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THERMOCOUPLES POSITIONING FOR EARLY-WARNING DETECTION OF THERMAL RUNAWAY

[1]MATTEO RIZZOTTO, [2]FEDERICO FLORIT, [3]RENATO ROTA, [4]VALENTINA BUSINI

Politecnico di Milano, Dipartimento di Chimica, Materiali e Ingegneria Chimica "G. Natta"
matteo.rizzotto@polimi.it, federico.florit@mail.polimi.it, renato.rota@polimi.it,
E-mail: valentina.busini@polimi.it

Abstract - Runaway reactions have always been a serious issue for the chemical industry. Failures that may lead to this type of accident are different: block of the impeller, loss of the reactor temperature control, error in the loading of reagents, just to name a few. The rapid detection of this phenomena is crucial. One of the most widely used preventive systems is the so-called early warning system, which allows to give an early warning at the beginning of the fugitive reaction. Due to non-homogeneity of the temperature inside the reactor, the positioning of the sensors is of crucial importance. In fact, an incorrect localization of the temperature probe could lead to a false alarm, which would undermine the early warning system. The objective of this work is the computational fluid dynamic (CFD) simulation of different failure scenarios, in order to determine the best location of the temperature sensors.

Index Terms - CFD, Early Warning System, Runaway, Thermocouples

I. INTRODUCTION

In the field of the chemical industry, despite numerous and significant improvements in the safety of the processes, accidents due to thermal runaway still occur [1][2]. Failures that may lead to this type of accident are for example the block of the impeller or control system failure(mechanical failure), or an error in the loading of reagents (human error), and these are the scenarios taken into account in this work. It is therefore necessary to promptly identify and understand these phenomena, especially when they can lead to dangerous situations. One of the most widely used preventive system is the so-called early warning system [3], which allows to give an early warning at the beginning of the fugitive reaction. Due to non-homogeneity of the temperature inside the reactor, the positioning of the sensors is of crucial importance. In fact, an incorrect localization of the temperature probe could lead to a false alarm, which would undermine the early warning system. The computational fluid dynamics (CFD), solving the mass equations, momentum, energy and species in a reactive system, can be very useful for this purpose, also considering the difficulty of carrying out experiments of this type in the laboratory, because of the high cost and risks associated with the process. Several works have been carried out on this topic, in order to estimate the possibility of the globalthermal runaway propagation from appearing hotspots [4][5], or for the determination of temperature probe location for a polymerization reaction [6]. The objective of this work was the CFD simulation of two different cases with two different failure scenarios (block of the impeller, and loading error) using a Reynolds Averaged Navier-Stokes (RANS) approach, in order to determine the best location of the temperature sensors. All simulations in this work were performed with the software Fluent 16.2, from the ANSYS suite. Fluent is a CFD software which allows solution of transport equations in 2D or 3D geometries. It requires a mesh file as input, while available settings can be defined from the program user interface. Simulation of the system was performed with an iterative solution of discretized equations, starting from a first guess solution.

II. MATERIAL AND METHODS

A. RANS transport equations

The general form of a Reynolds averaged transport equation for a scalar φ, assuming isotropic quantities, is

$$\frac{\partial(\rho\varphi)}{\partial t} + \nabla \cdot (\rho \mathbf{v}\varphi) = \nabla \cdot \left(\Gamma_\varphi \nabla\varphi\right) + S_\varphi \qquad (1)$$

Where ρ is the density, **v** is the velocity vector, Γ_φ is the effective scalar diffusivity, and S_φ is the scalar source term. Source terms require additional models and, in the case of species transport, these are the so called Turbulence Kinetics Interaction (TKI) models. The time averaged species transport equation is

$$\frac{\partial(\rho\omega_k)}{\partial t} + \nabla \cdot (\rho \mathbf{v}\omega_k) = -\nabla \cdot (\rho \mathfrak{D}_{eff} \nabla\omega_k) + \overline{\dot{\Omega}_k} \qquad (2)$$

Where ω_k is the mass fraction of species k, $\overline{\dot{\Omega}_k}$ is the average massive reaction rate, and $\mathfrak{D}_{eff}$ is the effective diffusivity, expressed as sum of a molecular term (density times molecular diffusivity for species, thermal conductivity for energy and dynamic viscosity for momentum transport) and a turbulent term.

B. Laminar Rate Model

For an irreversible single-step reaction

$$\nu_A A + \nu_B B \rightarrow \nu_C C + \nu_D D \qquad (3)$$

$$A + B \rightarrow C + D \qquad (5)$$

in which pressure effects are negligible (incompressible fluids, like liquids), the species reaction rate can be computed with power law and Arrhenius rate constant:

$$\overline{\dot{\Omega}_k} = \nu_K K_0 \exp\left(-\frac{E_a}{RT}\right) MW_k \prod_{i=1}^{NC} c_i^{\alpha_i} \qquad (4)$$

where K_0 is the Arrhenius pre-exponential factor, E_a is the activation energy, R is the universal constant of gases, T is the absolute temperature, MW_k is the molecular weight of species k, c_i is the average molar concentration of species I, and α_i is the rate exponent of species i.

The intrinsic problem of this model is that it does not include turbulence effects at all,that is why it is generally called Laminar Rate (LR) model [7]. Anyway, this model is quite accurate in cases like the ones in exam, where the system is well mixed, so intrinsic reaction is dominant over transport in determining the overall production or consumption rate (Case 1), or steady (Case 2).

III. CASE 1: Loading Error

A. Introduction

A semi-batch reactor,as discussed in [4], [5] and [8], was used to simulate an accident in a pilot scale reactor. Dimensions in cm are reported in Figure 1.

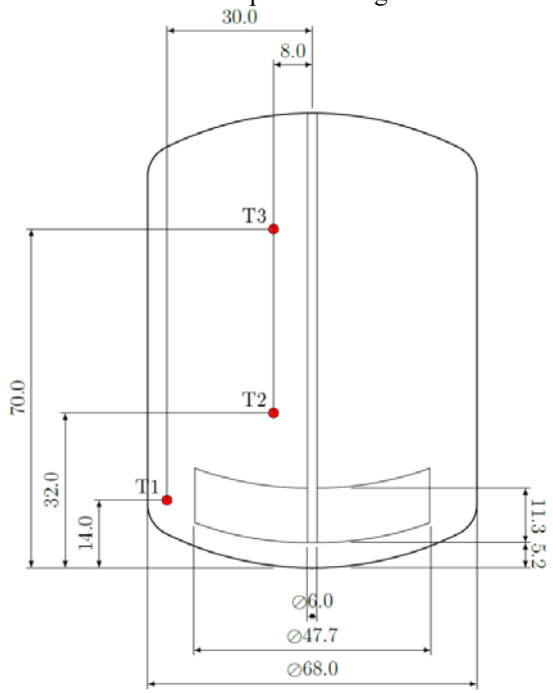

Figure 1 Reactor dimensions in [cm] and thermocouples positions.

In the simulation, theisoperibolic semi-batch pilot-scale reactor of nominal volume 340 L was used to perform a generic reaction between pure species A and B:

Reaction intrinsic kinetics is second order, first order with respect to each reagent:

$$r = K_0 \exp\left(-\frac{E_a}{RT}\right) c_A c_B \qquad (6)$$

Where $K_o = 9.72 \cdot 10^7$ m^3 $kmol^{-1}$ s^{-1}, $E_a = 82500$ J mol^{-1}. Reaction is exothermic with $\Delta H_R(298K) =$ -63.4 KJ mol^{-1}.

B. Accident scenario

The reactor is operated by charging 148 L A in the vessel and dosing stoichiometric B (106 L) over time while agitation is on (angular speed ω = 25 rpm). Reagents are preheated at 50 °C, while the jacket temperature is set to 90 °C. Possible accidental scenarios can be identified through the HAZOP analysis. In particular, an incorrect agitation procedure is considered. The operator correctly measures the quantity of reagents to be dosed but forgets to turn on the impeller and heating. After some time, the operator sees the reaction is not taking place and realizes the mistake. Agitation and heating are promptly turned on. After some time, there is a buildup of pressure due to temperature increase and liquid evaporation. The same scenario can happen if a malfunction of the electrical system happens, e.g. a power failure. The aim of this simulation was to find temperature fields of the reactor. Three thermocouples (located as in Figure 1) are used to measure temperature in three different positions inside the reactive mass.

C. Case setup

It was assumed reagents are stratified at the beginning, so pure B floats over pure A. The transient simulation starts when the operator switches on both agitation and heating. Pre-heating temperature is too low for a quantitative reaction, so no product is present at the beginning of simulation. Initial temperature is 323.15K. Walls are set to constant 363.15K (isoperibolic reactor) at the beginning. Impeller is considered as an adiabatic surface. Free surface is modeled with symmetry boundary conditions, so it is assumed to be flat at all times.

Simulation was done for liquid phase, so only the condensed fluid had to be meshed. The choice of single phase analysis allows to simplify the system. This simplification is even more valid as chemistry is assumed not to involve volatile species (e.g. from decomposition reactions). Evaporation was neglected, as well as volume changes due to composition variations.

Computational grid was made of about 180000 elements (tetrahedrons and wedges), after mesh independence analysis. Mesh minimum size was set to 1mm, and cell thickness was reduced close to walls in order to capture the boundary layer. Quality of the

mesh was measured with orthogonal quality and skewness; the minimum value of the former is 0.34, 0.88 on average (good quality), while the maximum value of the latter is 0.74, 0.21 on average (good quality). In order to model impeller rotation, the technique of Moving Reference Frame (MRF) was adopted. In the MRF method, the equations are expressed in a reference frame that rotates with the impeller speed [9] and solved in a stationary mesh. MRF is often used since it requires less resources than sliding meshand give satisfactory results [10]. A summary of solution settings is reported in Table 1. If not written otherwise, default parameters were used in the solution.

General	
Solver type	Pressure-based, Transient
Models	
Viscous	Standard κ-ε, standard wall function
Species	Species Transport, Volumetric reaction
Solution Methods	
Scheme	SIMPLE
Solution order	Second Order
Convergence Check	
Monitor	Integral of product molar concentration
Integration parameters	
Time step size	0.01-0.5 s
Iteration per time step	20-40

Table 1 Simulation parameters for Case 1

D. Results

A semi-batch reactor undergoing the analyzed accident can be treated as a batch system. A 0D model was adopted to compare CFD results with those of macroscopic balances [11]. In particular

$$\frac{dn_k}{dt} = \nu_k r(T, \boldsymbol{n})V \quad k = 1 \dots NC \tag{7}$$

$$\frac{dT}{dt} = \frac{-\Delta H_R(T) r(T, \boldsymbol{n})V + U\mathcal{A}(T_J - T)}{\rho \hat{c}_{p,mix}} \tag{8}$$

Where n_k is the total molar quantity of species k, V is the reaction volume, U is the global heat transfer coefficient, $\mathcal{A}$ is the heat exchange area, T_J is the jacket temperature, and $\hat{c}_{p,mix}$ is the massive constant pressure mixture specific heat.

The comparison of CFD and 0D model results is reported in Figure 2.

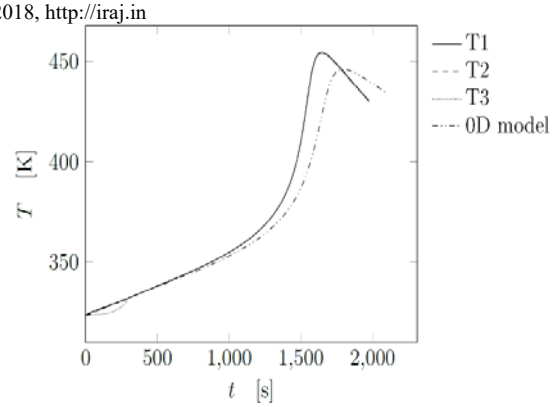

Figure 2 Temperature profiles of measuring devices for LR and 0D models for Case 1.

A close-up of the first few minutes of simulation is reported in Figure 3.

CFD results show that thermocouples T1 and T2 have almost the same response to impeller start-up. Thermocouple T3 has a delay instead, and this is due to its position in the reactor. T1 and T2 are close to impeller palettes, so in a region where mixing is fast. A further confirmation to this is the fact their thermal profile is very close to the one of perfect mixing, predicted by 0D model.

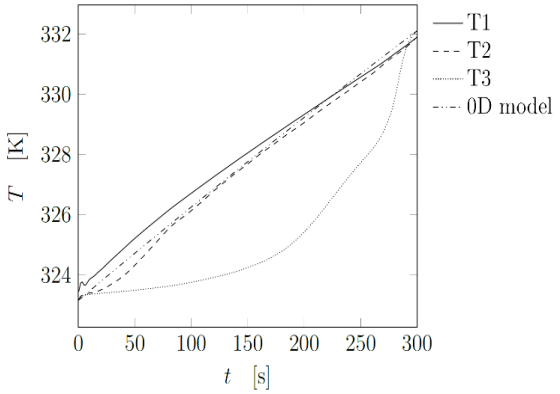

Figure 3 Temperature profiles of measuring devices for LR and 0D models for Case 1 in the first 300s of simulation.

T3 on the contrary is in a stagnant region at the beginning of simulation, so its profile is much different from the one of 0D model. The delayed behavior of thermocouple T3 suggest its positioning is not optimal in an early-warning framework. If only T3 was present, the onset of runaway would maybe be detected too late by both manual and automatic safety systems.

These non-homogeneities in temperature values can be seen in Figure 4, where the temperature distribution inside the reactor is presented at three different times.

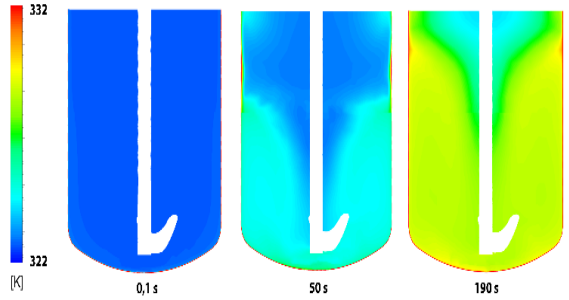

Figure 4 Temperature contours inside the reactor for Case 1 at three different times: 0,1 s, 50 s, 190 s.

Velocity contours are shown in Figure 5. As it is possible to note, in the first minutes of simulation the velocity is far from having auniform distribution inside the reactor. This situation particularly affects thermocouple T3, which is near the shaft, and can explain the differences shown in Figure 3.

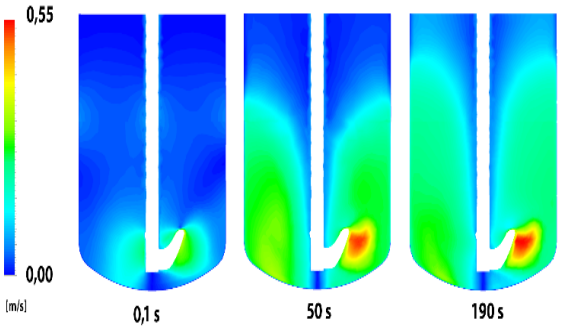

Figure 5 Velocity magnitude contours inside the reactor for Case 1 at three different times: 0.1 s, 50 s, 190 s.

IV. CASE 2: BLOCK OF THE IMPELLER

A. Introduction

The same reactor presented for Case 1, was used to simulate the block of the impeller in Case 2. The generic reaction between pure species A and B is:

$$A + B \rightarrow C + D \tag{9}$$

With reaction kinetics

$$r = K_0\, exp\left(-\frac{E_a}{RT}\right) c_{A,0}(1-\zeta)^{2.1} \tag{10}$$

Where $K_o = 4.3 \cdot 10^8$ m^3 kmol^{-1} s^{-1}, $E_a = 82300$ J mol^{-1}, and ζ is reactant conversion. Reaction is exothermic with $\Delta H_R(298K)$ = -66.6 KJ mol^{-1}.

B. Accident scenario

After a period of 6000 s of normal work (impeller normally working with angular speed ω = 25 rpm), the impeller suddenly blocks due to failure. Then, because of insufficient cooling, the temperature of the reacting mass significantly increases leading to a thermal runaway. Also in this case the simulation aim is to find temperature fields of the reactor. Three thermocouples (located as in Figure 1) are used to measure temperature in three different positions inside the reactive mass.For this case, experimental data are available up to normal operation time 6000 s. After this point, it would be too dangerous to get experimental data. CFD overcomes this problem, allowing to simulate any kind of situation.

C. Case setup

Simulation starts when the operator switches on both agitation and heating. Initial temperature is 320K. Walls are set to constant 333K (isoperibolic reactor) at the beginning. As for Case 1, impeller is considered as an adiabatic surface. Free surface is modeled with symmetry boundary conditions, so it is assumed to be flat at all times. Computational grid is the same used in Case 1, and a summary of solution settings is reported in Table 2. If not written otherwise, default parameters were used in the solution.

General	
Solver type	Pressure-based, Transient
Models	
Viscous	Standard κ-ε, standard wall function
Species	Species Transport, Volumetric reaction
Solution Methods	
Scheme	SIMPLE
Solution order	Second Order
Convergence Check	
Monitor	Integral of product molar concentration
Integration parameters	
Time step size	0.1-0.5 s
Iteration per time step	20

Table 2 Simulation parameters for Case 2

D. Results

The comparison of CFD, 0D model results, and experimental data [8] is reported in Figure 6.

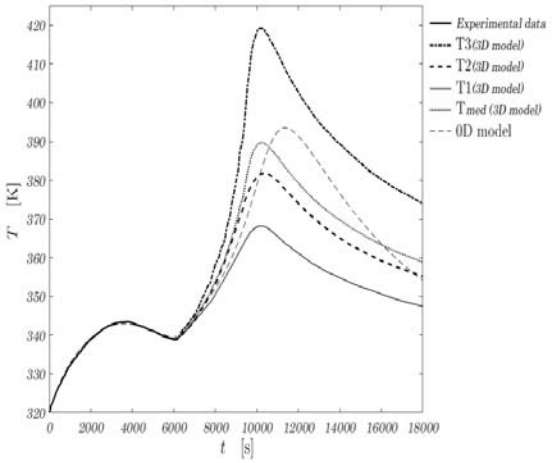

Figure 6Temperature profiles of measuring devices for LR and 0D models for Case 2.

During the period of correct operation there is a complete agreement between the results of the models and the experimental data. After the impeller fault (at time t = 6000s), the higher temperatures were correctly measured from thermocoupleT3, which represents the sensor located near the top of the reactor. Figure 7 shows a series of temperature contours at different times after the impeller stop, which immediately clarifies the unusual nature of the reagent fluid. The impeller block increases the temperature inside the reactor, the hot fluid rises upward and this explains the temperature trend with the quote.

Figure 7Temperature contours inside the reactor for Case 2 at three different times: 6000s, 8300s, 10200s.

The stratification visible in Figure 7 can be explained by the fact that after immediately the impeller fault, the fluid inside the reactor undergoes a slowdown, until it is almost completely stops about 200 seconds after the failure as seen in Figure 8, which allows to use the LR model.

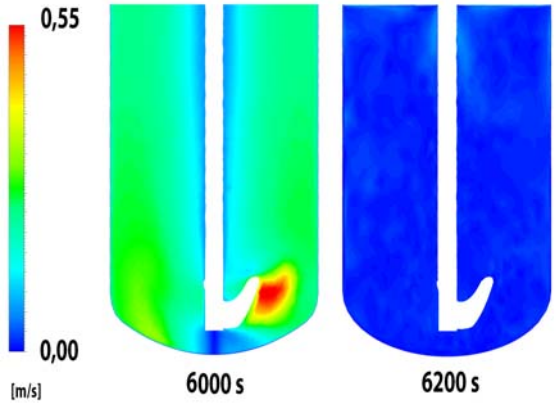

Figure 8 Velocity magnitude contours inside the reactor for Case 2 at two different times: 6000 s and 6200 s.

CONCLUSIONS

The technique of macroscopic equations is an alternative to CFD analysis and is generally adopted for safety assessments due to its simplicity. An important issue is the introduction of numerical simplifications. This reduces drastically the computational cost but may produce incorrect results. In Case 1 the 0D model is not able to describe in a correct way the temperature behavior registered by all the three thermocouples; while in Case 2, the 0D model predicts a slightly milder and delayed reaction, while CFD analysis leads to more conservative results. The simulations performed show the usefulness of CFD in analyzing these kind of problems and that there is no unique positioning of thermocouples which would be optimal to early-detect every runaway scenario. Here rises the importance of redundant measurements in a reactor.

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