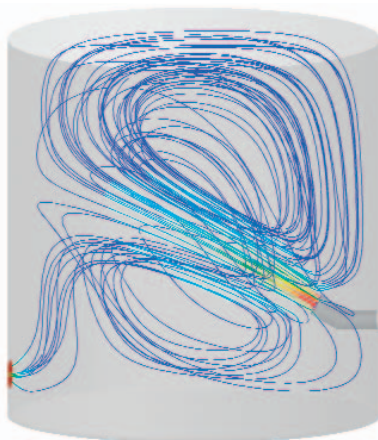
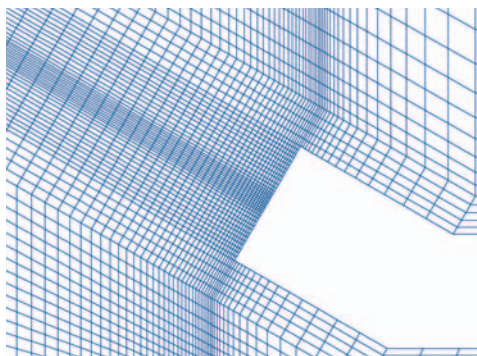


Preventing Runaway Reaction Accidents

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Solution domain and pathlines for the jet mixer studied



Grid near the inlet

RUNAWAY REACTIONS ARE AN ONGOING PROBLEM in the chemical industry, where they account for 26% of major accidents. Runaway reactions generate a sudden excess amount of heat, which can lead to an explosion. They can be stopped in two ways: by the addition of cold diluents and by the addition of an inhibitor, a chemical that acts to suppress the runaway reaction. The technology that involves the use of inhibitors is called shortstopping. Power failures are one of the main reasons for runaways, and after a power failure, the process of adding an inhibiting agent and mixing it with the reactor contents becomes a major problem in the shortstopping process. Jets or impellers, driven by a small generator, can be used for mixing under such circumstances.

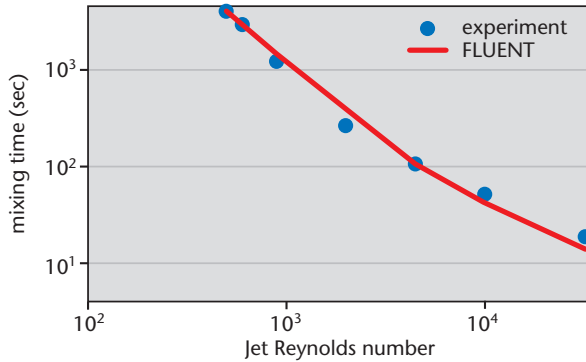
From a design standpoint, jet mixing is one of the simplest methods to achieve mixing. In jet mixing, a part of the liquid in the tank is drawn out through a pump and returned to the tank as a high-velocity jet through a nozzle, resulting in fluid mixing. In a recent project [1], CFD was used to compare the efficiency of jet mixers with impeller stirred vessels in shortstopping runaway reactions. On the basis of equal power consumption, this comparative study showed that jet mixers were ineffective when used for shortstopping, unless certain factors could be optimized. Due to the hazardous nature of runaway reactions, these factors cannot be determined with lab scale or pilot plant scale experiments, but CFD can be used to carry out virtual experiments instead.

Using FLUENT, mixing with a jet mixer was first investigated for different nozzle diameters and angles of injection. To account for the external circulating pump, user-defined functions (UDFs) were used to ensure that the mass fractions of all species entering the vessel through the inlet were equal to those leaving through the outlet at each timestep. Before simulating the reacting flow of the shortstopping process, the flow model alone was validated. Since overall mixing controls the process, the predicted mixing times were compared with the available experimental correlations [2, 3] and found to be in excellent agreement.

The converged flow results of the best jet configuration were then used for subsequent simulations of the runaway and inhibition reactions. Laminar volumetric reactions were modeled using UDFs. Guibert *et al.* [4] documented the kinetics of the considered runaway reaction. Before analyzing a specific runaway scenario, reactor conditions were varied and runaway behavior was studied. From all of the cases considered, the one with the fastest temperature increase was selected for further study, since it would be the most difficult to shortstop. For this scenario, as soon as the reactor temperature reached 450K, the inhibitor was added and the species transport equations for the inhibition reaction were solved simultaneously with the runaway reaction.

The results were used to identify the major and minor factors that contribute to effective shortstopping when using a jet mixer. These factors include the location for adding the inhibitor; the amount of the inhibitor; the rate of the inhibition reaction; the power input; the use of a cold diluent; and the use of multiple nozzles. The temperature distribution in the reactor after the shortstopping process and the decrease in the average reactor temperature were used to assess the importance of each factor.

For example, the temperature distribution on the mid-plane and an iso-surface of temperature equal to 500K (temperatures over 500K were considered hazardous) for two power levels was used to illustrate the importance of power input. The hotspots, or high temperature regions over 500K, decrease in size as the power is increased, which indicates improved shortstopping. In addition to the power input, the decrease in



Comparison of the predicted mixing time and experimental data for a range of jet Reynolds numbers [2]

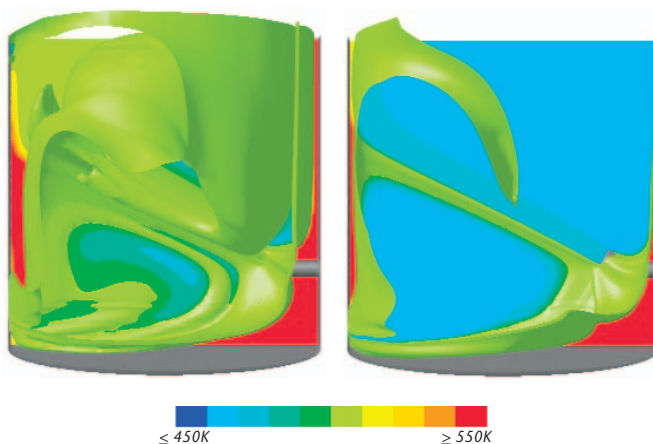
the final reactor temperature for the other factors was computed as well. When compared, the major factors that were found to contribute most to effective shortstopping were the use of cold diluents and the use of multiple nozzles. The factors found to be of less importance were the rate of the inhibition reaction, the location of the inhibitor injection, and the amount of inhibitor. The study clearly demonstrated the value of using CFD simulations in situations that are experimentally prohibitive. ■

Acknowledgements:

The authors acknowledge NSF for their support of this particular project, and Dr. Vivek V. Ranade and his student Dr. Avinash. R. Khopkar of IFMG, National Chemical Laboratories, Pune, India, for their technical contributions and inspiration.

References:

- 1 Dakshinamoorthy, D., Khopkar, A.R., Louvar, J.F. and Ranade. V.V.: CFD Simulations of Shortstopping Runaway Reactions in Vessels Agitated with Impellers and Jets. Accepted in the Journal of Loss Prevention in the Process Industries, 2005.
- 2 Lane, A.G.C. and Rice, P.: An Investigation of Liquid Jet Mixing Employing an Inclined Side Entry Jet. Transactions of Institute of Chemical Engineers, 60, 171-176, 1982a.
- 3 Lane, A.G.C. and Rice, P.: Comparative Assessment of the Performance of Three Designs for Liquid Jet Mixing. Industrial & Engineering Chemistry Process Design and Development, 21, 650-653, 1982b.
- 4 Guibert, M.R., Plank, A.C. and Gerhard, R.E.: Kinetics of the Propylene Oxide – Oxypropylated Glycerol Reaction. Industrial & Engineering Chemistry Process Design and Development, 10 (4), 497-500, 1971.



Contours of temperature on the mid-plane and an iso-surface of temperature at 500K illustrate the temperature distribution after shortstopping with less (left) and more (right) power input

Kinetic Details of Runaway and Inhibition

Runaway Reaction

Guibert *et al.* [4] studied the kinetics of the propylene oxide polymerization reaction. The rate of the reaction is defined as a function of temperature, propylene oxide concentration, and catalyst concentration. Monomer polymerizes to polymer in the presence of a basic catalyst. The kinetic expressions for the monomer concentration and temperature are as follows:

1.
$$\frac{dC_{monomer}}{dt} = -k_0 e^{-\frac{E}{RT}} C_{monomer} C_{catalyst}$$
2.
$$\frac{dT}{dt} = -k_0 e^{-\frac{E}{RT}} C_{monomer} C_{catalyst} \left(\frac{\Delta H}{c_p} \right)$$

Inhibition Reaction

The added inhibitor neutralizes the basic catalyst. The kinetic expression for the inhibition reaction is as follows:

3.
$$\frac{dC_{catalyst}}{dt} = -k_1 e^{-\frac{E}{RT}} C_{catalyst} C_{inhibitor}$$

Kinetic Data for Inhibition and Runaway Reactions

Activation Energy	E = 6.96E+08 J/kgmol
Heat of Reaction	$\Delta H = -1.63E+06$ J/kg(monomer)
Pre-Exponential Factor	$k_0 = 9.5E+11$ kg(total)/(kg(cat)-hr)
Specific Heat Capacity	$c_p = 2930$ J/kg(total)-K
Pre-Exponential Factor	$k_1 = 9.5E+11$ kg(total)/(kg(inh)-hr)
Gas Constant	R = 8314.34 J/kgmol-K