

First, second and nth order autocatalytic kinetics in continuous and discontinuous reactors



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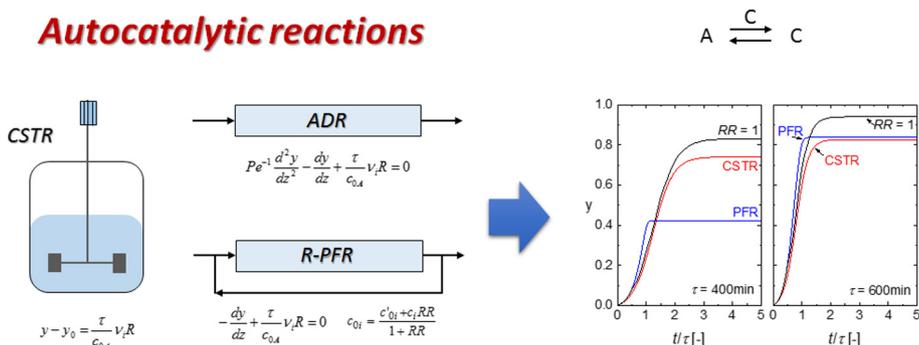
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HIGHLIGHTS

- First, second and nth order autocatalytic kinetics investigation.
- Methyl formate hydrolysis chosen as test reaction.
- Discontinuous and continuous reactors are considered.
- The reactors are analyzed by classical methods and numerical simulations.
- Optimization of both Pe and RR for nth order ($n = 1$) kinetics.

GRAPHICAL ABSTRACT



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ABSTRACT

Autocatalytic phenomena in chemical kinetics originate from various reasons, such as acid-catalytic effects of reaction products or change of the physical properties of the reaction mixture. The impact of autocatalytic kinetics on the chemical reactor design is crucially important leading to deviations from standard design rules. The impact of autocatalytic effects on first, second and nth order kinetics was investigated for batch, plug flow, backmixed, axial dispersion and recycled plug flow reactors was analyzed by classical approach and numerical simulations. Efficient numerical strategies were developed for the different reactor models. The results showed how an optimal degree of backmixing (Péclet number) and optimal recycle ratio can be determined for tubular reactors and how the reactor volume can be minimized for specific cases. Generic examples as well as hydrolysis of alkyl formate were considered as case studies.

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1. Introduction

Autocatalysis is a fascinating phenomenon in chemical kinetics, since the reaction rate increases as the reaction progresses. Typically, the rate falls at high conversions of the reactants. The kinetic curve recorded in a batch reactor has thus an S-shaped form as described by Fig. 1.

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Nomenclature

A, B, C, \dots	parameters	$\alpha, \alpha_0, \alpha_1, \alpha_l$	parameters
a, b, c, \dots	parameters	β, β_0, β_1	parameters
c	concentration, mol kg ⁻¹	γ	parameter in rate equation
Da	Damköhler number, –	δ	parameter in rate equation
D_z	axial dispersion coefficient, m ² s ⁻¹	λ	parameter
f, F	functions	ν	stoichiometric coefficient, –
g	function	τ	mean residence time, min
K	equilibrium constant, –	τ_0	recycle tube reactor mean residence time, min
k'	reaction rate constant, min ⁻¹	τ_{cell}	cell mean residence time, min
k_0	reaction rate constant, min ⁻¹	τ_{max}	mean residence time at max rate, min
k_1	reaction rate constant, kg mol ⁻¹ min ⁻¹	$\sqrt{\quad}$	parameter
L	reactor length, m		
N_{cell}	number (of cells), –	Subscripts and superscripts	
n	reaction order, –	0	time = 0 condition
Pe	Péclet number, –	i	general component index
R	reaction rate, mol kg ⁻¹ min ⁻¹	j	cell index in recycled PFR
RR	recycle ratio, –	opt	optimal
t	time, min	R	(recycle) reactor
V, V_{cell}	volume, m ³	*	equilibrium condition
V, V', V_R	volumetric flow rate, m ³ min ⁻¹		
w	flow velocity, m s ⁻¹	Abbreviations	
x	concentration of key component, mol kg ⁻¹	ADR	axial dispersion reactor
x_{max}	concentration of key component at max rate, mol kg ⁻¹	BR	batch reactor
y	dimensionless concentration, –	CSTR	continuous stirred tank reactor
y_{max}	dimensionless concentration at max rate, –	PFR	plug flow reactor
z	dimensionless length coordinate, –		

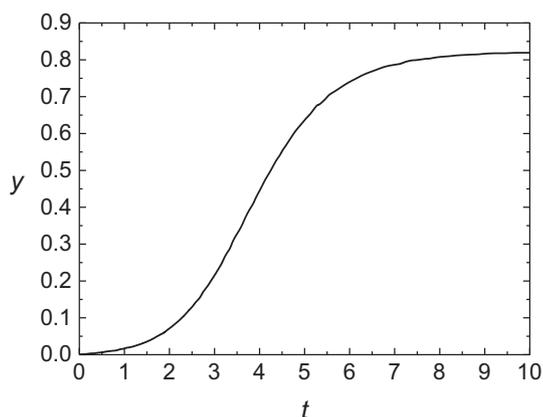


Fig. 1. Reactant conversion and product formation in an autocatalytic process.

The chemical reasons for autocatalysis can be several, but the characteristic feature is that the product molecules contribute to the reaction mechanism in such a way that the reaction rate is enhanced. A typical example is hydrolysis of esters – the process is acid-catalyzed; thus, the product acid molecules act as catalysts for the reaction and an autocatalytic effect is observed (Jogunola et al., 2011). A more exotic form of autocatalysis has been reported for homogeneously catalyzed chlorination of carboxylic acids. The reaction mechanism is based on the acid-catalyzed enolisation of the homogeneous catalyst, acid chloride. The halogenated carboxylic acid is a stronger acid than the reagent, the unchlorinated carboxylic acid (for instance, acetic acid has a pK_a -value of 4, while the pK_a -value of monochloroacetic acid is 1). For this reason, the acid-catalytic effect is continuously accelerated as the reagent molecule is transformed to the product molecule during the course of the reaction (Salmi et al., 1993).

Anyhow, similar autocatalytic mechanisms can be found in different process such as: nitration of phenol (Ducry and Roberge, 2005), thermoset curing for polymers (Kenny, 1994), aniline polymerization (Mu and Khan, 1996), quinone methide formation (Peterson and Fisher, 1986), and transition metal nanocluster formation (Watzky and Finke, 1997), even in electrochemistry science (Flätgen et al., 1999).

Levenspiel has analyzed the impact of autocatalytic kinetics on the selection of the optimal reactor configuration for autocatalytic processes (Levenspiel, 1999). In case that reactant conversions below the inflexion point of the kinetic curve (Fig. 1) are desired, the optimal reactor selection is a continuous stirred tank reactor (CSTR). After passing the inflexion point, the CSTR should be followed by a plug flow reactor (PFR) to minimize the total volume (space time at a fixed flowrate) of the reactor system. This kind of double-reactor construction might, however, be expensive and inflexible. If the optimum point (inflexion point) is shifted by some reasons, such as change of inlet concentrations or operation temperature, the operation point is shifted, too. This results in a change of sizing of the CSTR and PFR units in the system.

A further aspect that comes out from literature is that autocatalytic reactions can lead to multiple steady-states, due to small perturbations that die away exponentially, corresponding themselves to either stable or unstable solutions (Scott, 1983). This aspect is a well-known topic for chemical engineering. As a matter of fact, feedback problems can lead to bifurcations and instability. These aspects are nicely reviewed by Nobel laureates (Nicolis and Prigogine, 1977). For example, in 1983 and 1984 Gray and Scott modeled the different behavior of several kinds of autocatalytic reactions proceeding in a CSTR, demonstrating the presence of isolas and mushrooms in plots of conversion vs residence-times (Gray and Scott, 1983, 1984). In 1986 Puhl and Nicolis underline the importance of an ideal mixing in order to avoid a high instability of a CSTR, paying also the attention on the importance of premixing the different feed lines prior their injection to the reactor (Puhl

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