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# Simulation of $\text{Fe}_2\text{O}_3/\text{Al}$ combustion: Sensitivity analysis

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## Abstract

The sensitivity of a one-dimensional model, built to simulate the non-steady radial combustion propagation on thin circular samples of  $\text{Fe}_2\text{O}_3$ /aluminium thermite mixtures, was tested in relation to its least reliable thermophysical properties and to non-homogeneities in the initial reactant media. Zero order kinetics and conductive/radiative heat transfer were considered. The model is quite insensitive to variations of most of the properties studied. The highest sensitivity detected concerned aluminium conductivity. The non-uniform reactant mixing significantly affected the results, suggesting that experimental variability is partially explained by this feature.

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## 1. Introduction

The self-propagating high-temperature  $\text{Fe}_2\text{O}_3/\text{Al}$  thermite reaction is a known heat source to some engineering applications, such as (i) welding, cutting and perforation of materials by the molten products; (ii) production of alumina liners in situ for pipes; (iii) portable heat sources; (iv) pyrotechnics, propellants and explosive additives and components; (v) treatment of by-products and wastes from zinc and steel industries and (vi) synthesis of ceramic reinforced metal-matrix composites, magnetic films and iron aluminides. However, the combustion reactions, as the  $\text{Fe}_2\text{O}_3/\text{Al}$  thermite, are hard to follow by experimentation due to the extreme conditions developed. Hence, theoretical prediction of these processes represents a valuable guideline for experimental work.

The availability of experimental results of radial combustion on  $\text{Fe}_2\text{O}_3/\text{Al}$  disk shaped samples (Durães et al., 2006a)

has stimulated the derivation of a one-dimensional model to describe the combustion propagation (Durães et al., 2006b). The radial geometry was chosen for several reasons, namely, the possibility of easy detection of propagation heterogeneities, caused by deficient reactant mixing and/or different levels of compaction, and the testing of self-propagation in conditions of large energy losses to the surroundings, which is ensured by a very low sample thickness. Furthermore, with this geometry, no critical thickness extinction problems arise. Radial propagation modelling and simulation with the used experimental conditions allow the verification of self-propagation steady combustion mode, in the spatial scale of the sample radius. It is also a suitable tool for testing the influence of parameter changes on the combustion variables. The built model considers non-steady combustion propagation on thin circular samples of  $\text{Fe}_2\text{O}_3/\text{Al}$  mixtures, zero order kinetics and conductive/radiative heat transfer. All the properties of the system vary with the temperature and composition during the propagation and phase transitions are also contemplated, to achieve more realistic solutions, readily comparable with the experimental values. Adaptive numerical methods were used for the model solution. Fast moving steep front profiles were obtained, which were compared and validated by experimental results in

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Durães et al. (2006b). The experimental combustion velocities were used to adjust the kinetic constant of the model, to reach a good predictive capability.

The available data for the temperature dependence of some component properties are very scarce, making them unreliable. In this work, some of the least reliable properties were selected and the sensitivity of the model towards those properties was tested.

## 2. Model

The model tested was already described in detail in Durães et al. (2006b) and Brito et al. (2005). It is based on the following assumptions: (i) one-dimensional radial non-steady propagation; (ii) general reaction with mass stoichiometry  $\alpha_A A + \alpha_B B \rightarrow \alpha_C C + \alpha_D D$ ; (iii) zero order kinetics; (iv) conductive/radiative heat transfer mechanisms; (v) negligible relative movement between species and (vi) disk-shaped sample dimensions and confinement materials as described in experimental set-up presented in Durães et al. (2006a,b). Essentially, the model comprises energetic and mass partial balances:

$$\rho_M C_{PM} \frac{\partial T}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} \left[ k_M \left( r \frac{\partial T}{\partial r} \right) \right] + Q \cdot \mathbf{r} - \left[ (U_{\text{steel/air}} + U_{PMMMA/\text{air}})(T - T_0) + 2\sigma\epsilon_M(T^4 - T_0^4) \right] / Z, \quad (1)$$

$$\frac{dW_A}{dt} = -\alpha_A \mathbf{r}. \quad (2)$$

The reaction enthalpy ( $-Q$ ) considers the enthalpy variations (including phase transitions) at constant pressure of reactants and products in the temperature path  $T_0 - T$ . Reaction kinetics is defined as zero order, for temperature values beyond  $T_{\text{react}}$ :  $\mathbf{r} = H(T - T_{\text{react}})K$ , where  $H$  is the Heaviside function and  $K$  a non-temperature dependent kinetic constant. Heat losses through the sample top and bottom are accounted by the last term in Eq. (1). The problem is completed by the definition of initial and boundary conditions:

$$t = 0; \quad \begin{cases} 0 \leq r \leq R_0 \Rightarrow T = T_{\text{igni}}, \\ r > R_0 \Rightarrow T = T_0, \end{cases} \quad (3)$$

$$t > 0; \quad r = 0 \Rightarrow \frac{\partial T}{\partial r} = 0, \quad (4)$$

$$t > 0; \quad r = R \Rightarrow k_M \frac{\partial T}{\partial r} = - \left[ U'_{\text{steel/air}}(T - T_0) + \sigma\epsilon_M(T^4 - T_0^4) \right]. \quad (5)$$

Eq. (3) simulates ignition by a temperature spatial pulse. A symmetry condition and conductive/radiative heat transfer are considered at the inner and outer boundaries, respectively.

The assumption of variable temperature and composition thermophysical properties in the studied system implied a wide bibliographic data review for heat capacity, density, thermal conductivity and emissivity property variation with temperature. The thermophysical properties of the pure components ( $\text{Fe}_2\text{O}_3$ , Al, Fe,  $\text{Al}_2\text{O}_3$  and air), its dependence relations with temperature, the mixing rules and the confinement material properties were resumed in Brito et al. (2005). Out of the temperature ranges available in the literature, property values were fixed as the last value known. Furthermore, phase transitions of the components were considered, over  $\Delta T = 1$  K, by means of an equivalent  $C_P$ :  $C'_{Pi} = C_{Pi} + L_i/\Delta T$ .

The model was solved using non-uniform centred finite difference approximations to estimate spatial derivatives and DDASSL numerical integrator to perform time integration. An adaptive strategy converts the original problem in a set of sub-problems generated by a subgrid selection procedure, in each time step, as described in Brito et al. (2005). It was chosen to execute temporal step adaptation only, fixing the maximum refinement level of the spatial grid as 2.

The model solution comprises temperature and composition spatial and temporal profiles. The combustion wave propagation velocity was estimated using the composition front position vs. time. The location of the front was obtained by the 50% conversion point. The average maximum front temperature was computed using the temperature profiles located between 50% and 80% of the samples' radius ( $R$ ).

In this work, the kinetic constant adjusted in Durães et al. (2006b) and a stoichiometric ratio of reactants were used. The general data for the simulations are presented in Table 1.

Table 1  
General data for simulations

$Q _{T_0}$ (J/kg)	$T_0$ (K)	$P$ (Pa)	$T_{\text{igni}}$ (K)	$T_{\text{react}}$ (K)	$\Delta r$ (m)	
5,322,746	298.15	101,325	2300	1200	$1 \times 10^{-5}$	
$R$ (m)	$R_0$ (m)	$Z$ (m)	$\tau$ (s)	$T'$ (K)	$v_{\text{air}0}$	
0.025	0.0015	0.0015	0.1	1000	0.392	
$K$ (kg/m <sup>3</sup> s)	$\omega_{A0}$	$\omega_{B0}$	$\alpha_A$	$\alpha_B$	$\alpha_C$	$\alpha_D$
$9 \times 10^4$	0.747	0.253	−1	−0.33792	0.69943	0.63848
DDASSL tol.	Algorithm tol.	Finite diff. points		1st and 2nd level grid nodes		
$1 \times 10^{-6}$	$1 \times 10^{-2}$	5		41; 81		

Table 2  
Thermophysical properties selected and conditions for sensitivity test runs

Parameter/property	Ref. run conditions	Run test	Value/ref run value	Run test	Slope value
p1— $k_{\text{Fe}_2\text{O}_3}$	Constant	1	5	—	—
		2	10	—	—
p2— $\rho_{\text{Fe}_2\text{O}_3}$	Constant	—	—	9	−0.2
		—	—	10	−0.3
p3— $\rho_{\text{Al}_2\text{O}_3}$	Constant	3	0.8	11	−0.2
		4	1.2	12	−0.275
p4— $k_{\text{Al}}$	Constant for $T > 1300$ K	5	0.8	13	0.02
		6	1.2	14	0.03
p5— $\rho_{\text{Al}}$	Constant for $T > 1400$ K	—	—	15	−0.2
		—	—	16	−0.275
p6— $k_{\text{Fe}}$	Constant for $T > 1600$ K	7	0.8	—	—
		8	1.2	—	—

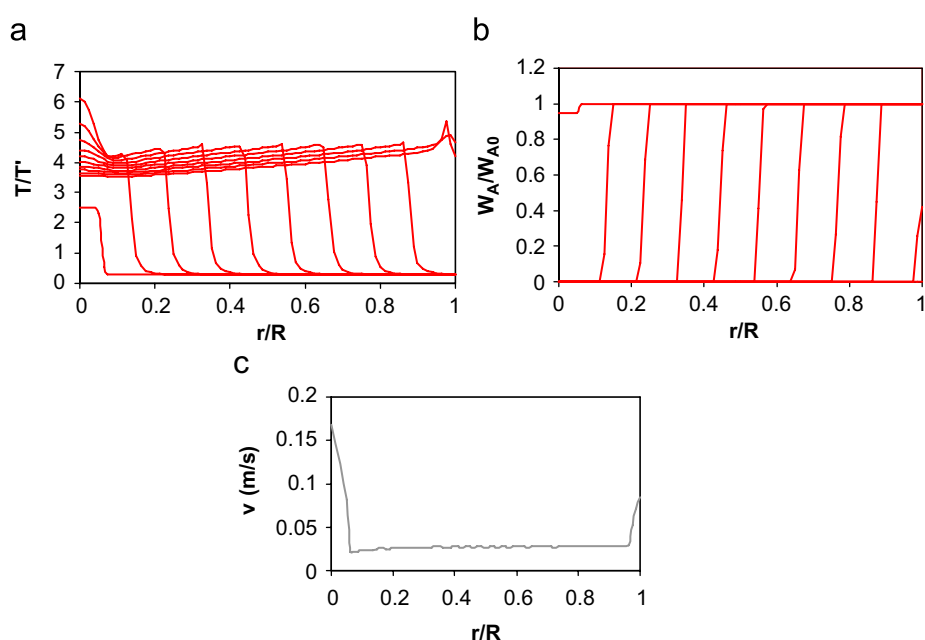


Fig. 1. Temperature (a), concentration (b) and front velocity (c) profiles in the reference run conditions. Time gap between profiles = 0.1 s.

### 3. Sensitivity analysis

The sensitivity analysis towards the least reliable thermophysical properties was performed considering non-temperature dependence (constant values); linear temperature dependence for temperatures beyond a known value (slopes). The selected properties were  $\text{Fe}_2\text{O}_3$ , Fe and Al thermal conductivity, and Al,  $\text{Fe}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$  densities (Table 2).

The influence of non-homogeneous mixing of the reactants was also studied, using randomly generated initial reactant concentration profiles centred on the average value. For that purpose, a sequence of pseudo-random numbers  $x_i$  was generated:

$x_0 = \text{seed}$ ;

$$x_{i+1} = q_1 \times \text{mod}(x_i, N) + q_2, \quad i = 0, 1, 2, 3, \dots, \quad (6)$$

where seed,  $q_1$ ,  $q_2$  and  $N$  are the generation parameters. These parameters were tuned to create an apparently random succes-

sion, normalized and centred on unity within a band defined by  $UB - LB$ :

$$y_i = LB + \frac{\text{mod}(x_i, N)}{N} \times (UB - LB), \quad i = 0, 1, 2, 3, \dots, \quad (7)$$

where  $UB = 1 + \text{Var B}/100$  and  $LB = 1 - \text{Var B}/100$ . To increase the apparent randomness of the succession, the admitted elements must be beyond a specified position  $\text{ini}$ , with a fixed interval  $j$  between them. Once the succession is established, the values are used as generators for the reactant's initial mass concentration profiles, multiplying  $y_i$  by the average mass concentration of the reactant at each node and starting from the inner boundary position. In this way, the initial reactant mass concentration is allowed to vary  $\pm \text{Var B}$  (%) around the average value used in the reference run. It must be ensured that the total reactant mass remains the same.

Table 3  
Sensitivity results for selected runs

	V (m/s)	Variation (%)	$T_{\max}$ (K)	Variation (%)
Ref. run	0.0273		4608	
Test 1	0.0284	+4	4611	+0.06
Test 2	0.0284	+4	4615	+0.15
Test 13	0.0299	+9.5	4612	+0.09
Test 14	0.0299	+9.5	4614	+0.13

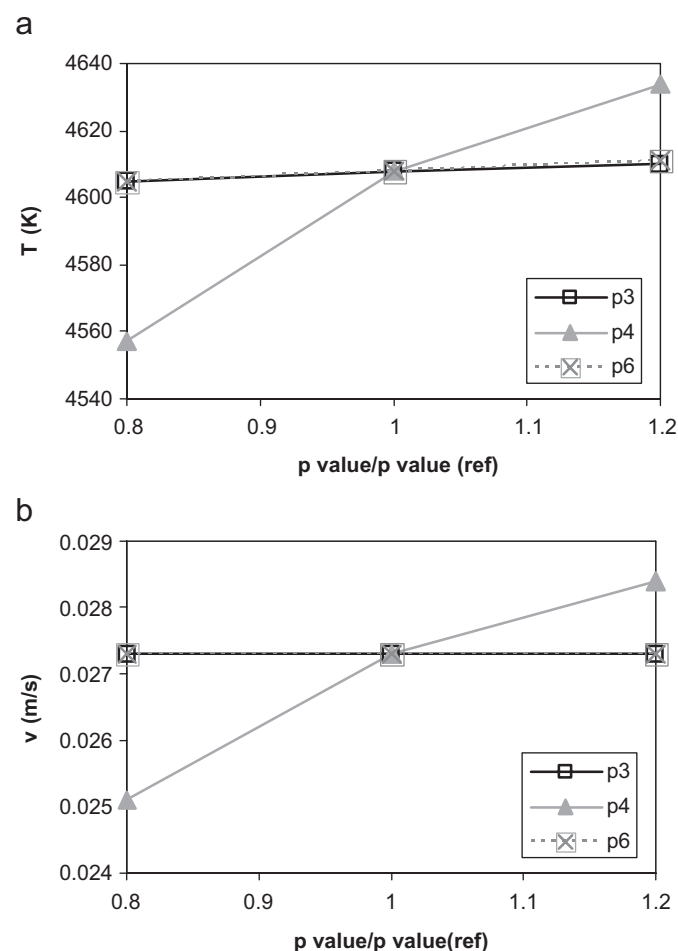


Fig. 2. Sensitivity analysis for Tests 3–8 in relation to (a)  $T_{\max}$  and (b)  $v$ .

#### 4. Results and discussion

Fig. 1 presents the typical concentration, temperature and wave propagation velocity profiles, obtained in the conditions defined as reference.

The test runs performed are presented in Table 2. For each test, the results monitored were the asymptotic thermal wave propagation velocity ( $v$ ) and the average maximum front temperature ( $T_{\max}$ ). The most uncertain and thus the most important parameter tested was the  $\text{Fe}_2\text{O}_3$  thermal conductivity, due to a considerable lack of information related to this property. Therefore, in previous works (Brito et al., 2005; Durães et al., 2006b) a non-temperature dependent value (0.59 W/m K) for pressed powder was used. This is a relatively low value that may affect the average conductivity of the mixture, which was calculated using a serial rearrangement of the components (Durães et al., 2006b). Therefore, only larger values of this property were tested (Table 2—Tests 1, 2). It was concluded that an increase by a factor of 5 was needed to produce visible changes on the results (Table 3). For the other properties (Tests 3–8),  $\pm 20\%$  deviations in relation to the reference run values were tested and the results are resumed in Fig. 2. It is concluded that the model seems relatively insensitive to the variation of most of the properties studied, including the less reliable one, p1. The highest sensitivity detected concerned p4, which

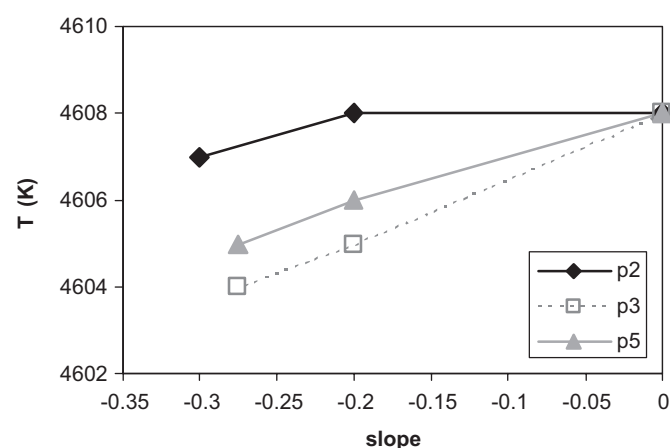


Fig. 3. Sensitivity analysis for Tests 9–12 and 15–16 in relation to  $T_{\max}$ .

Table 4  
Pseudo-random parameters used to generate the initial mass concentration profiles

Succession	Seed	$N$	$q_1$	$q_2$	ini	$j$	Variation (Var B)
A	50,000	1,000,000	369	300,001	20	1	20%
B	49,000						
Initial mass concentration profiles							
$\text{Fe}_2\text{O}_3$				Al			
run0	Constant profile—ref. run			Constant profile—ref. run			
run1	Generated by succession A			Generated by succession B			
run2	Generated by succession A			Constant profile—ref. run			

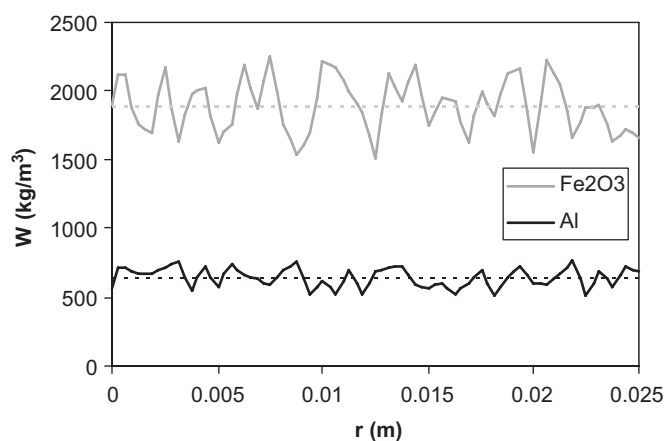


Fig. 4. Initial mass concentration profiles for run1.

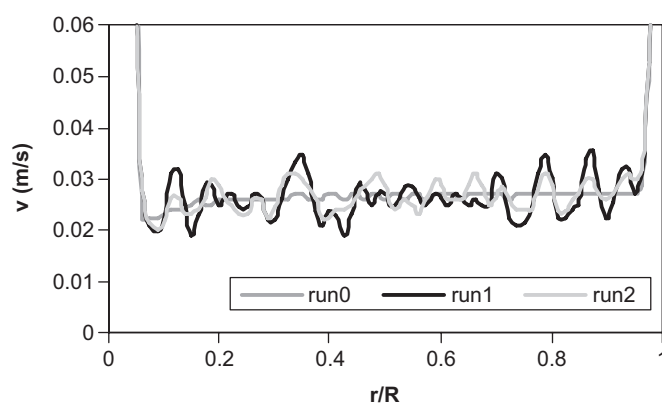


Fig. 6. Propagation front velocity profiles comparison.

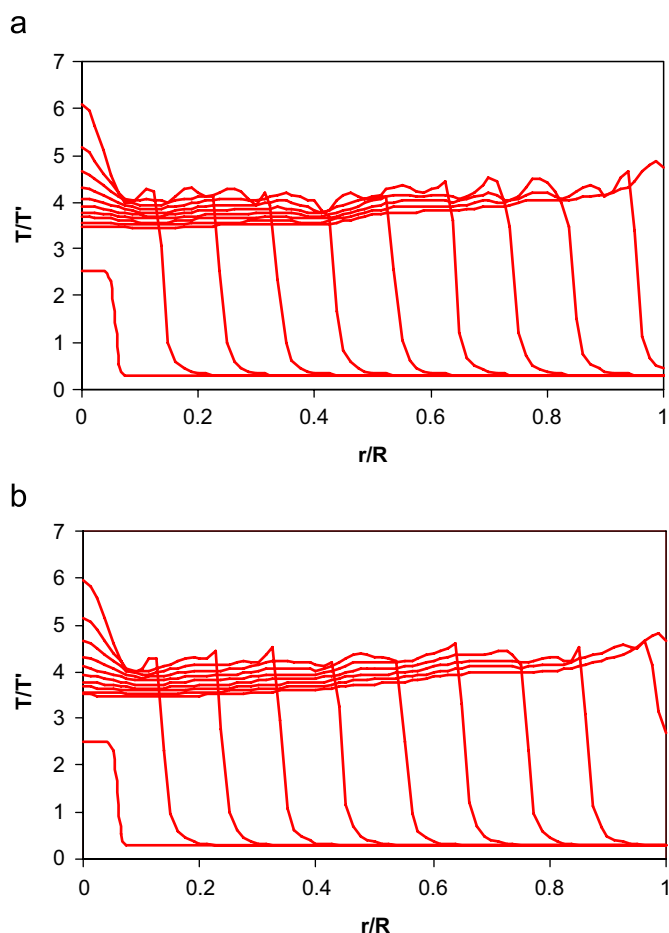


Fig. 5. Temperature profiles for (a) run1 and (b) run2. Time gap between profiles = 0.1 s.

reasonably affects the propagation velocity. The introduction of a linear dependence of properties on temperature was also tested (Tests 9–16) and the results are shown in Table 3 and Fig. 3. The influence of the temperature variation is even smaller than that reported above, with the exception of  $p_4$ .

Therefore,  $p_4$  is the most critical property to affect the simulation results.

Concerning the influence of non-homogeneous mixing, two test runs were defined as presented in Table 4. Fig. 4 shows the initial concentration profiles for run1. The resulting thermal wave propagation and velocity profiles are resumed in Figs. 5 and 6. It is concluded that these profiles are significantly affected by the non-homogeneity of the initial reaction media, the thermal wave propagation becoming more unstable. The velocity profiles show oscillations around the average reference value, with no definition of an asymptotic value. The simulated profiles are now more realistic, compared with experimental propagation results (Durães et al., 2006a). This suggests that experimental variability can be partially explained by non-uniform mixing of reactants.

## Notation

$C_p$	heat capacity, J/kg K
$k$	thermal conductivity, W/m K
$K$	zero order kinetic constant, kg/m <sup>3</sup> s
$L$	latent heat, J/kg
$Q$	reaction heat, J/kg
$\mathbf{r}$	reaction kinetic rate, kg/m <sup>3</sup> s
$r$	radial coordinate, m
$R$	sample radius, m
$R_0$	ignition zone radius, m
$T$	temperature, K
$T_{\text{igni}}$	ignition temperature, K
$T_{\text{react}}$	reaction temperature, K
$T'$	temperature normalization constant, K
$U$ or $U'$	heat transfer coefficient, W/m <sup>2</sup> K
$W$	mass concentration, kg/m <sup>3</sup>
$Z$	sample thickness, m

## Greek letters

$\alpha$	mass stoichiometric coefficient
$\varepsilon$	emissivity
$\rho$	density, kg/m <sup>3</sup>
$\sigma$	Steffan–Boltzman constant, W/m <sup>2</sup> K <sup>4</sup>

$\tau$	time normalization constant, s
$v$	volume fraction
$\omega$	mass fraction

#### Subscripts

$M$	mixture
$i$	arbitrary component
$A$	$\text{Fe}_2\text{O}_3$
$B$	Al
$C$	Fe
$D$	$\text{Al}_2\text{O}_3$
0	initial or surrounding conditions

Durães, L., Campos, J., Portugal, A., 2006a. Radial combustion propagation in iron(III) oxide/aluminum thermite mixtures. *Propell. Explos. Pyrot.* 31 (1), 42–49.

Durães, L., Brito, P., Campos, J., Portugal, A., 2006b. Modelling and simulation of  $\text{Fe}_2\text{O}_3$ /Aluminum thermite combustion: experimental validation. In: 16th European Symposium on Computer Aided Process Engineering and Ninth International Symposium on Process Systems Engineering, Part A, Computer Aided Chemical Engineering, vol. 21. Elsevier, Amsterdam, pp. 365–370.

#### References

Brito, P., Durães, L., Campos, J., Portugal, A., 2005. Modelling and simulation of  $\text{Fe}_2\text{O}_3$ /Al thermite combustion. In: Proceedings of the Ninth International Chemical Engineering Conference (CHEMPOR 2005), Chem. Eng. Dept., Univ. Coimbra, Coimbra, p. 157 & CD-ROM.