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CFD Modelling and Divergence Criterion for Safety of Chemical Reactors

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Abstract

The main aim of the performed studies was to develop a practical method to prevent runaway events in batch and semibatch chemical rectors. A use of computational fluid dynamics (CFD) techniques is here proposed to determine local temperatures and local reactants concentrations inside of the reactor. Series of CFD simulations have been executed for the exothermic reaction, being the homogeneous esterification reaction of the 2-butanol with the propionic anhydrite catalysed by the sulphuric acid. Basing on the results obtained from CFD simulations and the divergence calculation algorithm (Bosch *et al*., 2004), local temperature and concentrations have been converted into a spatial map of the local divergence of the system. Then, comparing the obtained local divergences to the divergence criterion of runaway boundary ($div > 0$), runaway regions inside the reactor have been detected. The elaborated conclusions can be further employed to indicate a number of temperature sensors and their location inside the reactor, so to apply efficiently the divergence criterion for on-line measurements.

Keywords: CFD modelling, divergence criterion, batch reactors, runaway prevention, reactor safety

1. Introduction

A safe operation of chemical reactors is a problem of great importance for performance of chemical plants. Despite significant investments to improve a safety of chemical processes, still a lot of serious runaway events occur in industrial batch and semibatch reactors (Westerterp and Molga, 2004).

The loss of temperature control in chemical reactors (*thermal runaway*) may occur for exothermic reactions, when for some reasons the rate of heat generation by chemical reaction exceeds the rate of heat removal by cooling. Then, a sudden increase of reactor temperature is provoking, so also further increase of the reaction rate and the rate of heat generation. Due to this auto-acceleration effect, the temperature of the reaction mixture may reach such a high value, at which dangerous side and/or decomposition reactions are triggered, so a serious accident or even explosion may be expected.

A lot of studies dedicated to prevention of thermal runaway in considered reacting systems can be found in the literature – e.g. see a review given by Zaldivar *et. al*.

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(2003). Among others, the early warning detection method for runaway initiation has been recently developed using the chaos theory (Strozzi *et al*., 1999). This general criterion, which helps to distinguish between a dangerous situation and non-dangerous one, is based on the divergence of the system. Furthermore, Zbilut *et al.* (2002) and Bosch et al. (2004) proved, that the divergence of the system could be reconstructed using only one temperature measurement.

A quality of mixing of the reactor content has a crucial influence on the reactor performance - i.e. on contacting of reactants, but also on removal of heat generated due to the reaction progress. For strongly exothermic reactions carried out in industrial reactors, it is particularly important where local "hot-spots" may appear in the reactor mixture, provoking a global thermal runaway. Temperature non-uniformities inside the reactor are also important for a practical application of the above mentioned early warning detection system – i.e. for non-uniform temperature distribution, it becomes important, what is a number of temperature sensors and how they are located inside the reactor.

In this paper a use of computational fluid dynamics (CFD) techniques has been proposed to determine a distribution of local temperatures and reactants concentrations inside of the reactor. Basing on the divergence calculation algorithm (Bosch *et al*., 2004), the obtained local temperatures and concentrations have been converted into a spatial map of local divergences of the system. Then, comparing obtained local divergences to the divergence criterion of runaway boundary ($div > 0$), the runaway regions inside the reactor have been detected. This directly helps to indicate a number of temperature sensors and their location inside the reactor, so to apply efficiently the divergence criterion for on-line measurements. Furthermore, elaborated CFD models of reactors, due to predicting in advance the reactor performance at different operation conditions, may play a significant role for designing of safe industrial reactors.

The proposed procedures and the obtained results have been demonstrated and discussed for the catalytic and strongly exothermic esterification reaction, carrying out in a bench scale stirred tank batch reactor.

2. CFD Modelling

CFD technique becomes increasingly important as an effective tool for numerical investigation of fluids flow (also in multiphase systems) - e.g. see Naude *et al.,* (1998), Lane *et al.,* (2002). Recently more complex systems with flow, chemical reaction and heat release are considered – for representative reviews of CFD applications in chemical reactor engineering see papers by: Kuipers & van Swaaij (1997), Dudukovic *et al*. (1999) and Baldyga (2001).

In this study the bench scale stirred tank batch reactor has been modelled using the CFD approach and local and instantaneous values of liquid velocity, temperature and reactants concentrations inside the reactor have been determined at operating conditions leading to thermal runaway.

4.1. Model equations

For homogenous liquid reaction system the appropriate mass, momentum, energy and species conservation equations have been formulated as follows:

$$\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial x_i}(\rho u_i) = 0 \tag{1}$$

$$\rho\left(\frac{\partial u_i}{\partial t} + u_j \frac{\partial u_i}{\partial x_j}\right) = -\frac{\partial p}{\partial x_i} + \frac{\partial}{\partial x_j}\left[\mu\left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} - \frac{2}{3}\delta_{ij}\frac{\partial u_l}{\partial x_l}\right)\right] + \frac{\partial}{\partial x_j}\left(-\rho\overline{u_i' u_j'}\right) \tag{2}$$

$$\rho c_p\left(\frac{\partial T}{\partial t} + u_j \frac{\partial T}{\partial x_j}\right) = \frac{\partial}{\partial x_i}\left(\left(\lambda + \frac{c_p \mu_t}{\mathrm{Pr}_t}\right)\frac{\partial T}{\partial x_i}\right) + H \tag{3}$$

$$\rho\left(\frac{\partial X_i}{\partial t} + u_j \frac{\partial X_i}{\partial x_j}\right) = \frac{\partial}{\partial x_i}\left(\left(\rho D_i + \frac{\mu_t}{Sc_t}\right)\frac{\partial X_i}{\partial x_i}\right) + R_i \tag{4}$$

where ρ – is the density, u – the liquid velocity, X – the mass fraction of the component, T – the temperature, H – the energy source due to chemical reaction and R - the mass rate of production or consumption by chemical reaction.

The "Reynolds stresses" appearing in Eq. 2 are modelled by employing the Bussinesq hypothesis - for more details see Wilcox (2002) and Fluent (2003).

For the considered reacting system, the reaction rate for each reactant - R_i (in Eq. 4) - has been evaluated using the appropriate kinetic expressions (Galvan *et al*., 1996), while the energy source - H (in Eq. 3) - has been estimated as the power generated due to the chemical reaction.

The elaborated model has been implemented in a CFD code based on the finite volume method. For a purpose of these studies, the FLUENT 6.1 software by Fluent Inc. has been employed. Basing on the results obtained previously (Rudniak *et al*., 2004), CFD calculations have been performed in a 3D domain. Standard boundary conditions (no slip on the tank wall and constant wall temperature) and the MRF (Moving Reference Frame) technique have been applied – see Fluent (2003). Top symmetry condition – i.e. zero normal velocity and zero normal gradients of all variables at a symmetry plane have been taken.

4.2. Reactor geometry and system specification

The reactor vessel geometry has been designed with a MixSim and a TGRID preprocessors. The mixed hexagonal/tetrahedral grid has been generated with MixSim - see Fig. 1. An appropriate discretization of the calculation domain has been performed: the obtained grid consists of approx. 70k cells, the volume of each cell is between 3.16 10^{-10} and 1.76 10^{-7} m^3, while a total reactor volume is 1.5 10^{-3} m^3.

At this stage of studies, physico-chemical properties of the reaction mixture have been taken as constants independent on the temperature and the reaction mixture composition. This simplification allows us to significantly reduce a calculation time by not solving flow equations during the reaction progress. Firstly, velocity profiles for the liquid reaction mixture have been calculated without taking reaction into account then, they have been kept the same during unsteady simulation of the reaction progress.

To examine an influence of the liquid viscosity on mixing efficiency, so also on non-uniformity of temperature distribution inside the reactor, two series of CFD simulations have been carried out for two viscosities of the reaction mixture: for the system S1 with

a moderate liquid viscosity $\mu = 0.6\ 10^{-3}$ [Pa s] and the system S2 with a large liquid viscosity $\mu = 0.615$ [Pa s]. So, two different viscous models have been applied in CFD modelling (Fluent, 2003): the k-ε realizable model for the system S1 and the laminar model for the system S2.

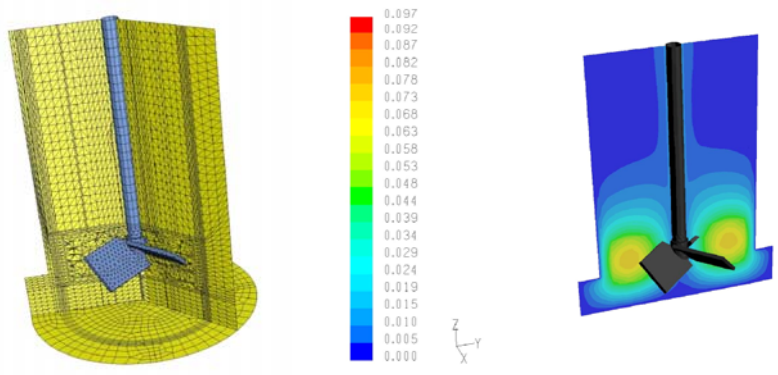

Figure 1. Grid generated for the reactor vessel (left) and velocity profiles obtained for the viscous system S2 (right).

3. Divergence Criterion

Recently, a new criterion to delimit runaway boundaries in chemical reactors has been developed (Strozzi *et.al.*, 1999, Zaldivar *et al.*, 2003). This criterion is based on the divergence of the system and it is defined as when the divergence of the reactor becomes positive on a segment of the reaction path – i.e. $div > 0$. The divergence is a scalar quantity, defined at each point as a sum of the partial derivatives of the mass and energy balances with relation to the correspondent variables – temperature and conversions (Zaldivar *et. al.*, 2005). So, the analytical divergence is defined as the trace of the Jacobian matrix of the system, **J**:

$$\mathbf{J} = \begin{bmatrix} j_{11} & j_{12} \\ j_{21} & j_{22} \end{bmatrix} = \begin{bmatrix} \dfrac{\partial(\partial\zeta/\partial t)}{\partial\zeta} & \dfrac{\partial(\partial\zeta/\partial t)}{\partial T} \\ \dfrac{\partial(\partial T/\partial t)}{\partial\zeta} & \dfrac{\partial(\partial T/\partial t)}{\partial T} \end{bmatrix} \tag{5}$$

i.e. as the sum of the diagonal elements:

$$div = j_{11} + j_{22} \tag{6}$$

where T is the reactor temperature and ξ – the conversion of the key reactant.

An application of the divergence criterion to on-line runaway detection in batch and semibatch chemical reactors is presented and widely discussed in a number of the above cited papers. A special version of the presented approach elaborated by Zbilut *et al.* (2002), in which only a single temperature measurement is needed and which is robust against noise contamination can be particularly useful for industrial practice. A use of the divergence criterion with single temperature measurement is related to the problem, where this temperature sensor should be located inside the reactor.

In this paper, basing on the results obtained from CFD simulations, the local values of the divergence have been calculated as a function of the reaction time. Comparing these values to the runaway criterion (*div* > 0), a proper location of temperature sensors can be indicated.

4. Results, Discussion and Conclusions

Two series of CFD simulations have been carried out for both considered types of the reacting systems: the system with low liquid viscosity (S1) and the system with large liquid viscosity (S2), respectively. Liquid velocity, reactants concentrations and temperature profiles inside the reactor vessel have been obtained as a function of the reaction time, by solving a set of the model equations.

A typical velocity profile for the viscous system (S2) is shown in Fig. 1, where zones of relatively weak mixing intensity can be clearly distinguished in the upper and the central parts the reactor vessel.

For the same viscous system (S2), profiles of the temperature and the concentration of the key reactant (propionic anhydrite) are displayed in Fig. 2, where distinct non-uniformities of temperature and concentration distribution are visible. A relatively high temperature in the stagnant zones inside of the reactor can be observed. For the system (S1), with a moderate viscosity of the reaction mixture, this non-uniformity of the temperature distribution is less pronounced.

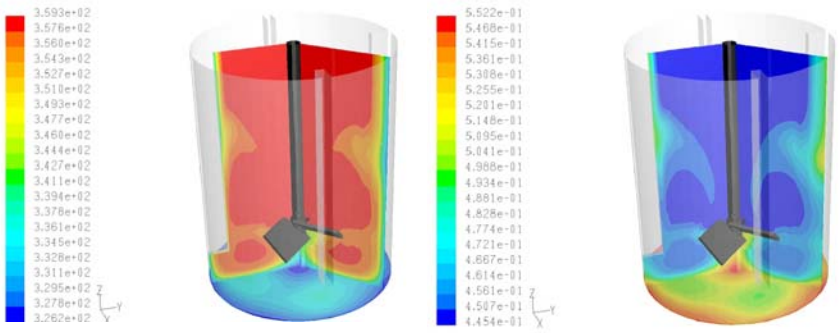

Figure 2. Results of CFD simulations for viscous system (S2), at the reaction pathway approaching runaway: t = 100 s. Temperature profiles (left) and concentrations of the propionic anhydrite (right).

For both tested reacting systems (S1 and S2), following equations 5 and 6, values of the local divergences have been calculated and spatial distributions of the divergence of the system are shown in Fig. 3. The appropriate partial derivatives have been estimated numerically with use of the results obtained from CFD simulations, applying a three point backward method. Values of the local divergence, displayed in Fig. 3, indicated that the both systems approach a dangerous pathway leading to a global runaway (div > 0). For the system S1, local non-uniformities of temperature and divergence are less pronounced, while they become essential for the viscous system (S2). The obtained results can be very useful for the parametric sensitivity analysis as well as for practical use of the divergence criterion by indicating a number and location of temperature sensors.

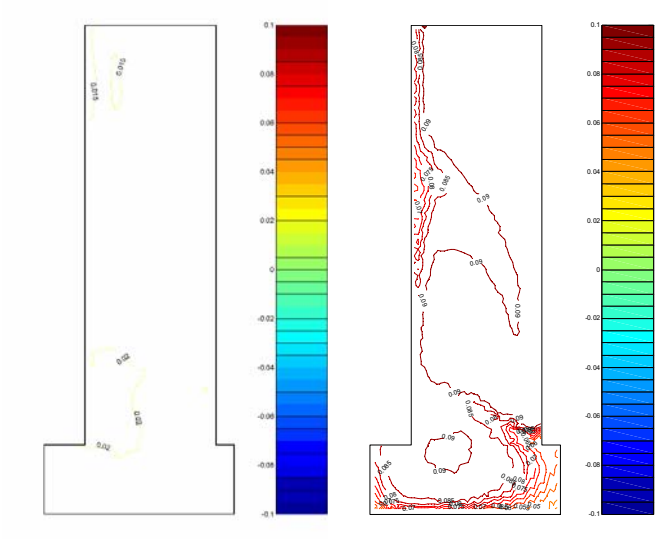

Figure 3. Local divergences of the reacting system as estimated from CFD results at the reaction time t = 80 s: (right) for the low viscosity system (S1), (left) for the high viscosity system (S2).

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