

# MODELING FOR HETEROGENEOUS FIXED-BED REACTOR FOR PEROXYCARBOXYLIC ACID PRODUCTION

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## Summary

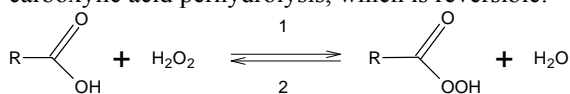
Synthesis of different peroxycarboxylic acids such as peroxyacetic and peroxypropionic acid from hydrogen peroxide and the parent carboxylic acids was performed over a heterogeneous ion-exchange resin catalyst in a continuous fixed-bed reactor at different temperatures and flow rates. Heterogeneous catalyst can replace a homogeneous catalyst, thus leading to green production technology. Different correlations demonstrated that pressure drop, internal and external mass and heat transfer can be neglected in the fixed-bed reactor. A pseudo-homogeneous model was applied to describe the reactor. Based on our experiments, the use of the fixed-bed reactor technology is more advantageous than a batch reactor.

## Keywords

Green CRE.

## Introduction

The applications of peroxycarboxylic acids<sup>1</sup> (PCA) as a disinfectant and bleaching agent are widely spread in industry. In this study, a “green” oxidation of the parent carboxylic acid (CA) with aqueous hydrogen peroxide (HP) is used<sup>2</sup>. Scheme 1 represents the reaction of carboxylic acid perhydrolysis, which is reversible:



Scheme 1. Synthesis of PCA from the parent carboxylic acid and hydrogen peroxide

Due to a slow reaction kinetics, an acid catalyst is needed to increase the velocity of the reaction. Sulfuric acid is the most common mineral acid used as a homogeneous catalyst. A greener way is to shift to heterogeneous catalyst, e.g., cation exchange resins bearing a sulfonic acid group. After studying this reaction catalyzed by Amberlite IR-120 in a batch reactor<sup>3</sup>, a fixed-bed reactor was developed to check our kinetic model and to explore the possibilities for continuous operation.

## Experimental section

The catalytic fixed-bed reactor consisted of catalyst layers and inert materials (for sampling). It was operated in

upstream mode and was put in a diagonal position to ease the sampling and prevent back-mixing. Samples were withdraw from different position in the reactor.

Table 1. Reactor characteristics

Reactor length [m]	0.6
Reactor diameter [m]	$1.45 \cdot 10^{-2}$
Loading of quartz ball [g]	67.4
Loading of wet Amberlite IR-120 [g]	36.3
Flow rate [ $\text{ml} \cdot \text{min}^{-1}$ ]	0.7-2.6
Temperature [ $^{\circ}\text{C}$ ]	30-60
$[\text{CA}]_0$ [ $\text{mol} \cdot \text{l}^{-1}$ ]	5.4-5.94
$[\text{H}_2\text{O}_2]_0$ [ $\text{mol} \cdot \text{l}^{-1}$ ]	6.3-6.97
$[\text{H}_2\text{O}]_0$ [ $\text{mol} \cdot \text{l}^{-1}$ ]	24.8-27.5

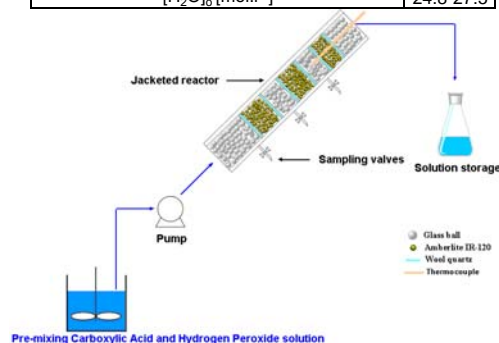


Figure 1. Schematic view of the fixed-bed reactor for peroxycarboxylic acid production.

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## Residence time distribution (RTD)

Pulse experiments with HCl as a tracer molecule were done to determine the RTD, the liquid volume and axial dispersion. Figure 2 displays the E-curves registered at different flow rates.

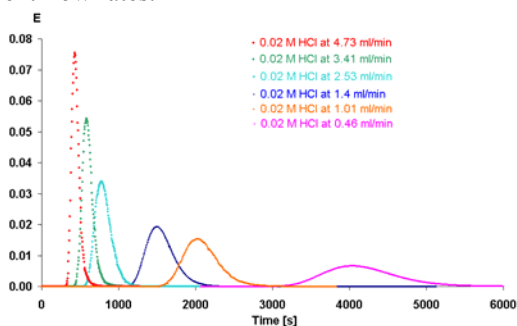


Figure 2. E-curves at 30°C by using HCl as a tracer.

One can notice that the distribution is symmetric, and the mean residence time was determined from these data. The mean residence time and the flow are related by  $\bar{t} = \frac{V_L}{F}$ ,

where F is the flow rate and  $V_L$  represents the void volume of the tube reactor, i.e. the volume of the liquid. Figure 3 represents the flow rate versus inverse of the mean residence time at 30 and 50°C.

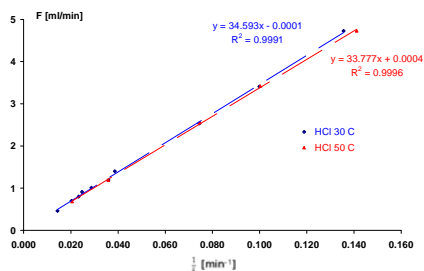


Figure 3. Flow rate versus inverse of the mean residence time.

As can be noticed, the flow pattern does not depend to the temperature, and the liquid volume in the reactor can be assumed to be in the range of 33.8-34.5 ml according to the pulse experiment with HCl. The Péclet number was calculated to be higher than 100, which implies that axial dispersion can be neglected in our system.

## Modeling

The pressure drop, evaluated by Ergun equation; external and internal mass transfer phenomena, evaluated by several correlations<sup>4,5</sup>, were found to be negligible. Then a steady-state pseudo-homogeneous model was applied to the fixed-bed reactor:

$$\dot{n}_{i,in} + r_{i,tot} \rho_{LB} \Delta V_L = \dot{n}_{i,out}$$

$$\Leftrightarrow \frac{dn_i}{dt} = r_{i,tot} \rho_{LB} F$$

$$\Leftrightarrow \frac{dC_i}{dt} = r_{i,tot} \rho_{LB}$$

where  $\rho_{LB}$  represents the amount of dried catalyst (kg) per volume of void ( $V_L$ ) in each section. The rate expression  $r_{tot}$  of the system has been described in a previous paper<sup>3</sup>.

$$r_{tot} = r_{hom} + r_{het} = \left[ \frac{k_{hom} \sqrt{K_{CA,diss}} [CA] [W]}{[W]} + \frac{k_{het} [-SO_3H]_0}{1 + K_{ads,CA,PCA}^C ([CA] + [PCA]) + K_{ads,W}^C [W]} \right] \left[ [CA] [HP] - \frac{1}{K^C} [PCA] [W] \right]$$

where  $r_{hom}$  and  $r_{het}$  represent the kinetic rate due the dissociation of the carboxylic acid itself and due to the presence of active site (i.e., sulfonic group) on the heterogeneous catalyst.

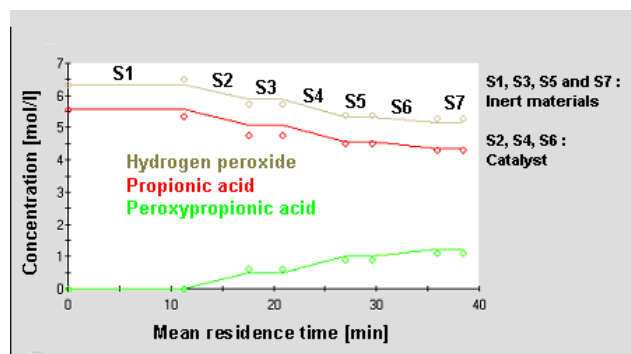


Figure 5. Fit of the model to the experiments for the perhydrolysis of propionic acid at a flow rate fixed to  $10^{-3}$  l/min at 30°C.

## Conclusion

The pseudo-homogeneous model fits the preliminary data obtained with the fixed-bed reactor. The kinetic parameters estimated in batch and continuous reactor are similar, e.g., the rate constants is  $10^3$  l.mol<sup>-1</sup>.s<sup>-1</sup> and the energy of activation is 50 kJ/mol in case of propionic acid. By comparing batch and continuous mode, it seems that the second one is more advantageous for the production.

## References

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