Journal of Thermal Analysis, Vol. 46 (1996) 67-84

INFLUENCE OF THE HEATING CONDITIONS ON THE THERMAL AND CHEMICAL BEHAVIOUR OF SOLID PARTICLES UNDERGOING A FAST ENDOTHERMIC DECOMPOSITION

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(Received December 5, 1994; in revised form April 13, 1995)

Abstract

This paper deals with models describing the thermal and chemical behaviour of solid particles undergoing fast endothermic reactions under the influence of an external heat flux. The heat source temperature is supposed to be constant, to increase with time, or to deliver a simple thermal flash. It is shown that the pyrolysis conditions (reaction temperature, conversion, etc.) depend on the chemical characteristics of the reaction and also to a large extent on the external heating conditions. Relationships are proposed to take into account these parameters. The results are applied to the thermal decomposition of $NaHCO_3$. The pyrolysis of cellulose is finally chosen in order to show how these operating parameters can also affect the selectivity of a more complex reaction.

Keywords: cellulose pyrolysis, endothermic reactions, heat transfer, modelling, $NaHCO_3$ decarbonation, particles, reaction temperature

Introduction

Reactions of solid particles of the type Solid + Fluid → Products, constitute an important domain of chemistry [1]. The endothermic reactions of simple decompositions occurring without the action of a fluid reactant (pyrolysis of organic compounds such as coal, biomass or polymers and decompositions of mineral products such as $CaCO_3$, $NaHCO_3$, etc. [2–4] are also important.

Much information is available on the kinetics of such reactions, and on temperatures of decomposition of various materials. Unfortunately, it is very difficult in practice to measure the real temperature of the reacting solid. Also, because of a strong coupling between chemical and transfer processes, the temperature of the solid may be quite different from that of the heat source. Consequently, many of these results are probably inaccurate.

0368–4466/96/ $ 5.00

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The purpose of the present paper is to study the change in actual particle temperature and the conversion as the reaction proceeds in different cases:

- Cold particle introduced into a medium at a constant high temperature
- Cold particle exposed to a thermal flash
- Cold particle introduced into a medium at an increasing temperature
- Particle reacting according to a complex chemical scheme

Standard conditions

Modelling was made with the following main assumptions:

– the particle undergoes thermal decomposition with a flat temperature profile inside the solid (no internal gradient);

– the fluid products escape freely from the inside of the solid towards the surface of the particle (no diffusional resistance);

– there is no volume change during the reaction;

– the rate of the chemical reaction is assumed to obey a first order law of the type $r = \rho_1 A \exp(-E/R_g T_S)$ (r is defined as the mass of solid transformed into fluids per unit time and unit solid volume [2]);

– the reaction is endothermic with an enthalpy change ΔH supposed to be independent of the temperature T_S of the solid (the case $\Delta H = 0$ will also be considered);

– the particle is a sphere (diameter dp or characteristic length $L = d_p/6$ [5].

The chemical regime imposes that the thermal Biot number Bi_T is lower than 0.1 [5]:

$$Bi_T = \frac{hL}{\lambda_1} < 0.1 \tag{1}$$

where the heat transfer coefficient h is supposed to be constant.

The heating conditions are represented by the heat transfer time constant t_e:

$$t_e = \frac{L\rho_1 C_{p1}}{h} \tag{2}$$

If, for example, the heat transfer occurs by radiation from a heated surface at a constant temperature of $T_W = 1000$ K and with a reacting particle at $T_S = 400$ K having an emissivity of 1, the heat transfer coefficient is close to $100\ \mathrm{W{\cdot}m^{-2}{\cdot}K^{-1}}$. With for example $t_e = 0.45$ s, a product $\rho_1 C_{p1}$ close to $2{\cdot}10^6\ \mathrm{J{\cdot}m^{-3}{\cdot}K^{-1}}$ and a thermal conductivity $\lambda_1 = 0.9\ \mathrm{W{\cdot}m^{-1}{\cdot}K^{-1}}$, the calculated particle size, from Eq. (2) is $d_p = 135{\cdot}10^{-6}$ m ($L = 22.5{\cdot}10^{-6}$ m) and the Biot number, from Eq. (1) is $2.5{\cdot}10^{-3}$.

If the transfer occurs by convection with a streaming gas, the values of h and L must fulfil condition (1) associated with a Nusselt number ($= 6\,hL/\lambda_g$) > 2 corresponding respectively to the two conditions $hL < 0.09\ \mathrm{W{\cdot}m^{-1}{\cdot}K^{-1}}$ and $hL > 6.67{\cdot}10^{-3}\ \mathrm{W{\cdot}m^{-1}{\cdot}K^{-1}}$ ($\lambda_g = 0.02\ \mathrm{W{\cdot}m^{-1}{\cdot}K^{-1}}$). With for instance $hL = 0.03\ \mathrm{W{\cdot}m^{-1}{\cdot}K^{-1}}$, a value of $t_e = 0.45$ s leads to a particle size of $d_p = 493{\cdot}10^{-6}$ m ($L = 82{\cdot}10^{-6}$ m) and a heat transfer coefficient of $365\ \mathrm{W{\cdot}m^{-2}{\cdot}K^{-1}}$. The Nusselt number is then 9, a quite possible value for a gaseous convective heat transfer, if the Nusselt number is expected to follow a Ranz and Marshall type law [5]. The Biot number calculated from (1) is then $3.3{\cdot}10^{-2}$. These calculations were made with $\lambda_g = 0.02\ \mathrm{W{\cdot}m^{-1}{\cdot}K^{-1}}$, a realistic value of the thermal conductivity for a gas at 300 K. Taking $\lambda_g = 0.06\ \mathrm{W{\cdot}m^{-1}{\cdot}K^{-1}}$ at 1000 K, the same assumption for hL and t_e leads to another quite possible value of 3 for the Nusselt number.

These calculations are typical examples, many other values could of course fit the imposed conditions.

Modelling will be applied to two practical examples: decomposition of $NaHCO_3$ to represent a pure one-step first-order reaction; cellulose flash pyrolysis to represent a more complex kinetic scheme.

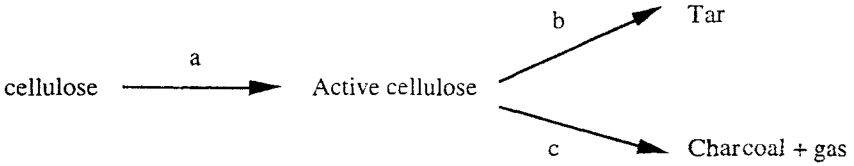
The characteristics chosen for the decarbonation reaction of $NaHCO_3$

$$2NaHCO_3 \rightarrow Na_2CO_3 + H_2O + CO_2 \tag{3}$$

are [3]: $A = 2.2{\cdot}10^{10}\ \mathrm{s^{-1}}$; $E = 95\,000\ \mathrm{J{\cdot}mol^{-1}}$; $\Delta H = 1.6{\cdot}10^{6}\ \mathrm{J{\cdot}kg^{-1}}$ (The theoretical case $\Delta H = 0$ will also be considered in order to determine the influence of the enthalpy on the results).

The mass density ρ_1; heat capacity C_{p_1} and thermal conductivity λ_1 of the compound $NaHCO_3$ are respectively $2159\ \mathrm{kg{\cdot}m^{-3}}$; $1042\ \mathrm{J{\cdot}kg^{-1}{\cdot}K^{-1}}$ and $0.9\ \mathrm{W{\cdot}m^{-1}{\cdot}K^{-1}}$.

The primary pyrolysis of cellulose will be considered in order to study the influence of the heating conditions on the selectivity of a more complex reaction. The selected mechanism is [6–8]:



(4)

The following kinetic constants for each first order process are considered as:

$$A_a = 2.8{\cdot}10^{19}\ \mathrm{s^{-1}};\quad E_a = 242\,000\ \mathrm{J{\cdot}mol^{-1}}$$

$$A_b = 3.3\cdot 10^{14}\ \mathrm{s^{-1}};\quad E_b = 197\,000\ \mathrm{J\cdot mol^{-1}}$$

$$A_c = 1.3\cdot 10^{10}\ \mathrm{s^{-1}};\quad E_c = 151\,000\ \mathrm{J\cdot mol^{-1}}$$

The enthalpy ΔH_a is sufficiently low to be supposed close to 0 [7]. In order to simplify the theoretical treatments and to observe the qualitative variations of the phenomena, it will be also supposed that $\Delta H_b = \Delta H_c = 0$.

The density ρ_1, heat capacity C_{p_1} and thermal conductivity λ_1 of cellulose and active cellulose will be assumed to be the same: $\rho_1 = 700\ \mathrm{kg\cdot m^{-3}}$; $C_{p_1} = 2800\ \mathrm{J\cdot kg^{-1}\cdot K^{-1}}$; $\lambda_1 = 0.2\ \mathrm{W\cdot m^{-1}\cdot K^{-1}}$ [7].

For both reactions (of $NaHCO_3$ and cellulose) the chosen standard value of the heat transfer time constant t_e will be 0.45 s, with some examples corresponding to 0.1 and 1 s.

High and constant heat source temperature

The first-order reaction is supposed to be of the type $\nu_1 S_1 \rightarrow \nu_2 S_2$ + (fluids).

The densities and heat capacities of S_1 and the mixture of S_1 and S_2 at conversion X are ρ_1, C_{p_1} and ρ, C_p, respectively. The heat and mass balances at the particle level are:

$$h(T_W - T_S) = Lk\rho_1(1 - X)\Delta H + L\rho C_p \frac{dT_S}{dt} \tag{5}$$

$$\frac{dX}{dt} = k(1 - X) \tag{6}$$

with the initial condition: $X = 0$, $T_S = T_o$.

The conversion yield X is defined as

$$X = \frac{m_o - m_1}{m_o} \tag{7}$$

where m_o is the mass of the solid S_1 before the beginning of the reaction and m_1 the mass of solid S_1 remaining at conversion X.

After elimination of time t between (5) and (6) one obtains the differential equation:

$$h(T_W - T_S) = Lk\rho_1(1 - X)\Delta H + L\rho_2 C_{p_2} k(1 - X)\frac{dT_S}{dX} \tag{8}$$

This equation can be written in the reduced form, based on dimensionless numbers [4]:

$$\text{Reduced temperature: } y = T_S/T_W \tag{9}$$

$$\text{Chemical time constant: } t_W = \rho_1/r_W \tag{10}$$

(r_w is the theoretical chemical rate defined at T_W)

$$\text{Activation criterion: } \gamma = E/R_gT_W \tag{11}$$

$$\text{Thermicity criterion: } H = \Delta H/C_{p_1}T_W \tag{12}$$

The variations of the physical properties of the solid as the reaction proceeds are represented by the number B:

$$B = \frac{\rho C_p}{\rho_1 C_{p_1}} = 1 + X\left[\frac{\nu_2 M_2 C_{p_2}}{\nu_1 M_1 C_{p_1}} - 1\right] \tag{13}$$

(B is most of the times close to 1, mainly for low conversion)

Under these conditions, Eq. (8) becomes:

$$B\frac{dy}{dX} = \frac{t_W}{t_e}\frac{1-y}{1-X}\exp\left(\gamma\frac{1-y}{y}\right) - H \tag{14}$$

The changes in conversion yield X have already been studied as a function of the temperature of the solid in a wide range of values of these dimensionless parameters. The main conclusions are as follows [4, 9].

The curves $X(y)$ have similar shapes with a sudden start of the reaction as soon as the temperature of the solid attains a given value T_R, very often much lower than T_W. As the reaction proceeds, a noticeable stabilization of the temperature of the solid is observed such that the term dy/dX can often be neglected in Eq. (14). Such behaviour is the result of two phenomena:

– Competition between heat fluxes required for the heating of the solid and for the endothermic reaction.

– The reaction occurring in a relatively short time.

The temperature T_R at which the reaction starts is mainly dependent on the activation energy E while it is only moderately sensitive to other parameters such as t_e, T_W, ΔH. In all cases the reaction temperature T_S differs significantly from T_W (several hundred degrees of difference for T_W = 1000 K).

The results have been validated for the thermal decomposition of $NaHCO_3$ [4, 9]. An example is reported in dimensional form in Fig. 1 for T_W = 1000 K.

It is seen that while ΔH has little influence on the temperature at which the reaction starts, it greatly influences the temperature stabilization. Table 1 shows

Table 1 Particle temperature at conversions 5% and 95% for different external heating conditions (example of the decomposition of $NaHCO_3$)

T / K	Heating conditions			
	Constant T_W (1000 K)		Increasing value of T_W with α =	
	ΔH	$\Delta H = 0$	$1.67 \cdot 10^{-3}$ K·s^{-1}	1.67 K·s^{-1}
T_S (X = 5%)	474	504	324	395
T_S (X = 95%)	532	595	363	456
T_S (5%) – T_S (95%)	58	91	39	61

that the difference in temperatures of the solid corresponding to 5 and 95% conversion is 91 K for $\Delta H = 0$, and it is only 58 K if ΔH is taken into account. It can also be shown that the heating rate dT_S/dt of the particle (calculated from Eq. (5)) is close to 10^3 K·s^{-1} for $\Delta H = 0$ (the heat exchanged with the source at T_W is only used for heating the particle) while it is reduced to about 100 K·s^{-1} if ΔH is not neglected.

Particle exposed to a thermal flash

It is supposed that a particle (T_{So} = 300 K; X_o = 0) is introduced into a hot medium (T_W = 1000 K) until it attains a given temperature T_{Si} and a conversion X_i. It is then immediately introduced into a cold medium (T_W = 300 K). Such a situation corresponds to the case of a particle exposed to a thermal flash. Practical applications could be: passing of a particle through a high energy zone (focus of solar or image furnace); passing of a particle through a hot gas boundary layer after bouncing on a surface [10]; in all cases of quenching of a reacting solid by immersion into a cold medium.

In order to solve the problem, Eq. (8) is used first with T_W = 1000 K, T_{So} = 300 K and X_o = 0 until given values of T_{Si} and X_i, and secondly with T_W = 300 K, T_{So} = T_{Si} and X_o = X_i. The heat-exchange conditions are supposed to be identical in both cases (the same values of t_e). The calculations are made for three possible values of X_i and for the thermal decomposition of the compound $NaHCO_3$.

Figure 2 shows a very important effect of the enthalpy change ΔH on the possible change in X after immersion of a particle into a cold medium. When ΔH is taken into account, only a few percent increase in X can be observed after quenching: asymptotic values X_∞ are close to X_i. Quenching is thus very efficient under these conditions, and after a few milliseconds (a few millimetres for a particle travelling at 1 m·s^{-1}) the reaction is stopped. For the assumption of $\Delta H = 0$, the reaction continues after cooling and the conversion may attain asymptotic values X_∞ much higher than X_i, sometimes close to 1, showing that

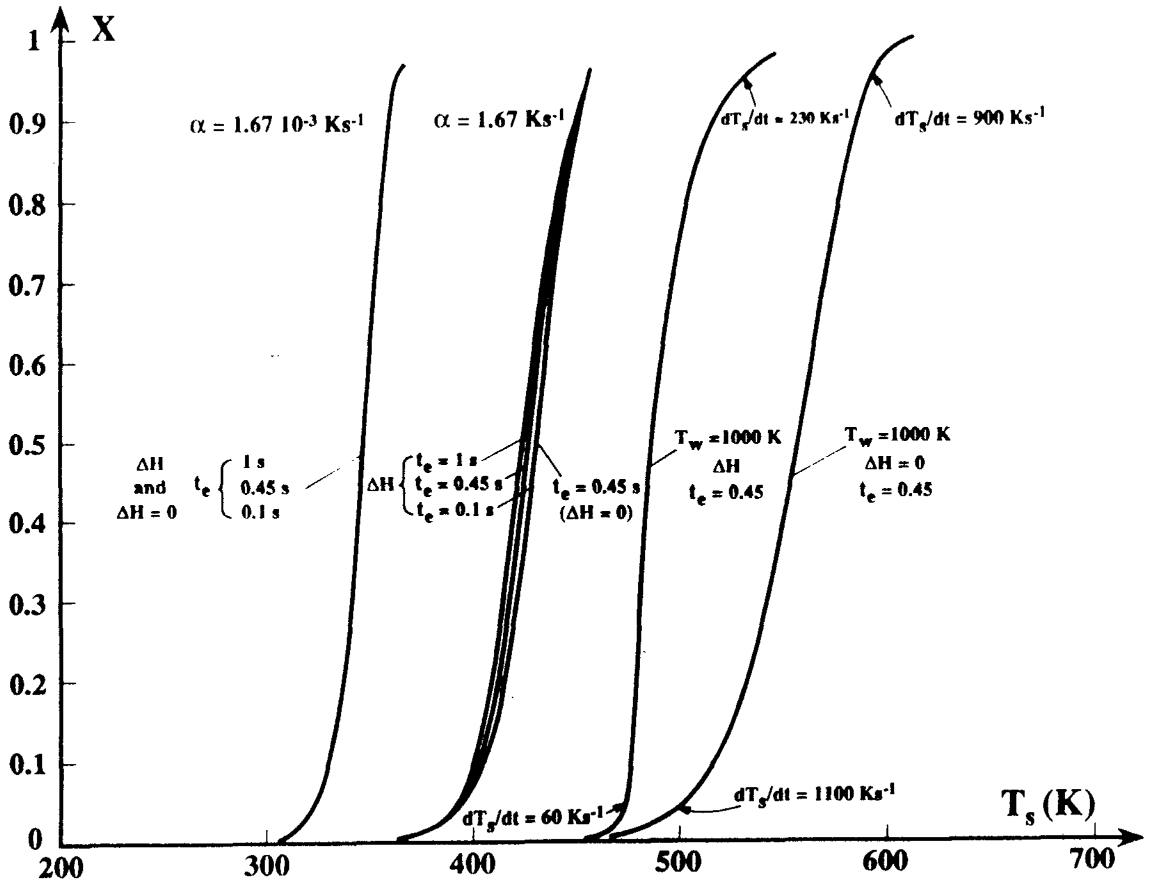


Fig. 1 Variations of conversion X as a functin of particle temperature T_S for different external heating conditions (constant heat source temperature T_W or temperature T_W increasing with time at a rate of α); several heat transfer time constants t_e; two assumptions on the enthalpy (ΔH or $\Delta H = 0$). The results relate to the decomposition reaction of $NaHCO_3$

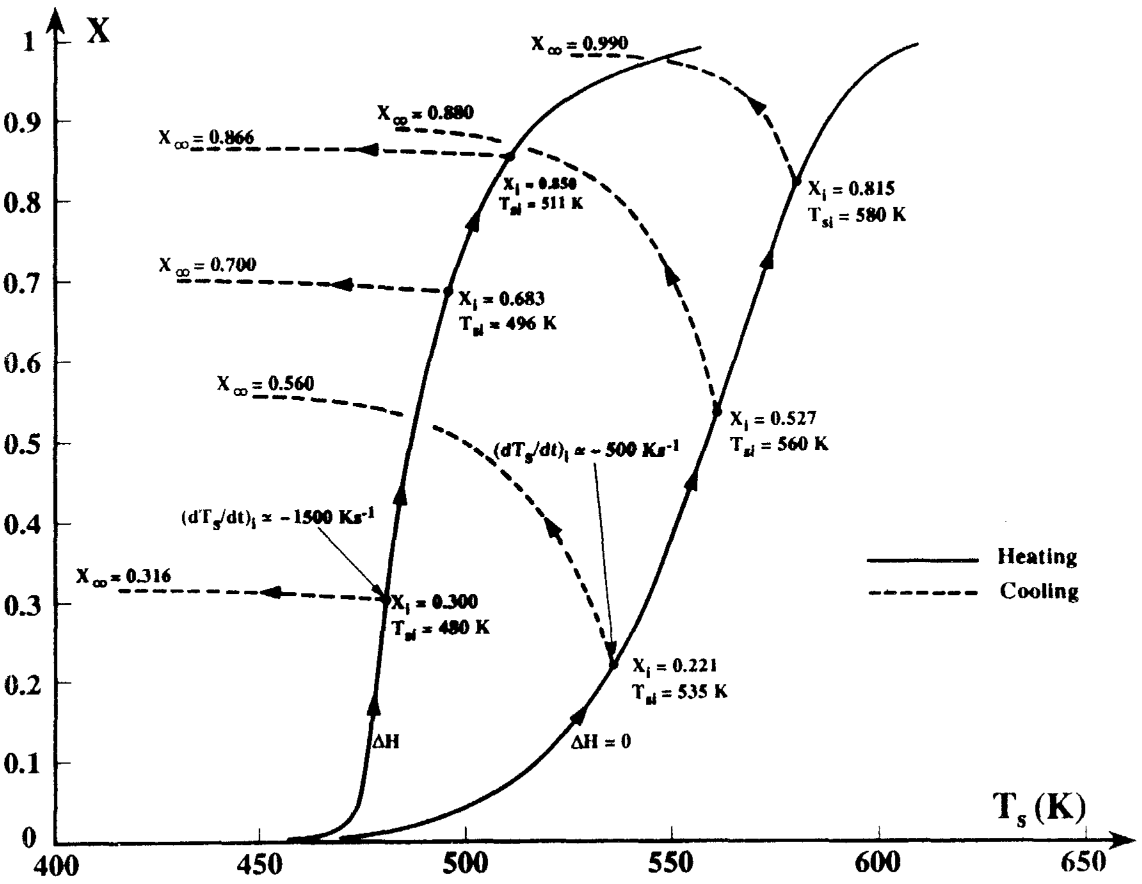


Fig. 2 Variations of conversion X as a function of particle temperature T_S under conditions of a thermal flash with two possible assumptions on the enthalpy (ΔH or $\Delta H = 0$). X_i and T_i are the values corresponding to the moment of cooling, X_∞ is the final asymptotic value of X. The results relate to the decomposition reaction of $NaHCO_3$

quenching is inefficient. However, this result shows that, on the other hand, a simple short flash heating could be sufficient for achieving a given high conversion. Figure 2 shows, in the same way, that the cooling rate dT_S/dt calculated at $X = X_i$ is logically slower when $\Delta H = 0$. It is interesting to note that the result is opposite for the heating rate (Fig. 1). In other words, the heating rate is faster and cooling rate slower for the assumption $\Delta H = 0$, compared to the case where a finite value of ΔH is taken into account. These logical observations show that if the solid may decompose in several possible elementary chemical processes, the selectivity will be different during the heating and cooling phases. These results are qualitatively similar to those obtained with other values of t_e, the cooling rates being strongly enhanced with small values of t_e.

The heat source temperature increases with time

In order to simplify the problem, three assumptions will be made:

– The temperature of the heat source is supposed to increase according to a linear function:

$$T_W = T_o + \alpha t \qquad (15)$$

– The heat transfer coefficient is constant with time

– There is no change in the physical properties of the particle ($\rho_1 = \rho_2$; $C_{p_1} = C_{p_2}$).

Under these conditions, the heat and mass balances (5) and (6) become:

$$\frac{T_o + \alpha t - T_S}{t_e} = k\,(1 - X)\,\frac{\Delta H}{C_{p_1}} + \frac{dT_S}{dt} \qquad (16)$$

$$\frac{dX}{dt} = k\,(1 - X) \qquad (17)$$

with $X = 0$ at $T_S = T_o$, and after elimination of dt:

$$\frac{dT_S}{dX} = \frac{T_o + \alpha t - T_S}{t_e\,k\,(1 - X)} - \frac{\Delta H}{C_{p_1}} \qquad (18)$$

Such a situation may be encountered in many practical situations and, for instance, in dynamic thermogravimetric analysis where most of the devices operate with $0.1 \le \alpha\ (\mathrm{K \cdot min^{-1}}) \le 100$ or $1.67 \cdot 10^{-3} \le \alpha\ (\mathrm{K \cdot s^{-1}}) \le 1.67$ [11]. Of course, in thermogravimetric experiments, temperature gradients are often observed inside the sample. But, if this sample is made of several small particles, each one has its own uniform temperature (and its own value of h) so that the qualitative conclusions of this model (formulated for single spheres) are always valid.

Values of the temperature of the solid T_S

Three approaches are considered for estimating the variations of T_S.

In a first simplified approach, it is supposed that $\Delta H = 0$. Equations (16) and (17) are independent, and the temperature of the particle T_S varies independently of the chemical reaction. The integration of (16) leads to:

$$T_S = T_o + \alpha t_e \left(\exp\left(-\frac{t}{t_e} \right) + \frac{t}{t_e} - 1 \right) \tag{19}$$

$$\frac{dT_S}{dt} = \alpha \left(1 - \exp\left(-\frac{t}{t_e} \right) \right) \tag{20}$$

The solution of Eq. (17) associated to Eq. (19) shows that the reaction occurs for $50 \le t(\mathrm{s}) \le 100$ ($\alpha = 1.67\ \mathrm{K{\cdot}s^{-1}}$) and for $10^4 \le t(\mathrm{s}) \le 4{\cdot}10^4$ ($\alpha = 1.67{\cdot}10^{-3}{\cdot}\mathrm{K{\cdot}s^{-1}}$). Under these conditions, $\exp(-t/t_e << 1)$ and $t_e << t$. Thus, Eqs. (19) and (20) can be written as:

$$T_S = T_o + \alpha t \tag{21}$$

$$\frac{dT_S}{dt} = \alpha \tag{22}$$

It follows that the particle is at the same temperature as the heat source at every time. The mass balance (17) can then be written as:

$$\frac{dX}{dT_S} = \frac{k}{\alpha} (1 - X) \tag{23}$$

Figure 1 shows the corresponding variations $X(T_S)$ for the two extreme values of α for $t_e = 0.1$, 0.45 and 1 s with the assumption of $\Delta H = 0$. The times required by the solid to attain the temperature at which $X = 1$ are approximately $3{\cdot}10^4$ s (8.3 h) for $\alpha = 1.67{\cdot}10^{-3}\ \mathrm{K{\cdot}s^{-1}}$ and 72 s for $\alpha = 1.67\ \mathrm{K{\cdot}s^{-1}}$, values much higher than the time constants t_e.

A second simplified approach supposes that, during the reaction, the term dT_S/dt is small compared to $\Delta H/C_{p1}$ in Eq. (18) as reported for most experimental conditions [4]. Under these conditions, Eq. (18) becomes:

$$T_o + \alpha t - T_S = t_e\, k\, (1 - X) \frac{\Delta H}{C_{p1}} \tag{24}$$

The corresponding $X(T_S)$ variations are depicted in Fig. 1. It is observed that the results are similar to those corresponding to the assumption of $\Delta H = 0$ at small heating rates ($\alpha = 1.67 \cdot 10^{-3}$ K·s^{-1}). There is only a very small difference in the case of $\alpha = 1.67$ K·s^{-1}.

In a third approach, no assumption is made and Eqs (16) and (17) are numerically integrated. The results obtained are similar to those derived from the previous assumptions of $\mathrm{d}T_S/\mathrm{d}X = 0$.

As a conclusion, it appears that whatever the assumptions made for the enthalpy, the calculated variations $X(T_S)$ are roughly identical and that the simplified expression (23) may represent the phenomena. Then it can be supposed that the particle temperature is the same as that of the heat source at every moment of the reaction. This is the most fundamental difference from the case of constant heat source temperature which is often much higher than the true reaction temperature T_S. This is a logical consequence of the fact that low values of T_W and heating rates α (a few degrees per min) are associated with small heat transfer time constants t_e (a fraction of seconds). Figure 1 shows that for constant heat source temperature, the heating rates of the solid are always much higher ($\mathrm{d}T_S/\mathrm{d}t = 60$ to 900 K·s^{-1}) than in the case of experiments made with increasing values of T_W where $\mathrm{d}T_S/\mathrm{d}t$ is always close to α.

All these calculations have been made with the assumption of a constant heat transfer coefficient h. This is for example encountered in the case where the heat source is a preheated flowing gas exchanging energy with the particle by convection. However, heating is very often ensured by radiation from a wall whose temperature increases with time. Under these conditions, the heat transfer coefficient $h_W = \sigma\varepsilon\,(T_W^4 - T_S^4)/(T_W - T_S) = \sigma\varepsilon\,(T_W^2 + T_S^2)\,(T_W + T_S)$ increases with T_W and the equations of the model are more complicated. Equation (5) of the heat balance becomes

$$\sigma\varepsilon\,[(T_o + \alpha t)^4 - T_S^4] = Lk\rho_1\,(1 - X)\,\Delta H + L\rho C_p \frac{\mathrm{d}T_S}{\mathrm{d}t} \qquad (25)$$

With assumption of $\Delta H = 0$, $\rho_1 = \rho$ and $C_{p_1} = C_p$, the numerical integration of Eq. (25) with $\varepsilon = 1$ gives similar variations of T_S with time t than those derived from Eq. (19) for given values of L, ρ_1, C_{p_1}. The values of T_S are then always very close to those of T_W and the variations $X(T_S)$ are the same as in the case of h = constant.

Domains of reaction temperatures

In all the cases, Fig. 1 shows that the reaction occurs within a relatively narrow range of temperature of the particle. Table 1 gives the values of $T_S(X = 5\%)$ and $T_S(X = 95\%)$. It can be seen that the difference between these values is smaller when α is small (only 39 K for $\alpha = 1.67 \cdot 10^{-3}$ K·s^{-1}). For very small heating rates α and constant values of T_W, the reaction can be considered as quasi-isothermal up to ≅ 60% conversion. Figure 1 and Tables 1, 2 and 3 show that because of the low sensitivity of T_S to changes in t_e and T_W, the ranges of reaction temperatures are never identical, but depend strongly on the experimental situation: slow or fast heating rate or constant value of T_W. These ranges are roughly: 324–363 K for $\alpha = 1.67 \cdot 10^{-3}$ K·s^{-1} 395–456 K for $\alpha = 1.67$ K·s^{-1}; 474–532 K for $T_W = 1000$ K. Thus, it would always be quite interesting to perform measurements in each of these situations in order to enlarge the experimental ranges of temperatures and to test, for example, the validity of kinetic laws with greater accuracy [3, 12].

Sensitivity of the variations $X(T_S)$ to changes in the operating parameters (comparison with the case T_W = constant)

Influence of enthalpy change ΔH

As previously observed, ΔH has only little influence in the case of progressive heating (Fig. 1), the process being controlled by the heating rate α of the heat source. Table 2 reveals, for $X = 50\%$, a difference of only 5 K in the reaction temperature. In the case of constant values of T_W, while ΔH has only a small effect on the temperature at which the reaction starts (Fig. 1), it greatly influences the domain of reaction temperature: Table 1 shows that the reaction

Table 2 Influence of the external heating rate α and heat transfer time constant t_e on the temperature of a reacting particle at 50% conversion (example of the decomposition of $NaHCO_3$)

t_e / s	External heating rate α / K·s^{-1}	
	$1.67 \cdot 10^{-3}$	1.67
0.1	347	431
0.45	347	427 (432 for $\Delta H = 0$)
1	347	424

Table 3 Influence of the temperature of heat source T_W and heat transfer time constant t_e on the temperature T_R at which the reaction starts (example of the decomposition of $NaHCO_3$)

t_e / s	Constant T_W / K	
	1000	500
0.1	504	489
0.45	473	460
1	458	446

occurs in a range of 91 K for $\Delta H = 0$ and only 58 K if ΔH is taken into account.

Influences of t_e and T_W

For T_W = constant, an empirical relationship has been proposed [4] for representing the variations of the temperature T_R at which the reaction starts:

$$\frac{1}{T_R} = \frac{R_g}{E} \ln \left(2A \frac{\Delta H}{C_{p_1}} \frac{t_e}{T_W} \right) \tag{26}$$

showing that the effective parameter is the activation energy E, the other parameters appearing in the logarithm. In the case of the decomposition of the compound $NaHCO_3$ this equation becomes:

$$T_R = \frac{11\,418}{\ln \left(6.75 \cdot 10^{13} \frac{t_e}{T_W} \right)} \tag{27}$$

Table 3 shows the relatively small influence of t_e on the value of T_R ($\cong$ 45 K for a factor of 10 in t_e). It also appears that the phenomena are only very slightly dependent on the heat source temperature: changing T_W from 1000 to 500 K has almost no effect on T_R for a given t_e (maximum variation of only 15 K in the values of T_R).

These results confirm that modification of the experimental values of granulometry d_p, heat transfer coefficient h or heat source temperature T_W would have practically no effect on the particle reaction temperature T_S.

For increasing values of T_W, Fig. 1 and Table 2 show that t_e has no influence on T_S (at X = 50%) for $\alpha = 1.67 \cdot 10^{-3}$ K·s^{-1} and only a very small effect (only 7 K for the highest value of α = 1.67 K·s^{-1}. This is a logical consequence of the fact that $T_S = T_W$ at any time for all values of α. As in the previous case, these results show that changing h and/or L has no appreciable effects on the reaction temperature of the solid. The sensitive parameter is the heating rate of the source ($\approx$ 80 deg difference for extreme values of α). As a consequence of these observations, the published values of decomposition temperatures of different solid reactants have no sense if α is not mentioned. Of course, this important parameter must always be taken into account in the calculation of kinetic constants derived from thermogravimetric measurements (Eq. (23)).

Influence of the heating conditions on the selectivity of a complex reaction

The results in the previous part of this paper have shown that changes in the heating conditions may cause significant differences in the temperature ranges in which the decomposition of a solid proceeds. It results that if several primary or secondary competitive reactions with different activation energies are possible, the selectivity may be highly affected by the transfer conditions. In order to bring evidence of these phenomena, the example of the pyrolysis of cellulose will be presented Eq. (4). The first-order step gives rise to active cellulose: the results of the previous sections apply to this process that occurs at given cellulose temperatures. After this step, two other first-order processes are possible, producing tar or solid charcoal. Supposing that we want to minimize charcoal formation, let us define the instantaneous yield of tar φ at a given reaction temperature T_S:

$$\varphi = \frac{k_b}{k_b + k_c} = \frac{1}{1 + A_o \exp\left(\frac{E}{T_S}\right)} \tag{28}$$

with $A_o = \frac{A_c}{A_b} = 3.96 \cdot 10^{-5}$ and $E_o = \frac{E_b - E_c}{R_g} = 5.53 \cdot 10^3\ K$

It is interesting to study the change in φ with the conversion X_C of cellulose as the reaction proceeds, and for various heating conditions:

$$X_C = \frac{\text{Initial mass of cellulose} - \text{remaining mass of cellulose}}{\text{Initial mass of cellulose}} \tag{29}$$

For sake of simplicity, the primary process (a) is supposed to occur without any change in particle properties (ρ_1, C_{p_1} and d_p). Two cases are considered: constant and increasing heat source temperature T_W.

Constant T_W

Combination of Eqs (5) and (6) with definition (28) and with the assumption of $\Delta H_a = 0$ leads to the following differential equation:

$$\frac{d\varphi}{dX_C} = \frac{\varphi(1-\varphi)}{E_o}\left(\ln\frac{1-\varphi}{A_o\varphi}\right)^2 \frac{T_W - T_S}{t_e k_a (1 - X_C)} \tag{30}$$

The elimination of T_S between (28) and (30) leads to another equation, the numerical integration of which yields the variations of φ with X_C. Figure 3 shows (for $t_e = 0.4$ s) that after a more or less steep increase in φ, at the beginning of the reaction, φ rapidly reaches constant values (for $X_C > 0.1$) which are strongly dependent on T_W, that appears as a very important parameter in determining the selectivity. The tar yield is much higher for high values of T_W as often observed in the literature: 30% for $T_W = 500$ K; 72% for 600 K; 87% for 700 K and 91% for 1000 K (at $X_C = 50\%$).

Increasing values of T_W

The law of variation is supposed to be given by Eq. (15). Calculations are made with the assumption that $T_S = T_W$ at any time.

Combination of Eqs (23) and (28) leads to a new equation:

$$\frac{d\varphi}{dX_C} = \frac{\varphi(1-\varphi)}{E_o}\left(\ln\frac{1-\varphi}{A_o\varphi}\right)^2 \frac{\alpha}{k_a(1-X_C)} \tag{31}$$

Figure 3 shows that, in contrast with the case of T_W = constant, the selectivity φ is not constant but increases while the reaction proceeds. Moreover, for a given conversion X_C, the selectivity always strongly depends on the heating rate: φ is 25 to 30% higher for the highest heating rate applied of 1.67 K·s^{-1}. In other words, a given selectivity φ at a given cellulose temperature T_S could be observed at very low or very high conversions X_C, according to the value of α

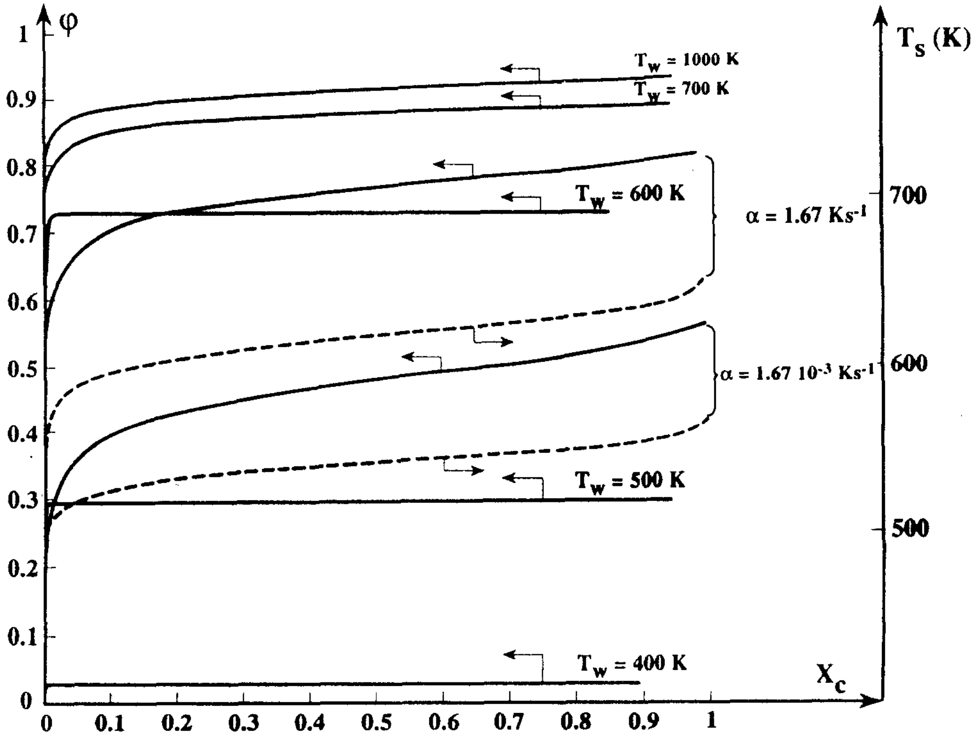


Fig. 3 Variations of the instantaneous selectivity φ as a function of conversion X_C for two different external heating rates α and for the case of a constant heating source temperature T_W. The results relate to the pyrolysis of cellulose, φ being the instantaneousyield of tar

(for example, $\varphi = 0.55$ and $T_S = 560$ K would correspond to $X_C \cong 0$ with $\alpha = 1.67$ K·s^{-1} and to $X_C \cong 1$ with $\alpha = 1.67 \cdot 10^{-3}$ K·s^{-1}). It can also be shown that for a given cellulose temperature T_S, the selectivity φ is always higher in the case of constant T_W. These results allow the conclusion that the conversion yield and selectivity are not only dependent on the instantaneous temperature of cellulose but, to a large extent, also on the external heating conditions.

Conclusions

The modelling of the endothermal decomposition of solid particles was carried out under strong coupling conditions between reaction and transfer heat fluxes. As an example, the equations were applied to the thermal decomposition reaction of $NaHCO_3$, but the results are qualitatively valid for every solid pyrolysis reaction of the type $S_1 \rightarrow S_2 +$ (fluids).

When a cold particle is introduced into a hot medium, a simple heating of the solid is first observed until a given temperature is attained at which it reacts in a relatively narrow temperature range. The reaction conditions are controlled by both the chemical characteristics of the reaction and the heat transfer processes. The influence of the main effective parameters was underlined. When a cold particle is introduced into a medium the temperature of which increases with time, the reaction conditions are mainly controlled by the heating rate of the heat source. A consequence is that the reaction conditions (temperature, conversion, experimental parameters, etc.) may be quite different from those observed with a constant heat source temperature.

The difference in behaviour is also very important when the chemical processes are more complex as observed in the case of the pyrolysis of cellulose where the selectivity strongly depends on the conditions.

The case of a particle undergoing a thermal flash has also been studied and also the parameters controlling the efficiency of quenching. The influence of the enthalpy change on the rate of heating and cooling of the particle has also been underlined.

The main conclusions are that if the enthalpy and activation energy of a reaction are important parameters, the rate of heating (or cooling) may also greatly affect the conditions of particle pyrolysis. Speaking of "reaction temperature", "pyrolysis temperature" or "decomposition temperature" of a solid material has no sense if the conditions of heating are not given, the results being only valid for a given apparatus and set of experimental conditions. It results that these phenomena have to be mentioned and taken into account in the calculation of Arrhenius parameters from experimental results. Hence, many of the published kinetic constants must be considered and used very carefully.

Notations

A, A_a, A_b, A_c	Preexponential factor of the Arrhenius law equation and of processes a, b, c / s^{-1}
A_o	Ratio A_c/A_b
B	Dimensionless parameter describing the evolution of ρ and C_p as a function of X
Bi_T	Thermal Biot number
C_p	Heat capacity of the solid at conversion X / $J\cdot kg^{-1}\cdot K^{-1}$
C_{p1}, C_{p2}	Heat capacity (of solid S_1; of solid S_2) / $J\cdot kg^{-1}\cdot K^{-1}$
d_p	Particle diameter / m
E, E_a, E_b, E_c	Activation energy of processes a, b, c / $J\cdot mol^{-1}$
E	Ratio $(E_b - E_c)/R_g$ / K
h	Heat transfer coefficient / $W\cdot m^{-2}\cdot K^{-1}$
h_W	Radiation heat transfer coefficient / $W\cdot m^{-2}\cdot K^{-1}$
H	Thermicity criterion
k	First order kinetic constant / s^{-1}
L	Characteristic particle size (volume to external surface area ratio, $= d_p/6$ for a sphere) / m
m_o	Initial mass of solid S_1 / kg
m_1	Mass of solid S_1 remaining at conversion X / kg
M_1	Molecular weight of solid S_1 / $kg\cdot mol^{-1}$
M_2	Molecular weight of solid S_2 / $kg\cdot mol^{-1}$
r, r_W	Rate of chemical reaction at T_S and T_W / $kg\cdot m^{-3}\cdot s^{-1}$
R_g	Gas constant / $J\cdot mol^{-1}\cdot K^{-1}$
S_1, S_2	Solid reactant and product
t	Time / s
t_e	Heat transfer time constant / s
t_W	Chemical time constant / s
T_{So}, T_S, T_{Si}, T_R	Particle temperature (initial; at time t; at the time of quenching; when the reaction starts) / K
T_W	Heat source temperature / K
X_o, X, X_i, X_C	Conversion (initial; at time t; at the time of quenching; in the pyrolysis of cellulose)
y	Reduced temperature

Greek letters:

α	Heating rate of the heat source / $K\cdot s^{-1}$
ΔH	Reaction enthalpy / $J\cdot kg^{-1}$
ε	Emissivity
φ	Instantaneous yield of tar

γ	Activation criterion
λ_1, λ_g	Thermal conductivity (of solid S_1; of the carrier gas) / $W \cdot m^{-1} \cdot K^{-1}$
ρ	Density of the solid at conversion X / $kg \cdot m^{-3}$
ρ_1, ρ_2	Density (of solid S_1; of solid S_2) / $kg \cdot m^{-3}$
σ	Boltzmann constant ($5.67 \cdot 10^{-8}$ $W \cdot m^{-2} \cdot K^{-4}$)

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