

EXPERIMENTAL MEASUREMENT OF ABLATION RATE OF WOOD PIECES, UNDERGOING FAST PYROLYSIS BY CONTACT WITH A HEATED WALL.

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1. INTRODUCTION

The conventional pyrolysis of biomass yields about equal amounts of gases, char and tar. When pyrolysis is carried out in severe heating conditions, the reaction products can be almost entirely gaseous and contain significant amounts of light unsaturated hydrocarbons. Authors involved in such research, generally recommend several types of conditions: small wood particles, high temperatures, high heating rates, high heat fluxes, etc. Few of them [1,3,5,6] have associated the idea of ablation regime, to the observation of the fast pyrolysis reaction. Actually, the apparent rate of reaction is a function of two competitive processes within the wood particle: the rate of heat transfer and the rate of chemical decomposition of wood itself. If chemical processes are very fast, the heat transfer is rate controlling: this is the so called ablation regime characterized by a thin superficial layer of reacting wood. Such a regime can be represented by the rate at which the reacting layer moves towards the cold unreacted core of the piece of wood (ablation rate v) and the thickness of this reacting layer (e).

2. EXPERIMENTAL SET UP (Fig. 1)

The experimental system consists in a stainless steel disks (diameter: 7.5×10^{-2} m) spinning at a constant velocity (of the order of 1 m.s^{-1}) and heated by four gas burners located under the disk. The mean temperature is measured with a thermocouple pressed on the upper face. Rods of beech wood ($2,3,4,6$ and 10×10^{-3} m diameter) are vertically applied on the hot surface under known and variable pressures. A jet of argon is directed towards the contact surface in order to prevent spontaneous inflammation in air. No significant rise of wood temperature and no subsequent reaction is observed when the spinning disk is not heated. This eliminates the possibility of frictional heating effects. The experiments reported here are carried out in conditions of independence of reaction rate upon disk velocity. It is to be noticed that no change in the apparent rate was observed when a notched disk was used.

The reaction produces gases and liquids undergoing further gasification on the disk surface. The presence of interstitial fluid between wood and steel acts as a kind of lubricant making the frictional contacts smoother.

The apparent rate of reaction v is obtained by direct measurement of the time required for a known length of rod to be consumed. The thickness of the ablation layer e is estimated by microscopic measurement of the extent of the uniformly darkened zone near the surface.

3. EXPERIMENTAL RESULTS

The variations of v and e were studied as a function of disk temperature (T_W), rod diameter (d), and pressure (P) under which the rods were pressed onto the disk. The pressure was controlled by placing known weights on the upper part of the rod (Fig. 1).

3.1. Variations of e with v

Fig. 2 shows some typical values of e as a function of v for $T_W = 873 \text{ K}$ and $d = 3 \times 10^{-3} \text{ m}$. The large dispersion of points is explained by the difficulty of measurement of e : wood is a very heterogeneous material and the boundary between fresh and partially reacted wood cannot be defined with accuracy. This boundary is also blurred by capillary migration of strongly coloured liquid between the grains

of the wood (this liquid is mainly water coloured by traces of tar). Despite this lack of accuracy, Fig. 2 shows that the ablation thickness roughly decreases as ablation rate increases. For high values of v , e is too small to be accurately measured (extreme ablation conditions).

3.2. Variations of v with P

A logarithmic plot of v against P shows that v can be represented by a simple relationship

$$v = a P^\beta \quad 1)$$

The accuracy of experiments is not sufficient to detect any influence of d . This shows that fast pyrolysis can be carried out with large pieces of wood and not only with small particles, as often stated in the literature. From figure 3 a straight line fitting yields the following β values: $\beta = 0.99$ ($T_w = 873$ K), $\beta = 0.97$ ($T_w = 973$ K), $\beta = 1.02$ ($T_w = 1073$ K), $\beta = 1.01$ ($T_w = 1173$ K). Therefore, we may adopt a linear dependence $v = aP$.

Fig. 3 also shows that under high temperature and pressure, the ablation rate becomes very high and may exceed $3 \times 10^{-2} \text{ m s}^{-1}$ in agreement with other determinations [1]. In these conditions, the apparent massic rate of wood consumption reaches 0.24 kg hr^{-1} ($d = 2 \times 10^{-3} \text{ m}$) and 6 kg hr^{-1} ($d = 10^{-2} \text{ m}$).

4. INTERPRETATION AND DISCUSSION OF RESULTS

4.1. Signification of a

In the same manner as the ablation reaction is controlled by heat transfer inside the wood, it will be supposed that the reaction is also limited by heat transfer from the disk to the surface of wood. The variations of v will be attributed to the variations of the heat flux with T_w and P . It will be also assumed that the temperature T_d of the surface of pyrolyzing wood is constant whatever the experimental conditions. In these conditions :

$$\phi = h(T_w - T_d) = v \rho C_p (T_d - T_o) + \rho v \Delta H \quad 2)$$

It is difficult to select an accurate value for the reaction enthalpy ΔH . Direct measurements [7] by rapid pyrolysis of wood have given values close to zero around 773 K. Reed et al. [2] proposed a model assuming that the reaction occurs in several steps: the wood is first sensibly heated without any transformation up to the reaction temperature where it is depolymerized to yield a solid which subsequently melts before vaporizing. If the tars are mechanically wiped away the heat input corresponds to sensible heat and heat of fusion. The latter has been estimated to about $4 \times 10^4 \text{ J kg}^{-1}$ at 773 K, which represents only 3.6% of the heat required to heat the wood from 373 to 773 K. Thence:

$$\phi = h(T_w - T_d) \approx v \rho C_p (T_d - T_o) \quad 3)$$

Thanks to 1) with $\beta = 1$ and 3) it can be deduced that h is proportional to P :

$$h = KP \quad 4)$$

3) and 4) show that $\frac{v}{P}$ is a linear function of T_w , allowing the calculation of T_d and K :

$$\frac{v}{P} = \frac{K}{\rho C_p} \left(\frac{T_w}{T_d - T_o} - \frac{T_d}{T_d - T_o} \right) \quad 5)$$

As expected, Fig. 4 shows that the variation is linear. With $T_o = 373$ K, $\rho = 700 \text{ kg s}^{-1}$ and $C_p = 2800 \text{ J kg}^{-1} \text{ K}^{-1}$ the following values are deduced:

$$K = 0.02 \text{ W m}^{-2} \text{ K}^{-1} \text{ Pa}^{-1} \quad \text{and} \quad T_d = 753 \pm 30 \text{ K}$$

4.2. Discussion

4.2.1. About the heat transfer coefficient h

The variations of h deduced from relation 3) and from experimental measurements are reported in Fig. 5. It appears that h is independent of d and T_w and is only a function of P . Of course, a best fitted straight line leads to the same values of K ($0.02 \text{ W m}^{-2} \text{ K}^{-1} \text{ Pa}^{-1}$) and β (0,998) as previously optimized:

The three significant modes of heat transfer are convection, radiation and more or less direct contact with the disk. There are few chances that convection may occur significantly because of transpirational cooling effect. The radiation heat transfer coefficient can be defined as: $h_R = \sigma \epsilon (T_w^2 + T_d^2)(T_w + T_d)$. Assuming $\epsilon = 0.5$ and $T_d = 753 \text{ K}$, $h_R (\text{W m}^{-2} \text{ K}^{-1})$ has the following values: 62 (873 K), 74 (973 K), 89 (1073 K), 106 (1173K). These are much lower than the experimental values of h , especially at high pressure (Fig. 5).

Direct heat transfer by interface contact between the disk and the rod can take place by combined mechanisms of conduction across true contact points and conduction across entrapped interstitial fluid. The prediction of theoretical h values is difficult: they depend on the thermal conductivity of fluid and solids, surface finish, and hardness, contact pressure, etc. Extreme values of h compiled by Rohsenow et al. [8] have been reported in Fig. 5 (dashed lines). In spite of very different experimental conditions (contact materials are metals, gap materials are metals or gases). The order of magnitude is correct. However, it is difficult to find a physical justification to the linear variation of h with P . For explaining this, theories of lubrication might be invoked if the whole heat transfer was supposed to take place across a continuous layer of insulating fluid between the two solid surfaces.

In anyway, the coefficient h is very high, showing that the mechanisms of heat transfer by contact must not be underestimated in the study of reactors where solid particles are pyrolysed by contact on the hot walls of the vessel (cyclone reactor for instance [3,8,10]).

4.2.2. About the surface temperature T_d

T_d has been assumed independent of T_w and P . The good linearity observed in Fig. 4 is a first confirmation of this. Fig. 4 also shows that $v = 0$ for $T_w = 753 \text{ K}$, in good agreement with the experimental observation that no fast reaction significantly occurs when $T_w < 753 \text{ K}$. These observations are also in agreement with thermogravimetric measurements showing that pyrolysis of dry wood is essentially complete at 773 K [4]. Let us also remind the model proposed in [2] assimilating fast pyrolysis to a three phases reaction: heating to 773 K, melting at 773 K, vaporization of tars.

Thus it seems fairly reasonable to assume that the temperature of the wood surface is of the order of 753 K whatever T_w and P . According to this mechanism, it could be wrong to say that wood is heated at the temperature of the walls of a reactor before decomposing.

4.3. Relationship between v and e

There are three different ways for establishing a simple relationship between v and e .

Let us suppose that e is the distance between the two isothermal surfaces $T = 473 \text{ K}$, $T_d = 773 \text{ K}$, and that the heat transferred is used to increase the wood temperature:

$$v \rho C_p (T_d - T) = \frac{\lambda}{e} (T_d - T) \quad \text{or} \quad v e = \frac{\lambda}{\rho C_p} = \alpha \quad (6)$$

where α is the thermal diffusivity of wood.

Assuming that penetration of heat into the rod takes place by simple one-dimension conduction, the expression giving T as a function of depth z in the solid at steady state is [8]:

$$\frac{T - T_0}{T_d - T_0} = \exp \left(- \frac{vz}{\alpha} \right) \quad 7)$$

Taking $T = 437$ K, $T_0 = 373$ K and $T_d = 773$ K, z is considered to be equal to e and then:

$$ve = 1.39 \alpha \quad 8)$$

. A model has been proposed [5] for representing the thermal volatilization of solid particles, where the equations of simultaneous heat and mass balances are numerically solved. Assuming a constant surface temperature, this model yields:

$$v = \frac{1}{b\rho} \left(\frac{\lambda r}{C_p} \right)^{1/2} \quad \text{and} \quad e = \frac{5}{b} \left(\frac{\lambda r}{rC_p} \right)^{1/2} \quad 9)$$

b is a constant number close to 2.6 when $\Delta H = 0$, r is the chemical rate of reaction and e is the thickness of the solid layer where 99 % of the reaction occurs. From expressions 9) we obtain:

$$ve = \frac{5}{b^2} \frac{\lambda}{\rho C_p} \approx 0.74 \alpha \quad 10)$$

. From the three methods above it can be deduced that

$$0.7 \alpha < ve < 1.4 \alpha \quad 11)$$

Several values of α have been proposed in the literature: $10^{-7} \text{ m}^2 \text{ s}^{-1}$ [6], $0.82 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$ [2], 0.6 to $1.5 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$ [11], 1.4×10^{-7} to $3.4 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$ [12]. These different estimations lead to: $0.4 \times 10^{-7} < ve (\text{m}^2 \text{ s}^{-1}) < 5 \times 10^{-7}$.

Fig. 2 shows that the experimental results (mean value $ve = 0.8 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$) are in agreement with this rough estimation (dashed lines).

As an illustration, for the highest ablation rate measured (fig. 3): $32.5 \times 10^{-3} \text{ m s}^{-1}$, the thickness of the ablation layer e is predicted to be about $3 \times 10^{-6} \text{ m}$.

5. CONDITIONS REQUIRED FOR THE OBSERVATION OF ABLATION

Relation 3) shows that fast pyrolysis in ablation regime (high value of v and small value of e) is expected when high heat fluxes are available as for example in solar concentrators or image furnaces. A few experiments have been done with an image furnace (mean flux density: $5 \times 10^5 \text{ W m}^{-2}$) focused on the end of a beech wood rod ($d = 8 \times 10^{-3} \text{ m}$), automatically adjusted as the reaction proceeds. The rod is placed inside a transparent glass vessel in steam atmosphere.

The apparent rate of reaction is measured to about $2 \times 10^{-4} \text{ m s}^{-1}$ while the theoretical value is $8.5 \times 10^{-3} \text{ m s}^{-1}$ (calculated on the basis of 3) with $\rho = 700 \text{ kg m}^{-3}$, $C_p = 2800 \text{ J kg}^{-1} \text{ s}^{-1}$, $T_d - T_0 = 400 \text{ K}$). The reaction produces also large amounts of char. How can this discrepancy be explained? The primary products remain for some time at the surface (there is no mechanical elimination) until they disappear by partial decomposition under the effect of high local temperature and by gasification with steam. This relatively thick layer of products partially prevents the radiation to reach fresh parts of wood and a part of the flux is consumed by the endothermal reaction of char gasification. Consequently, the overall reaction takes place in slow pyrolysis regime.

As a conclusion, it appears that fast pyrolysis of wood in ablation regime is observed if two conditions are fulfilled: high available heat flux density and efficient elimination of primary products from the surface of wood.

REFERENCES

- [1] J.P. DIEBOLD. Proceedings of Specialists' Workshop on Fast Pyrolysis of Biomass

- Copper Mountain Co (USA), October 19-22 (1980), p. 237
- [2] T.B. REED, J.P. DIEBOLD and R. DESROSIERS. *Ibid.*, p. 7
- [3] J. LEDE, F. VERZARO, B. ANTOINE and J. VILLERMAUX. *Ibid.* p. 327
- [4] F. SHAFIZADEH. *Ibid.* p. 79
- [5] J. VILLERMAUX and B. ANTOINE. *Rev. Gen. Therm. Fr.* 227 (1980), 851
- [6] J. VILLERMAUX, J. LEDE and F. VERZARO. *Rev. Gén. Therm. Fr.* 227 (1980), 861
- [7] A. ROLIN. Thesis. Centre agréé régional CNAM, Nancy (F) (1981)
- [8] W.R. ROHSENOW and J.P. HARTNETT. *Handbook of Heat Transfer*. McGraw Hill (1973)
- [9] J. LEDE et J. VILLERMAUX. *La Recherche* 134 (1982) 787
- [10] J.P. DIEBOLD and J. SCAHILL. *Fundamentals of Thermochemical Biomass Conversion* YMCA of the Rockies, Estes Park Co (USA) October 18-22 (1982)
- [11] G. LESGOURGUES and J.L. HOUZELOT. Private communication. Laboratoire des Sciences du Génie Chimique. Nancy (F) (1981)
- [12] R. CHARUEL, J.C. ROSSELET and J.M. SERRA-TOSIO. *Colloque Sciences et Industries du Bois*. Grenoble 20-22 Septembre (1982)

NOMENCLATURE

a,b,k	Constants
C_p	Heat capacity of wood
d	Rod diameter
e	Thickness of ablation layer
h, h_R	Heat transfer coefficient: Experimental, by pure radiation
P	Pressure
r	Chemical rate of reaction
T_o, T_d, T_w	Temperatures: initial (373 K), of the surface of pyrolysing wood, of the disk
v	Ablation rate
z	Depth in the rod
α	Thermal diffusivity of wood
β	Exponent
ΔH	Enthalpy of the reaction
ϵ	Emissivity
ϕ	Density of flux
λ	Thermal conductivity of wood
ρ	Mass density of wood
σ	Boltzmann constant ($5.67 \times 10^{-8} \text{ W m}^{-2} \text{ K}^{-4}$)

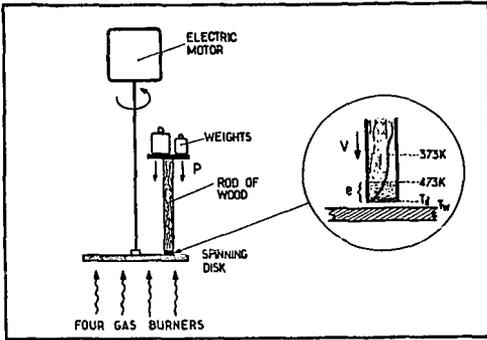


Figure 1. Scheme of experimental set-up

Figure 2. Variations of the thickness of ablation layer e as a function of ablation rate v .

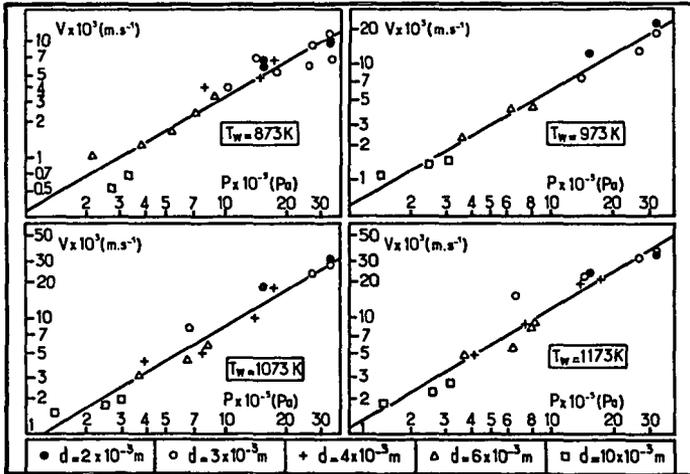
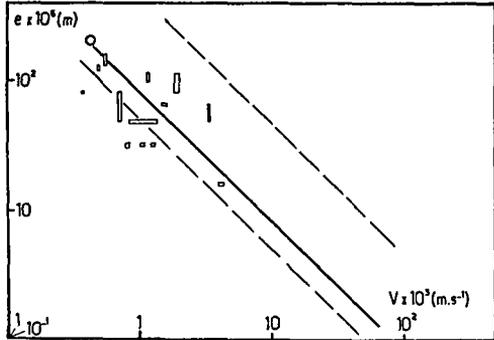


Figure 3. Experimental variations of ablation rate v as a function of pressure P for four values of disk temperature T_w .

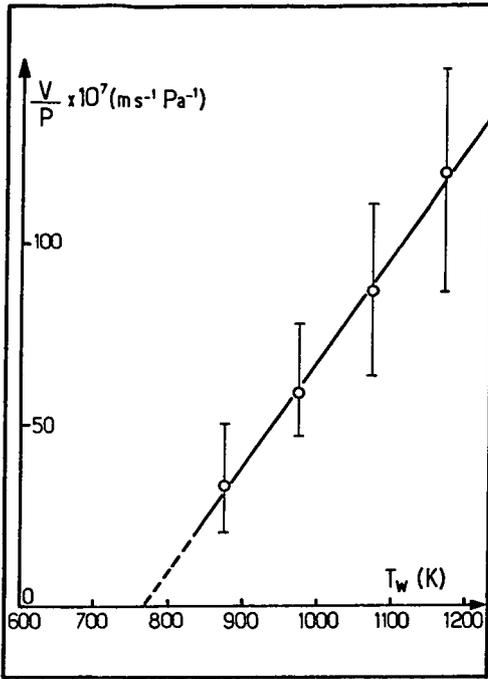


Figure 4. Variations of the ratio
 Ablation rate v
 Pressure P
 as a function of disk
 temperature T_w .

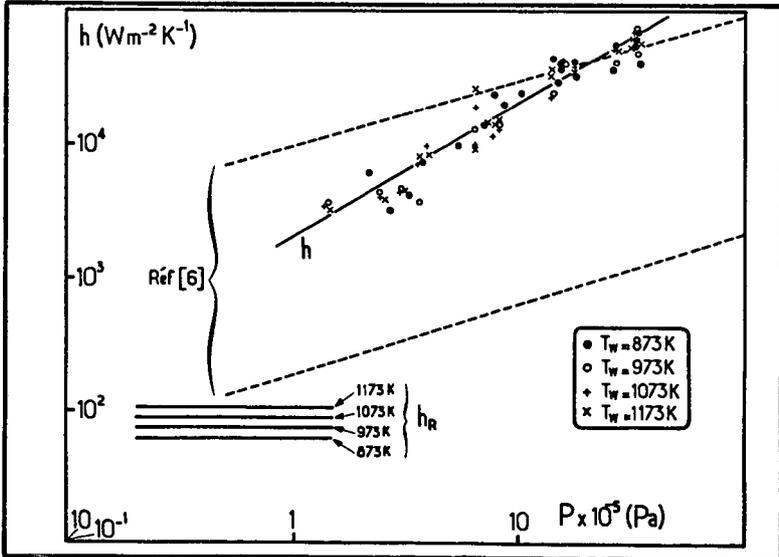


Figure 5. Variations of heat transfer coefficient h as a function of pressure p .