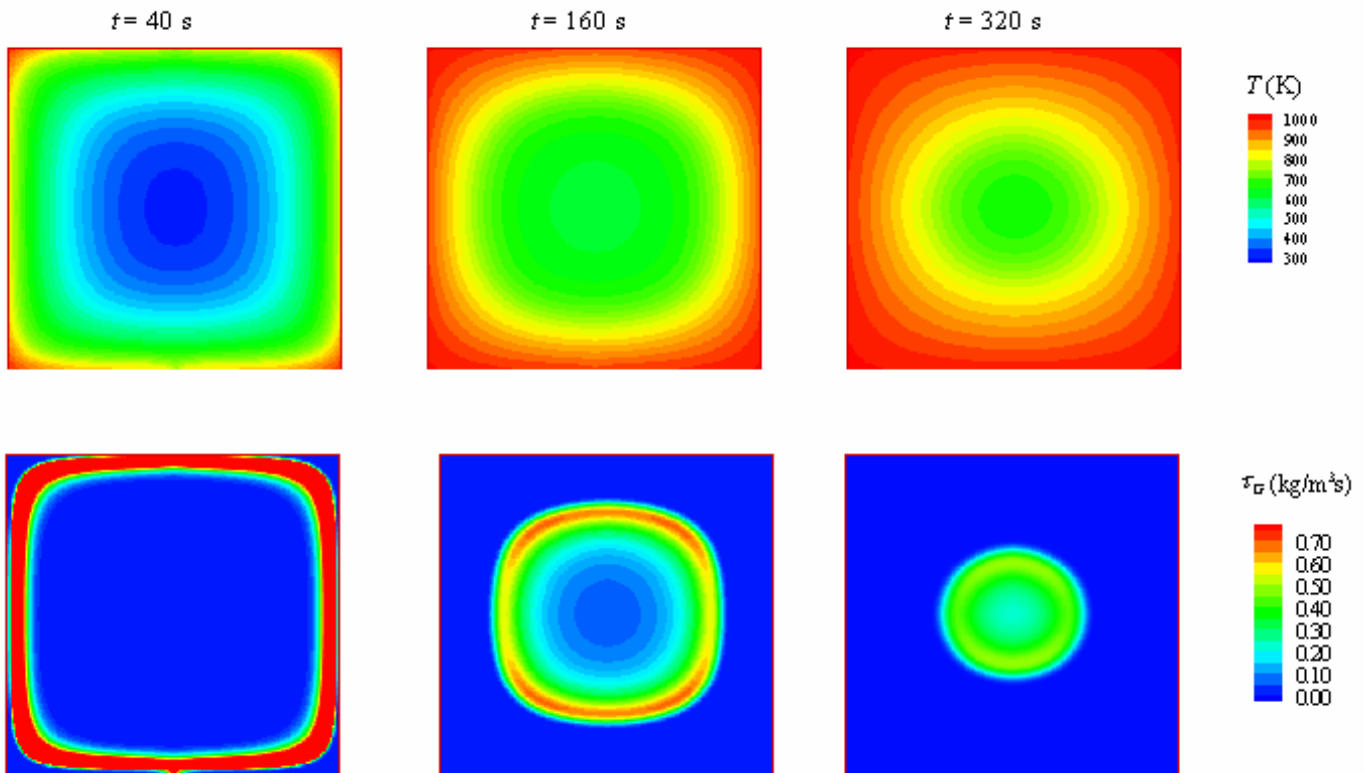
	Virgin wood	char
$\lambda_{//}$	0.150 W/m/K	0.10 W/m/K
$\lambda_{\perp}$	0.105 W/m/K	0.07 W/m/K
$K_{//}$	$10^{-14} \text{ m}^2$	$10^{-11} \text{ m}^2$
$K_{\perp}$	$10^{-18} \text{ m}^2$	$10^{-12} \text{ m}^2$

**Table 3: Characteristics of the wood's heterogeneities[12,13]**

Figure 2 allows one to follow the change in time of the temperature contour at  $360^{\circ}\text{C}$ . Actually, in a study on pyrolytic behavior of different wood varieties, it has been put forward that pyrolysis occurs for redwood at  $360^{\circ}\text{C}$  when irradiated with heat flux of about  $50 \text{ kW.m}^{-2}$  [14].



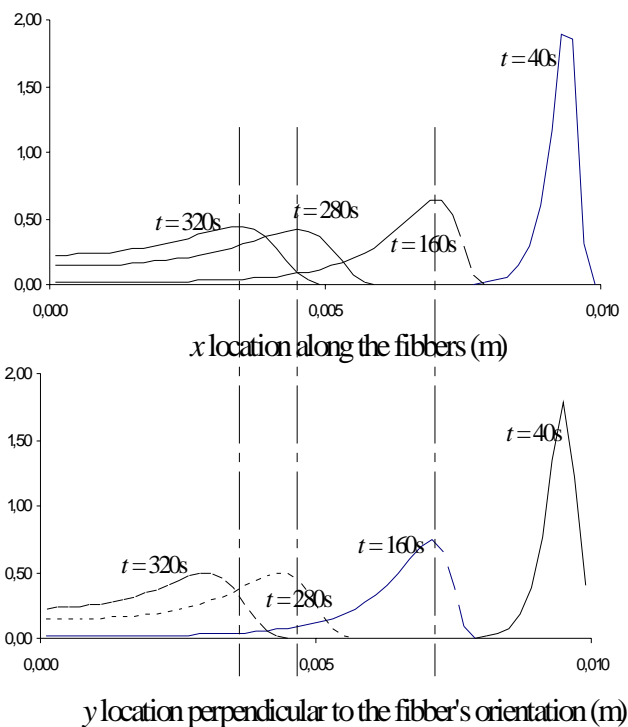
**Figure 2: Change of iso-contours at  $T=360^{\circ}\text{C}$  - time delay of 40s between each curve**



**Figure 3 Change of T temperature field and the  $\tau_g$  gas production rate at  $t=40, 160$  and  $320\text{s}$**

Then, according to the chosen geometry, the temperature contour organizes first in a square shape. This behavior arises up to  $t = 160$ s. For  $t \geq 200$ s, the shape of the contour begins to evolve progressively toward a more elliptic one. For instance, such a change is clearly detectable at 320 s. Thus, it implicitly means that the rate of spread of the pyrolysis reaction front is greater in the  $y$  direction than in the  $x$  one. In order to emphasize this change, Figure 3 shows the contour of the whole temperature field and the  $\tau_g$  rate of gas production. It is also interesting to note that the front reaction is relatively thin in the first instant of heating and becomes larger with time. The profile of  $\tau_g$  along the  $Ox$  and  $Oy$  axis are also plotted (Figure 4) at  $t = 40, 160, 200$  and  $320$ s.  $\tau_g$  profiles are characterized by a peak at a maximum level. The latter is relatively sharp at  $t = 40$  s on both  $x$  and  $y$  directions and the more the reaction front advances in the material, the smaller the maximum and the larger the peak. Such a behavior in the change of the gas production rate is typical of the front reaction spread under pyrolysis.

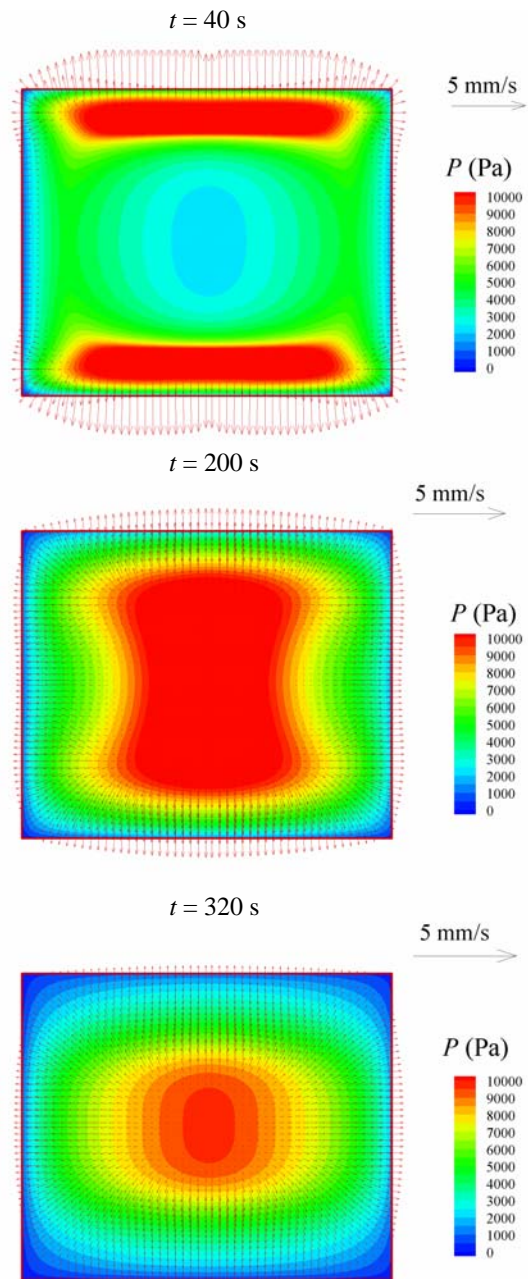
Considering the scale of thermal diffusivity (in the  $x$  and  $y$  directions), an inhomogeneous behavior was expected during pyrolysis but not in that way. Due to a higher level of  $\lambda$  in the fiber direction, it should have emphasized the kinetics along the fibers; in this case, the elliptic shape would have been in the  $y$ -direction instead of the  $x$ -direction. How can we explain such a conflicting behavior?



**Figure 4: Profiles of  $\tau_g$  in the  $x$ -direction and  $y$ -direction, i.e. parallel to and perpendicular to the fibers respectively**

At  $t=40$ s, high pressure region develops near the external boundary for direction parallel to wood fibers whereas pressures are still low in the perpendicular direction. However the wood surfaces are subjected to the same thermal stress but due to a

smaller permeability in the  $y$ -direction, higher pressure develops at the vicinity of the surface.



**Figure 5: Pressure and associated velocity vectors during pyrolysis process**

Thus, at this location, velocities are greater in the  $y$  than  $x$ -direction. A similar trend is also observed at  $t = 200$  s even if the two velocity components are more or less comparable. On the contrary, at  $t = 320$  s, velocities in the  $x$ -direction are significantly higher than those observed in the  $y$ -direction. Along the fibers, pressure gradients are significant, which favors convection fluxes. Then, convection fluxes balance conductivity flux to such a point that pyrolysis kinetics is delayed along the fiber direction.

## CONCLUSION

A two-dimensional simulation of large redwood sample has been carried out. As far as we know, this is the first time such an analysis was performed with a three competitive reactions scheme to describe pyrolysis. In order to integrate homogeneities of wood, convective as well as conductive fluxes were estimated by taking into account the direction in which transfers occur.

A main and favored direction is the one parallel to the redwood's fibers offering higher conductivity level and by far permeability coefficient greater than in the perpendicular direction. Nevertheless and according to the presented results, transfers are surprisingly faster in the perpendicular direction leading to an elliptic shape behavior during pyrolysis. Such a behavior is due to the fact that conductive transfers are balanced by strong convection fluxes along fiber's direction. An interaction between transfers in the two directions may also be at the origin of the different transfers according to the direction. To check the latter, comparison between one-dimensional and two-dimensional results should be performed. Whatever the causes, the results underline the necessary multi-dimensional approach for a better description of large wood sample pyrolysis.

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