Modelling of chromatographic reactors

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Highlights

- A new chromatographic reactor model was developed.
- Methyl acetate hydrolysis was simulated.
- The performances were compared with most advanced existing model.
- Model implemented in gPROMS ModelBuilder.

1. Introduction

The esterification of carboxylic acid with alcohols is a hot topic of the modern bio-refinery, to produce, for example, solvents, plasticizers [1]. Nowadays, a lot of effort is in progress to optimize the synthesis of several esters. The right reactor should optimize the physical characteristics of the system that is, as before mentioned, a liquid-solid reaction. Among the different choices, the use of a chromatographic reactor [2]. For example, Mazzotti et al., instead, used the simulated moving bed reactor (SMBR) packed with Amberlyst-15 catalyst to perform acetic acid esterification to ethylacetate, demonstrating that the resin can be used both to catalyze the reaction and separate the stream. It is important to underline that to design such apparatus, accurate and reliable models are needed, involving profiles along different coordinates (time, reactor radius, reactor axis and catalyst radius) [3-5], the knowledge of physical and chemical properties, and powerful tools to reach a reliable solution. In the present work, the development of a reactor model, that can be used to interpret experimental data collected in chromatographic reactors will be presented. Methyl acetate hydrolysis catalyzed by DOWEX 50W-X8 catalyst was chosen as case study [6].

2. Methods

The developed model can be considered an advancement respect to the recent efforts published in the literature [6]. The breakthrough idea is to develop a model where no rate-determining-step is considered, writing the opportune mass balance equations on both the liquid bulk and intraparticle phases (see Table 1 for details). All the physical parameters were calculated from existing correlations.

Table 1. Model hypothesis and upgrades with existing strategy.

<table>
<thead>
<tr>
<th>Vu and Seidel-Morgenstern [6]</th>
<th>Present research</th>
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<tbody>
<tr>
<td>Pseudo-homogeneous model</td>
<td>Fluid-solid model</td>
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<tr>
<td>Lumped axial dispersion</td>
<td>Axial dispersion</td>
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<td>Kinetic regime</td>
<td>Fluid-solid mass transfer resistance</td>
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<tr>
<td>Kinetic regime</td>
<td>Intraparticle diffusion</td>
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The liquid bulk and intraparticle mass balance equations are respectively reported in Eq.s 1-2.

\[
\frac{\partial C_{i,B}}{\partial t} = -u \frac{\partial C_{i,B}}{\partial z} + D_z \frac{\partial^2 C_{i,B}}{\partial z^2} - k_{n,i} a_{wp} (C_{B,i} - C_{i,L})_{r_p=r_c} \\
\frac{\varepsilon}{\partial C_{i,L}} + (1-\varepsilon)K_{r_p} \frac{\partial C_{i,L}}{\partial t} = \frac{D_p}{r_p} \frac{\partial}{\partial r_p} \left( r_p \frac{\partial C_{i,L}}{\partial r_p} \right) + (1-\varepsilon)D_{r_p} \frac{\partial}{\partial r_p} \left( r_p \frac{\partial K_{r_p} C_{i,L}}{\partial r_p} \right) + (1-\varepsilon)\psi_{i,r_p}
\]

The model was implemented in gPROMS ModelBuilder v.4 software, by solving the axial and particle radial partial derivatives with a centered finite difference method with respectively 150 and 25 discretization points.
3. Results and discussion

Methyl acetate (MA) hydrolysis kinetic rate laws with related parameters are fixed and directly taken from literature [6]. The following simulation conditions were set: flowrate=0.75 mL/min, temperature=298K-328K, stream=pure water. The results of the developed model were compared with the output obtained by Vu and Seidel Morgenstern. Firstly, a simulation of an unreactive system was made with the two models (present and literature model), by injecting a three-component pulse (MA, acetic acid, methanol, 0.5 mol/L each) at the inlet of the column. The results reported in Figure 1-left clearly demonstrates that two models show the same output. Even if the output is very similar, the novelty of our model is that all the necessary physical parameters are estimated with existing correlations, i.e. the diffusivities. This is clearly a novelty in the field, because the existing models lump the intraparticle diffusion in adjustable semi-empiric parameters fitted on the peak width, having no physical meaning. Thus, our model is characterized by a more predictive power.

![Figure 1. Comparison with literature model (left): symbols represent the output obtained with Vu and Morgenstern model [6], lines the output of our model; description of experimental data [6] (right): symbols are experimental data, lines the model description.](image)

A second simulation was performed by considering the reaction, by simulating the injection of 100μL 0.5mol/L MA in water at different temperatures (Figure 1-right). As it can be seen, our model correctly describes the experimental data reported in the literature, with no additional fitting parameters.

4. Conclusions

A novel chromatographic reactor model was developed to interpret experimental data dealing both with the esterification of carboxylic acids and with the hydrolysis of organic esters. The model is advanced respect to the state of the art because no rate-determining steps are considered. All the physical and chemical phenomena are taken into account. In perspective, the model can be applied in optimizing the esterification/hydrolysis processes.

References


Keywords

Reactive chromatography; modelling; esterification; heterogeneous catalysis.
Short history

Vincenzo Russo was born in Naples on 02/05/1985. On 09/05/2014 he got his PhD title in Chemical Sciences in the Chemical Sciences Department of the University of Naples "Federico II", with a thesis entitled “Kinetic and Catalytic Aspects in Propene Oxide Production”, on the synthesis of propene oxide subject, from propene and hydrogen peroxide in the presence of TS-1 catalyst, investigating both the kinetic and catalytic aspects. From May 2014 to July 2016 he was a Post-Doctoral Researcher at the Department of Chemical Sciences of the University of Naples "Federico II" (Napoli, Italy), working on reaction modelling, catalysis and kinetic investigation. From July 2016 till September 2017 he worked at Åbo Akademi University (Turku, Finland) on multiphase reactors modelling as senior researcher. From September 2017 till now he is working as Assistant Professor (RTD-A) at the at the Department of Chemical Sciences of the University of Naples "Federico II" (Napoli, Italy).

Scientific contributions and research field of interest

- Author of 43 papers appeared on international peer-reviewed Journals and 2 book chapters.
- His main scientific activities deal with:
  - Reaction and reactor modelling of multiphase systems
  - Kinetic investigation of catalytic reactions
  - Safety criteria for exothermic reactions
  - Design and realization of lab-scale pilot plants
  - Plant automation and control

- His scientific activities are carried out in collaboration with public and private partners:
  - Åbo Akademi University, Turku (FI)
  - Eindhoven University of Technology, Eindhoven (NL)
  - Fraunhofer ICT-IMM, Mainz (D)
  - Dipartimento di Ingegneria Civile, Chimica, Ambientale e dei Materiali, Università di Bologna, Bologna (IT)
  - Dipartimento di Ingegneria Civile Edile e Ambientale, Università degli Studi di Napoli “Federico II”, Napoli (IT)
  - Dipartimento di Ingegneria chimica, dei Materiali e della Produzione industriale, Università degli Studi di Napoli “Federico II”, Napoli (IT)
  - Istituto per i Polimeri, Compositi e Biomateriali (IPCB) – CNR, Portici/Pozzuoli (IT)
  - CONSER S.p.A., Roma (IT)
## Job experiences and formation

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<th>Date</th>
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<th>Subject</th>
<th>Qualification</th>
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<td>04/09/2017 – today</td>
<td>University of Naples “Federico II” – Chemical Sciences Department</td>
<td>Industrial Chemistry (CHIM/04)</td>
<td>Assistant Professor (RTD-A).</td>
</tr>
<tr>
<td>01/01/2016 – 19/07/2016</td>
<td>University of Naples “Federico II” – Chemical Sciences Department</td>
<td>Industrial Chemistry</td>
<td>Research grant: “Studio della sintesi di poliesteri e poliammidi da acido succinico ottenuto da brodi di fermentazione e scale-up del processo”, ambito disciplinare Scienze Chimiche, BioPolIS (PON03PE_00107_1/1 CUP E48C14000030005).</td>
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<td>09/05/2014</td>
<td>University of Naples “Federico II” - Chemical Sciences Department</td>
<td>Industrial Chemistry</td>
<td>PhD in Chemical Sciences</td>
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<tr>
<td>01/11/2013 - 28/02/2014</td>
<td>Åbo Akademi– Laboratory of Industrial Chemistry and Reaction Engineering</td>
<td>Industrial Chemistry</td>
<td>Visiting student</td>
</tr>
<tr>
<td>15/09/2010-01/03/2011</td>
<td>University of Naples “Federico II” - Chemical Sciences Department</td>
<td>Industrial Chemistry</td>
<td>Fellowship holder: &quot;Metodi innovativi per la produzione di oli Epossidati&quot;, cooperation with Mythen SpA.</td>
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<tr>
<td>23/06/2010</td>
<td>University of Naples “Federico II” - Chemical Sciences Department</td>
<td>Industrial Chemistry</td>
<td>Master degree in Sciences and Technologies of Industrial Chemistry - 110/110 cum laude.</td>
</tr>
<tr>
<td>28/03/2008</td>
<td>University of Naples “Federico II” - Chemical Sciences Department</td>
<td>Industrial Chemistry</td>
<td>Bachelor degree in Industrial Chemistry - 110/110 cum laude.</td>
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Scientific contributes

Papers on magazines


Conference papers (Scopus source)


Book chapters


PRIZES

Conferences contributes

Chairman activity

1. Chair activity at CHISA 2016 - 27-31 August 2016 Prague, Czech Republic.

Oral presentations


Poster presentations

Reviewer activity

- Chemical Engineering Journal
- Bioresource Technology
- Canadian Journal of Chemical Engineering
- Industrial & Engineering Chemistry Research
- Chemical Engineering Communications
- Adsorption
- International Journal of Oil, Gas and Coal Technology
- International Journal of Thermal Sciences
- Fuel Processing Technology

Teaching activity

Since 2014 for the Chemical Science Department of the Università di Napoli “Federico II” (Consiglio del Dipartimento di Scienze Chimiche n. 2 del 20/02/20), for CHIM04 sector (Industrial Chemistry), he is part of the exam commissions of the following teachings:
1. Introduzione alla Chimica industriale e al calcolo di processo
2. Principi di Chimica Industriale con esercitazioni
3. Chimica Industriale I
4. Tecnologie Avanzate nei processi chimici industriali
5. Qualità, sicurezza e tutela bervettuale nell'industria chimica

Invited lectures

1. Lecture entitled “Reactor simulations” for the course “Principles of Chemical Reaction Engineering”, held for students of the English Master’s program in Chemical Engineering, Åbo Akademi University, Turku, Finland on October 17th, 2016.
2. Lecture entitled “Reactor simulations” for the course “Kemisk Reaktionsteknik” (“Chemical Reaction Engineering”), held for students of the Master’s program in Chemical Engineering, Åbo Akademi University, Turku, Finland on December 9th, 2016.

Co-advisor activity

Master degree thesis


Bachelor degree thesis

Activity in national and EU projects

01/01/2016 – 19/07/2016 BIOPOLIS PON 2007-2013. Activity: “Studio della sintesi di poliesteri e poliammidi da acido succinico ottenuto da brodi di fermentazione e scale-up del processo”


12/05/2014 – 15/05/2015 PON04_a2F B&SAVE-AQUASYSTEM-SIGOLD (CUP E61H2000170005), BORS 14 DICEA/2014. Activity: “Modellazione di colonne di adsorbimento fluido-solido”


Activity in cooperation with industrial partners

2011 – 2015 Propene oxide synthesis in cooperation with CONSER S.p.A.

15/09/2010 – 01/03/2011 Epoxidized soybean oil production in cooperation with Mythen S.p.A.

Attended schools


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