A new model for the design and analysis of trickle bed reactors

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HIGHLIGHTS

► A new model for the design and analysis of catalytic trickle bed reactors was developed.
► Local liquid distribution is obtained as a function of operating conditions and physical properties of all three phases.
► Impact of local incomplete wetting on conversion is taken into account.
► Modeling of the kinetics and mass transport on a particle as well as on a reactor scale.
► Performance is demonstrated by comparison of model predictions to experimental data.

ABSTRACT

A new discrete model was developed for the design and analysis of catalytic trickle bed reactors operating in the low interaction regime based on the local structure of packed beds. By detailed comparisons of model predictions to experimental data the performance of the new model is demonstrated. By means of this model the steady-state behavior of trickle bed reactors can be studied in terms of operating conditions, physical properties of all three phases, transport parameters and isothermal reaction kinetics on a particle as well as on a reactor scale.

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1. Introduction

Catalytic trickle bed reactors are multiphase systems consisting of a fixed bed of catalytic particles with in most cases concurrent downflow of liquid and gas. The behavior of trickle bed reactors is very complex and depends on mass and heat transfer as well as on hydrodynamics [1]. At low liquid flow rates, as encountered in the low interaction regime, maldistribution of liquid flow is found to occur. Such maldistribution may arise from a large number of potential reasons, e.g. improper initial distribution of feed, varying local structural properties of the packing, wall effects, wetting characteristics of the catalyst, liquid properties as well as operating conditions. It can result in incomplete wetting, existence of hot spots and catalyst deactivation. Therefore, detailed information about the liquid flow distribution inside the packing is essential for a proper design of trickle bed reactors [2,3].

For a quantitative prediction of the reactor performance mathematical models are needed which are able to represent the local interactions between liquid and solid on a reactor as well as on a particle scale [4]. In the past several models have been proposed in the literature which can be classified according to their basic assumptions with respect to the representation of liquid flow.

• Pseudohomogenous models represent the liquid flow as continuous functions of local position [5–9] thus totally ignoring the discrete structure of liquid flow in the trickling regime. It has been shown that these models are able to satisfactorily predict trickle bed performance provided that all model parameters and their dependencies are known, the liquid is distributed uniformly and all particles are completely wetted [10]. However this is not a realistic description of the low interaction trickle flow regime in packed bed reactors [11,12].

Partial wetting conditions may be taken into account by use of a global wetting parameter as done by Lluita et al. [13,14].

• Discrete models represent liquid flow as a result of single discrete transport processes occurring at the particle scale. Therefore, they are ideally suited for representing the discrete structures of liquid flow in the trickling regime. Furthermore, experimental investigations have shown that the liquid–solid interactions in the low interaction regime are locally random but stable with time. Basically these models rely on a representation of the pore space as a combination of recurring basic elements, i.e. cells, comprising one or more particles or even only a part of a particle itself [15–17]. Liquid flow distribution is obtained by balancing the
inflow and outflow of all interconnected cells. Similarly, percolation models represent the pore space as a body-centered cubic lattice consisting of sites and bonds. Liquid flow through the lattice is modeled as a percolation process based on statistical calculations (Monte Carlo method) [12].

Based on a detailed knowledge of the geometry of the pore space, the liquid flow can also be simulated using a Lagrangian approach, i.e. interpreting the entire trickling liquid flow as the sum of distinctive motions of individual liquid elements [18]. According to the authors a liquid element can encounter various actions (e.g. roll, split or coalescence) while traveling through the packed bed. At every geometric location of the packing the respective action is randomly chosen out of a set of possible actions.

In view of the discrete structure of the liquid flow in trickle bed reactors operating in the low interaction regime, Lagrangian methods are regarded to be the most promising methods for simulating the liquid flow on a particle scale. It is the objective of this contribution to demonstrate that by using a Lagrangian method the three-dimensional liquid distribution inside the packing can be obtained in terms of physical properties of the liquid–solid system used. Moreover, it will be shown that the impact of partial wetting on conversion can be reliably predicted provided the kinetics and the mass transport of the reaction system under consideration is known.

2. Model development

2.1. Packing generation

Maldistribution of liquid flow arises from a large number of potential reasons, among others the varying local structural properties of the packing are found to be dominant. Therefore, in order to account for maldistribution effects, the model is based on a detailed knowledge of the local structure of the packed bed. Unfortunately, these geometrical data can only be obtained with large experimental effort.

As was shown by Schnitzlein [19], computer generated sphere packings closely resemble real packings, i.e. predicted radial voidage distributions are in good agreement with reported literature data. Recently, the packing generation procedure has been extended to account for other particle geometries, e.g. cylindrical extrudates, too. Therefore, as a remedy all the necessary information about the local structural properties of the packed bed are retrieved from such simulated packings. By specifying type (e.g. sphere, cylinder), size and catalytic activity for every particle a polydispersed packing inside a cylindrical container can be generated. It is noted that the hydrodynamic model shown below is confined to spherical particles. A small section of a simulated packed bed with catalytic (bright color) and non-catalytic (dark color) particles is shown in Fig. 1. It is possible to generate realistic packings with several thousands of particles.

![Computer generated sphere packing with catalytic (bright color) and non-catalytic (dark color) particles.](image-url)
2.2. Hydrodynamics

Following the approach of Spedding and Spencer [18] the liquid flow distribution is simulated by considering a large number of discrete liquid elements of finite size introduced at the top of the packing. On its way through the packed bed a liquid element (dynamic liquid holdup) can appear either as rivulet, film or single drop (see Fig. 2b–d). Moreover, the liquid can be trapped at contact points between two or more particles thus contributing to the static liquid holdup (see Fig. 2a) [13].

Based on the information about the local position of every single particle inside the packed bed the stagnant liquid bonds between two particles and between a particle and the wall can be predicted in terms of the liquid–solid properties. Therefore, the surface tension, the contact and the half filling angle as well as the critical separation distance have to be experimentally determined for each liquid–solid system under consideration. The good agreement between predictions and experimental data is noted (see Fig. 3). Details of the calculation are given elsewhere [20].

While traveling through the packed bed each discretized liquid element evolves through local interactions with other elements and its environment as well as with external forces. In contrast to the original approach of Spedding and Spencer [18], the various actions a liquid element can encounter are mainly governed by the physical properties of the liquid–solid system [21,22] and only to a small extent by random processes. In order to identify the relevant actions and to quantify their impact, a large number of experiments have been carried out varying the physical properties of the liquid, the material of the spherical particles, the wettability and the properties of the packed bed as well [23]. The respective experimental conditions are summarized in Table 1.

Experimentally, the liquid distribution inside the reactor can be obtained by varying the reactor height and measuring the liquid distribution at the outlet via the mixing-cup technique, provided

![Fig. 2. Different appearances of a liquid element.](image)

![Fig. 3. Comparison between calculated and measured static liquid holdup for different liquid–solid systems and geometrical properties (20% variance)](image)
that the packing structure is not disturbed by the collector device. This was achieved by using a new collector type consisting of hemispherical caps arranged in a structure similar to an ordered packing of spheres as shown in Fig. 4 [24].

The liquid leaving the reactor in every interstice comprised by contacting particles is collected into compartments, which are in turn connected to separate liquid reservoirs. The content of each reservoir is obtained gravimetrically. It is noted that by applying different combinations of compartments the liquid flow distribution can be obtained with a high local resolution. Prior to each experiment the packing was prewetted according to Levec et al. [25]. Moreover, in order to measure the dynamic liquid holdup during the experiments the reactor was suspended on a tension S-type load cell.

Fig. 5 exemplarily shows a simulated liquid distribution as well as a radial flow distribution for a sphere packing with a reactor-to-

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Table 1
Varied parameters for the liquid distribution measurements.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Range of variation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle material</td>
<td>Glass, polyoxymethylene, Vitrified clay</td>
</tr>
<tr>
<td>Surface tension</td>
<td>0.032–0.079 N/m</td>
</tr>
<tr>
<td>Liquid density</td>
<td>991–1181 kg/m³</td>
</tr>
<tr>
<td>Liquid viscosity</td>
<td>1–2.5 and 100 mPas</td>
</tr>
<tr>
<td>Contact angle</td>
<td>0–75°</td>
</tr>
<tr>
<td>Particle diameter</td>
<td>0.004–0.014 m</td>
</tr>
<tr>
<td>Cylinder diameter</td>
<td>0.05 and 0.10 m</td>
</tr>
<tr>
<td>Packing height</td>
<td>0.004–0.70 m</td>
</tr>
<tr>
<td>Liquid load</td>
<td>0.6–6 kg/(m²s)</td>
</tr>
<tr>
<td>Liquid distribution</td>
<td>Single central, Uniform distribution</td>
</tr>
</tbody>
</table>

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Fig. 4. Collector – schematic (left) and photography (right).

**Fig. 5.** Simulated liquid distribution (left, dark colored spheres are in contact with liquid) and radial flow distribution over the height (right).

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particle-diameter ratio of $d_t/d_p = 10$ for different horizontal cuts through the reactor at distinct heights.

Despite the fact that the simulated packings closely resemble experimental packings the actual positions of individual spheres may be different. Therefore, one cannot expect an exact local agreement of the simulated liquid flow distribution with experimental data. In order to provide a reasonable means for comparison, the maldistribution coefficient as proposed by Marcandelli et al. [26] was used. Fig. 6 shows a comparison of the maldistribution coefficients as obtained for simulated and experimentally obtained liquid flow distributions. Despite the fact that liquid flow in packed beds is to a certain extent governed by random processes, the model is able to predict the maldistribution in packed beds in good agreement with experimental data for all liquid–solid systems under consideration.

Knowing the liquid flow distribution inside the packed bed the dynamic holdup is calculated by summing over all discrete liquid elements inside the packing. A comparison between experimental and simulated dynamic liquid holdup is shown in Fig. 7. Moreover, local degree of wetting can be calculated for each single particle by additionally considering the local static holdup.

### 2.3. Network model

In order to account for the mixing characteristics of liquid flow inside the packing the obtained liquid distribution is transformed into a three-dimensional directed graph structure [27], the vertices and the edges of which are represented by contact points and elements of liquid flow (see above), respectively. Small basic reactor types (e.g. Plug Flow Reactor PFR, Continuous Stirred Tank Reactor CSTR, Dispersed PFR) of different size are attributed to the vertices and edges as shown in Fig. 8.

By choosing an appropriate reactor type with an exchange volume the interaction between static and dynamic liquid elements [28] is accounted for, as well. The characteristic parameters for each basic reactor (e.g. type, size) are retrieved from tracer experiments. These experiments have been carried out by injecting an electrolyte sample at the top of the bed and monitoring its spread at the outlet with respect of time (axial dispersion) and radial position (radial dispersion).

Since the radial tracer distribution is mainly governed by the structural properties of the packing, only axial tracer distributions are used to obtain values for the model parameters for the individual basic reactor types (e.g. $D_{ax}$, $\alpha'$ and $\beta'$). The axial dispersion coefficient is obtained by fitting the axial tracer distribution as obtained by means of a one-dimensional dispersion model to experimental data. Subsequently, the remaining parameters are iteratively adjusted until a good agreement is achieved (see Fig. 9).

The instationary mass balance equations for each basic reactor are formulated in terms of concentrations in both phases taking into account the respective catalytic surface or catalyst mass (see Eqs. (1)–(7)).

#### Continuous Stirred Tank Reactor:

$$\frac{\partial c}{\partial t} = -\frac{qL}{V} (c_0 - c) + \frac{\rho}{\rho_s} r(c)$$

#### Plug Flow Reactor:

$$\frac{\partial c}{\partial t} = -u \frac{\partial c}{\partial z} + \frac{\rho}{\rho_s} r(c)$$

#### Dispersed Plug Flow Reactor:

$$\frac{\partial c}{\partial t} = -u \frac{\partial c}{\partial z} + D_{ax} \frac{\partial^2 c}{\partial z^2} + \frac{\rho}{\rho_s} r(c)$$

#### Continuous Stirred Tank Reactor with Exchange Volume:

![Fig. 6. Measured and simulated maldistribution factor [26] (0.2 deviation).](image)

![Fig. 7. Comparison between experimental and simulated dynamic liquid holdup (0.05 deviation).](image)

![Fig. 8. Simulated liquid flow (left) and representation by a three-dimensional network of minireactors (right).](image)
The entire arrangement yields a mathematical model consisting of a very large number of (partial) differential equations which are locally discretized via a finite volume approach [29]. The resulting set of differential equations is integrated following the approach of Cochlovius and Schnitzlein [30].

2.4. Kinetics

Knowing the local degree of wetting, the amount of the local catalytic surface attributed to each graph element can be obtained for every basic reactor. Thus, for a given reaction system the performance of each basic reactor can be calculated provided the parameters for the kinetics and the mass transport processes are known. A schematic representation of the relevant intraphase mass transfer steps is shown in Fig. 10.

For heterogeneous reactions partial wetting of porous catalyst particles may result in an increased global reaction rate [31]. Therefore, gas–solid as well as liquid–solid mass transfer steps have to be taken into account.

The kinetic as well as the mass transport parameters are determined by preliminary experiments using a laboratory-scale co-current trickle bed reactor as well as a liquid-full recycle reactor [23].

3. Validation

In order to validate the reactor model, experiments were carried out using a laboratory-scale trickle bed reactor (reactor diameter 3 cm and reactor height 21 cm) using a porous 0.3 wt.% eggshell Pd/Al₂O₃-catalyst (Süd-Chemie, particle diameter 2–4 mm, BET surface area 61.54 m²/g). The hydrogenation of alpha-methylstyrene to cumene was chosen as model reaction [23,32–35]. Due to the large excess of the liquid reactant the reaction can be regarded to be first order with respect to hydrogen. The kinetic parameters are determined using the experimental strategy as proposed by Morita and Smith [35]. Due to the small catalytic layer (thickness of the active layer 200 μm) internal diffusion effects are neglected throughout.

In order to demonstrate the impact of partial wetting on reactor performance exclusively, the conversion should be concentration independent. This was achieved, by operating the trickle bed
reactor as differential recycle reactor (see Fig. 11). The differential operating conditions have been verified experimentally.

All experiments have been carried out at 1 bar and liquid flow rates within the trickle flow regime. The conversion was obtained by measuring the concentration of the liquid reactant by means of a sonic probe featuring an excellent time resolution [36]. Prior to each run, the bed was flooded with alpha-methylstyrene (99% purity). The liquid as well as the pure hydrogen were injected at the top of the packed bed. The reactor was kept isothermal at a temperature of 40.6 °C by a double jacket.

Fig. 12 shows the obtained conversion as a function of liquid flow rate. The good agreement between model predictions and experimental data is noted. The nonlinear decrease of conversion is an indication, that in this case incomplete wetting governs the overall reaction rate.

This is further exemplified in Fig. 13, where conversion is plotted as a function of space time. Again, the model is able to predict the experimental data with good agreement. Moreover, predicted conversions are shown which are calculated by means of the well-established PDE model [32,33,37] with and without considering incomplete wetting by means of a global wetting efficiency [38]. The large deviations between these model predictions and the experimental data indicate, that incomplete wetting is a local phenomenon which cannot be adequately accounted for by using a global wetting parameter. The superiority of the new model which accounts for the relevant processes at a particle scale is evident.

4. Conclusions

It is well known that in trickle bed reactors operating in the low interaction regime the impact of local incomplete wetting on conversion is dominant. The reliable prediction of the phenomenon demands a reactor model which is able to account for the local properties of liquid flow in packed beds at a particle scale. Since the new reactor model meets these conditions, it is able to reliably predict the performance of catalytic trickle bed reactors.

Due to the flexible structure and the modular setup the hydrodynamic model can be easily extended to incorporate other particle geometries, provided all the model parameters characterizing the liquid–solid interactions are known. Since the network model is based on the liquid distribution it can be applied in this case without any modifications.

Further extensions will include amongst others a detailed representation of the fluid dynamics of the gas phase, thus extending the applicability of the model beyond the limits of the low interaction regime.

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