

## FUSION-LIKE BEHAVIOUR OF BIOMASS PYROLYSIS

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### INTRODUCTION

Considering a thermal reaction of a Solid  $\rightarrow$  Fluid type, the apparent rate of reaction can be controlled by chemistry, thermal and mass transfer resistances. If the chemical processes are very fast, and if the fluid products are easily eliminated from the medium, the overall rate of reaction is controlled by heat transfer resistances. This is the case of the ablation regime [1], characterized by a steep temperature gradient at the wood surface and consequently by a thin superficial layer  $e$  of reacting solid moving at a constant velocity  $v$  towards the cold unreacted parts of the solid.

Suppose now that heat is provided by a surface at  $T_w$ . A theoretical increase of the surface temperature  $T_d$  of the solid (by increasing  $T_w$ ) would lead to a subsequent increase of the heat flux demand. Such a demand would be satisfied by an equal external heat flux supply, a condition fulfilled only with large temperature gradients ( $T_w - T_d$ ). The consequence would be a stagnation of  $T_d$ , leading to a fusion like behaviour of the reaction.

Wood pyrolysis carried out in conditions of high available heat fluxes and efficient elimination of products occurs in ablation regime with production of very low fractions of char [2,3,4] and could therefore behave as a simple fusion. This paper presents a brief outline of the main ideas and results obtained to this effect and issued from different approaches. More details can be found in related papers [5,6,7,8].

The reaction has been carried out in three different conditions : heating against a hot spinning disk ; against a fixed heated surface ; in a continuous cyclone reactor. In the first two cases, the behaviour of the reaction is compared to that of solids undergoing simple fusion in the same conditions.

### SPINNING DISK EXPERIMENTS

The melting of ice, paraffin and "rilsan" (polyamide 11) and the pyrolysis of wood have been carried out by applying under known pressures  $p$ , rods of the corresponding solids against a hot spinning stainless steel disk (temperature  $T_w$ ) [5,6]. In wood experiments, the reaction produces almost exclusively gases and liquids, the solids being mainly ashes deposited on the disk. The liquids produced are rapidly extracted from the wood surface and eliminated by the fast moving disk on which they undergo further decomposition to gases at a rate depending on  $T_w$ . The presence of the thin liquid layer acts as a kind of lubricant.

Figure 1 reveals that under comparable values of  $p$ , the behaviour of  $v$  as a function of  $v_R$  is similar, the orders of magnitude of  $v$  being the same for the four types of solids. For  $v > 2 \text{ m s}^{-1}$ ,  $v$  increases with  $p$  following :

$$v = a p^F$$

(1)

a depends on  $T_w$  and F on the material. The mean values of F (ice : 0.035 ; paraffin : 0.29 ; "rilisan" : 0.83 ; wood : 1) can be fairly well represented by :

$$F(\text{melting solid}) = \frac{Cp_s(T_f - T_o)}{Cp_s(T_f - T_o) + L} \quad \text{or} \quad F(\text{wood}) = \frac{Cp_s(T_d - T_o)}{Cp_s(T_d - T_o) + \Delta H} \quad (2)$$

F being close to 1 for wood shows that it is probable that  $\Delta H$ , the enthalpy of pyrolysis, is small with respect to sensible heat in agreement with literature.

The equations of heat flux density balances between the disk and the rod are :

$$\begin{aligned} \text{melting solid} : h(T_w - T_f) &= v\rho_s Cp_s (T_f - T_o) + v\rho_s L \\ \text{wood} : h(T_w - T_d) &= v\rho_s Cp_s (T_d - T_o) + v\rho_s \Delta H \end{aligned} \quad (3)$$

Assuming that the heat transfer coefficient h is the only parameter depending on the pressure ( $h = Kp^F$ ) it can be deduced :

$$\frac{v}{p^F} (\text{melting solid}) = \frac{K}{\rho_s Cp_s (T_f - T_o) + L} \frac{T_w - T_f}{p^F} ; \quad \frac{v}{p^F} (\text{wood}) = \frac{K}{\rho_s Cp_s (T_d - T_o) + \Delta H} \frac{T_w - T_d}{p^F} \quad (4)$$

In agreement with (4), Figure 2 shows that the variations of  $\frac{v}{p^F}$  with  $T_w$  are linear for the three melting solids and also for wood. The values of  $T_f$  calculated from the extrapolation of the straight lines to  $v = 0$  are in very good agreement with the known values of melting points (better than 2 % accuracy). The corresponding "fusion temperature" of wood is then calculated close to 739 K.

The values of heat transfer coefficients obtained from the slopes of the straight lines in figure 2 are of the same order of magnitude (around  $10^4 \text{ W m}^{-2} \text{ K}^{-1}$ ) whatever the solid showing that the mechanisms of heat transfer are probably similar for wood and melting solids. For wood, h varies as  $h = 0.017 p (\text{W m}^{-2} \text{ K}^{-1}) [5]$ . These values reveal very efficient transfers.

#### FIXED HEATED WALL

The same experiments as before have been made with rods of ice, paraffin and wood pressed against a stationary piece of brass heated at  $T_w$ .

An analytic solution has been found for representing the rate of ablative melting of a solid cylinder pressed against a horizontal wall maintained at  $T_w$  [7]. In steady state, a liquid layer of constant thickness is formed between the hot surface and the rod, with a radial flow of liquid. The resolution of the equation of liquid flow associated with that of energy balance between the two surfaces allows to derive the following relationship:

$$v = \frac{\rho_l}{\rho_s} \left[ \frac{2}{3} \frac{\alpha_l^3}{\mu_l R^2} Pe^3 (Ph) p \right]^{1/4} \quad (5)$$

where Pe is a Peclet number, a function of a phase change number

$$Ph = \frac{Cp_l (T_w - T_f)}{L} \quad \text{as} \quad Pe = \frac{Ph}{1 + Ph^{5/6}/3}$$

The relation (5) shows that v varies as  $p^{0.25}$  whatever the type of solid. In reduced form, (5) can be written as follows :

$$v = \frac{2}{3} [Pe^3 P]^{1/4} \quad (6)$$

with 
$$v = \frac{\rho_s R}{\rho_l \alpha_l} v \quad \text{and} \quad P = \frac{R^2}{\mu_l \alpha_l} p$$

By plotting  $V$  against  $\left[\frac{2}{3} Pe^3 P\right]^{1/4}$  one should obtain a straight line of slope one whatever the nature of melting solid and wall temperature.

As in the case of ice and paraffin [7], ablation rate  $v$  for wood pyrolysis varies as  $P^F$  with a mean value of  $F$  (0.29) close to the theoretical one (0.25) (Fig. 3). The figure 4 gathers all the experimental points according to (7). The physical properties used for the calculation of  $V$  and  $P$  for ice and paraffin are reported in ref. [7,8]. In the case of wood, the factor containing these properties in equation (5) has been fitted to the experimental results (fig. 3) leading to  $v = 1.55 \times 10^{-3} (Pe^3 p/p_0)^{1/4} (m s^{-1})$ . The fitted constant associated with estimated values for  $\rho_l$  ( $500 \text{ kg m}^{-3}$ ),  $Cp_l$  ( $3.65 \text{ kJ.kg}^{-1}\text{K}^{-1}$ ) and  $\alpha_l$  ( $0.3 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$ ) allows to calculate  $\mu_l = 72.5 \times 10^{-3} \text{ Pa.s}$ , a reasonable value for the viscosity of a liquid at a melting point of 739 K [7,8].

#### CYCLONE REACTOR EXPERIMENTS

The continuous fast pyrolysis of wood sawdust has been studied in a Lapple type ( $2.8 \times 10^{-2} \text{ m}$  diameter) cyclone reactor heated between 893 and 1330 K [2]. The wood particles carried away by a flow of steam enter tangentially into the cyclone on the inner hot walls of which they move and undergo decomposition. Mass balances show in all the cases, a very low fraction of char (< 4 %) while the gasification yield increases with wall temperature  $T_W$ . It appears from figure 5 that the reaction seems to occur only for wall temperatures greater than about 800 K in good agreement with fusion temperature of 739 K. In such a model, the decomposition temperature of particles being roughly constant, the gasification yield increase with  $T_W$  would then result from further vaporization and/or decomposition of primary products (mainly liquids) at the wall and/or in the gas phase with an efficiency depending on  $T_W$ .

#### DISCUSSION

All these results obtained in different experimental conditions, show striking similarities between ablative wood pyrolysis and melting of solids. Nevertheless the equivalent fusion temperature of 739 K has been calculated from relation (4) based on the assumption that  $T_d$  is constant. Let suppose now that  $T_d$  depends on external physical conditions ( $p$ ,  $T_W$ ) under the assumption that  $\Delta H \ll v \rho_s Cp_s (T_d - T_0)$ . The heat flux density balance equation is :

$$h(T_W - T_d) = \rho_s Cp_s v (T_d - T_0) \quad (7)$$

The reaction occurring in ablation condition concerns only a thin external wood layer  $e$  inside which the equation of mass balance  $ke = v$  associated with  $ev = \alpha_s$  [5] leads to a relationship between the ablation velocity and the chemical first order kinetic constant  $k$  :  $k = v^2/\alpha_s$  and finally to :

$$T_d = \frac{h T_W + T_0 \sqrt{k \lambda_s \rho_s Cp_s}}{h + \sqrt{k \lambda_s \rho_s Cp_s}} \quad (8)$$

Figure 6 shows the variations of  $T_d$  with  $T_w$  ( $\lambda_s = 0.2 \text{ W m}^{-1} \text{ K}^{-1}$ ;  $C_{p_s} = 2800 \text{ J kg}^{-1} \text{ K}^{-1}$ ;  $\rho_s = 700 \text{ kg m}^{-3}$ ) with  $h$  as a parameter. The first order rate constant for the formation of "active cellulose" [9]  $k(\text{s}^{-1}) = 2.83 \times 10^{19} \exp -29000/T_d$  has been supposed to fit the present case of wood primary decomposition.

It can be observed that the smaller the values of  $h$ , the shortest the domain of wall temperature where  $T_d = T_w$  (for the lowest values of  $h$ ,  $T_d/T_w$  becomes less than one as wood begins to decompose). In most of usual experimental devices wood temperature is then very different from source temperature. Consequently, the direct determination of pyrolysis rate laws would have sense only for low wall temperatures ( $< 750 \text{ K}$ ).

Figure 6 shows that  $T_d$  varies with  $T_w$  and  $h$  indicating that strictly speaking, the fusion model is not appropriate. But it can be observed (specially for the low  $h$ ) that as soon as  $T_d/T_w < 1$ ,  $T_d$  increases more and more slowly with  $T_w$  and rapidly reaches a roughly constant value. Fusion model seems then to be an excellent first approximation.

The hatched zone reported in figure 6 is bounded by the extreme values of  $h$  determined in ref. [5] and by the extreme values of  $T_w$  explored. The "fusion temperature" of  $739 \text{ K}$  appears to be well situated inside the hatched surface. Such a fair agreement shows that the chosen kinetic law is a good approximation for wood decomposition. The "fusion temperature" must then be considered a mean value lying roughly between  $660$  and  $725 \text{ K}$  for  $T_w = 773 \text{ K}$  and between  $700$  and  $800 \text{ K}$  for  $T_w = 1173 \text{ K}$ .

## CONCLUSION

The behaviour of wood rods undergoing ablative pyrolysis by more or less intimate contact with a hot surface has revealed strong similarities with a phase change phenomenon. The principal reasons developed are the followings : quite similar behaviour of wood rods with true melting solids when applied on moving or fixed surfaces : same orders of magnitude of  $v$  and  $h$  ; same dependance law with applied pressure with a power  $F$  showing probable low values of the enthalpy of reaction ; same  $p^{0.25}$  dependance of  $v$  in the case of fixed surface ; same low of variations of  $v$  with wall temperature. Ablative pyrolysis carried out with sawdust in a cyclone reactor proves that no fast reaction occurs for wall temperatures lower than  $\sim 800 \text{ K}$ .

A consequence of these conclusions is that the accurate direct determination of kinetic rate constant of wood decomposition is a difficult task, likely impossible over wide ranges of temperatures in most of experimental devices (upper limit around about  $800 \text{ K}$ ). Even if such high temperatures could be reached, the system should be designed in such a way that the products of the reaction could also be removed from the reacting surface with high efficiencies. For example, figure 6 shows that  $T_d = T_w = 800 \text{ K}$  would be observed for  $h = 10^6 \text{ W m}^{-2} \text{ K}^{-1}$ . Assuming that the available heat flux is controlled by conduction through the oil layer, such a heat transfer coefficient would be effective for an equivalent layer thickness of  $0.1 \mu\text{m}$  ! (calculation made with a thermal conductivity of  $0.1 \text{ W m}^{-1} \text{ K}^{-1}$  for oil). Of course, an efficient removal of these liquids would prevent also the extent of their subsequent decomposition to secondary products and then to reduce the formation of new thermal isolating layers.

All these conclusions are in agreement with the analysis of other authors. Diebold pointed out in 1980 the efficiency of "solid convection" for carrying out the reaction of ablative pyrolysis of biomass (demonstration of

"sawing" biomass [4]. The same author stated also recently that cellulose passes probably through a liquid or plastic unstable state ("active cellulose") during pyrolysis before further decomposition [14] in agreement with Antal who points out the strong analogies observed between cellulose pyrolysis at high heating rates and phase change phenomena [10,11] with an upper limit at which pyrolysis occurs of 773 K. Evidence of such an upper limit is explained by a competition between heat demand from biomass and available external heat flux [12]. The same author [12] notices also the difficulty and indeed impossibility of achieving conditions whereby pyrolysis kinetics could be studied at very high temperatures. Finally, it must be reminded that in 1980, Reed [13] proposed a model for estimating the enthalpy of flash pyrolysis of wood based on several steps : heating of biomass up to a reaction temperature of 773 K, followed by a depolymerisation to form a solid which subsequently melts, melted matter being afterwards able to vaporize, following the temperature.

#### NOMENCLATURE

a	Constant ( $m s^{-1} Pa^{-F}$ )
Cp	Specific heat capacity ( $J kg^{-1} K^{-1}$ )
e	Thickness of reacting wood layer (m)
F	Exponent
h	Heat transfer coefficient ( $W m^{-2} K^{-1}$ )
H	Specific enthalpy ( $J kg^{-1}$ )
K	Constant ( $W m^{-2} K^{-1} Pa^{-F}$ )
k	First order kinetic constant ( $s^{-1}$ )
L	Heat of fusion ( $J kg^{-1}$ )
p	Pressure (Pa)
p <sub>o</sub>	Atmospheric pressure (Pa)
P	Reduced pressure
Pe	Peclet number
Ph	Phase change number
R	Radius of the solid cylinder (m)
T <sub>d</sub>	Wood surface temperature (K)
T <sub>f</sub>	Fusion temperature of a melting solid (K)
T <sub>o</sub>	Ambient temperature (K)
T <sub>w</sub>	Wall temperature (K)
v	Ablation velocity of the solid cylinder ( $m s^{-1}$ )
X	Gasification yield
V	Reduced velocity
α	Thermal diffusivity ( $m^2 s^{-1}$ )
λ	Thermal conductivity ( $W m^{-1} s^{-1}$ )
μ	Viscosity (Pa s)
ρ	Density ( $kg m^{-3}$ )

#### Subscripts :

s	solid cylinder
ℓ	liquid layer

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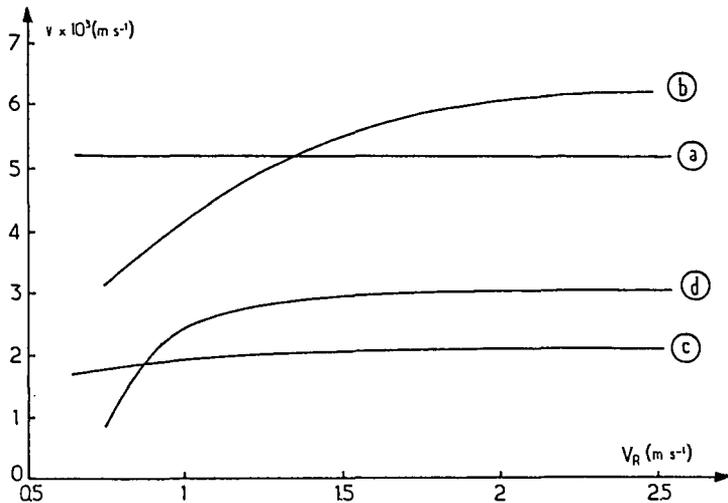


Fig. 1. Experimental variations of ablation velocities  $v$  with disk velocity  $V_R$  for four kinds of solids : a(ice,  $T_W = 348 \text{ K}$ ,  $p = 2 \times 10^5 \text{ Pa}$ ), b("rilsan",  $T_W = 723 \text{ K}$ ,  $p = 3,45 \times 10^5 \text{ Pa}$ ), c(paraffin,  $T_W = 373 \text{ K}$ ,  $p = 3,45 \times 10^5 \text{ Pa}$ ), and d (wood,  $T_W = 1073 \text{ K}$ ,  $p = 3,7 \times 10^5 \text{ Pa}$ ) (From [8]).

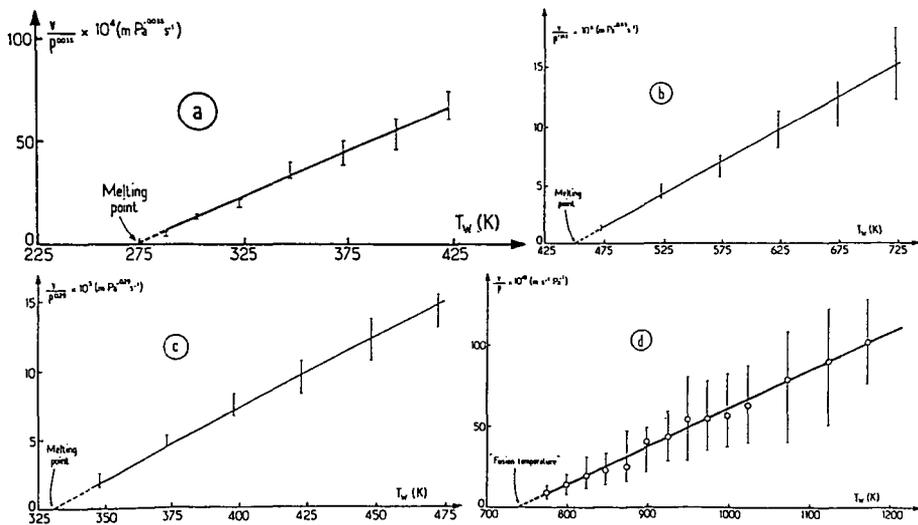


Fig. 2. Experimental variations of  $v/p^E$  with disk temperature  $T_W$  for : a(ice), b("rilsan"), c(paraffin) and d(wood) (From [8]).

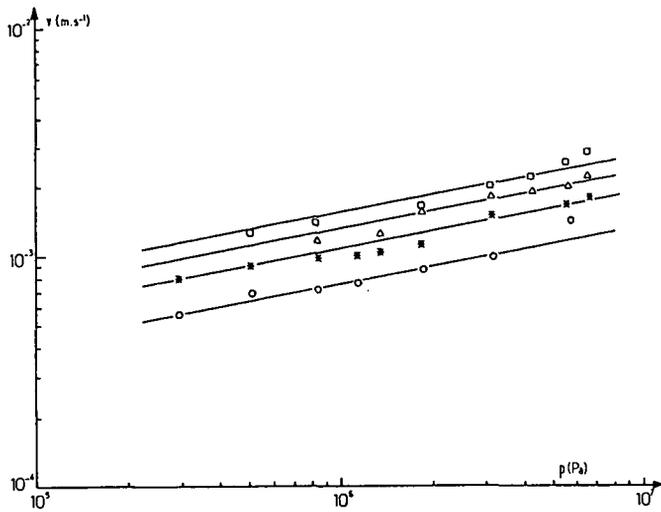


Fig. 3. Ablative pyrolysis rate of wood  $v$  as a function of applied pressure  $p$  for different wall temperatures -  $\circ$ : 823 K ;  $*$ : 873 K ;  $\Delta$ : 923 K ;  $\square$ : 973 K

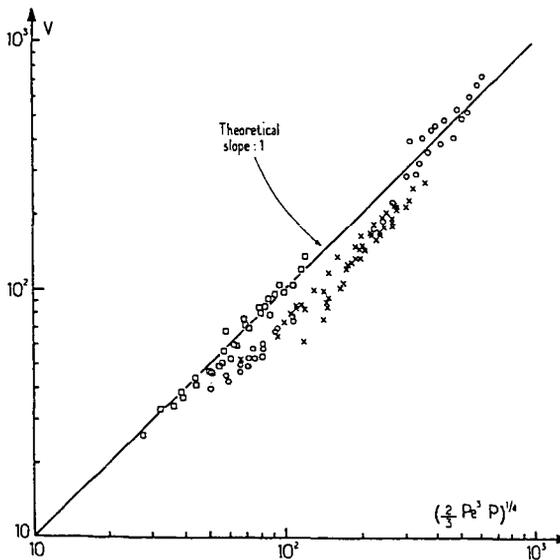


Fig. 4. Dimensionless representation of reduced velocity  $V$  as a function of reduced pressure  $P$  for three kinds of solids -  $\circ$ : paraffin ;  $x$ : ice ;  $\square$ : wood ...

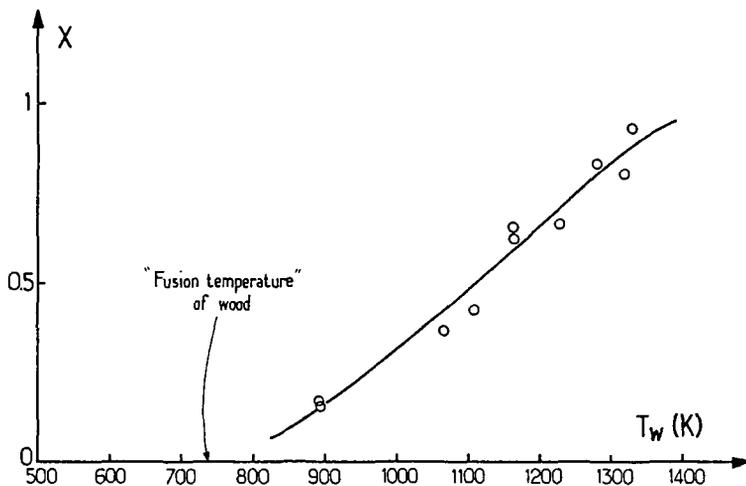


Fig. 5. Variation of the gasification yield  $X$  as a function of wall temperature  $T_W$  in the fast pyrolysis of wood sawdust in a cyclone reactor : comparison with the "fusion temperature" of 739 K.

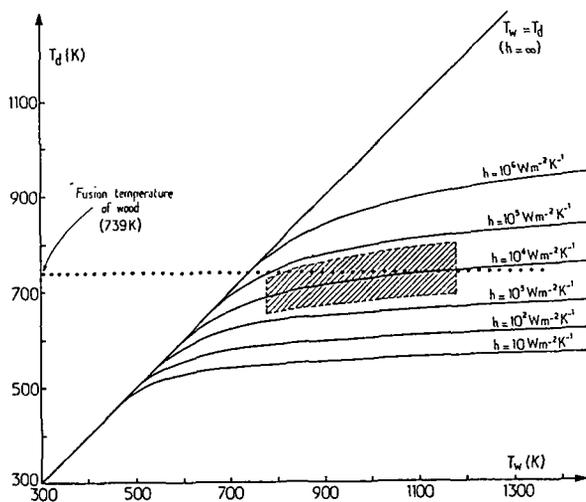


Fig. 6. Theoretical variations of wood surface temperature  $T_d$  as a function of heat source temperature  $T_W$  for different values of the external heat transfer coefficient. The hatched surface corresponds to the experimental domain ( $776 \leq T_W(K) \leq 1176$  and  $10^3 < h(W m^{-2} K^{-1}) < 6 \times 10^4$ ).