

Chemical Reaction Engineering for Process Optimization: The Importance of Primary Processes on the Molecular Level

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Abstract: Any innovative design of a chemical or biological reactor has to consider the dynamics of the primary physical and chemical steps involved in the overall process. For homogeneous highly viscous systems the mixing time is of crucial importance for the product quality. In heterogeneous systems, product selectivity and reactor performance can be optimized under dynamic conditions.

Keywords: Micromixing · Periodic operation · Unsteady state

1. Introduction

Chemical reaction engineering is a diverse and evolving science. Its ultimate aim is the appropriate design of chemical and biological reactors ensuring safe and efficient process operation. Chemical and biological processes should be de-



signed to be inherently safe and environmentally benign. Hazards associated with materials and operations used in the process should be eliminated or at least reduced to a minimum. Raw materials and energy should be sparingly used and the formation of waste in the manufacturing process should be minimized. The preference is avoidance of waste generation at the source rather than elimination of unwanted and harmful co- and by-products. 'End of pipe' solutions must be replaced by 'production integrated environmental protection'.

The above-mentioned targets can only be reached by an integrated approach based on chemistry, physics and engineering sciences. The design and sizing of chemical reactors must consider physical and chemical kinetics. This was first understood by Damköhler, who formulated the importance of the characteristic reaction time in relation to the diffusion time in heterogeneous systems. Based on systematic studies on chemical transformations in flowing systems, he rationalized the relationships between the characteristic reaction time and space time in homogeneous and quasi-homogeneous systems [1][2]. These innovative ideas were further developed by Danckwerts in his pioneering paper in 1958 on the influence of the micro mixing time on the global reaction rate, reactor performance and product selectivity [3].

During the past decades fundamental knowledge has been gained in the physico-chemical processes taking place at different time scales, ranging from microseconds for chemical reactions up to several hours for chemical reactors. Any development of a new catalyst, the design of a novel process, and its efficient control has to consider the dynamics of the underlying physical and chemical processes. This will be illustrated with the following examples.

2. The Influence of Mixing on Homogeneous Reactions

For the proper design of homogeneous reactors macroscopic mixing characterized by the residence time distribution as well as mixing on the molecular level are of primary importance to obtain high product yields and to discriminate against unwanted secondary reactions.

2.1. Macromixing in Tubular Reactors

The performance of tubular reactors is impaired by the occurrence of unfavorable flow profiles and, even more, by convective fluctuations due to density gradients *e.g.* provoked by temperature gradients. These problems become important for reactions with relatively slow kinetics necessitating large space times and/or for reactions in high viscous me-

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dia. Different means are proposed to circumvent large backmixing in tubular reactors, which all have in common that an enforced radial exchange of fluid elements is superimposed on the longitudinal fluid flow. In other words, the radial mixing time has to be short compared to the residence time of the reactant in the reactor. To avoid excessive pressure drop and fluid maldistribution the use of structured packings with high voidage under laminar flow conditions is favored. Such characteristics are provided by some motionless mixers. Therefore, detailed studies have been carried out to characterize different types of motionless mixers with particular emphasis on the range of low Reynolds numbers. Residence time distribution measurements were performed in aqueous systems, non-reactive and reactive polymer mixtures in a wide range of viscosities from 0.5×10^{-3} Pa s to 3×10^3 Pa s [4][5]. For Reynolds numbers below 100 the dispersion is independent of flow rate and the Bodenstein number for Sulzer SMX mixers was found to be $Bo \cong 80$ per meter, corresponding to about 40 ideally mixers in series per meter. The results obtained led to the design of tubular reactors for enzymatic-catalyzed reactions [6–13] and for homogeneous polymerization and co-polymerization [4][14–22].

2.2. Micromixing

The results from RTD measurements show that effective macroscopic radial mixing can be achieved but do not yield any information about the micromixing time, *i.e.* the characteristic time for ensuring a homogeneous composition on the molecular level. If the reaction time is short compared to the micromixing time the system is said to be segregated. Segregation occurs in reacting systems with very fast reactions, *e.g.* in flames, or in high viscous liquids even at moderate reaction rates. The ratio between characteristic mixing time and reaction time determines the degree of segregation. For homo-polymerizations, the degree of segregation affects the molecular mass distribution and the heterogeneity index. Whereas for co-polymerizations, the time of micromixing will strongly influence the product characteristics in terms of mean molecular mass and its distribution on one hand, and the composition distribution and the sequence of monomer units on the other hand. In order to investigate and estimate the degree of micromixing, a novel test reaction using in-line sensor was developed and tested [23–25].

The free radical bulk polymerization of styrene in the presence of a chain transfer agent was used as a test reaction to characterize the micromixing in a tubular loop reactor. Under otherwise constant reaction conditions (temperature, concentrations of monomer and transfer agent), the average molecular mass depends strongly on the mixing intensity, which is a function of the specific power dissipation (ϵ) and the mixing device used.

To estimate the segregation, a linear scale between total segregation (TS) and perfect micromixing (MM) is assumed. Based on the obtained mean molecular masses (\bar{M}_w (ES)), a segregation index X_s is defined as follows:

$$X_s = \frac{\bar{M}_w(ES) - \bar{M}_w(MM)}{\bar{M}_w(TS) - \bar{M}_w(MM)} \quad (1)$$

To evaluate the experimental results, a micromixedness ratio (α) is introduced:

$$\alpha = \frac{1 - X_s}{X_s} = a \left(\frac{t_r}{t_m} \right)^b \quad (2)$$

Relying upon several observations and simulations Villermaux and coworkers [26][27] suggested that α can be correlated with the ratio of two characteristic times: t_m , the micromixing time and t_r the characteristic reaction time.

Under laminar flow conditions t_m is proportional to $(\nu/\epsilon)^{1/2}$ [28][29] and Eqn. 2 becomes:

$$X_s = \left[1 + a' \left(t_r \sqrt{\epsilon/\nu} \right)^b \right]^{-1} \quad (3)$$

Experimental results for the segregation index as a function of t_r/t_m are shown in Fig. 1 for three different mixing devices. They correspond to the Sulzer mixer types SMXL, SMX and a developed 'high-mixing' device. Analysis of Fig. 1 allows a quantitative comparison of the

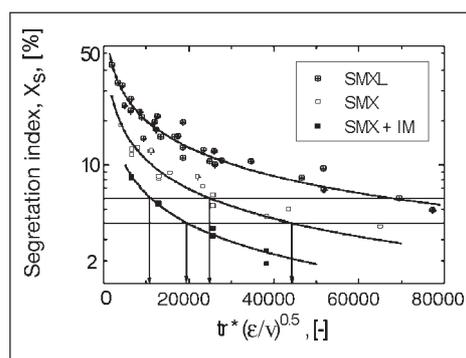


Fig. 1. Segregation index as function of the reaction and mixing time (t_r/t_m)

mixing efficiencies. It follows for identical power dissipation in the reactor that the characteristic mixing time in a SMXL mixer is twice as long as in a SMX mixer. It is even six times longer compared to the special mixer unit. Based on the micromixing studies a co-polymerization process was developed. The experimental results from the pilot plant confirmed the high efficiency of the designed mixer and the *a priori* predicted uniform composition of the produced co-polymer [22].

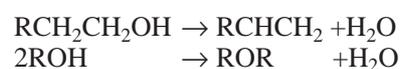
3. Dynamic Operation of Chemical Reactors

Process development and engineering has traditionally been focused on running chemical production units stationary. The process parameters are selected to provide the best possible operating level for the desired objectives. In the search for further improvement of continuous processes within a given range of parameters such as temperature, pressure, concentration and flow-rate, unsteady state or forced periodic operation of chemical reactors was proposed [30–33]. Dynamic behavior of the reactor, or unsteady state of the catalyst in heterogeneous systems, is used as an additional tool for process optimization.

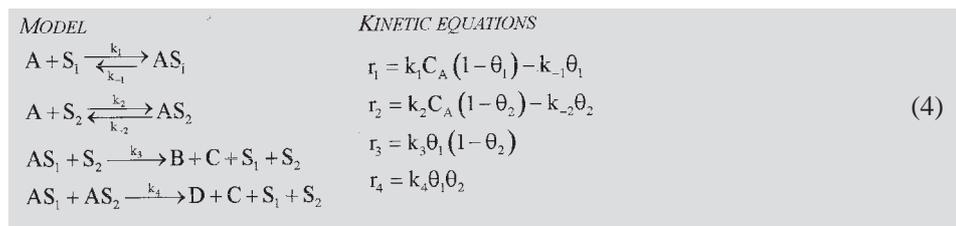
In heterogeneous catalysis different physical and chemical steps like mass transport, adsorption, surface reaction and desorption influence the global reaction rate. Therefore, the concentration of surface species under forced concentration variations may differ considerably from the steady state resulting in a change of the various surface reaction rates, thus altering the product selectivities.

The behavior of catalysts during non-steady state operation is intrinsically connected to the dynamics of chemical processes occurring on its surface. As these processes are in general fast, important effects can only be reached at periods in the range of the characteristic times of the surface processes.

One of the examples for the increased reaction rate by periodic variation of reactant concentration in the reactor is the dehydration of alcohols over amphoteric oxides, *e.g.* Al_2O_3 [34–37].



The kinetics of this reaction can be described by considering a model with two different active sites i involved in the catalytic action [38–40]. The proposed



reaction scheme and the resulting kinetic equations are given above.

Alcohol (A) is strongly adsorbed on an acid site (S_1) and weakly on the basic S_2 . An adjacent empty basic site (S_2) is required for the formation of an olefin, while the production of ether necessitates two occupied sites (AS_1 and AS_2).

Under steady state conditions the rate of olefin formation increases with the reactant concentration C_A up to a maximum value. A further concentration increase leads to a decrease of the reaction rate due to the blocking of free S_2 sites (Fig. 3).

In order to increase the yield of the olefin it was proposed to stop periodically the feed of alcohol in the reactor inlet (see Fig. 2). After a feed stop, the alcohol desorbs rapidly from S_2 but not from S_1 . As a consequence, the surface concentration of empty S_2 sites rises quickly, which results in an increase of the instan-

taneous reaction rate of olefin formation until the accumulated surface compound (AS_1) has been consumed. At the same time ether formation is suppressed.

The attainable reactor performance and olefin selectivity depends strongly on the amplitude and frequency of the imposed concentration variations. The optimal cycle period is related to the adsorption capacity of the catalyst and must be in the range of the characteristic time of the surface processes.

When the forced cycling is repeated sufficiently often, the results within the periods become identical. For these cycle invariant conditions the predicted mean production rate as a function of the reactant concentration and length of period is shown in Fig. 3 for a constant cycle split of $\gamma=0.9$ [39]. The mean reaction rates are considerably higher compared to the maximum at steady state for concentrations exceeding the optimal steady state

value. If the adsorption equilibrium for sites 2 is attained rapidly, high frequencies for the concentration oscillations are required to achieve a maximal average reaction rate. If instantaneous adsorption equilibrium is assumed, the optimal length of period approaches zero ($t_p = >0$).

Due to the high inertia of conventional reactors the attainable frequencies of concentration oscillations are in the order of 10^{-4} to 10^{-2} Hz. To increase the frequency, reactors with low inertia and narrow residence time distribution are required. Compared to conventional randomly packed beds microchannel reactors are much more suitable for periodic operation at high frequencies, due to their small dimensions and well-defined structure. As the channel diameters are in the order of several micrometers, microreactors operate under laminar flow conditions resulting in a parabolic velocity profile. But, due to the short radial diffusion times the radial concentration profile is flat, leading to a narrow residence time distribution of the reactants [37]. The latter characteristic is of crucial importance for non-steady-state operation. Only reactors with a uniform residence time can be used to get the full advantage of forced concentration variations.

For the catalytic dehydration of isopropanol a special microchannel reactor consisting of microstructured stacked plates was designed and constructed (Fig. 4) [37]. The geometry of the plates and of the stack itself was optimized to avoid mixing in the entrance and outlet area and to distribute evenly the flow between the different channels [41].

The reactor, plates as well as the housing, was constructed of stainless steel. Each plate contains rectangular channels of $300 \mu\text{m}$ width, $240 \mu\text{m}$ depth and 20 mm length. The developed microchannel reactor can be operated efficiently at frequencies up to 1 Hz.

In Fig. 5 the instantaneous outlet concentrations of the reactant, isopropanol and the products, propene and diisopropylether are shown for a cycle period of $t_p = 30 \text{ s}$ and a space time of $\tau = 0.165 \text{ s}$. An important phase shift between the concentration oscillations of isopropanol and the propene is observed, whereas the for-

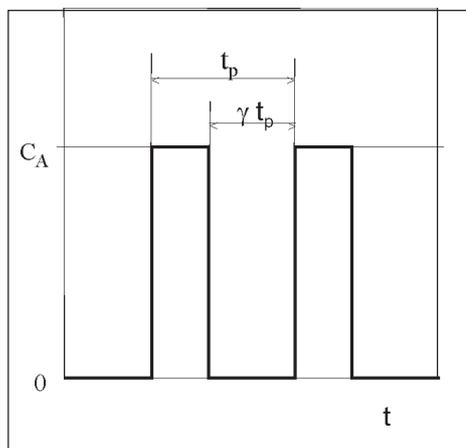


Fig. 2. Schematic presentation of forced periodic variation of reactant concentration

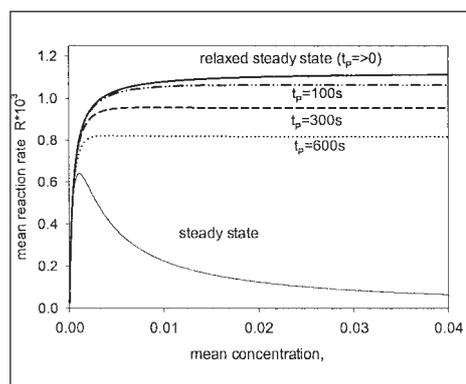


Fig. 3. Mean reaction rate over a period as function of the mean feed concentration for different length of period and a cycle split of $\gamma=0.9$

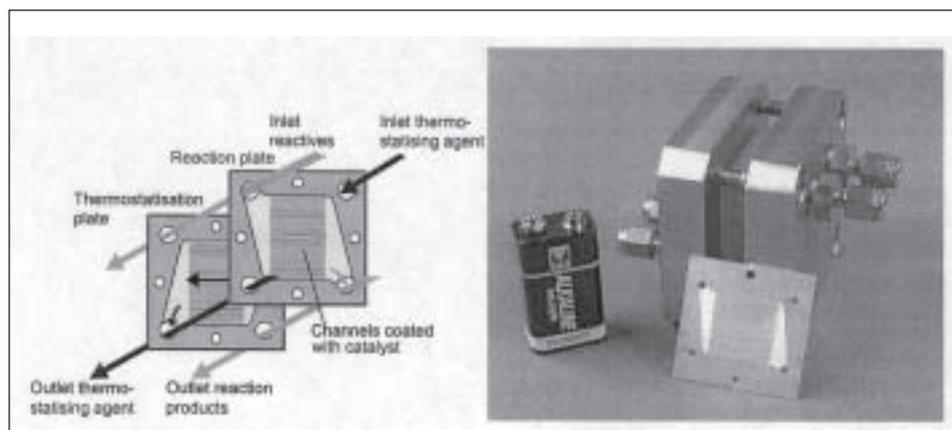


Fig. 4. Photo and sketch of fluid flows in the microstructured reactor (Institut für Mikrotechnik, Mainz)

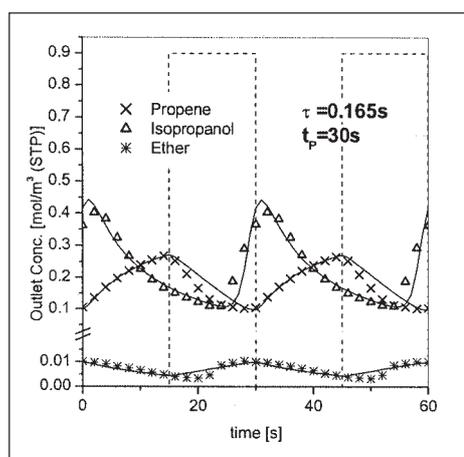


Fig. 5. Outlet concentrations as function of time. $T = 200\text{ °C}$, $P = 1.26\text{ bar}$, $C_{i\text{PrOH,average}} = 0.45\text{ mol/m}^3\text{ (STP)}$. Symbols: experimental values; lines: model simulation

mation rate of ether is proportional to the reactant concentration. This results in considerable changes in the conversion and the product selectivity (Fig. 6). Depending on the length of period, the conversion increases from 32% at steady state up to 51% under forced periodic operation. At the same time the olefin selectivity reaches 95% compared to 83% at steady state. In addition, the productivity for the target product could be nearly doubled (Fig. 7).

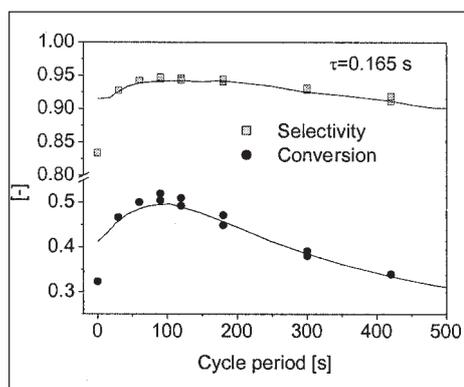


Fig. 6. Mean selectivity and conversion as function of cycle period. $T = 200\text{ °C}$, $P = 1.26\text{ bar}$, $C_{i\text{PrOH,average}} = 0.45\text{ mol/m}^3\text{ (STP)}$. Symbols: experimental values; lines: model simulation

4. Conclusions

The global rate of chemical reactions is the result of a complex interplay of different physical and chemical processes. Depending on the characteristic time of each primary step, the overall kinetics can change considerably affecting product selectivity and reactor performance.

In continuous homogeneous reactors, the average rate of reaction is in general influenced by the degree of local mixing on the molecular scale. Long micromixing times compared to the characteristic reaction time lead to concentration gradients and alter the product quality. This was demonstrated for bulk polymerization and co-polymerization. Quantitative relationships between mixing and reaction times were established for a proper reactor design.

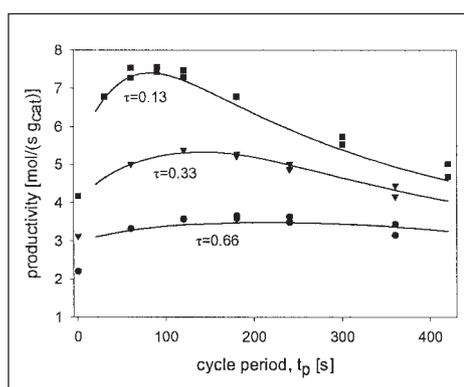


Fig. 7. Average reactor performance as function of cycle period and space time. $T = 200\text{ °C}$, $P = 1.26\text{ bar}$, $C_{i\text{PrOH,average}} = 0.45\text{ mol/m}^3\text{ (STP)}$. Symbols: experimental values; lines: model simulation

In general, the dynamics of the individual physical and chemical steps involved in a reacting system are quite different. Therefore, the composition of a reacting mixture in the reactor or on the surface of catalyst under non-stationary conditions can differ considerably from the values at steady state. This may lead to improved product selectivities and reactor performances, not attainable under stationary conditions. Repeated disturbance of the reacting system through pe-

riodic concentration variations is a powerful tool to optimize the performance of chemical and biological reactors. It is important to note that periodic operation can only be beneficial if the time-periods for the parameter variations are in the range of the characteristic time of the primary reaction steps. This was theoretically and experimentally shown for reactions with self-inhibition, e.g. the catalytic dehydration of alcohols on alumina.

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