

MODELLING OF SIMULTANEOUS REACTION AND DIFFUSION IN CHEMICAL REACTORS WITH PARTICLE SIZE DISTRIBUTIONS: APPLICATION OF ION-EXCHANGE RESINS IN HETEROGENEOUS CATALYSIS

Olatunde Jogunola^{1,*}, Tapio Salmi¹, Johan Wärnå¹, Sébastien Leveneur^{1,2}, J.-P. Mikkola^{1,3}

¹Åbo Akademi, Process Chemistry Centre, Industrial Chemistry and Reaction Engineering,
FI-20500 Åbo/Turku Finland

²INSA-Rouen, LSPC-Laboratoire de Sécurité des Procédés Chimiques,
BP08, 76801 Saint-Étienne-du-Rouvray France

³Umeå University, Technical Chemistry, Chemical-Biological Centre, Department of Chemistry,
SE-90187 Umeå Sweden

* jolatund@abo.fi

A general model and software for simultaneous reaction and diffusion in porous catalysts were developed. The model comprises multiple reactions, diffusion phenomena and catalyst particle size distributions. The applicability of the model was illustrated with two examples originating from green chemistry: hydrolysis of alkyl formate (formic acid process) and perhydrolysis of carboxylic acids (percarboxylic acid process). Cation exchange resins were used as catalysts in both cases. Experiments carried out in batch reactors as well as computations demonstrated in an unequivocal way that the reaction-diffusion model should be used in the application cases. The methodology presented is general, and it can be applied on any heterogeneously catalyzed liquid-phase reaction system.

1. INTRODUCTION

The interaction of intrinsic kinetics and mass transfer in porous catalyst particles is a classical topic of chemical engineering since the days of Thiele and Frank-Kamenetskii. The basic theory is well-known and it is nicely summarized in the monumental work of Aris (1975). However, real practical applications of the theory concerning reaction and diffusion in porous media are not that many. The main reason might be that the complex chemical systems appearing in industrial practice require a numerical solution of the catalyst particle model, coupled to the model of the chemical reactor. In this work, we demonstrate the necessity of the reaction-diffusion model in the green synthesis of chemicals through catalyzed liquid-phase reactions. Cation-exchange resins were used as catalysts.

Ion exchange catalysts are frequently used to enhance the rates of numerous chemical processes, such as esterification, ester hydrolysis, etherification and aldolisation reactions. The benefits of ion-exchange resins as catalysts are their well-defined active sites, good reproducibility and good durability.

Many research efforts have been dedicated to the product distribution and kinetic modelling of various reactions on ion-exchange resins, but very few of them comprise mass-transfer effects, namely the interaction between intrinsic kinetics and internal diffusion in porous resin particles (Xu and Chaung, 1999). However, particularly for industrial applications of these catalysts, it is necessary to use particles of the size about 1 mm to keep the pressure drop within a reasonable limit in continuous fixed bed reactors. Furthermore, commercially available ion-exchange resin materials are not monodisperse, but always have a particle size distribution.

2. MODELLING APPROACH

We have developed a very general modelling approach to describe simultaneous chemical reactions and diffusion in porous ion-exchange particles in chemical reactors. A pseudo-homogenous model was used, which

did not take into account the selective adsorption on the catalyst surface. However, the model takes into account the particle size distribution. Simultaneous reaction and diffusion in the porous catalyst particles is described by a dynamic model, coupled parabolic partial differential equations,

$$\frac{dC_i}{dt} = \frac{r_i \rho_p}{\varepsilon_p} + r_i + \frac{D_{ei}}{\varepsilon_p R_j^2} \left(\frac{d^2 C_i}{dX^2} + \frac{a-1}{X} \frac{dC_i}{dX} \right) \quad (1)$$

The boundary conditions are $C_{pi(X=1)} = C_i$ at the catalyst particle surface and $\left(\frac{dC_{pi}}{dX} \right)_{X=0} = 0$ at the particle center. Consequently, the reaction-diffusion model is solved for each catalyst particle size fraction. Experimentally determined particle size distribution is incorporated in the reactor model; for instance, for a batch reactor, the following model is applied:

$$\frac{dC_i}{dt} = a_p \sum_j y_j N_{ij} x_j^2 \quad (2)$$

Where a_p is the total outer particle surface area-to-liquid volume, y_j is the fraction of particles with the radius R_j . The reaction-diffusion model was solved by discretising the space derivatives originating from diffusion in eq. (1) by central difference formula, and thus transforming the PDEs to ODEs, which were solved numerically together with the reactor balance equation (2). Typically 10-20 discretisation points were used in the calculations. A stiff ODE-solver was applied to solve numerically the large initial value problem created. In general, the following approach was used: The intrinsic kinetics was determined for small particle sizes, in the absence of the internal diffusion limitations. This gave the numerical values of the rate constants. Experiments were performed with different catalyst particle fractions and molecular diffusion coefficients of the compounds were estimated from available correlations, such as Wilke-Chang equation. This information was incorporated in the complete model, eqs (1-2); in which the effective diffusion coefficients play a central role. The particle porosity-to-tortuosity ratio in the effective diffusion coefficients was adjusted in situ during the simulations by applying non-linear regression analysis. The parameters were estimated from the experimental data by using the objective function

$$Q(f) = \sum_{i=1}^n (y_i - \hat{y}_i)^2 \quad (3)$$

where y_i is the experimental value of component i in the mixture and \hat{y}_i is the corresponding model prediction. In the present work, y_i and \hat{y}_i represent the concentrations. The parameter estimation was carried out with simplex-Levenberg-Marquardt algorithm by minimizing the weighted sum of residual squares (Haario, 2007).

3. EXPERIMENTAL SECTION

3.1 Apparatus and experimental procedures

The hydrolysis reaction was carried out in a conventional 500ml Parr autoclave (made of zirconium metal). The reactor consists of a feeding vessel, a reaction vessel, a heating unit, a stirrer and a sampling line. The sampling line was equipped with a cooling bath and a filter. The temperature control requires two thermocouples and cooling air. Nitrogen was used for pressurizing the system and as a shielding gas. The reaction was performed at

a N₂-pressure of 20 bar and isothermally at temperature levels of 60°C and 90°C. The liquid samples were analyzed offline with a gas chromatography.

3.2 Catalyst properties and characterization

Amberlite IR 120 is a strongly acidic gel-type resin with sulfonic acid group. It is not porous in the true sense because its structure depends upon swelling when in contact with liquid. In their swollen state, we can identify an internal porosity in terms of equilibrium uptake of water or other liquid. Thus, it approximates a true molecular-scale solution (LeVan, 1993). Thus, pore diffusion model is very useful in describing the effectiveness factor. The properties of the catalyst according to the manufacturer are shown in Table 1.

Table 1. Properties of Amberlite IR 120 resin.

Properties	Specification
Bead type	gel
Cross linking (%)	8
Particle size range (mm)	0.3-1.2
Moisture content (% mass)	45
Density of wet catalyst (g/cm ³)	1.26
Maximum operating temperature	120°C
Capacity by dry weight (meq/g)	4.4

The catalyst was used in the dry form. Thus, it was washed with distilled water, filtered and then dried in an oven at 99°C for 48 hours until a constant weight was obtained. All experiments were done with the pre-treated resin. This is to know the exact quantity of water, which is one of the reactants in the system.

The particle size distribution (PSD) of the dried resins was determined in water at room temperature using a laser diffraction particle sizer, the Malvern 2600 series. The instrument working principle is based on the light scattering property of the particles using He-Ne laser diffraction system.

The acid sites capacity was measured by a conventional titration method (Zagrodnj, 2007), which has been described in an earlier publication (Jogunola et al., 2010).

4. RESULTS AND DISCUSION

4.1 Catalyst characterization

The acid sites capacity of the Amberlite IR 120 on dry basis obtained by taking the average of three measurements is 4.7 meq/g. The difference between our value and that of the manufacture might be due to experimental error and non-ideality of the titration mixture. The apparent Brønsted acid concentration [H]⁺ is calculated based on the cation exchange capacity by dry weight (meq/g):

$$[\text{H}]^+ = \frac{0.0047 * W_C}{V_L} \quad (4)$$

The particle size distribution of the dry resin immersed in water after few minutes as obtained with the particle sizer is depicted in Figure 1.

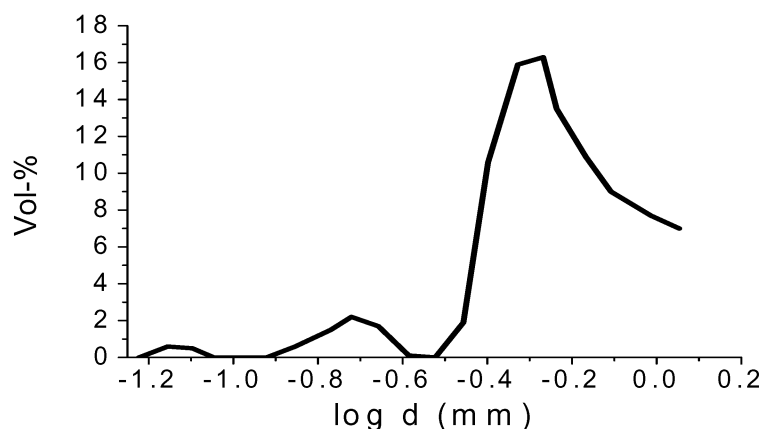
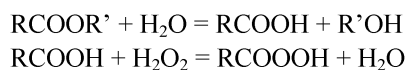


Fig 1. Particle size distribution of Amberlite IR 120 resins for hydrolysis of alkyl formate.

From the figure, the particle diameter range 0.06–0.08 mm makes up 0.8 vol-% of the distribution, while 0.12–0.26 constitutes 6.1 vol-%. The distribution is continuous in the particle size range 0.3–1.13 mm, which is 92.8 vol-%. The mean diameter of the particle according to the instrument is 0.53 mm. The specific surface area according to the Malvern 2600 series is $0.0156 \text{ m}^2/\text{cm}^3$ ($< 0.1 \text{ m}^2/\text{g}$). However, this value is not as reliable as that using a surface area specific technique e.g. argon or nitrogen adsorption porosimetry. However, it was difficult to obtain the specific surface area using nitrogen BET method because in the dry state, Amberlite IR 120 resin has no effective permanent porosity.

4.2. Kinetic modelling results and discussion

Two application examples were considered: hydrolysis of methyl and ethyl esters as well as perhydrolysis of carboxylic acids. The reaction schemes are displayed below,



Hydrolysis of formic acid esters is of relevance in the production of formic acid according to the Leonard process and perhydrolysis of carboxylic acids is the dominating reaction route in the production of percarboxylic acids, which are used for bleaching, sanitation purposes and chemical reagents.

The following rate equations were used to describe the intrinsic kinetics.

Hydrolysis :

$$\begin{aligned} r_{\text{tot}} &= r_{\text{hom}} + r_{\text{het}} \\ &= [k_{\text{hom}1} + k_{\text{hom}2} * [\text{RCOOH}] + k_{\text{het}} * [-\text{SO}_3\text{H}]_0] * \\ &\quad \left[[\text{RCOOR}'] * [\text{H}_2\text{O}] - \frac{1}{K^c} * [\text{RCOOH}] * [\text{R}'\text{OH}] \right] \end{aligned}$$

Perhydrolysis:

$$r_{\text{tot}} = r_{\text{hom}} + r_{\text{het}}$$

$$= \left[\frac{k_{\text{hom}} * \sqrt{K_4^C * [\text{RCO}_2\text{H}] * [\text{H}_2\text{O}]}}{[\text{H}_2\text{O}]} + \frac{k_{\text{het}} * [-\text{SO}_3\text{H}]_0}{1 + K_1^C * ([\text{RCO}_2\text{H}] + [\text{RCO}_3\text{H}]) + K_7^C * [\text{H}_2\text{O}]} \right] * \left[[\text{RCO}_2\text{H}] * [\text{H}_2\text{O}_2] - \frac{1}{K^C} * [\text{RCO}_3\text{H}] * [\text{H}_2\text{O}] \right]$$

where $-\text{SO}_3\text{H}$ refers to the sulphonic acid sites present in the ion-exchange resin. K_C is the concentration-based equilibrium constant and it is based on the liquid phase concentration, therefore an ideal liquid mixture is assumed and the liquid volume remains constant. The contribution of homogeneous catalysis (r_{hom}) is included in the rate equations, since the hydrolysis and perhydrolysis proceed to some extent also in the absence of an added catalyst. The estimated parameter values for the homogenous catalysis for methyl formate hydrolysis (MFH) are depicted in Table 2. The following values were used for the reaction enthalpies; methyl formate $\Delta H_R^o = +5.44$ kJ/mol at 25 °C (Roine, 2009).

Table 2. Estimated parameters of MFH in the absence of the catalyst.

Estimated Parameter	Parameter value	Relative error (%)	Correlation matrix					
			K_{eq}	$E_{A,\text{hom}}$	k_{hom}	k_{auto}	$E_{A,\text{auto}}$	
K_{eq}	0.111	2.4	1.000					
$E_{A,\text{hom}1}$	64.4 kJ/mol	19.8	-0.041	1.000				
$k_{\text{hom}1}$	1.68×10^{-5} L/mol min	19.1	0.228	0.465	1.000			
$k_{\text{hom}2}$	1.66×10^{-4} L ² /mol ² min	26.6	-0.248	-0.460	-0.997	1.000		
$E_{A,\text{hom}2}$	47.1 kJ/mol	30.2	0.035	-0.995	-0.487	0.485	1.000	

$T_{\text{mean}} = 75$ °C; Degree of explanation 99.4%, MFH = methyl formate hydrolysis

The values in Table 2 were used as input values to estimate heterogeneous catalysis parameters. A typical plot of the homogenous system for methyl formate hydrolysis is shown in Fig. 2.

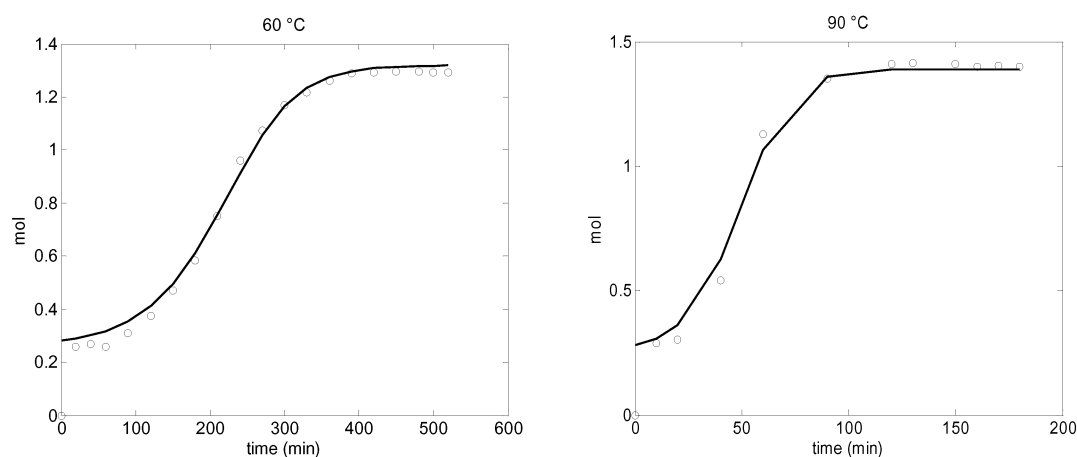
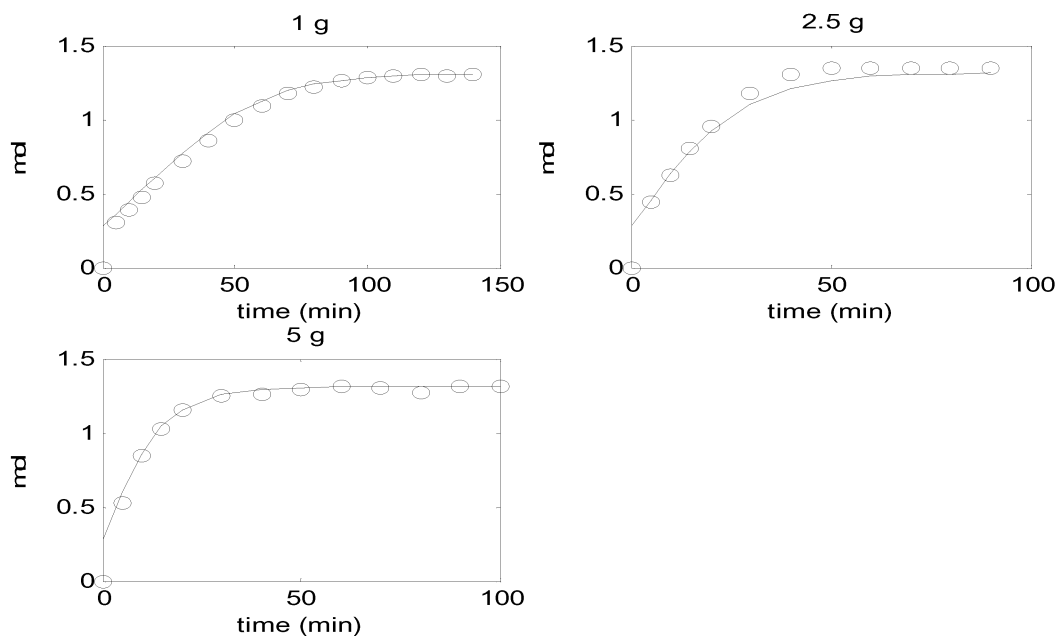


Fig. 2: Fit of the model to experimental data (alcohol) in the absence of solid catalyst for methyl formate hydrolysis

During the analysis of the samples, no side reaction (i.e. selectivity is 100%) was observed for all experiments. At a stirring speed range of 300-700 rpm, there was no external mass transfer limitation and attrition of the catalyst was not visible under the chosen reaction condition. So, 300 rpm was chosen for the entire experiments. The results were based on the analysis of the alcohol formed since alkyl formate analysis gave inconsistent results. It can be seen from the figure that Homogeneous catalysis play a significant role in the process since the system is auto-catalyzed (S-shape) in the absence of the resin.

A thorough analysis of both experimental systems revealed that internal diffusion in the catalyst (resin) particles plays a significant role in practice and thus the modelling approach was applied. Since the particle size range (0.3-1.2 mm) was broad, it was necessary to take the particle size distribution into account in the modelling. The effectiveness factors for the catalyst particles varied within the range of 0.55-1.0 for hydrolysis and 0.76-1.0 for perhydrolysis. Some kinetic curves are displayed in Fig. 3, which nicely illustrate the excellent fit of the kinetic model to the experimental data. The model enables the simulation of the concentration profiles inside the catalyst particle; examples are shown in Figs 4-5, which clearly demonstrate that concentration gradients appear inside the porous catalyst particles and that the concentration profiles and thus also the effectiveness factors strongly depend on the catalyst particle size.

(a)



(b)

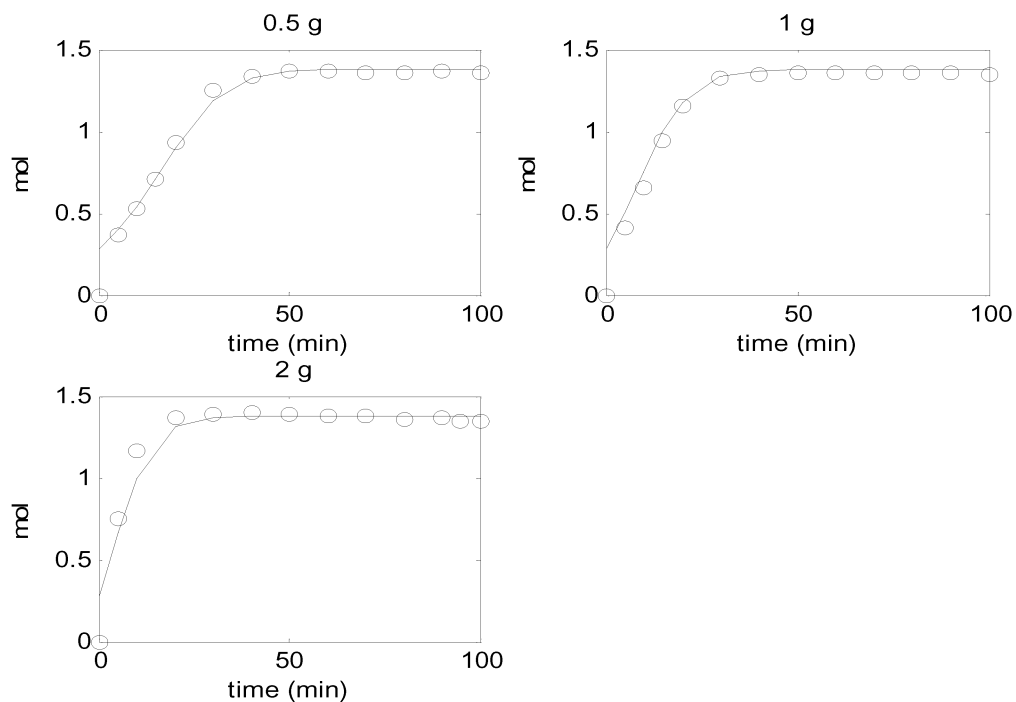
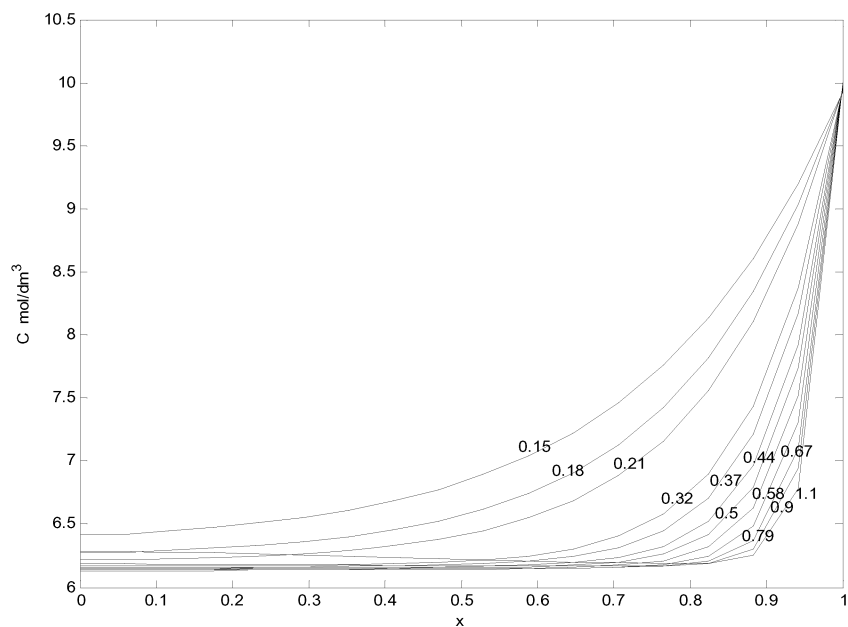


Figure 3. Fit of the model to the experimental data (methanol) for methyl formate hydrolysis at (a) 60°C and (b) 90 °C using different amounts of the solid catalyst; $H_2O/ester = 1.8$.

(a)



(b)

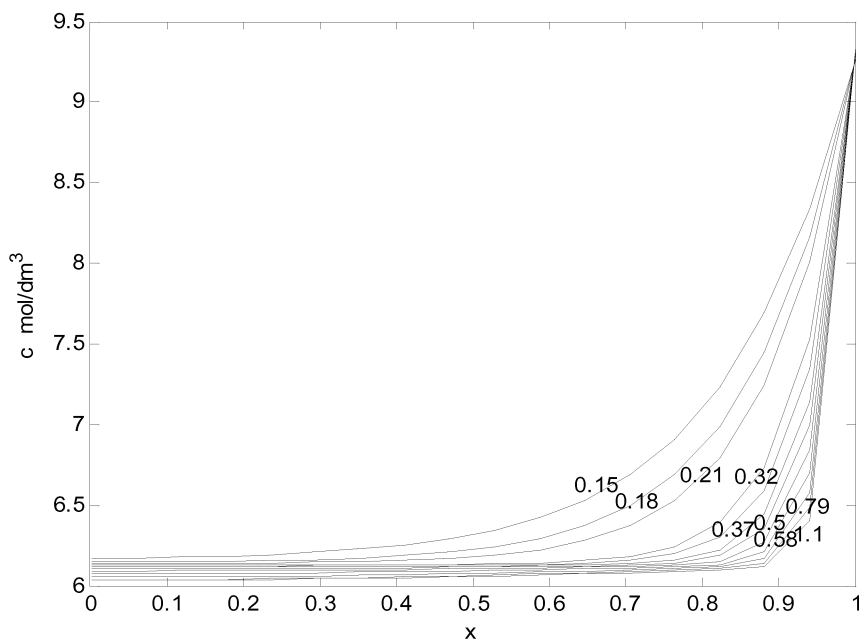


Figure 4. Concentration profiles of methyl formate hydrolysis inside the catalyst particle at (a) 60°C using 2.5 g catalyst and (b) 90 °C using 2g for different particle sizes (particle diameter in mm) in the beginning of the reaction (x -dimensionless coordinate); $H_2O/ester = 1.8$

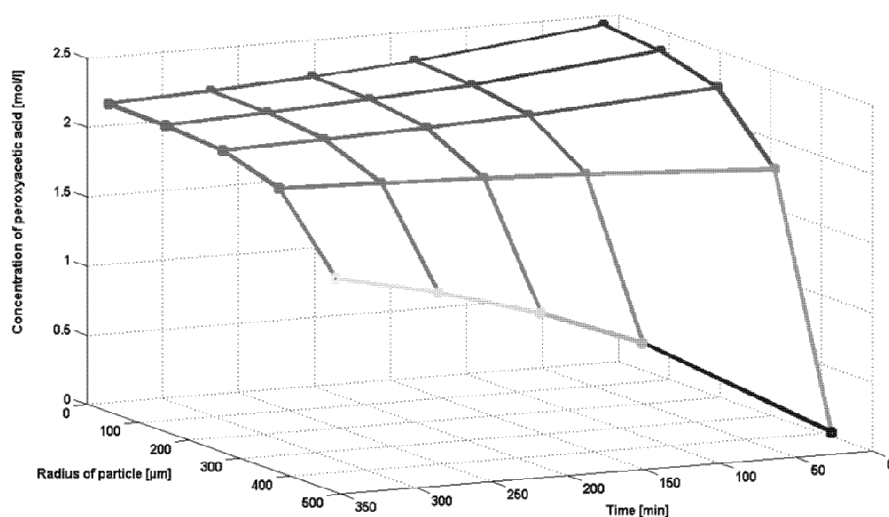


Figure 5. Concentration profile for peroxyacetic acid inside a particle of 898 μm at 30°C.

The parameter values for the catalytic reaction for methyl formate hydrolysis is collected in Table 3.

Table 3: Estimated parameter values for the catalytic reaction in the presence of diffusion limitation.

Estimated Parameter	Parameter value	Relative error (%)	Correlation matrix k_{het}
ε_p/τ_p	0.2 (fixed value)		
k_{het}	$1.0 \times 10^{-3} \text{ mol/g}_{cat} \text{ min}$	3.7	1.0
E_A	50.8 kJ/mol	5.3	E_A 1.308 1.0

The degree of explanation of the model result is 98% and the correlation matrix is reasonable. The activation energy (see From Table 3) of the resin-catalyzed methyl formate hydrolysis is consistent with that reported in the literature (Begum, 2001).

CONCLUSIONS

For a molecular-level understanding of the processes, this kind of approach is necessary. The general methodology proposed by us and the software developed can be used for scale-up purposes, not only for the demonstration examples discussed, but for any heterogeneously catalyzed liquid-phase reaction system, where porous solids and particle size distributions are involved. The modelling and simulation effort was focused on batch reactors; in future, it will be extended to continuous fixed bed reactors

NOTATION

a	shape factor of a catalyst particle
a_p	outer catalyst particle area-to-liquid volume
C	concentration
D	diffusion coefficient
D_{ei}	effective diffusion coefficient
d_p	particle diameter
EA	activation energy
het	heterogeneous
hom	homogeneous
$[H]^+$	Brønsted acid concentration
K	equilibrium constant
k	rate constant
N	diffusion flux
Q	degree of explanation
R_j	particle radius
r_i	generation rate for component i
r	radial coordinate
t	time
X	dimensionless particle coordinate ($X=r/R_j$)
x_j	normalized particle radius ($x_j=R_j/R_{average}$)
y_j	fraction of particles with the radius r_j
V_L	volume of solution

W_C	mass of catalyst
ε_p	porosity
ρ_p	density of a catalyst particle
τ_p	tortuosity of a catalyst particle

ACKNOWLEDGEMENT

This work is part of the activities of the Åbo Akademi Process Chemistry Centre (PCC) within the Finnish Centre of Excellence Programmes (2006-2011) by the Academy of Finland.

REFERENCES

- Aris R., 1975, *The Mathematical Theory of Diffusion and Reaction in Permeable Catalysts*, Clarendon Press, Oxford, United Kingdom.
- Begum S., 2001, Alkyl Formate Esters in Aqueous Medium: A Comparative study of Acid-catalyzed Hydrolysis, *Journal Chemical Society, Pakistan* 23 (3), 139-143.
- Haario, H., 2007. *ModEst 6– A User’s Guide*; Profmath Oy, Helsinki.
- Jogunola, O., Salmi, T., Eränen, K., Mikkola, J.-P., 2010. Qualitative treatment of catalytic hydrolysis of alkyl formates. *Appl. Catal. A, General* 384, 36-44.
- LeVan M. D, Carta G, Yon C. M. Adsorption and ion exchange. In: Green DW, editor. *Perry’s chemical engineers’ handbook*, 7th ed. New York: McGraw-Hill, 1997.
- Leveueur S., Murzin D.Yu., Salmi T., Mikkola J.-P., Kumar N., Estel L., Eränen K., 2009, Synthesis of peroxypropionic acid from propionic acid and hydrogen peroxide over heterogeneous catalysts, *Chemical Engineering Journal* 147, 323-329.
- Leveueur S., Wärnå J., Salmi T., Murzin D.Yu., Estel L., Eränen K., 2009, Interaction of intrinsic kinetics and internal mass transfer in porous ion-exchange catalysts: green synthesis of peroxy-carboxylic acids, *Chemical Engineering Science* 64, 4104-4114.
- Salmi T., Mikkola J.-P., Wärnå J., 2010, *Chemical Reaction Engineering and Reactor Technology*, Taylor & Francis CRC Press, Florida, United States.
- Roine, A., 2009. *HSc Chemistry 7.0*, Outokumpu Research Oy, Pori.
- Xu Z. P., Chuang K. T., 1997. Effect of internal diffusion on heterogeneous catalytic esterification of acetic acid. *Chemical Engineering Science* 52, 3011-3017.