

Enhancement of three-phase kinetic studies of complex reaction systems by semibatch reactor technology*

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A semibatch reactor concept was proposed for the determination of the kinetics in complex catalytic liquid and gas-liquid systems with reactions of highly varying rates. The method is based on continuous removal of liquid phase from the reactor, while the catalyst remains inside the reactor. The concept was demonstrated by catalytic hydrogenation of citral on Ni catalyst. The primary product (citronellal) is formed very rapidly, while the secondary (citronellol) and tertiary (3,7-dimethyloctanol) products appear much more slowly. With the proposed semibatch concept, the formation of the ultimate products was considerably accelerated and all of the rate parameters were successfully estimated by nonlinear regression analysis. The proposed approach can be extended to fixed beds with recycling as demonstrated by computer simulations.

1. INTRODUCTION

A majority of kinetic studies is carried out in batch reactors. The system is complicated by the presence of heterogeneous catalysts, since external and internal mass transfer resistances easily corrupt experimentally recorded kinetic data. The general recipe is to suppress the reaction rates, use vigorous stirring to remove external mass transfer resistance and to utilize as small as possible catalyst particles to diminish internal mass transfer resistance. These concepts are reasonable, as such, as complex reaction schemes are treated, where consecutive and parallel reactions appear.

* Invited article

The basic dilemma from a kinetic viewpoint is that the first reactions are very rapid, whilst the consecutive steps are slow. If a small amount of catalyst is placed in the reactor, it guarantees that the system operates in the kinetic regime, but the consecutive steps are far too slow to recognize the real kinetic behaviour. On the other hand, if larger catalyst amounts are placed in the reactor, the first reactions become influenced by external mass transfer limitations. A realistic way to surmount the dilemma is to change the catalyst-to-liquid ratio with time. At the initial stage of the reaction, a small amount of catalyst should be used to push the system towards the kinetic regime, while the relative amount of catalyst should be increased, as the reactions progress. It is more reasonable to start with a small catalyst-to-liquid ratio and increase it with time. In fact, a high liquid-to-catalyst ratio can be used in the beginning of the reaction, but it is decreased by feeding out the reaction liquid as the reaction advances. Thus the catalyst bulk density ($\rho_B = m_{cat}/V_L$) increases with time. In the sequel, we shall also envisage, how the idea works for a practical case, namely catalytic three-phase hydrogenation of citral on supported Ni catalyst. The products of citral hydrogenation are used for industrial production of fragrances.

2. THEORY

2.1. Mass balances for a semibatch catalytic three-phase reactor

The general mass balance for non-volatile components in a semibatch reactor with complete backmixing but with a decreasing liquid phase volume can be written as follows

$$\frac{dn_i}{dt} = r_i m_{cat} - \dot{n}_{i,out} \quad (1)$$

where n_i is the amount of substance, $\dot{n}_{i,out}$ the molar flow, r_i the generation rate and m_{cat} the mass of catalyst. Diffusion resistance inside the catalyst particle and in the surrounding liquid film are assumed to be negligible, as the catalyst particles are small and the reaction rates are low. Thus all the equations presented in the sequel presume the kinetic regime.

The mass balance equation can be written with concentrations, since the amount of substance is $n_i = c_i * V_L$, where both the concentration c_i and the liquid volume, V_L will be changed with the reaction time. We get from eq. (1),

$$d \frac{(c_i V_L)}{dt} = r_i m_{cat} - c_{i,out} * \dot{V}_{out} \quad (2)$$

Recalling that $\frac{dV_L}{dt} = -\dot{V}_{out}$ (a constant volumetric flow out, \dot{V}_{out} from the reactor) and $c_i = c_{i,out}$ because of perfect mixing simplifies the mass balance is thus simplified to

$$\frac{dc_i}{dt} = \rho_B r_i \quad (3)$$

where the bulk density (ρ_B) of the catalyst is defined by

$$\rho_B = \frac{m_{cat}}{V_{0L} - \dot{V}_t} \quad (4)$$

The generation rate r_i is determined by the stoichiometry, i.e. $r_i = \sum v_{ij} r_j$, where j denotes the reaction step.

2.2 Isothermal consecutive reactions of first order

We consider an isothermal case, where a component A reacts in three irreversible first-order reactions and the initial concentrations of the reaction products R, S and T are assumed to be zero. The reaction temperature is constant. For the reaction sequence



the mass balance equation (3) gives

$$\begin{aligned} \frac{dc_A}{dt} &= -k_1 c_A \rho_B \\ \frac{dc_R}{dt} &= (k_1 c_A - k_2 c_R) \rho_B \\ \frac{dc_S}{dt} &= (k_2 c_R - k_3 c_S) \rho_B \\ \frac{dc_T}{dt} &= k_3 c_S \rho_B \end{aligned} \quad (6)$$

For a general case of consecutive reactions, it is practical to solve the problem numerically in the Damköhler space. Balance equation system (6) can be rewritten to

$$\begin{aligned}
 \frac{dc_A}{dDa} &= \frac{-c_A}{1 - \frac{Da}{\alpha}} \\
 \frac{dc_R}{dDa} &= \frac{c_A - c_R\beta_1}{1 - \frac{Da}{\alpha}} \\
 \frac{dc_S}{dDa} &= \frac{c_R\beta_1 - c_S\beta_2}{1 - \frac{Da}{\alpha}} \\
 \frac{dc_T}{dDa} &= \frac{c_S\beta_2}{1 - \frac{Da}{\alpha}}
 \end{aligned} \tag{7}$$

It should be noticed that $\frac{Da}{\alpha} = \frac{k_1\rho_B t}{k_1\rho_B\tau_0} = \frac{t}{\tau_0}$ and $\beta_i = \frac{k_{i+1}\rho_B t}{Da} = \frac{k_{i+1}}{k_1}$ in eq. (7).

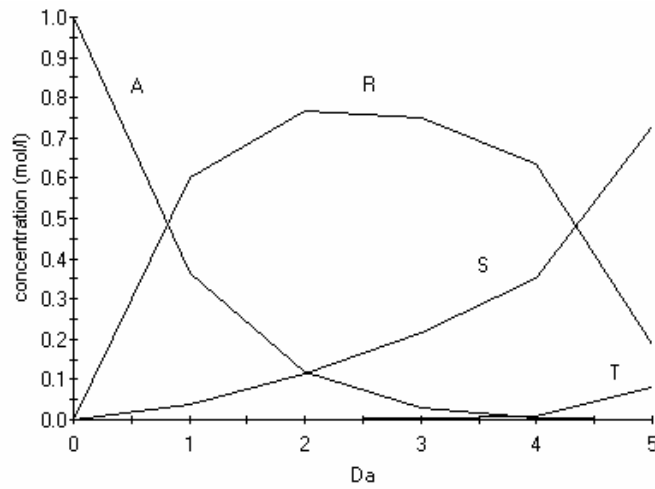
By using eq. (7), the concentration profiles for consecutive reactions for which $k_1 > k_2 > k_3 > k_4$ with and without pumping were investigated. Some results are depicted in Fig. 1 demonstrating the capability of pumping to enhance the formation of secondary and ternary products (S, T). Without pumping, it would be very difficult to obtain reasonable kinetic data for products S and T from a single experiment.

3. EXAMPLE: CITRAL HYDROGENATION

In the hydrogenation of citral, both parallel and consecutive reactions proceed simultaneously (Fig. 1) (Mäki-Arvela et al. 2002, Mäki-Arvela et al. 2005). Seven different pressure- and temperature levels were investigated. The following products were detected under the reaction conditions: citronellal, citronellol, geraniol, isopulegol, nerol, 3,7-dimethyloctanal and 3,7-dimethyloctanol. Some of these products were formed in trace quantities and thus the reaction scheme (Fig. 2) was considerably simplified. Two different reaction schemes were compared in kinetic modelling. In the reaction scheme 1 (Fig. 2) only consecutive reactions for citronellal and citronellol are included. In the modelling A denotes citral, B citronellal, C citronellol and D 3,7-dimethyloctanol. Reaction scheme 2 (Fig. 2) includes consecutive reactions with respect of citronellal and citronellol and one parallel reaction with respect of citronellal.

In the modelling according to this scheme, A denotes citral, B citronellal, C citronellol and D 3,7-dimethyloctanol; 3,7-dimethyloctanal (E) is hydrogenated further to 3,7-dimethyloctanol (D). In the experimental data, the concentration of 3,7-dimethyloctanal did not increase as a function of time and thus the influence of step 5 in the reaction scheme (Fig. 2) was neglected.

a)



b)

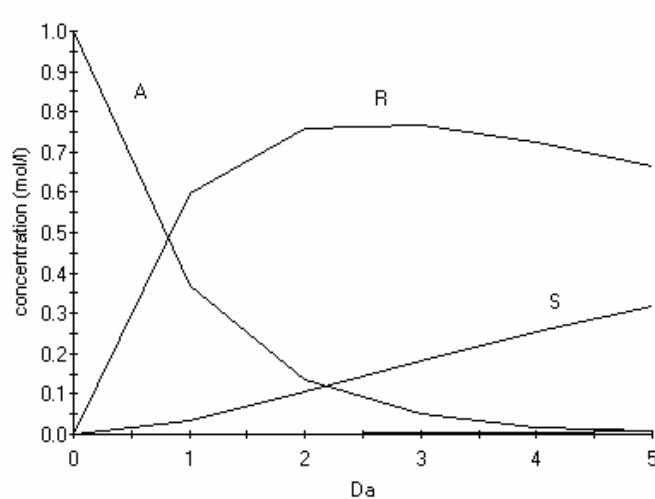


Fig. 1. Kinetics for first-order consecutive reaction system A6 R 6 S 6 T with a) and without b) liquid phase pumping. The kinetic parameters were: $k_1 = 0.5 \text{ min}^{-1}$, $k_2 = 0.05 \text{ min}^{-1}$, $k_3 = 0.005 \text{ min}^{-1}$, with liquid phase pumping $\tau_0 = [300, \infty]$, without pumping $\tau_0 = \infty$.

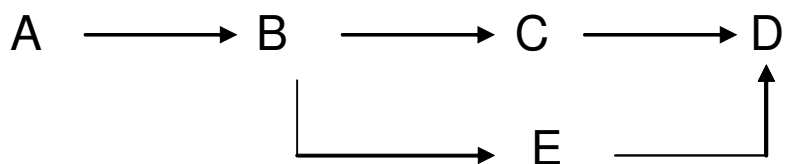


Fig. 2. Simplified reaction schemes for citral hydrogenation.

3.1. Experimental procedures

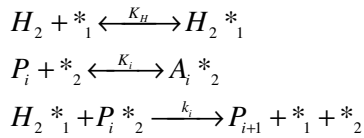
Citral (Alfa Aesar, 97%) hydrogenation kinetics was investigated in a semibatch autoclave (Autoclave Engineers) in 2-pentanol (>98%, Merck 807501) as a solvent in the temperature and pressure ranges of 50–90°C and 5–21 bar, respectively. The Ni/Al₂O₃ (20.2 wt.% Ni, BET surface area (nitrogen physisorption) 101 m²/g_{cat}, metal dispersion (hydrogen chemisorption) 15.7%) catalyst with a mean particle size of 13.5 μm (sieved to fractions less than 100 μm) was reduced prior to the experiment in situ at 270°C at 1 bar for 90 min under flowing hydrogen (99.999%, AGA). Typically, the initial citral concentration and the initial liquid phase volume were 0.1 mol/l and 325 ml, respectively. The catalyst mass was kept constant in all of the experiments (500 mg) and the stirring rate was 1500 rpm (Rushton turbine), which facilitated the hydrogenation under kinetic regime. In the experiments with an increasing catalyst bulk density, about 1 g/min liquid was continuously taken out from the reactor by using a needle valve and weighted in situ. The organic components were analysed with a gas chromatograph (Mäki-Arvela et al. 2002).

3.2. Langmuir-Hinshelwood kinetics

Langmuir-Hinshelwood mechanism was applied to citral hydrogenation kinetics. The mechanism is based on the assumption that all of the reactants adsorb on the active sites at a catalyst surface. Reactions occur only between the adsorbed reactants, after which they desorb releasing space to other reactant molecules to adsorb. Surface reactions were presumed to be rate determining in these two models. Molecularly adsorbed hydrogen was assumed to be the catalytically active species.

3.2.1. Kinetic model. This model is based on the assumption that hydrogen molecules are much smaller than the organic ones. The larger organic molecules give empty space between themselves during adsorption, while the smaller hydrogen molecules can be adsorbed on the active sites without any essential competition. The reaction steps in this model are described below. Also here the

surface reaction steps were assumed to be rate determining, while the adsorption steps were presumed to be in quasi-equilibria.



where $*$ and $*_{2}$ denote vacant sites for hydrogen and organic molecules adsorption, respectively.

The model gives to the following rate equations:

$$\begin{aligned} r_1 &= \frac{k_1 c_A c_H}{D_1 D_2} \\ r_2 &= \frac{k_2 c_R c_H}{D_1 D_2} \\ r_3 &= \frac{k_3 c_S c_H}{D_1 D_2} \end{aligned} \quad (8)$$

where $D_1 = 1 + K_H c_H$ and $D_2 = 1 + \sum K_i c_i$ and $i = A, B, C, D$. For the ultimate case that the adsorption effects are negligible, $D_1 \approx 1$ and $D_2 \approx 1$.

3.2.2. Generation rates. The generation rates for the components become according to the reaction scheme (Fig. 2),

$$\begin{aligned} r_A &= -r_1 \\ r_B &= r_1 - r_2 \\ r_C &= r_2 - r_3 \\ r_D &= r_3 \end{aligned} \quad (9)$$

3.3. Parameter estimation

The mole fraction of hydrogen (x_{H_2}) in 2-pentanol was obtained from the measurements of (Mäki-Arvela et al. 2002).

The temperature dependence of the rate parameters were calculated from the modified Arrhenius equation,

$$k_j = k_{0,j} e^{\frac{-E_{a,j}}{R} \left(\frac{1}{T} - \frac{1}{\bar{T}} \right)} \quad (11)$$

where $k_{0,j}$ is the rate constant at the average temperature (\bar{T}): $A = k_{0,j} e^{\frac{E_{a,j}}{RT}}$. The average temperature was 70°C.

The rate parameters were determined by non-linear regression analysis by minimizing objective function (Q), a difference between the experimental (c_i) and estimated concentrations (\hat{c}_i),

$$Q = \sum (c_i(t) - \hat{c}_i(t))^2 \quad (12)$$

4. ESTIMATION RESULTS

4.1. Hydrogenation of citral on nickel catalyst in semibatch mode

The kinetic model for hydrogenation of citral on the dispersed Ni/Al₂O₃ catalyst was investigated according to the reaction schemes 1 and 2 (Fig. 2). The estimated results from these two models are equally good and can describe the experimental data well. The degree of explanation exceeded 95 % in most cases. The standard errors of the parameters were reasonable. The most accurate estimations were achieved with reaction scheme 1 (Fig. 2), where all of the kinetic experiments were taken into account. The differences between reaction scheme 1 and 2 were, however, relatively small. The model fits are depicted in Fig. 3 and the values of the kinetic parameters are collected in Table 1.

As separate adsorption parameters K_A (for citral) and K_B (for citronellal) were used, the fit of the model to experimental data did not improve much. These two adsorption parameters were considered for in cases, which contained high amounts of citral (A) and citronellal (B) compared to the other components in the reaction mixture. Additionally, it can be mentioned that the numerical values for K_{AC_A} and K_{BC_B} were small and had just a minimal effect on the reaction kinetics under the prevailing reaction conditions. Modification of the models according to Langmuir-Hinshelwood kinetics impaired the estimation statistics compared to the models excluding adsorption parameters. The simple model ($D_1=D_2=1$) was able to describe the experimental data with a good enough accuracy.

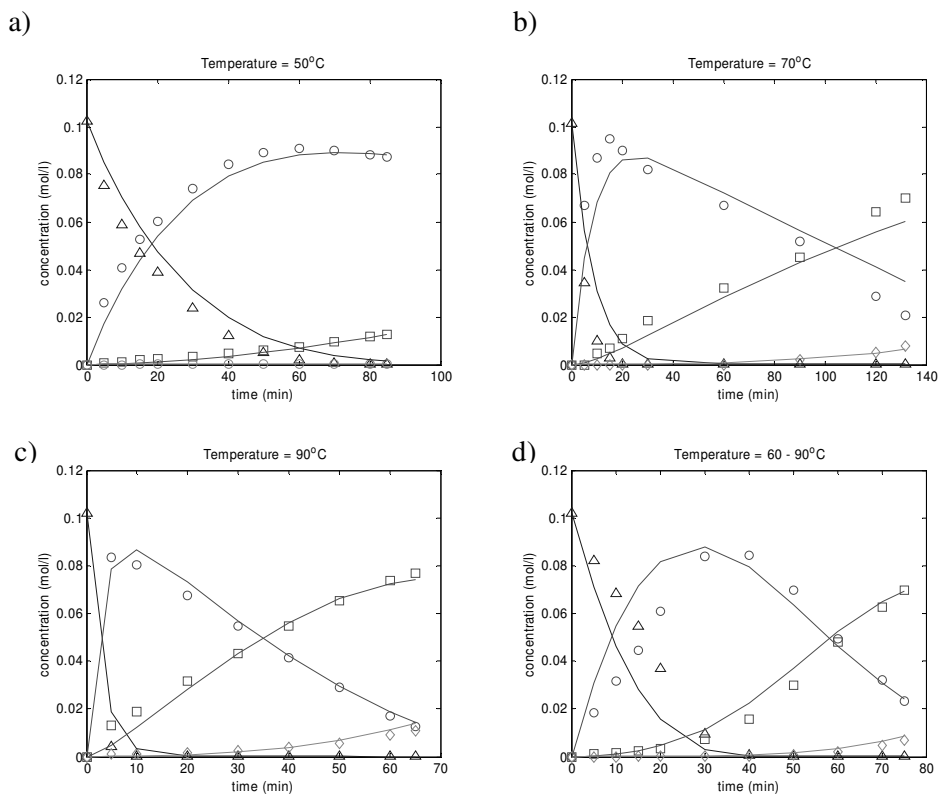


Fig. 3. Kinetics in citral hydrogenation at 10 bar hydrogen at a) 60°C, b) 70°C, c) 90°C and in the temperature programmed reaction between 60°C to 90°C, modeling according to model 1 and reaction scheme 1. Symbols: citral (Δ ◇), citronellal (o), citronellol (□) and 3,7-dimethyloctanol (◇).

Tab. 1. Kinetic models and parameter values for citral hydrogenation with pumping according to the reaction scheme 1.

Model	Parameter*	Estimated Parameters	Estimated Std Error	Est. Relative Std Error (%)
$r_1 = k_1 c_A c_H$	k_{01}	$0.454 \cdot 10^1$	$0.160 \cdot 10^0$	3.5
	k_{02}	$0.203 \cdot 10^0$	$0.771 \cdot 10^{-2}$	3.8
$r_2 = k_2 c_B c_H$	k_{03}	$0.439 \cdot 10^{-1}$	$0.881 \cdot 10^{-2}$	20.1
	E_{a1}	$0.524 \cdot 10^5$	$0.226 \cdot 10^4$	4.3
$r_3 = k_3 c_C c_H$	E_{a2}	$0.673 \cdot 10^5$	$0.314 \cdot 10^4$	4.7
	E_{a3}	$0.352 \cdot 10^5$	$0.178 \cdot 10^5$	50.6
$R^2=95.61\%$.	E_{a2}	$0.570 \cdot 10^5$	$0.297 \cdot 10^4$	5.2
	E_{a3}	$0.290 \cdot 10^5$	$0.189 \cdot 10^5$	65.2
	K_A	$0.161 \cdot 10^2$	$0.995 \cdot 10^1$	61.7
	K_B	$0.211 \cdot 10^2$	$0.119 \cdot 10^2$	56.5
	k_{03}	$0.443 \cdot 10^{-2}$	$0.181 \cdot 10^{-2}$	40.9
	E_{a1}	$0.572 \cdot 10^5$	$0.243 \cdot 10^4$	4.2
	E_{a2}	$0.635 \cdot 10^5$	$0.326 \cdot 10^4$	5.1
	E_{a3}	$0.540 \cdot 10^5$	$0.255 \cdot 10^5$	47.2

*The rate constants values (k_1 , k_2 , k_3) are reported at average temperature (70°C)

5. FIXED BED WITH RECYCLE

The idea of increasing the catalyst mass-to-liquid volume is by no means limited to slurry reactions, but can be expanded to a fixed bed with recycle and a liquid storage tank. A conceptual flowsheet is sketched in Fig. 4. For the fixed bed, a dynamic balance equation for a volume element ΔV can be written as

$$\dot{n}_{i,in} + r_i \rho_B \Delta V = \dot{n}_{i,out} + \frac{dn_i}{dt} \quad (13)$$

By denoting $\dot{n}_{i,out} - \dot{n}_{i,in}$ by $\Delta \dot{n}_i$, recalling that the amount of substance in the volume element is $n_i = c_i \Delta V$ and letting $\Delta V \rightarrow 0$, we obtain the differential equation

$$\varepsilon_L \frac{dc_i}{dt} = \rho_B r_i - \frac{dn_i}{dV} \quad (13a)$$

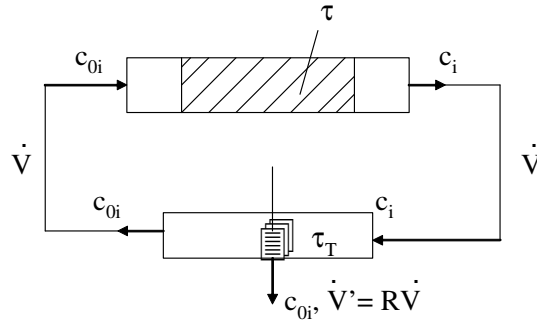


Fig. 4. Circulating fixed bed system – conceptual flowsheet.

Since the volumetric flow rate (\dot{V}) for a such liquid-phase system can be considered to be virtually constant, the derivative becomes $d\dot{n}/dV = \dot{V}dc_i/dV$. By denoting $V/\dot{V} = \tau$ we get the hyperbolic PDE

$$\frac{dc_i}{dt} = \frac{1}{\varepsilon_L} \left(\rho_B r_i - \frac{dc_i}{d\tau} \right) \tag{14}$$

In case of low conversion per one passing cycle, the space derivative of the concentration is approximatively linear, $dc_i/d\tau \approx (c_i - c_{0,i})\tau$ and the PDE is converted to an ODE. Average concentrations can be used in the calculation of the generation rates (r_i).

In the storage tank is complete backmixing prevails, and no reactions take place there. The balance equation can thus be written as

$$c_i \dot{V} = c_{0,i} \dot{V} + c_{0,i} \dot{V}' + \frac{dn_{0,i}}{dt} \tag{15}$$

After introducing the definitions of volumetric flow rate $\dot{V}' = R\dot{V}$, and tank volume $V_T = V_{0,T} - \dot{V}'t$ and $n_{0,i} = c_{0,i}V_T$ we obtain

Tab. 2. Simulation of recycled fixed bed reactor for the system $A \rightarrow R \rightarrow S \rightarrow T$.

ε_L	0.5
τ	1 min
τ_{0T}	10 min
R	0...50
Kinetic parameters	
$k_1\rho_B$	1.0 min^{-1}
$k_2\rho_B$	0.7 min^{-1}
$k_3\rho_B$	0.5 min^{-1}

Initial conditions $c_A(t=0) = 1.0 \text{ mol/l}$, other concentrations zero

$$\frac{dc_{0,i}}{dt} = \frac{1}{\tau_r} (c_i - c_{0,i}) \quad (16)$$

where $\tau_r = \tau_{0,T} - Rt$. The model consists of coupled eqs (14) and (16), which were solved numerically for the first-order system $A \rightarrow R \rightarrow S \rightarrow T$ with the sets of parameters listed in Table 2.

Some sample calculations are displayed in Fig. 5. As the figure reveals, the concept should work in practice, we get a similar enhancement of the secondary and tertiary reactions as was obtained for the slurry reactor concept. For the fixed bed coupled to the storage tank, there is, however, more space for the adjustment of the experimental conditions, since the tank volume and space time (τ_T) can be varied within very large intervals.

6. CONCLUSIONS

A new reactor concept involving a gradual increase of the catalyst bulk density was proposed. The approach was illustrated by a case study, hydrogenation of citral on supported nickel.

The results indicated that the reaction rates are enhanced by increasing the catalyst bulk density, which is achieved by pumping out the liquid phase during the experiments. A kinetic model comprising the increase of the catalyst bulk density was used for the quantitative description of the reactor behaviour.

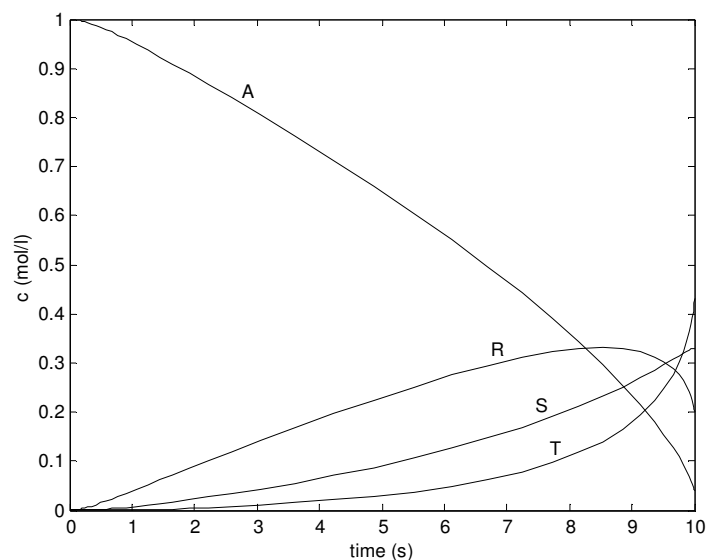


Fig. 5. Simulation of recycled fixed bed reactor for the system $A \rightarrow R \rightarrow S \rightarrow T$. The parameters are listed in Table 2.

The effect of the catalyst bulk density on the hydrogenation kinetics was demonstrated with the aid of kinetic model. The estimated parameters were used in the demonstration of the system behaviour in the Damköhler space. The semibatch concept proved to be useful in enhancing the efficiency for obtaining kinetic information from semibatch experiments, since the rate parameters of consecutive reaction schemes with successively decreasing parameter values can be obtained from a single experiment. With the conventional technology, this is not possible, but several separate experiments with different catalyst bulk densities, and initial concentrations are necessary. The methodology proposed by us contributes the intensification of kinetic studies of two- and three-phase catalytic systems. It is not limited to agitated slurry reactors only, but can be extended to fixed beds with recycle, as demonstrated by simulations.

Acknowledgements

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