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Heterogeneous thermochemical decomposition of a semi-transparent particle under high-flux irradiation: uniform versus non-uniform irradiation

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Abstract The effects of a semi-transparent reacting particle irradiation are analysed using a transient combined heat transfer model. Direct uniform irradiation is found to be favourable for particle heating and decomposition, decreasing the total reaction time by a factor of 3.3 as compared to that for non-uniform irradiation. In both cases heat transfer from the surface to the reaction zone is the process limiting mechanism.

List of symbols

A	Area (m^2)
$\bar{c}_p$	Specific heat at constant pressure ($\text{J mol}^{-1} \text{K}^{-1}$)
E_c	Activation energy of chemical reaction rate constant (J mol^{-1})
h	Heat transfer coefficient ($\text{W m}^{-2} \text{K}^{-1}$)
$\bar{h}$	Specific enthalpy (J mol^{-1})
I_λ	Spectral radiation intensity ($\text{W m}^{-2} \mu\text{m}^{-1} \text{sr}^{-1}$)
k_c	Chemical reaction rate constant ($\text{mol m}^{-2} \text{s}^{-1}$)
k_0	Pre-exponential factor of chemical reaction ($\text{mol m}^{-2} \text{s}^{-1}$)
k	Thermal conductivity ($\text{W m}^{-1} \text{K}^{-1}$)
N	Amount of substance (mol)
n	Refractive index
$\hat{n}$	Unit normal vector
p	Pressure (Pa)
$\dot{q}$	Heat flux (W m^{-2})

$\bar{R}$	Universal gas constant ($8.314 \text{ J mol}^{-1} \text{K}^{-1}$)
r	Radius (m)
$\bar{r}$	Reaction rate ($\text{mol m}^{-3} \text{s}^{-1}$)
$\hat{k}$	Unit vector into the z -direction
S_v	Volume based specific surface area ($\text{m}^2 \text{m}^{-3}$)
$\dot{S}$	Volumetric heat source (W m^{-3})
T	Temperature (K)
t	Time (s)
$\bar{V}$	Molar volume ($\text{m}^3 \text{mol}^{-1}$)
V	Volume (m^3)
x, y, z	Cartesian coordinates (m)
X	Reaction extent

Greek symbols

β	Extinction coefficient (m^{-1})
$\Delta H_{298\text{K}}^0$	Standard enthalpy of reaction (J mol^{-1})
λ	Wavelength (μm)
ν	Stoichiometric coefficient
$\bar{\rho}$	Molar concentration (mol m^{-3})
ρ	Reflectivity
θ	Polar angle (rad)
σ	Stefan–Boltzmann constant ($\sigma = 5.6704 \times 10^{-8} \text{ W m}^{-2} \text{K}^{-4}$)

Subscripts

a	Absorption
b	Blackbody
CaCO ₃	Calcium carbonate
CaO	Calcium oxide
CO ₂	Carbon dioxide
chem	Chemical
cond	Conduction
eff	Effective
em	Emission

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ext	External
gr	Grain
i	Component index
p	Particle particle surface
rad	Radiative
λ	Spectral
0	Initial

Other symbols

∇ Del operator

1 Introduction

Chemically reacting particles exposed to high-flux irradiation are often encountered in high-temperature solar thermochemical processes [1–3]. Optically large semi-transparent particles of non-uniform composition and morphology are used in the solar thermal lime and cement production [4–7], and solar thermochemical CO₂ capture [8–10]. In these applications, particles are found in multiple configurations such as moving/mixing beds [4–6], stationary beds [7] and fluidized beds [9, 10], resulting in different particle irradiation conditions. Non-uniform irradiation of optically large particles results in non-uniform temperature and chemical reaction rate that may significantly affect the overall decomposition time. Examples of previous pertinent studies of radiative heat transfer in optically large semi-transparent particles exposed to non-uniform external irradiation can be found in [11, 12].

In this work, we extend the conjugate heat transfer analyses of uniformly-irradiated large and semi-transparent CaCO₃ particles undergoing thermal decomposition presented in [13, 14] to investigate the effects of non-uniform particle irradiation. The model predicts the temperatures and chemical reaction extent for a range of physical parameters with their values matching conditions anticipated in solar thermochemical applications.

2 Problem statement

A non-gray, non-isothermal and non-uniform semi-transparent spherical particle in the size range of geometrical optics is exposed to high-flux irradiation and placed in a hot air flow as schematically shown in Fig. 1. The particle undergoes heterogeneous thermochemical decomposition according to [15]:

The chemical reaction rate is modelled by assuming the volumetric decomposition model with changing grain size described in [16] and employed in a combined heat transfer

model for a heterogeneous thermochemical decomposition of a semi-transparent particle under direct high-flux irradiation [14]. The rate of reaction (1) and the rate at which the radius of the CaCO₃ grains shrink are given by [16]:

$$\bar{r} \stackrel{\text{def}}{=} \frac{\bar{r}_i}{v_i} = \frac{1}{v_i} \frac{dN_i}{dV dt} = -S_{v,0} \bar{\rho}_{0,\text{CaCO}_3} \left(\frac{r_{\text{gr,CaCO}_3}}{r_{0,\text{gr,CaCO}_3}} \right)^2 \frac{dr_{\text{gr,CaCO}_3}}{dt},$$

$$i = \text{CaCO}_3, \text{CaO}, \text{CO}_2 \quad (2)$$

$$\frac{dr_{\text{gr,CaCO}_3}}{dt} = -k_c \bar{V}_{0,\text{CaCO}_3} f(p_{\text{CO}_2}), \quad k_c = k_0 \exp\left(-\frac{E_c}{RT}\right) \quad (3)$$

where v_i are the stoichiometric coefficients in Eq. (1), $v_{\text{CaCO}_3} = -1$ and $v_{\text{CaO}} = v_{\text{CO}_2} = 1$; $\bar{R}$ is the gas constant, T is the reaction temperature, $\bar{V}_{0,\text{CaCO}_3}$ is the molar volume of non-porous CaCO₃, $S_{v,0}$ is the initial volume-based specific surface area, and $f(p_{\text{CO}_2})$ is a function of the CO₂ partial pressure [14, 16]. The local and overall extents of the reaction (1) are defined as [13, 14]:

$$X_{\text{local}}(r, \theta, t) \stackrel{\text{def}}{=} 1 - \frac{\bar{\rho}_{\text{CaCO}_3}(r, \theta, t)}{\bar{\rho}_{0,\text{CaCO}_3}},$$

$$X_{\text{overall}}(t) \stackrel{\text{def}}{=} \frac{2\pi \int_0^\pi \int_0^{r_p} r^2 X_{\text{local}}(r, \theta, t) \sin \theta dr d\theta}{\frac{4}{3}\pi r_p^3} \quad (4)$$

Fig. 1 Optically large and semi-transparent particle undergoing heterogeneous decomposition under: **a** diffuse and uniform particle irradiation and **b** collimated and partial particle irradiation

The parameters of the calcination reaction and the morphological parameters of CaCO_3 and CaO are taken in this study for the Blanca limestone [16].

Two cases of the external particle irradiation are considered: (a) diffuse and uniform irradiation of the whole particle surface approximating irradiation conditions of a fast rotating and moving particle exposed to a collimated flux; and (b) partial irradiation of the particle surface by a collimated flux approximating irradiation conditions of an immobilized particle. Note that the assumption of non-uniform and directional irradiation of an immobilised particle is an idealization and is considered here as a limiting case. In a practical application, an immobilised particle will radiatively interact with other particles and/or reactor walls. The external irradiation is time-independent, has the spectral distribution of a blackbody at 5,777 K to approximate the solar spectrum, and is equal to $\dot{q}_0 = 1 \text{ MW m}^{-2}$ in both cases. The particle surface is assumed to be grey-diffuse with the initial surface reflectivity of $\rho = 0.0925$. The porous CaO is assumed to be non-reflective. The air outside the particle flows with the free-stream velocity $u_\infty = 0.09 \text{ m s}^{-1}$, pressure $p_\infty = 1 \text{ atm}$, and temperature $T_\infty = 1,500 \text{ K}$ to approximate conditions in a solar reactor for CaCO_3 decomposition [4, 5]. The external convective heating and mass transfer at particle surface is uniform over the entire particle surface. The particle radius remains unchanged with time. The initial pressure in the particle is $p = 1 \text{ atm}$. The gas phase in the pores inside the particles is radiatively non-participating. The dense CaCO_3 is assumed to be non-scattering. The irregularly shaped and randomly oriented CaO grains formed during the calcination reaction are assumed to be spherical. For simplicity, it is assumed that the partial pressure of CO_2 is constant and equal to the partial pressure of CO_2 in the atmospheric air, $p_{\text{CO}_2} = 39.5 \text{ Pa}$. As the reaction (1) proceeds, the specific surface area, porosity, properties (optical, radiative, thermal), composition and temperature of the particle undergo transient variations.

3 Heat transfer model

The energy conservation equation is formulated for the solid phase [13, 14]:

$$\bar{\rho} \bar{c}_p \frac{\partial T}{\partial t} = \nabla \cdot (k_{\text{cond}} \nabla T + k_{\text{rad}} \nabla T) + \dot{S}_{\text{chem}} \quad (5)$$

where T , $\bar{\rho}$, $\bar{c}_p$, and $\dot{S}_{\text{chem}}$ are the time-dependent temperature, molar density, molar specific heat, and the volumetric heat source, respectively. The internal radiative transport in the particle is modeled using the Rosseland

diffusion approximation with time-dependent non-gray extinction coefficient of the particle material [13, 14, 17]:

$$k_{\text{rad}} = \frac{16n_{\text{eff}}^2 \sigma T^3}{3\beta_R}, \quad \frac{1}{\beta_R} = \frac{\pi}{4\sigma T^3} \int_{\lambda=0}^{\infty} \frac{1}{\beta_\lambda} \frac{dI_{b\lambda}}{dT} d\lambda \quad (6)$$

where β_λ is the spectral extinction coefficient of the medium inside the particle and n_{eff} is the effective refractive index. The volumetric heat source due to the chemical reaction is:

$$\dot{S}_{\text{chem}} = -\bar{r} \sum_j \bar{h}_j v_j = -\bar{r} [\bar{h}_{\text{CaO}}(T) + \bar{h}_{\text{CO}_2}(T) - \bar{h}_{\text{CaCO}_3}(T)] \quad (7)$$

The initial condition and the boundary conditions are:

$$T(r, t = t_0) = T_0 \quad (8)$$

$$\nabla T|_{r=0} = 0, \quad (9a)$$

$$(k_{\text{cond}} + k_{\text{rad}}) \nabla T|_{r=r_p} = h_{\text{ext}}(T_\infty - T) + \dot{q}_a - \dot{q}_{\text{em}} \quad (9b)$$

where $\dot{q}_a$ and $\dot{q}_{\text{em}}$ are the absorbed portion of the incident external flux and the flux emitted from the particle. The external heat transfer coefficient at the particle surface h_{ext} is obtained using the correlation for a flow over a sphere by Whitaker [18]. The surface reflectivity is modeled as a weighted sum of the reflectivities for CaCO_3 and CaO , $X_{\text{local}} \times 1 + (1 - \rho)(1 - X_{\text{local}})$. The portion of the external radiative flux absorbed at the particle surface is calculated as:

for diffuse and uniform particle irradiation

$$\dot{q}_a = [1 - \rho(1 - X_{\text{local}})] \frac{\dot{q}_0}{4} \quad (10)$$

for collimated and partial particle irradiation

$$\dot{q}_a = \begin{cases} [1 - \rho(1 - X_{\text{local}})] \dot{q}_0 \hat{\mathbf{k}} \cdot \hat{\mathbf{n}} & 0 \leq \hat{\mathbf{k}} \cdot \hat{\mathbf{n}} \leq 1 \\ 0 & \text{else} \end{cases} \quad (11)$$

where $\dot{q}_0$ is the external collimated flux in the z -direction, $\hat{\mathbf{n}}$ is the outward pointing normal surface unit vector and ρ is the total-hemispherical reflectivity of the particle surface. Note that Eqs. (10) and (11) result in the same amount of radiative power absorbed by the entire particles in both cases.

The 2D finite volume method in spherical coordinates and the explicit Euler time-integration scheme are applied to numerically solve the mathematical model, Eqs. (2)–(11) [19].

4 Results

The baseline simulation parameters and the material properties used in this study follow those used in [14]. The

baseline simulation parameters are used in the computations unless stated otherwise.

The temperatures of the uniformly and non-uniformly irradiated particles are shown in Figs. 2 and 3. Transient temperature profiles at selected locations $r/r_p = 0, 0.5$ and 1 are shown in Figs. 2a and 3a for the two cases, respectively. The temperatures of the uniformly irradiated particle increase at the same rate at any location from the initial 300 to 800 K—temperature corresponding to the onset of the endothermic chemical reaction. With the progress of the chemical reaction, heat transfer becomes the limiting mechanism of the decomposition process,

corroborated by the characteristic shape changes in the temperature profiles at $t \approx 11$ s and 7 s at $T \approx 950$ K for $r/r_p = 0$ and 0.5, respectively. When the decomposition approaches completion, excess heat becomes available for local heating resulting in accelerated local particle heating. The uniformly-irradiated particle reaches a uniform steady-state temperature of 2,035 K after 25 s. For the non-uniformly irradiated particle, the surface temperature increases at the highest rate at $\theta = 0^\circ$ due to the maximum in the absorbed radiative flux at this location. The onset of the chemical reaction at 800 K is reached in less

Fig. 2 Temperature profiles of a uniform particle irradiation: **a** particle temperatures at selected locations and **b** temperature profiles across the particle at selected times

Fig. 3 Temperature profiles of a non-uniform particle irradiation: **a** particle temperatures at selected locations and **b** temperature profiles across the particle at selected times

than 0.5 s, after which the temperature continues to increase at a diminishing rate to 2,844 K at $t = 42.1$ s, when the decomposition is complete. The surface temperature decreases with the increasing angle θ due to the decreasing incident radiative flux, which drops to zero at $\theta = 90^\circ$. For $\theta > 90^\circ$ the surface temperature further decreases approaching minimum at $\theta = 180^\circ$. At $t \approx 20.7$ s the temperature at the centre of the non-uniformly irradiated particle exceeds the surface temperature at $\theta = 90^\circ$. For $\theta = 180^\circ$, this effect is observed already at $t \approx 0.55$ s. The characteristic changes in the temperature profiles support the hypothesis of heat transfer limitation of the decomposition reaction in the non-uniformly irradiated particle, similarly to that for the uniformly irradiated particle. These changes differ with θ due to different durations of the decomposition process. The steady-state temperature distribution is spatially non-uniform due to the asymmetric boundary conditions, with the maximum of 2,844 K for $r/r_p = 1$ and $\theta = 0^\circ$ and a minimum of 1,157 K for $r/r_p = 1$ and $\theta = 180^\circ$.

Spatial temperature profiles at selected times are shown in Figs. 2b and 3b for the uniformly and non-uniformly irradiated particles, respectively. For the uniformly irradiated particle, symmetric spatial temperature profiles are observed due to the symmetric boundary conditions. The characteristic changes in the temperature profiles observed at $t = 5$ and 10 s, indicate the location of the reaction zones and support the hypothesis of heat transfer limitation of the decomposition reaction discussed in [14]. The reaction zone remains approximately isothermal at around 950 K, while heat is transferred to the unreacted core. For the non-uniformly irradiated particle, the spatial temperature profiles along the x axis show symmetric distributions due to the boundary conditions symmetric with respect to the x -axis. The temperature decreases along the z axis from the irradiated front to the non-irradiated back of the particle. The characteristic changes in the temperature profiles, corroborating again heat transfer limitation of the decomposition process, indicate the movement of the reaction zone from the irradiated front towards the non-irradiated back of the particle.

The overall extent of the decomposition reaction for both irradiation models is shown in Fig. 4 as a function of time. Until $t \approx 2.3$ s, the non-uniform model predicts a higher reaction extent, $X_{\text{overall}} = 0.17$, due to the higher temperature in the vicinity of the irradiated particle surface. However, as the calcination process proceeds, the average distance between the reaction zone and the irradiated surface increases, and heat transfer limitation leads to decomposition rate decreasing faster for the non-uniformly irradiated particle than for the uniformly irradiated one. The non-uniform irradiation of the CaCO_3 particle extends its decomposition time by a factor of 3.3.

Fig. 4 Overall extent of the calcination reaction as a function of time

5 Summary and conclusions

The effect of non-uniform irradiation of an optically large semi-transparent reacting CaCO_3 particle has been analysed using a numerical model coupling radiation, conduction and convection heat transfer modes to the chemical kinetics of the decomposition reaction. The Rosseland diffusion approximation was employed to model the internal radiative transport. For both non-uniformly and uniformly irradiated particles heat transfer from the surface to the reaction zone is the limiting mechanism of the chemical reaction leading to characteristic shape changes in the spatial temperature profiles. Uniform particle irradiation is highly favourable for particle heating and decomposition, decreasing the total reaction time by a factor of 3.3 as compared to that for non-uniform irradiation. However, higher reaction rates are initially obtained for the non-uniformly irradiated particle due to a faster particle heating in the vicinity of the irradiated surface. As the reaction proceeds, the decreasing heat transfer rate to the reaction zone leads to a drastic reduction in the decomposition rate of the non-uniformly irradiated particle. The results show that the highly non-uniform irradiation is undesired for fast particle heating and decomposition.

The effect of uniform versus non-uniform particle irradiation has been studied for a specific physical system as motivated by the particular solar thermochemical applications including solar lime and cement production, and solar thermochemical CO_2 capture. The analysis can be further extended to generalise the results for a class of chemical reactions involving internally non-uniform non-isothermal

semi-transparent particles with parameterised geometry, material properties, and reaction rates.

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