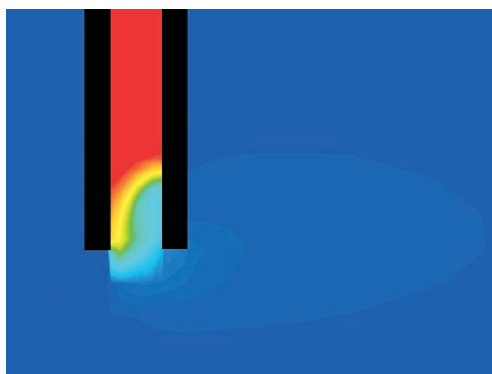


# Improving Reaction Selectivity by Clever Mixing

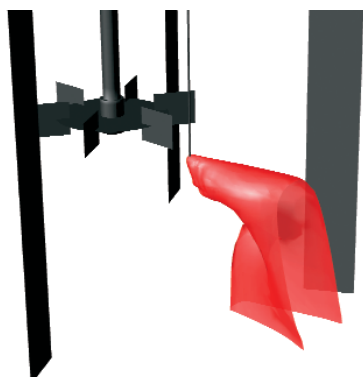
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Backmixing effect – chemical reaction takes place through back diffusion into the feed pipe

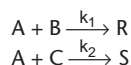


Contours of concentration of the secondary product S in the stirred tank reactor



Visualization of reaction zone in the semibatch stirred tank reactor

In the pharmaceutical industry, many chemical reactions leading to desirable intermediate and end-products are accompanied by side reactions producing undesired by-products. By-products decrease reaction yield and complicate product separation. The simplest system that reveals this behavior is one of two parallel reactions with two reagents, B and C, present in a homogeneous mixture and competing for a common reagent, A. Competing reactions result in the formation of the desired product, R, and the undesired product, S:



A competitive-consecutive reaction scheme that behaves in a similar manner<sup>1</sup> involves only reagents A and B, but delivers by-products through a reaction of A with R. An understanding of the process parameters that govern the competitive-parallel scheme therefore can be applied to the competitive-consecutive scheme as well.

To improve selectivity, the competition between reactions can be enhanced. For example the addition of a homogeneous catalyst can increase the rate of the first, desired reaction, resulting in a more selective synthesis of R. However, there is a limit for such a procedure. When the first reaction becomes very fast, its rate becomes controlled by mixing, rather than the reaction kinetics. Competition is then between the mixing-controlled first reaction and the slower second reaction, which is often also affected by mixing. The problem of reactive mixing arises and is further complicated when the flow is turbulent and the Reynolds averaging procedure is applied.

To model this process, it is useful to check which of the sequence of mixing processes can directly or indirectly affect the course of the chemical reactions. Comparison of the characteristic times for mixing and reaction can provide this information. For very long reaction times (minutes to hours) only the process time is relevant (feed time in the case of semibatch stirred tank reactors or mean residence time in continuous stirred-tank reactors (CSTRs)). When the reaction time is between seconds and minutes, consideration of the flow

pattern (macromixing) and turbulent diffusion (mesomixing) is required, but concentration fluctuations of reacting species can be neglected. For reaction times that are significantly smaller than 1 second, the reaction rate becomes micromixing-dependent and the effects of concentration fluctuations should be included.

A general modeling approach has been developed and linked to FLUENT 6 through user-defined functions (UDFs). It incorporates all three regimes, and can be applied when the first reaction is instantaneous and the second one is fast. Involving macromixing, mesomixing, micromixing, and reaction kinetics<sup>2,3</sup>, it can be applied to semibatch or continuous operation. To model micromixing, a non-equilibrium multiple-time-scale mixing model is applied. The model includes mixing in the inertial-convective, viscous-convective and viscous-diffusive subranges of the spectrum. This means that the effects of the molecular diffusivity and viscosity on the rate of turbulent mixing are included. To express the averaged reaction rate in terms of other dependent variables, a conditional moment closure based on a linear interpolation of local instantaneous reactant concentration values is applied. The reactant concentrations are expressed by means of the mixture fraction, whereas the distribution of the mixture fraction is approximated using a beta distribution function.

The model has been applied<sup>2,3</sup> to a semibatch stirred tank reactor and a CSTR, predicting well all the trends observed in experiments, including the effects of residence and feed times, impeller speed, feed concentrations, feed pipe position, and backmixing. The results illustrate that by using this approach, it is possible to design the way in which the reagents are contacted and mixed to obtain the goals specific for the process, that is, to improve selectivity. ■

## references:

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- 3 J. Bałdyga and Ł. Makowski, *Chem. Eng. Technol.*, **27**(3), pp.225-230, 2004.