Study of heterogeneous catalytic microreactors

Internship - 3A Option GREEN/ Master Génie de procédé
Ecole Centrale Marseille

Xiaotong ZHAN

Tutor : Françoise Duprat (M2P2)
Co-tutor : Damien Hérault (ISM2)

2015/9/11
Acknowledgement

First of all, I would thank my supervisor and tutor Prof. Françoise Duprat for having offered me the opportunity to do the internship and thesis in laboratory M2P2. I appreciated a lot her help and patient instructions about the literature research, the experiment and the report during my internship and her help during all my 3A in Centrale Marseille. I would thank Dr. Damien Hérault, for sparing his time to help me to do experiments in laboratory ISM2, for giving me advices and teaching me a lot about chemistry.

I would also thank M. Arnaud Treuvey, who have offered me lots of help to carry out experiments, especially the UV-vis. spectroscopy. Many thanks to my colleagues of ISM2, who are very nice and helpful.

I’m also grateful to Ecole Centrale Group and projet CSC, for giving me this opportunity of living and studying in France.
Abstract

As a part of the PhD thesis, the objective of this internship is the study of heterogeneous catalytic microreactors, in order to well prepare the following PhD work. The works of internship are composed by two sections: research of literature and experiments.

The research of literature section is mainly concentrated in the industrial application of microreactors and the modeling study of heterogeneous catalytic microreactors. The microreactors utilized in industry and pilot plant and examples of industrial production with microreactors are introduced. The research status, modelings and kinetic studies, and the performance comparison of different heterogeneous catalytic microreactors are summarized.

In the experimental section, a simple and fast reaction is chosen, and a packed-bed microreactor system is set up. The analysis of reaction conversion and kinetic is presented.
I Introduction

Microreactors, the miniaturized reaction systems with dimensions in the millimeter and submillimeter range, have gained gain in popularity for chemistry and chemical process industry in the past two decades.

The advantages of microreactors have been discussed extensively. The small dimensions of microreactors ensure a short radial diffusion time leading to a narrow residence time distribution (RTD)\cite{1}, and allow usage of minimal amounts of reagent to precisely control the reaction and provide high selectivity towards the desired product \cite{2}. In addition, their high surface area-to-volume ratio in the range of 10000 to 50000 m$^{-1}$ compared to traditional reactors, provide a large interfacial area between different phases, which can largely improve the efficient of heterogeneous catalysis \cite{2}\cite{3}. The microreactors have high heat and mass transfer, which allow to utilize the full potential of catalysts during highly endothermic or exothermic reactions and avoid hot-spots formation \cite{4}. Besides that, the environmental benefits of microreactors should be mentioned. The amount of energy consumed per unit temperature rise can be made extremely small, according to their efficient heat transfer, and the reactions involving reactive, toxic or explosive intermediates can be carried out in safety in microreactors, because the small instantaneous volumes \cite{5}.

In chemistry laboratories and chemical industries, batch processes are usually adopted because they are clean, well developed and easy to handle. However, continuous flow processes are gaining more and more attention, not only in the productions of heavy chemicals, but also in fine chemical and pharmaceutical industries. With the continuous flow processes, the scale-up problems can be easily solved, meanwhile, the use of hazardous chemicals can be enabled safely, and some dangerous reactions and flash reactions can be controlled and finished in the flow condition.\cite{6}\cite{7}

As we all known, catalysis owns an irreplaceable status in the chemical industry. It is regularly stated that over 90% of all chemical products have at least one catalytic step in their manufacture.\cite{8} Both homogeneous and heterogeneous catalysis find wide application in chemicals production. Each may offer advantages in particular cases.\cite{9} Particularly, heterogeneous catalysts gains more attention in the industrial production because they are cheap, easy to get, and have good thermal stability. What’s more, heterogeneous catalysts, especially the solid catalysts, can be easily separated in the process, and they make it possible to use the fixed-bed reactor to improve the production efficiency \cite{10}.

Combing heterogeneous catalysis with continuous flow microreactors technology has several penitential advantages, as discussed in some reviews \cite{3}\cite{11}. In summary, this method could cut back production costs to a large degree, and improve the
production efficiency simultaneously. Generally, there are three main types of heterogeneous catalytic microreactors: packed-bed microreactor, wall-coated microreactor (and macro-monolithic reactor) and micro-monolithic reactor.

![Figure 1](image)

Figure 1  Schematic representation of the cross-section of a microchannel in a) packed-bed, b) monolithic, and c) wall-coated microreactors.\textsuperscript{[3]}

This five months internship is the first part of the PhD thesis. The general objective of the thesis is the study of heterogeneous catalytic microreactors with the aim of industrial level production. This study contains the efficiency comparison of different heterogeneous catalyst system and the improvement in catalytic reaction brought by the microreactor. The final objective of thesis is to synthesize the chiral heterogeneous catalysis then apply it into a continuous flow microreactor system set up by ourselves. Therefore, the objective of this internship, is to well understand the thesis, to grasp the basic knowledge of microreactors and to attempt the primary experiment.

The main work of the internship is composed by two sections.
1) The first section is the research of literature published, mainly about the industrial application of microreactors and the modeling of heterogeneous catalytic microreactors. The different microreactors applied in industry and pilot plant and the industrial production examples will be introduced. The different heterogeneous catalytic microreactors: Packed-bed, Monolithic and Wall-coated microreactors will be presented and compared with each other. The correlations of mass transfer, heat transfer and pressure drop will be summarized.
2) The second section is the experimental section. All the experiments are carried out in laboratory ISM2. A packed-bed microreactor system has been established in the lab. A fast and simple model reaction and commercial catalyst will be chosen to test the instruments and the operating process for the following thesis. The kinetic of the model reaction will be studied.
References

II  Literature research section 1: Industrial application of microreactors

The advantages of microreactors have been discussed in the previous part. The question remaining is whether these microreactor devices are able to meet the expectations for industrial use raised in the academic environment. In the last fifteen years, a lot of companies have started to study microstructured devices as tools for process intensification, such as Lonza, Corning, IMM and so on. But a fact is that, not all chemical reactions can profit from microreactors. In this part, different types of microreactors utilized in pilot and industry will be introduced. What’s more, different types of reactions that well suit the microreactors will be presented.

However, industry is not very active in publishing not only because of confidentiality reasons but also because of the absence of direct need for a profile. Therefore, it has to be accepted that some information is missing among this part and that this is only the tip of the iceberg.

1  Type of reactors

1.1  CPC Cytos

1.1.1  Cytos Lab System/Cytos Pilot System

![Figure 2  Cytos Pilot System](image)
The Cytos Pilot System (Fig. 2) is 10-times external parallelized but has the identical fluidic behavior as the Cytos Lab System. The Cytos Lab System is characterized by dimensions of 100 × 150 × 10 mm with a channel width of less than 0.1 mm, a weight of 1.2 kg and an internal volume of 1.1 mL (reactant side, after mixing) and 12 mL (heat exchanger), respectively.

Dana Kralisch et al.\[^{[1]}\] have analyzed the ecological potential of microreaction technology with Cytos Pilot System. In this article, the product flow of m-anisaldehyde with Cytos Lab System is 0.06 kg/h. The yield amounted to 88% of the theory, at 273K.

### 1.1.2 Cytos College System

![Figure 3 CYTOS College System\[^{[2]}\]](image)

The Cytos College System microreactor (Fig. 3) consists of several stacked plates with microstructures in the submillimeter range (width approximately 100 μm). The volume of the microreactor itself is 2 mL, and that of the RTU 45 mL, so the total volume (V total) of the system is 47 mL. Maximal residence time in the microreactor (plus residence time unit, RTU) is approximately 2 h.

In the research of Davy R. J. Acke et al.\[^{[2]}\], Cytos College System is applied in the Baylis-Hillman reaction, at room temperature or 40 °C, with the conversion max. 100% and yield max. 95%.

In the research article of Ellen Van Meenen et al.\[^{[3]}\], this system is used in the synthesis of α-aminophosphonates, at temperature 50 °C, 80 °C, and 100 °C, with the
conversion max. 100% and yield max. 91%. The flow rate was adjusted to 0.3 mL/min.pump resulting in a residence time of 78 min. The residence time (t_r) was calculated by the following formula: t_r = V_{total}/r_{total} with r_{total} = 0.6 mL/min. The continuous process allowed us to synthesize more than 10 grams α-aminophosphonate per hour (or more than 250 g per day).

Thomas S. A. Heugebaert et al. [4] used this system in the acetone cyanohydrin synthesis. The best result that can be attempted in a batch is: the temperature 30 °C, the flow rate 120ml/h, the field 99% and the output 39.1g/h.

In the synthesis of 3,4-diamino-1H-isochromen-1-ones [5], different reaction conditions have been tested, at 50 °C. The maximum output is 2.28g/h with the yield 75% after the crystallization. The residence time varies from 23 to 50 mins in different conditions.

1.1.3 Other CPC microreactor

Ch. Wille et al. [6] have investigated the synthesis of pigments in a three-stage microreactor pilot plant. The details of this microreactor have not been discussed. The temperature is 15 °C. And output of the MRT-pilot plant is about 1 kg/h.

1.2 Corning microreactor

Multi-injection Corning microreactor

Figure 4  Corning Multi-Injection Microreactor[7,8]
Dominique M. Roberge et al.\textsuperscript{[7][8]} have researched on the continuous multi-Injection reactor for multipurpose production. This reactor (Fig.4) is an assembly of four microstructures made of glass into a frame, comparable to an engineered skid. Typical dimensions of a microstructure are $161 \times 131 \times 8$ mm and the typical footprint of the reactor is $600 \times 320 \times 320$ mm. The total internal volume of the reactor including the four microstructures is $35$ mm.\textsuperscript{[7]}

The temperature of the experiments is -40°C. This production can be ramped up to 2 tons of final product within four weeks with five reactors, the annual capacity of the installation being then 25 metric tons of final product. Operation at high flow rate is in the range of 80–100 g/min.\textsuperscript{[8]}

1.3 ESK ceramic production reactor

![ESK ceramic production reactor](image)

Figure 5  ESK ceramic production reactor (3M, Kempten) in the experimental setup (a) and plate design of the mixing module (b).\textsuperscript{[9]}

Sebastian Schwolow et al.\textsuperscript{[9]} have investigated a michael addition in microreactors. The reaction channel is with a square cross section (2.0 mm $\times$ 2.0 mm). The flow rate is 50 mL/min ($Re \approx 300$). The temperature is from 0 °C to 55 °C.
1.4 Tubular microreactor

<table>
<thead>
<tr>
<th>caterpillar minimixer: characteristic properties</th>
<th>specifications</th>
</tr>
</thead>
<tbody>
<tr>
<td>mixer construction material</td>
<td>stainless steel 1.4571 (SS 316 Ti)</td>
</tr>
<tr>
<td>number of plates needed to form minimixer channel</td>
<td>2</td>
</tr>
<tr>
<td>minimixer channel: initial width: maximum width</td>
<td>1200 μm: 2400 μm</td>
</tr>
<tr>
<td>minimixer channel (both plates): initial depth: maximum depth</td>
<td>1200 μm: 1700 μm</td>
</tr>
<tr>
<td>microstructure in one plate: initial depth: maximum depth</td>
<td>600 μm: 850 μm</td>
</tr>
<tr>
<td>minimixer stage: length</td>
<td>2400 μm</td>
</tr>
<tr>
<td>number of mixing stages</td>
<td>8</td>
</tr>
<tr>
<td>total length of caterpillar minimixer</td>
<td>19.2 mm</td>
</tr>
<tr>
<td>device outer dimensions</td>
<td>50 mm × 50 mm × 10 mm</td>
</tr>
</tbody>
</table>

Figure 6 Specifications and dimensions of the steel caterpillar minimixer\cite{10}

In the experiments of V. Hessel et al.\cite{10} using the pilot-scale configuration with the caterpillar minimixer, the maximum yield of 89% obtained with the laboratory configuration using the caterpillar mixer could be confirmed also with the pilot-scale configuration equipped with the same device. The best result was achieved at 10 °C and 10 s. Moreover, the results show that even for long residence times (about 4 times longer as for the laboratory configuration) and tubes of large inner diameter, no significant decrease of yield was observed at the two lowest temperatures applied, 10 and 20 °C. In the laboratory configuration with the same device, when the flow rate is 10L/h, the mass of product is 43.83g, with the yield 81%. \cite{10}
Iwasaki and Yoshida\textsuperscript{[11]} designed and constructed an industrially-suited pilot plant (3.5 m * 0.9 m) for the free radical polymerisation of methylmethacrylate (MMA) with a capacity of 10 t/a, which was installed at the industrial site at the Idemitsu Company in Japan. Eight micro-reactor blocks are arranged in a parallel manner (see Fig. 7). Each of these blocks contains three micro-tube reactors (500 mm internal diameter, 2 m length) in series. The performance of this pilot plant was similar (polydispersity index, yield and average number-based molecular weight) to that of a single micro-reactor tube. This demonstrates that external numbering-up concepts can be successfully applied to industrial use.

1.5 Micorchannel chip
Shigenori TOGASHI et al. [12] have researched on the yield improvement of chemical reactions by using microreactors and have developed a pilot plant using the numbering up of microreactors. The microreactor is divided into a lower case with two inlet fittings, an upper case with one outlet fitting, and a micro channel chip between the upper and the lower cases. The lower and upper cases are made of corrosion-resistant Hastelloy-C276. The thermocouple is set up in the neighborhood of channel walls neighborhood of the upper case.

Figure 8 shows the microchannel chip, which is made of quartz glass and which has a diameter of 42 mm. Two kinds of liquids flow (Reactant-A and Reactant-B) from the edge to the center in a multilayer state, and they mix in the gradually narrowing microchannel. The height of the channel is 150 µm, and the minimum width of the channel is 250 µm.

Figure 11 shows a structure of a pilot plant that involves the numbering up of microreactors. The pilot plant was 1500 mm wide, 900 mm long, and 1500 mm high. The total maximum flow rate when 20 microreactors was $10^4$ mm$^3$/s, which corresponds to 72 t/year when operated at rates less than 10h/d for 200 days.
Figure 12 shows the yield of mono-nitrophenols and 2,4-dinitrophenol. The yields of the main product were evaluated at 298.15K over 30min of continuous running. \cite{12}

<table>
<thead>
<tr>
<th></th>
<th>Mono-nitrophenols [%]</th>
<th>2,4-Di-nitrophenol [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Batch reactor</td>
<td>77.0</td>
<td>7.7</td>
</tr>
<tr>
<td>One microreactor</td>
<td>86.3</td>
<td>2.3</td>
</tr>
<tr>
<td>Pilot plant</td>
<td>88.1</td>
<td>1.7</td>
</tr>
</tbody>
</table>

Figure 13  Lab-Plate reactor for development purposes and typical setup of plate stack reactor with A6 and A5 size \cite{13}
With this microreactor developed by Lonza\textsuperscript{[13]}, 700 kg of isolated material were produced in a pilot campaign leading to more than 10m$^3$ of processed solution through the reactor setup. The mass flow and the isolated yield are shown in Fig.14. A second campaign was performed to produce more than 2 tons of isolated material in 2009.

\begin{center}
\begin{tabular}{|c|c|c|c|c|}
\hline
Reactor & $\dot{m}_{\text{MR}}$ [g/min] & $T_{\text{out}}$ [$^\circ$C] & $\Delta p$ [bar] & Isolated yield [%] \\
\hline
Static mixer 3/8" & 33 & 9 & 0.3 & 88 \\
Static mixer 3/8" & 148 & 41 & 1.6 & 84 \\
Glass MR 0.5 mm & 33 & $-$14 & 0.4 & 86 \\
Glass MR 0.5 mm & 148 & 15 & 3.2 & 88 \\
Lonza MR-A6 0.5 mm & 33 & $-$22 & 0.9 & 89 \\
Lonza MR-A6 0.5 mm & 140 & $-$16 & 8.8 & 90 \\
Lonza MR-A5 0.7 mm & 150 & $-$20 & 3.4 & 90 \\
Lonza MR-A5 1.0 mm & 150 & $-$21 & 2.0 & 88 \\
Lonza MR-A5 1.0 mm & 237 & $-$16 & 4.5 & 88 \\
\hline
\end{tabular}
\end{center}

Figure 14  Comparison of different reactors and flow rates for scale-up of the lithiation reaction\textsuperscript{[13]}

In 2011, F. Ebrahimia et al.\textsuperscript{[16]} have demonstrated one of the most underutilized principles of micro reaction technology, that of increased process safety, by means of investigating on-site raw material production-to minimize handling and transportation risks.

\begin{center}
Figure 15  Channel configuration on a reaction plate (a) and arrangement of heat transfer (b)\textsuperscript{[16]}
\end{center}

Continuous syntheses of performic and peracetic acids were performed in a microstructured reactor(Fig.15).
The synthesis reactions of the acids are shown in Eq. (1) (performic acid) and in Eq. (2) (peracetic acid). Both reactions were carried out in the presence of a homogeneous sulfuric acid catalyst. Both reactions seemed to be rather fast because with performic acid equilibrium was reached in 4 min at 313 K and with peracetic acid in 10 min at 343 K.

The influence of the channel sizes on production capacity was examined in order to find alternatives for channel dimensions. At first, the width of the channels was fixed to 15 mm and it was assumed that 18 m channel can be machined on the surface of the reaction plate. Based on these decisions, the required number of reaction plates for the desired production capacity was calculated at different channel depths. The required total length was computed on the basis of the measured kinetics and with the assumption of plug flow. The results for performic acid are shown in Fig. 16.

Based on Fig.16, alternatives for the depth of the channel are 3 or 4 mm taking into account that the maximum required production capacity for performic acid was 12 kg/h. In such a case, 9 (4 mm) or 14 (3 mm) reaction plates are needed to satisfy the required production capacity. The required production capacity of peracetic acid is higher (20 kg/h) and residence time is longer compared to the reaction of performic acid. This leads to higher number of plates in the unit as can be seen in Fig.16. 18 plates (4 mm) or 24 (3 mm) plates are needed to reach desired production capacity for peracetic acid.

<table>
<thead>
<tr>
<th>Reaction temperature [K]</th>
<th>Residence time [min]</th>
<th>Production capacity [kg/h] (total flow rate [dm^3/h])</th>
<th>Mass fraction of the percarboxylic acid in the product mixture [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Performic acid</td>
<td>303</td>
<td>1–12 (5–80)</td>
<td>13</td>
</tr>
<tr>
<td>Peracetic acid</td>
<td>333</td>
<td>1–20 (5–80)</td>
<td>23</td>
</tr>
</tbody>
</table>

Figure 16  Number of the reaction plates required to production capacity at different channel depth. Capacity window is shown in grey shade. [16]
The concept is flexible in terms of production capacity producing 1–12 kg/h (max. 100 t/a) performic acid and 1–20 kg/h (max. 170 t/a) peracetic acid. The structure of the reactor is rather simple and it can be designed as a compact and transferable unit.

### 1.6 StartLam 3000 microreactor

The StarLam 3000 reactor was designed by IMM (Institute of Microtechnique, Mainz, Germany). There are the dimensions and operating conditions.

<table>
<thead>
<tr>
<th>Name</th>
<th>Star Laminator 3000</th>
<th>Star Laminator 3000</th>
</tr>
</thead>
<tbody>
<tr>
<td>Order number</td>
<td>StarLam 3000</td>
<td>StarLam 3000</td>
</tr>
<tr>
<td>Mixing principles</td>
<td>Multi-Lamination</td>
<td>Multi-Lamination</td>
</tr>
<tr>
<td>Size (L x B x H)</td>
<td>220 x 429 x 486</td>
<td>95 x 95 x 150</td>
</tr>
<tr>
<td>Connectors (Inlet/Outlet)</td>
<td>DN 80/N 50</td>
<td>DN 150/N 25</td>
</tr>
<tr>
<td>Standard mixing channels (μm)</td>
<td>250</td>
<td>250</td>
</tr>
<tr>
<td>Standard material</td>
<td>Body: 1.4571 foil: 1.4401</td>
<td>Body: 1.4571 foil: 1.4401</td>
</tr>
<tr>
<td>Options</td>
<td>Other materials like Hastelloy, Monell or Titan on request</td>
<td>Other materials like Hastelloy, Monell or Titan on request</td>
</tr>
</tbody>
</table>

**Operating Conditions**

<table>
<thead>
<tr>
<th>Order number</th>
<th>StarLam 3000</th>
<th>StarLam 3000</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td>for FKM: -20 to +220; for FFKM: -20 to +315; for glass: -30 to +180</td>
<td>100</td>
</tr>
<tr>
<td>Pressure stability (bar)</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Flowrate (l/h)</td>
<td>5000 – 30000</td>
<td>600 – 8000</td>
</tr>
<tr>
<td>Residence time (ms)</td>
<td>180-1100</td>
<td>72 – 960</td>
</tr>
<tr>
<td>Inner volume (ml)</td>
<td>1500 (623 mix section)</td>
<td>160</td>
</tr>
<tr>
<td>Max Viscosity (mPas)</td>
<td>10000</td>
<td>10000</td>
</tr>
<tr>
<td>Leakage Class</td>
<td>&lt; 1 x 10⁻¹</td>
<td>&lt; 1 x 10⁻¹</td>
</tr>
</tbody>
</table>

![Figure 17 Dimensions of StarLam 3000][14]

In the article [14], authors have described the incorporation of a microreactor into an existing production plant in Austria, with the aim of doubling the current production capacity. After using StarLam 3000 microreactor, they discussed the successful implement of this technology into the current process, reporting the development of a process with the production capacity of 3.6 t/h, at the temperature up to 130 °C. The StarLam 3000 was installed in June 2005. Since then the reactor has been in permanent production use. No signs of corrosion were observed after ten months of production use.
1.7 Summary of pilot and industrial microreactors

The main parameters of industrial and pilot microreactors are summarized as below.

<table>
<thead>
<tr>
<th>Microreactor</th>
<th>Productivity</th>
<th>Size</th>
<th>Flow rate</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cytos Pilot System[1]</td>
<td>0.06 kg/h</td>
<td>1000 x1500 x100mm</td>
<td></td>
<td>273K</td>
</tr>
<tr>
<td>Cytos College System [2][3][4][5]</td>
<td>250 g/day</td>
<td></td>
<td>0.6 mL/min</td>
<td>30 °C to 100 °C</td>
</tr>
<tr>
<td></td>
<td>39.1 g/h</td>
<td>47 mL</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.28 g/h</td>
<td>47 mL</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Multi-injection Corning microreactor[7][8]</td>
<td>25 metric tons/year</td>
<td>161 x 131 x 8 mm</td>
<td>80–100 g/min</td>
<td>-40 °C</td>
</tr>
<tr>
<td>ESK ceramic production reactor[9]</td>
<td></td>
<td>2.0mm x 2.0mm (cross section)</td>
<td>50 mL/min</td>
<td>0 °C to 55 °C</td>
</tr>
<tr>
<td>caterpillar minmixer[10]</td>
<td>43.83g/h</td>
<td>50mm x 50 mm x 10 mm</td>
<td>10L/h</td>
<td>10 °C</td>
</tr>
<tr>
<td>A pilot plan of MMA[11]</td>
<td>10 t/a</td>
<td>3.5m * 0.9m</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Micorchannel chip[12]</td>
<td>72 t/year</td>
<td>L=900mm H=1500 mm W=1500 mm</td>
<td>10^4 mm^3/s</td>
<td></td>
</tr>
<tr>
<td>Micorchannel chip of Lonza[13]</td>
<td>2 t/year</td>
<td>A5 1.0mm</td>
<td>237g/min</td>
<td></td>
</tr>
<tr>
<td>Micorchannel chip[16]</td>
<td>Max 170t/a</td>
<td>d=3mm</td>
<td>5-80dm^3/h</td>
<td>313K and 343K</td>
</tr>
<tr>
<td>StartLam3000 microreactor[14]</td>
<td>3.6 t/h</td>
<td>95x95x150mm</td>
<td>600-8000l/h</td>
<td>-20 to 315°C</td>
</tr>
</tbody>
</table>

2 Type of reactions

2.1 Fast or slow kinetics

2.1.1 Baylis-Hillman Reaction (slow kinetics)

The Baylis-Hillman reaction has received a lot of attention because of the possibility of creating highly functionalized building blocks in a one-pot reaction. Usually, the Baylis-Hillman reaction is a slow reaction requiring days or weeks to go to completion.
Davy R. J. Acke and Christian V. Stevens\textsuperscript{[2]} have optimized the Baylis-Hillman reaction under microreactor conditions, using DABCO as a catalyst. After optimization, the reaction could be performed continuously and approximately 30% faster compared to batch conditions, however at a quite low flow rate.

![Investigated Baylis-Hillman reaction\textsuperscript{[2]}](image)

2.1.2 Grignard reactions (fast kinetics)

The Grignard reaction is of type A (highly exothermic and very rapid) and has a low yield which is attributed to a hot spot formed in the mixing zone of the reactor. The reaction yield could be significantly increased by applying the multi-injection principle, leading to better thermal control in the microreactor.

![Reaction of a Grignard reagent with an acyl chloride](image)

Dominique M. Roberge et al. \textsuperscript{[8]} have conducted the reactions in three different Corning microstructures: the single mixing plate design (without thermal fluid layer), the mono-injection design (NIM), and the multi-injection design (MJ). The results is in Fig.20.
Figure 20  Validation in terms of yield of the industrial Corning microreactor at high flow rates and different temperatures.

### 2.2 Highly toxic reactants or byproducts

Thomas S. A. Heugebaert et al.\textsuperscript{[4]} have proposed a safe production method for acetone cyanohydrin with microreactors. Acetone cyanohydrin is a widely used source of hydrogen cyanide. Although the synthesis of acetone cyanohydrin is well described in the literature, it mostly involves the generation of one or more equivalents of hydrogen cyanide in the reaction. This poses high risks: in case of spillage or accidental leakage, large amounts of hydrogen cyanide will be liberated into the working environment.

![Acetone cyanohydrin synthesis](image)

**Figure 21** Acetone cyanohydrin synthesis\textsuperscript{[4]}

An easily amenable method is presented to produce acetone cyanohydrin on mole scale (output 39 g/h), using a continuous flow system to overcome the high risks associated with the large-scale use of hydrogen cyanide.
Entry 9 (Fig. 22) presents a yield of 99% and an output of 39 g/h, a scale which one would hesitate to attempt in a batch. Although this output is somewhat lower than that for entries 1 and 2, only a small amount (1%) of HCN is lost during this reaction, as opposed to 36% and 29% for entries 1 and 2. Therefore, this entry represents a satisfactory method to produce acetone cyanohydrin in a straightforward way.

Davy R. J. Acke and Christian V. Stevens\cite{5} have studied a known reaction procedure, using in situ generated HCN. A safe reaction setup was created to avoid the release of the hazardous gas during the process. The 3,4-diamino-1H-isochromen-1-ones were produced continuously in moderate to good yields.

![Figure 23: Formation of 3,4-diamino-1H-isochromen-1-ones (R = aryl)](image)

2.3 Side/consecutive products

V. Hessel et al.\cite{10} have investigated the replacement of a former batch process by a continuous-flow process with microfluidic devices, which results in a notable process intensification for the Phenyl Boronic Acid Process with regard to product yield, reduction of side/consecutive products, and energy expenditure.
The best result of the investigations was an HPLC yield of 89% (preparative confirmed: 81%). This is nearly 25% higher as compared to the established Phenyl Boronic Acid Process, when being industrially performed in a batch-wise manner, and about 18% more than the laboratory-scale batch. The side- and consecutive products are reduced to levels below 1%, thereby increasing selectivity and facilitating separation by elimination of the distillation step. As a result, a product of higher purity (99%) is achieved.

2.4 Unstable intermediates

The continuous flow microreactor systems enable the use of a short-lived intermediate because the residence time can be greatly reduced to the order of milliseconds, keeping the flexibility of the addition order of reaction components (flash chemistry).
Aiichiro Nagaki et al.\textsuperscript{[15]} have achieved a sequential introduction of three electrophiles into 1,3,5-tribromobenzene based on Br/Li exchange reaction using an integrated flow microreactor system consisting of six micromixers and six microtube reactors. This method enables flash synthesis of TAC-101 and its analogues within 13 s in good yields on a preparative scale.

\section{2.5 Highly exothermic}

Dana Kralisch and Guenter Kreisel\textsuperscript{[1]} have taken the two-step synthesis of m-anisaldehyde from m-bromoanisole as a model reaction. Because of its highly exothermic behavior, this synthesis can only be carried out under significant safety precautions and with a high cooling energy effort in conventional batch reaction equipment. The application of micro-structured devices allows a continuous isothermal reaction setup at T = 273K.

On the industrial scale, the authors compared the synthesis of m-anisaldehyde in a 400 L vessel, cooled down to 193K by a cryogenic system, and in the continuous Cytos Pilot System at T = 273K. 10 Cytos microreactors were running with a cumulative product mass flow of 0.6 kg/h. Compared to the microreaction mode, the
same yield of 88% can be expected if the reaction temperature of the batch process can be held under 193 K.

Sebastian Schwolow et al.\cite{9} have discussed several steps of process development in flow chemistry and have proposed a systematic approach for the transfer of lab experiments in microstructured devices to the conditions of small-scale production processes, using an exothermic Michael addition of piperidine to ethyl acrylate as an example.

\[
\text{NH} + \text{O} \rightarrow \text{O}
\]

Figure 27 Synthesis of 3-piperidinopropionic acid ethyl ester

Preliminary calculations, which focus on characteristic times of transport phenomena, can be used in order to ensure the operability of the production scale reactor. Further experiments for reactor characterization provide additional information to describe mixing, residence time distribution, and heat transfer in the examined reactors. It is exemplarily shown how preliminary experiments can be the basis for the prediction of scale-up effects and the development of a continuous production process. Plug flow behavior and short mixing times could be confirmed for all investigated flow reactors. Furthermore, interactions of reaction kinetics and the formation of hot spots in the reactor channel were investigated. For the examined reaction, the simulations predicted the product yield under production conditions in good accuracy.

\subsection*{2.6 Conclusion}

In these cases, the microreactor can be used to control the reaction speed, reduce the release of the highly toxic reactants or byproducts, reduce the side- and consecutive products, enable the use of a short-lived intermediate and stabilize the highly exothermic reaction. It also works well in the low-temperature environment. The efficiency of these reactions can be also improved greatly in the microreactor system.
3  Examples of Industrial production

3.1  Nitroglycerin microstructured pilot-plant (Xi’an Huian Industrial Group, China)

A nitroglycerin pilot plant (15kg NG/h, investment 5M €) has been installed at Xi’an site in China and has started up in 2005 [17]. The manufactured nitroglycerin will be used as medicine for acute cardiac infarction. Therefore, the product quality must be on highest grade, and initial tests already revealed higher selectivity and purity. The plant is foreseen to operate safely and fully automated. As a second step, a plant for downstream purification, of notably larger size and complexity as the reactor plant, is going to be developed. Environmental pollution should be excluded by advanced waste water treatment and a closed water cycle. Thus, the purification plant will have parts for washing and drying of the nitroglycerin and, in a final stage, also encompass formulation and packaging.
3.2 Pilot plant for radical polymerization running at Idemitsu site in Japan

Iwasaki and Yoshida\textsuperscript{[11]} designed and constructed an industrially-suited pilot plant for the free radical polymerisation of methylmethacrylate (MMA) with a capacity of 10t/a, which was installed at the industrial site at the Idemitsu Company in Japan. Eight micro-reactor blocks are arranged in a parallel manner (see Fig. 7). Each of these blocks contains three micro-tube reactors (500 mm internal diameter, 2 m length) in series. The performance of this pilot plant was similar (polydispersity index, yield and average number-based molecular weight) to that of a single micro-reactor tube. This demonstrates that external numbering-up concepts can be successfully applied to industrial use.

3.3 Production of a polymer with FZK microreator at DSM fine Chemicals GmbH in Linz, Austria

![FZK microreator](image)

Figure 29 FZK microreator with the size of ‘shoe-box’. This apparatus was used for manufacture of a high-value product for plastics industry at DSM in Linz/Austria\textsuperscript{[11,18]}

At the Institut fur Mikroverfahrenstechnik (IMVT) in the Forschungszentrum Karlsruhe, the group of Schubert et al. developed a customised microstructured reactor of about shoe-box size for use at the company DSM Fine Chemicals GmbH in Linz/Austria\textsuperscript{[11][18]}. During a ten-weeks lasting production campaign over 300 tons of a
high-value product were manufactured for plastics industry. The central element of this new production plant is a microstructured reactor, made from a special Nickel alloy, being 65 cm long and 290 kg heavy. This device is operated at a throughput of 1,700 kg liquid chemicals per hour and transfer of a power of 100 kW. (see Fig. 29).

The pre-term 'micro' thus relates to the interior of the microstructured reactor; in the micro-mixer unit, the reactants are fed via several ten thousands of micro channels and thereafter react in such micro-flow patterned fluidic environment. In this way, a central reaction route at DSM is replaced, which was conducted before in a very large reactor tank encasing several thousands of explosive and corrosive chemicals. The micro-reactor yield could be increased thereby as compared to the former route; the process safety for handling the corrosive chemicals was still enhanced when using the micro-reactor process. The use of raw materials and the waste streams were reduced, improving the cost analysis and eco-efficiency of the process.

4 Conclusions

In this part, literature research about industrial application of microreactors has been carried out. Different types of microreactors utilized in pilot and industry have been presented, such as Cytos Pilot and college System, Corning Multi-Injection Microreactor, Starlam microreactor....The parameters and productivities of these microreactor systems have been summed up. The chemical reactions with very fast or slow kinetics, with highly toxic reactants or byproducts, with unstable intermediated and with highly exothermic behavior can profit from microreactor because of its accuracy control and high security. Then some examples of industrial production with microreactor have been introduced. We could conclude that the microreactors can largely improve the industrial productivity compared with the current classic reactor, and ensure the security of process.

However, as we have told, industry is not very active in publishing. Thus, one cannot expect that the ongoing developments can be shown with a similar degree of completeness, clarity and detailedness, as this is possible for reviewing scientific contributions from academy with a wealth of peer-reviewed papers. The information of major interest of what has been transferred to production and how do the companies make profit with the new technology is usually kept secret.
5 References


(b) T. Iwasaki and J.-I. Yoshida; Proceedings of the "8th International Conference on Microreaction Technology, IMRET 8", (10 - 14 April 2005); Atlanta, USA.

[13] Norbert Kockmann, Michael Gottsponer, Dominique M. Roberge, Scale-up concept of single-channel microreactors from process development to industrial production, Chemical Engineering Journal 167 (2011) 718–726


   http://pubs.acs.org/cen/coverstory/83/8322finechemicals.html

III  Literature research section 2:
heterogeneous catalytic microreactors

In the chemical phenomenon occurred in catalytic reactors, there are different steps of mass and heat transfer in the surface and inside of catalyst. These transfers depend on the type of reaction and catalyst, and also on the size of reactor and catalyst. Generally speaking, in microreactors, the reduction of size can modify the transfer rate, but it’s necessary to figure out that how the size influences the kinetic and transfer of microreactor, and whether the correlations in classic reactors are also applicable in microreactors.

In this part, many types of heterogeneous catalytic microreactors will be introduced, and their performances will be discussed and compared. The modeling studies of these microreactors will be presented. The correlations of mass transfer, heat transfer and pressure drop of different microreactors will be summarized.

1  Introduction of major parameters

1.1  Mass transfer

In a heterogeneous reaction sequence, mass transfer of reactants first takes place from the bulk fluid to the external surface of the pellet. The reactants then diffuse from the external surface into and through the pores within the pellet, with reaction taking place only on the catalytic surface of the pores. If a catalyst particle in an industrial reactor were operating with an extremely low turnover frequency, diffusive transport of chemicals to and from the catalyst surface would have no effect on the measured rates. If the chemical reaction proceeds very fast, the overall rate may be controlled by the transport of reactant from the fluid to the external surface of the catalyst particle or by diffusion inside the pores of the catalyst particle\[1,2\].

![Figure 30  Mass transfer and reaction steps for a catalyst pellet\[1\]](image-url)
1.1.1 External mass transfer

When a chemical reaction occurs on an active surface, the rates of intraparticle diffusion and chemical reaction are in steady state and simultaneously take place. For a given component “A”, the reaction rate in first order can be defined as:

\[ r_{Ai} = k_r C_{Ai} \]

where \( r_{Ai} \) is the reaction rate of the component “A” at surface (kmol/m\(_p^2\)s), \( k_r \) is the rate coefficient of the reaction (m\(_f^3\)/m\(_p^2\)s), \( C_{Ai} \) is the concentration of A at the surface (kmol/m\(_f^3\)). \[3\]


The consumption of A at the interface has to be compensated for by transport from the bulk fluid, the flux of which can be written:

\[ N_A = k_g (C_A - C_{Ai}) \]

where \( N_A \) is mass flux with respect to the fixed solid surface (kmol/m\(_p^2\)s), \( k_g \) is the mass transfer coefficient (m\(_f^3\)/m\(_p^2\)s), \( C_A \) is the concentration of A in bulk stream (kmol/m\(_f^3\)).

The two rates\( (r_{Ai} \text{ and } N_A) \) must be equal for steady state, and this is used to eliminate the unmeasured surface concentration \( C_{Ai} \)

\[ r_{Ai} = N_A = r_A \]

So,

\[ C_{Ai} = \frac{k_g}{k_r + k_g} C_A \]

and

\[ r_A = \left( \frac{1}{k_g} + \frac{1}{k_r} \right)^{-1} C_A = k_0 C_A \]

\( k_0 \) is the overall rate coefficient.

To relate the reaction time to the transport phenomena rate occurring in a reaction system, the Damköhler number can be defined as:

\[ Da = k_r C_0^{n-1} \tau \]

where \( C_0 \) is the initial concentration, \( n \) is the reaction order, \( \tau \) is the mean residence time.

In reacting systems that include interphase mass transport, the second Damköhler number (Da\(_{II} \)) is defined as the ratio of the chemical reaction rate to the mass transfer rate:

\[ Da_{II} = \frac{k_r C_0^{n-1}}{k_g S_a} \]

\( S_a \) is the interfacial area.
Löffler & Schmidt (1975)\textsuperscript{[3]} illustrated that in order to determine the reaction rates with only 10% error due to mass transfer, the Damköhler number (Da) should be less than 0.1.

The mass transfer coefficient, $k_g$, can be calculated by the correlations of the experimental data (Satterfield, 1970 as cited in Forni, 1999), between the Sherwood, Schmidt, and Reynolds numbers.

\[
\begin{align*}
    Sh &= k_c D_p / D_{AB} \\
    Sc &= \mu / (\rho \cdot D_{AB}) \\
    Re &= D_p \rho u_s / \mu
\end{align*}
\]

where, $D_p$ (m) is the diameter of the catalyst particle. $D_{AB}$(m$^2$ s$^{-1}$) is the diffusion coefficient or diffusivity of component A in component B. $\rho$ (g m$^{-3}$) and “$\mu$” (Pa.s) are the density and viscosity of the fluid, respectively. “$u_s$” (cm s$^{-1}$) is the superficial flow rate of the fluid referred to the overall cross section of the catalyst bed.

There are several correlations of the structure about the relationship of $Sh$, $Sc$ and $Re$:

\[ Sh = f(Re, Sc) \]

For example, for flow around spherical particles, the Sherwood number is correlated to the Schmidt number, $Sc$, and the Reynolds number, $Re$:

\[ Sh = 2 + 0.6 Re^{1/2} Sc^{1/3} \]

However, most mass-transfer results are correlated in terms of the $J_D$ factor proposed by Satterfield-Chilton-Colburn:

\[ j_D = k_g Sc^{2/3} / u \]

In the gas, if 3<Re,2000,

\[ j_D = \frac{0.357}{\varepsilon Re^{0.359}} \]

In the liquid,

If 0.006<Re<55,

\[ j_D = \frac{1.09}{\varepsilon Re^{0.67}} \]

If 55<Re<1500,

\[ j_D = \frac{0.250}{\varepsilon Re^{0.31}} \]

These $J$ factor plots are available in most textbooks on mass transfer. If one can estimate the fluid density, velocity, viscosity, diffusivity, and catalyst particle size, then a reasonable approximation of the mass-transfer coefficient can be found.
1.1.2 Internal mass transfer

According to the mole balance for diffusion and reaction inside the catalyst pellet as described by Fick's law, the internal diffusion rate "\(N_A\)" (mol m\(^{-2}\) s\(^{-1}\)) is defined as:

\[ N_A = -D_e \left( \frac{\partial C_A}{\partial z} \right) \]

where \(C_A\) is the number of moles of A per unit of the open pore volume, the effective diffusion coefficient (diffusivity) \(D_e\) (m\(^2\) s\(^{-1}\)) is given by:

\[ \frac{1}{D_e} = \frac{1}{D_{b,e}} + \frac{1}{D_{k,e}} \]

where \(D_{b,e}\) and \(D_{k,e}\) are the effective diffusion coefficients for bulk and Knudsen diffusions, respectively. They can be calculated using the equations as demonstrated by Satterfield (1970) as:

\[ D_{b,e} = \frac{D_b \theta}{\tau} \]

\[ D_{k,e} = 1.94 \times 10^4 \frac{\theta^2}{\tau S_g \rho_p} \sqrt{\frac{T}{M}} \]

where \(D_b\) (m\(^2\) s\(^{-1}\)) is the bulk diffusion coefficient, \(\theta\) is the internal void fraction of the solid particle, \(\tau\) is the tortuosity factor of the pores, \(S_g\) (m\(^2\) g\(^{-1}\)) is the specific surface area of the catalyst, \(\rho_p\) (g m\(^{-3}\)) is the particle density, \(T\) (K) is the reaction temperature, and \(M\) (g mol\(^{-1}\)) is the molecular mass of the diffusing species.

An effectiveness factor, \(\eta\), can be defined as the ratio of the observed rate of reaction for the particle as a whole to the intrinsic rate at the surface conditions:

\[ \text{Internal effectiveness factor} = \eta = \frac{\text{Actual rate of reaction}}{\text{Reaction rate if entire interior surface is exposed to concentration at the external pellet surface}} \]

The magnitude of the effectiveness factor is range from 0 to 1. For \(\eta\) near unity, the entire volume of the pellet is reacting at the same high rate because the reactant is able to diffuse quickly through the pellet. For \(\eta\) near zero, the pellet reacts at a low rate. The reactant is unable to penetrate significantly into the interior of the pellet and the reaction rate is small in a large portion of the pellet volume. The pellet’s diffusional resistance is large and this resistance lowers the overall reaction rate.

In the general procedure, a key step in estimating the catalyst effectiveness factor, \(\eta\), is the calculation of the dimensionless parameter, the Thiele modulus \(\phi\) or the Weisz
criterion $\Phi$. Both measure the relative rate of reaction to that of diffusion, that is, the reaction is said to be diffusionally constrained when the rate of diffusion can’t keep up with the rate of reaction. The Thiele modulus requires the knowledge of the intrinsic reaction rate constant and the kinetic order of the reaction, while the Weisz criterion is expressed in observable reaction rate terms without the need to know the detailed kinetics.\(^4\)

Thiele modulus is given by (for the first-order reaction):

$$\phi = L \left( \frac{k}{D_e} \right)^{1/2}$$

$L$ is the particle volume/external area (e.x. for the sphere, $L=V/S=d/6$ where $d$ is the diameter of sphere). $D_e$ is the effective diffusion coefficient = $D_m \varepsilon_p \tau$ where $D_m$ is the molecular diffusion, $\varepsilon_p$ the porosity, $\tau$ the tortuosity.

The Weisz-Prater Criterion is given by (for the first-order reaction):

$$\Phi = \eta \phi^2 = \frac{L^2 (-r_A)_{obs}}{C_{A_s} D_e}$$

Where $C_{A_s}$ the reactant concentration at the particle surface.

For large values of the Thiele modulus, the rate of reaction is much greater than the rate of diffusion, the effectiveness factor is much less than unity, and we say the pellet is diffusion limited. Conversely, when the diffusion rate is much larger than the reaction rate, the effectiveness factor is near unity, and we say the pellet is reaction limited. Figure 31 shows the relationship between the effectiveness factor and the Thiele modulus.

![Figure 31](image)

Effectiveness factor as a function of Thiele modulus $\phi$ for an isothermal particle

Three regions indicated: $\leftarrow G; G-H; H \rightarrow$\(^4\)
There are three regions:

1. Negligible pore-diffusion resistance (up to point G):
   \[ \phi < 0.5, \; \eta \to 1 \]
2. Significant pore-diffusion resistance (G-H):
   \[ 0.5 < \phi < 5, \; \eta = (\tanh \phi) / \phi \]
3. Strong pore-diffusion resistance (beyond point H):
   \[ \phi > 5, \; \eta \to 1/\phi \]

For a first order reaction and different particle shapes:

<table>
<thead>
<tr>
<th>Region</th>
<th>Slab ((\omega = x/x_p))</th>
<th>Cylinder (^{(a)}) ((\omega = \bar{r}/R_p))</th>
<th>Sphere ((\omega = \bar{r}/R_p))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\phi)</td>
<td>(x_p \sqrt{\frac{k}{D_{IA}}})</td>
<td>(R_p \sqrt{\frac{k}{D_{IA}}})</td>
<td>(R_p \sqrt{\frac{k}{D_{IA}}})</td>
</tr>
<tr>
<td>(\psi = C_A/C_{AS})</td>
<td>(\frac{\cosh(\phi \omega)}{\cosh(\phi)})</td>
<td>(\frac{I_0(\phi \omega)}{I_0(\phi)})</td>
<td>(\frac{\sinh(\phi \omega)}{\omega \sinh(\phi)})</td>
</tr>
<tr>
<td>(\eta)</td>
<td>(\frac{\tanh(\phi)}{\phi})</td>
<td>(\frac{2I_1(\phi)}{\phi I_0(\phi)})</td>
<td>(\frac{3}{\phi} \left[ \frac{1}{\tanh(\phi)} - \frac{1}{\phi} \right] )</td>
</tr>
</tbody>
</table>

\(^{(a)}i\) is a modified Bessel function of order \(i\).

**Figure 32** Influence of catalyst particle geometry on concentration profile and effectiveness factor for a first-order, isothermal, isobaric reaction\(^{(4)}\)

### 1.2 Heat transfer

Similarly, the fluid to particle interfacial heat transfer resistances can be described by:

\[ (-\Delta H) r_A = h_f a_m (T_S^5 - T) \]

The heat transfer coefficient \(h_f\) is also correlated with respect to the Reynolds number by means of a \(j\)-factor expression:

\[ j_H = h_f Pr^{2/3} / c_p \rho u \]

where
- \(c_p\) is the mass heat capacity
- \(Pr\) is the Prandtl Number, \(Pr = \mu c_p / \lambda\)

For 15 < \(\text{Re} < 1500\), \(j_H = 1.2 j_0\)

Similarly with the Sherwood \(Sh\) presented, the Nusselt number can be used to calculate the heat transfer coefficient. Nusselt number is obtained from:
\[ \text{Nu} = \frac{h \cdot d_p}{\lambda} \]

where \( \text{Nu} \) is the Nusselt number, \( \lambda \) is the thermal conductivity and \( d \) is the diameter of grain.

The heat transfer coefficient in is usually formulated in terms of the dimensionless groups:

\[ \text{Nu} = f(\text{Re}, \text{Pr}) \]

\( \text{Re} = \text{Reynolds Number} \)
\( \text{Pr} = \text{Prandtl Number} \)

In many cases, the mechanisms of heat and mass transfer are similar, the Chilton-Colburn analogy (Westerterp et al., 1984) is often used:

\[ \text{Nu} = \text{Sh} \left( \frac{\text{Pr}}{\text{Sc}} \right)^{1/3} \]

Plenty of other correlations have been given to establish the relationship between these dimensionless numbers.

Concentration and temperature gradients between the catalyst exterior surface and the fluid are usually negligible in commercial reactors. For very moderate reactions with moderate heat effects, it may not be necessary to distinguish between the conditions in the gas and on the catalyst surface, or even inside the catalyst.

In pseudo-homogeneous models, it is assumed that inter-phase composition and temperature gradients are sufficiently small. Nakamura et al. (1970) have shown that the catalyst surface reaction is the rate-determining step. Therefore, in most of research, we can assume that diffusion effects inside the catalyst are lumped into the kinetic parameters of the reaction rate expressions. The above assumption can be justified by using Mears' criterion (1971) for detecting the onset of interphase gradients. If the following Mears criterion is satisfied, then the observed reaction rate will deviate less than 5 % from the true chemical rate\(^6\)

\[ \frac{(-\Delta H) \cdot r \cdot \rho_b \cdot d_j}{2 \cdot h_f \cdot T} < 0.15 \cdot \frac{RT}{E}. \]

Therefore, the interphase gradients can be easily neglected in the model equations

### 1.3 Pressure drop

Pressure drop is an important parameter in the process design and performance of microreactors as it affects the energy requirements and hence the operating cost and sizing of the reactor.
Operations of multiphase processes, especially packed-bed reactors, are always associated with pressure losses because of the inner design of the reactors. Pressure drop represents the energy dissipated caused by fluid flow through the reactor bed. High pressure drop through the system not only requires high energy input to the system, it also prohibits the unit from being operated at high gas and liquid velocities, and thus the throughput is limited. Starting from Ergun (1952), the estimation of pressure drop along packed beds has been well documented over the years.

For example, The pressure drop through a gas-solid packed bed can be described by the equation first proposed by Ergun (1952)\cite{30} and corroborated by many later workers:

\[ \frac{-\Delta P}{H} = 150 \frac{\mu U (1 - \varepsilon)^2}{x^2 \varepsilon^2} + 1.75 \frac{\rho_f U^2 (1 - \varepsilon)}{x \varepsilon^2} \]

H: Height of the packed bed (m)
x: Spherical equivalent particle diameter (m)
\(\varepsilon\): Bed voidage
\(\rho_f\): Density of the fluid flowing through the packed bed (kg/m\(^3\))
U: Superficial fluid velocity (m/s)
\(\mu\): Viscosity of the fluid flowing through the packed bed (Pa.s)

in which the total energy loss in the fixed bed is treated as the sum of kinetic energy loss \(1.75 \frac{\rho_f U^2 (1 - \varepsilon)}{x \varepsilon^2}\) and viscous energy loss \(150 \frac{\mu U (1 - \varepsilon)^2}{x^2 \varepsilon^2}\).

\section{Packed-Bed microreactors}

Filling microchannels with catalyst powders or pellets is the easiest way to incorporate the catalyst into MR. The micropacked-bed is commonly used for catalyst screening. But there are also examples for the use of micropacked-beds for the distributed production of chemicals. In catalyst activity testing, packed-bed microreactors are the most commonly used devices.

The advantage of packed-bed microreactors stems from the fact that traditional and optimized catalyst can be easily implicated. And the packed bed microreactors also have advantages such as high catalyst loading, fairly easy characterization and quantification of the catalyst, a large range of catalytic supports, and easy fabrication of the catalytic device by filling the channels with functional catalytic particles. However, limitations can be uncontrolled fluid dynamics, heat transfer limitation and
significant pressure drops developing along the microchannel.\[8\]

### 2.1 Research status of packed-bed microreactor modeling

Ayman Karim et al.\[10\] have compared the performance of a packed-bed microreactor to a wall-coated microreactor for steam reforming of methanol on a commercial CuO/ZnO/Al\(_2\)O\(_3\) catalyst. They have developed a 2D pseudo-homogeneous model of the packed-bed reactors to study the impact of reactor size on the apparent catalyst activity. They also used a 2D model for the wall-coated reactor to study the effect of catalyst wall-coating thickness and that of reactor diameter on the apparent catalyst activity. The diameter of the reactor they used is from 1mm, 1.75mm and 4.1mm.

Their modeling results show that the reactor productivity per weight of catalyst is independent of reactor diameter and catalyst coating thickness. For the same reactor diameter, the thicker the catalyst coat the higher the reactor volumetric productivity.\[10\]

The reactivity results showed that the packed bed reactor suffered from significant temperature gradients, and this was confirmed by the analysis of heat transfer limitation using a 2D pseudo-homogeneous model. The wall-coated reactor was shown to be free from any transport limitations. Their modeling results showed that a 530 mm reactor with 95 mm coating thickness is isothermal and free from diffusion limitation. They also found that their coating process does slightly lower the catalyst activity, however, they believe that the wall-coated reactor still offers a better solution to achieve high catalyst activity without the penalty of pressure drop.\[10\]

Teuvo Kilpiö et al.\[11\] have presented a modeling study for the direct synthesis of hydrogen peroxide with methanol as the solvent in a continuous three-phase packed-bed reactor. The modeling study used data from an experimental study performed with a Pd/CeS catalyst in a reactor with the diameter of 1.15cm.

Fig.34 presents the parameter values used in their experiments.
<table>
<thead>
<tr>
<th>variable</th>
<th>values</th>
<th>units</th>
</tr>
</thead>
<tbody>
<tr>
<td>liquid feed flow rate</td>
<td>0.5, 0.75, 1.0, and 2</td>
<td>mL/min</td>
</tr>
<tr>
<td>gas feed flow rate</td>
<td>0.5, 1, 2, 7, 4, 6, 9, and 12 (whole-reaction-set studies)</td>
<td>mL/min</td>
</tr>
<tr>
<td></td>
<td>0.5, 1, 2, 7, 4, 6 (separate decomposition studies)</td>
<td>mL/min</td>
</tr>
<tr>
<td>pressure</td>
<td>10 and 20</td>
<td>bar</td>
</tr>
<tr>
<td>temperature</td>
<td>263</td>
<td>K</td>
</tr>
<tr>
<td>catalyst particle size</td>
<td>0.5–1</td>
<td>mm</td>
</tr>
<tr>
<td>H$_2$O$_2$ concentration in the liquid feed</td>
<td>0.00 (whole-reaction-set studies)</td>
<td>mol/L</td>
</tr>
<tr>
<td></td>
<td>0.125 (separate decomposition studies)</td>
<td>mol/L</td>
</tr>
<tr>
<td>reactor diameter</td>
<td>1.15</td>
<td>cm</td>
</tr>
<tr>
<td>catalyst bed length</td>
<td>0.5</td>
<td>cm</td>
</tr>
</tbody>
</table>

Figure 34  Parameter Values Used in the Experiments$^{[11]}$

They have also proposed the steps of modeling work:

1. Data Selection Based on Focus and Consistency

- focus of the direct- and total-decomposition studies: complete ranges of flow rates studied
- focus of the whole-reaction-set study: higher-selectivity and productivity conditions
- data filtering: inconsistent data removed (needed only for the whole-reaction-set study)

2a. Experimental Reactor Data

- direct decomposition
- total decomposition
- all four reactions

2b. Separate Reactor Models

- direct decomposition (single-reaction model)
- total decomposition (model with two reactions)
- whole reaction set (model with all four reactions)

2c. Results of Each Reactor Model

- direct-decomposition rate parameter
- hydrogenation rate parameter
- synthesis and oxidation rate parameters
- liquid hold-up parameters
- gas–liquid mass-transfer parameters
- flow-rate correction parameters (required because of operation in the higher-flow-rate interaction regime)

3. Tracer Test Data and Model

- test data for the whole reactor setup (including the catalyst or having the catalyst replaced by fine sand)
- main result of the tracer tests: estimate for the Peclet number (then used in all reactor models)

4. Separate Particle Model (All Four Reactions Included)

- main result of the particle model: estimate for the effectiveness improvement potential
- Damköhler analysis done to verify the numeric particle model for each reaction separately

Figure 35  Modeling Steps$^{[11]}$
R. Rajasree et al.\textsuperscript{[12]} have studied the steam methane reforming (SMR) process using a dynamic 2D pseudo homogeneous model. The key chemical reactions of the SMR process are given by:

\[
\begin{align*}
\text{CH}_3 + \text{H}_2\text{O} & \rightleftharpoons \text{CO} + 3\text{H}_2, \quad \Delta H_{298} = 206.2 \text{ kJ/mol} \\
\text{CH}_4 + 2\text{H}_2\text{O} & \rightleftharpoons \text{CO}_2 + 4\text{H}_2, \quad \Delta H_{298} = 164.9 \text{ kJ/mol} \\
\text{CO} + \text{H}_2\text{O} & \rightleftharpoons \text{CO}_2 + \text{H}_2, \quad \Delta H_{298} = -41.1 \text{ kJ/mol}
\end{align*}
\]

The mathematical model used to describe the SMR reactor with adsorbent dilution is a dynamic 2D pseudo homogeneous model that considers the nonisothermal, nonadiabatic, and nonisobaric nature of operation. Many model assumptions have been used. The reactor diameter studied is from 25 mm to 2 mm, keeping a catalyst loading of 6.45 g. The reaction was assumed to be carried out at $T_f = 773$ K.

Ivana Denčić et al.\textsuperscript{[13]} have published the first engineering paper on enzymatic microreactors that gives a complete kinetic description, clear-cut benchmarking to a batch process, study on enzyme stability, and an outline on enzymatic microreactor production performance. The transesterification of ethyl butyrate with butyl butyrate was studied in a batch reactor and in a packed-bed microreactor with Novozym 435 as a catalyst. A tubular reactor with an inner diameter of 4.5 mm and a length of 103 mm was packed with 635–660 mg of Novozym 435 beads with diameters of 500–710 μm by introducing the beads with a funnel and tapping on the side of the reactor.

The packed-bed microreactor allows for higher specific enzyme loading and shorter diffusion pathway than that of the batch reactor, therewith enabling higher overall conversion and higher reaction rate per unit of catalyst volume. A benchmarking between the batch reactor and the microreactor performance is illustrated in following figure.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Batch Reactor</th>
<th>Microreactor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactor volume, mL</td>
<td>100</td>
<td>1.64</td>
</tr>
<tr>
<td>Enzyme loading, mg</td>
<td>350</td>
<td>660</td>
</tr>
<tr>
<td>Maximum conversion, %</td>
<td>87</td>
<td>99.9</td>
</tr>
<tr>
<td>Residence time, min</td>
<td>30</td>
<td>4</td>
</tr>
<tr>
<td>Observed activity, mol/(m$^3$CALB/s)</td>
<td>0.34</td>
<td>0.42</td>
</tr>
</tbody>
</table>

This work demonstrates that how a milliscale packed-bed reactor can be used for complex chemistries, such as transesterification by providing good mixing and controlled reaction conditions. If expensive enzymatic catalysts are used, continuous packed-bed operation is more favorable than that of batch because it eliminates high shear and enzyme erosion. The described packed-bed microreactor could also be used for evaluation of process parameters for industrially important
enzyme-catalyzed processes, because a wide range of process conditions could be tested in a short period of time.

Andrej Pohar et al.\textsuperscript{[14]} have studied the methanol decomposition on Pt/CeO\textsubscript{2}/ZrO\textsubscript{2} catalyst inside a packed bed microreactor in the temperature range of 300-380 °C. A 1D mathematical model, which incorporates diffusion, convection and mass transfer through the boundary layer to the catalyst particles, as well as a 3D computational fluid dynamics model, are developed to describe the methanol decomposition process inside the packed bed.

The microreactor (Fig. 37) consisted of inflow and outflow ports for fluidic connections (ϕ 2.6 mm), 4 mounting ports (ϕ 4.5 mm), and a service port for the insertion of the catalytic spheres. The use of spherical catalyst particles for the packed bed is advantageous, since closed areas inaccessible to the flow and stagnant zones are less likely to exist. The catalytic bed had the dimensions 33.8 * 3 * 41.4 mm (width * depth * length), which yielded approximately 4.2 cm\textsuperscript{3} reaction chamber space. The total microreactor size was 63.8 * 6 * 41.8 * mm.

![Figure 37](image-url) (a) The bottom layer of the LTCC (Low-temperature co-fired ceramic) microreactor displaying the catalytic bed with a grate at the inlet and outlet. (b) The assembled LTCC microreactor with metal fittings. (c) The model of the microreactor; units in meters. (d) A close-up of the grate connecting the inlet channel with the reaction chamber \textsuperscript{[14]}

Parham Sadooghi and Reinhard Rauch\textsuperscript{[15]} have reported a two dimensional heterogeneous model simulation and experimental study of steam reforming of methane mixture with propylene in a packed bed reactor filled with nickel based catalysts. The outside diameter of the reactor is 8 mm and the inside diameter of the
reactor is 7 mm. The height of the catalyst in the reactor is 0.1 m. The inlet temperature is 973K.

\[
\begin{align*}
\text{CH}_4 + \text{H}_2\text{O} & \leftrightarrow \text{CO} + 3\text{H}_2 \quad \Delta H_{298}^0 = +206 \text{ kJ/mol} \\
\text{CO} + \text{H}_2\text{O} & \leftrightarrow \text{CO}_2 + \text{H}_2 \quad \Delta H_{298}^0 = -41 \text{ kJ/mol} \\
\text{CH}_4 + 2\text{H}_2\text{O} & \leftrightarrow \text{CO}_2 + 4\text{H}_2 \quad \Delta H_{298}^0 = +165 \text{ kJ/mol} \\
\text{C}_3\text{H}_6 + 6\text{H}_2\text{O} & \leftrightarrow 3\text{CO}_2 + 9\text{H}_2 \quad \Delta H_{298}^0 = +110 \text{ kJ/mol}
\end{align*}
\]

Modeling result shows that high temperature gradients exist near the wall toward the center of the reactor at each axial position and are more significant close to the reactor entrance.

Air-water co-current (horizontal) flow experiments were carried out by Ion Iliuta et al.\cite{16} to measure pressure drop and liquid hold up in a 1 mm(ID) diameter glass tube packed with 55 mm nearly monodisperse glass spheres.

The measurements allowed calibration of a two-dimensional hydrodynamic model based on the volume-averaged mass and momentum balance equations to describe the concurrent two-phase flow in packed bed microreactors.

The model shows a significant sensitivity of two-phase flow with respect to capillary pressure, which has a tendency to help liquid spreading across the porous medium. The capillary pressure causes the liquid phase to displace from the high-porosity
region to the low-porosity region of the bed and as result a smaller/higher fraction of liquid/gas flowing through the micro-reactor cross section is subject to channeling. This leads to an increase/decrease of liquid/gas flow through the core area.

Two-phase pressure drop is very large, particularly for particles with small diameter, and is significantly influenced by capillary forces, especially at higher reactor-to-particle diameter ratios.

Bruno Tidona et al.\cite{17} have studied the liquid-to-particle mass transfer in micro packed beds of different hydraulic to particle diameter ratio $N$ and different channel geometries, i.e. circular and rectangular, with the copper dissolution method.

In this paper, they have demonstrate that the shape of the channel has no influence on the liquid-to-particle mass transfer as long as $N$ is constant. Moreover, higher Sherwood numbers were measured with increasing $N$ for $4 < N < 24.4$, but the opposite influence was observed for $N < 4$. In the case of $N > 4$ we highlight that the channeling effect, i.e. higher velocities in the wall region compared to the center of the packed bed, has a main impact on the mass transfer. For $N < 4$ the packed bed cross section cannot be differentiated anymore in a wall region and a center region, hence there is no wall effect and a better flow distribution through the packed bed cross section is induced which increases mass transfer, as proposed in this paper.

**Figure 39** Left: top view of the 250 $\mu$m*1000$\mu$m microreactor with copper particles, filter and outlet (dashed circle). Right: Qualitative sketch (drawn to scale) of the (a, b) 400$\mu$m*360$\mu$m and (c, d) 1000$\mu$m*250$\mu$m silicon/glass microreactor with (a, c) 75$\mu$m and (b, d) 149$\mu$m copper particles.\cite{17}

They also have discussed the calculation of porosities. They validated and compared the measured porosities with the equations of Tsotsas and Schlünder which were adapted from the empirical formula of Dixon.

$$
\varepsilon = 0.37 + \frac{0.05}{N} + \frac{1.0867}{N^2} \quad \text{(loose packing)}
$$
Minjing Shang et al.\textsuperscript{[18]} have described a new microflow process for the synthesis of adipic acid starting from cyclohexene and hydrogen peroxide in a packed-bed microreactor.

\[
\varepsilon = 0.37 + \frac{0.05}{N} + \frac{0.5344}{N^2} \quad \text{(dense packing)}
\]

What’s more, they have compared the batch reaction and flow reaction in packed bed microreactor.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Reactor</th>
<th>Residence time [min]</th>
<th>STY [kg L(^{-1}) h(^{-1})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Batch reactor [8]</td>
<td>480</td>
<td>0.03</td>
</tr>
<tr>
<td>2</td>
<td>Packed-bed microreactor</td>
<td>20</td>
<td>0.57</td>
</tr>
</tbody>
</table>

Figure 41  Comparison between batch reaction and flow reaction on the isolated yield of adipic acid\textsuperscript{[18]}

It is immediately clear that the direct oxidation reaction of cyclohexene to adipic acid in a packed-bed microreactor greatly improves the space time yield.

### 2.2 Summary of packed-bed microreactor modeling

#### 2.2.1 Mass transfer

In general, the mass transfer in a packed bed operating in the trickling-flow regime is not at all precisely known, and very broad ranges of mass-transfer coefficients have been observed.\textsuperscript{[11]}

Ivana Denčić et al.\textsuperscript{[13]} have calculated the mass-transfer coefficient \((k_c)\) at the liquid–solid interface using the correlation below, from Ratering et al.\textsuperscript{[19]}

\[
k_c\left(\frac{d_p + 2\delta}{D_{eff}}\right) = \left[2^{5.8} + \left\{0.61\left(\frac{1}{v}\right)\left(\frac{d_p + 2\delta}{D_{eff}}\right)^{4/3}\right\}^{0.58}\left(\frac{v}{D_{eff}}\right)^{1/3}\right]^{5.8}^{1/5.8}
\]
where \( d_p \) the average catalyst diameter not including catalyst shell, \( D_{\text{eff}} \) effective diffusivity, \( \delta \) catalyst shell thickness, \( \epsilon \) power input of the impeller, \( \nu \) kinematic viscosity.

They have also used the correlation from Dwivedi and Upadhyay\(^{[20]}\), where the authors correlated mass-transfer in fixed beds with particle Re number as

\[
\epsilon J_d = \frac{1.043}{Re^{0.82}} + \frac{0.95}{Re^{0.46}}
\]

where

\[
J_d = \frac{k_c}{u} Sc^{2/3}
\]

and

\[
Re = \frac{\rho u (d_p + 2\delta)}{\mu \epsilon}
\]

The effective diffusion coefficient of a certain compound in a resin particle depends on the value of the molecular diffusion coefficient of that compound in the pure liquid, porosity of the particle, and the tortuosity factor:

\[
D_{\text{eff}} = D \frac{\epsilon_{\text{cat}}}{\tau}
\]

The mass transfer coefficients \((k_{c,i})\) were calculated by Andrej Pohar et al.\(^{[14]}\) from the correlation for the Sherwood numbers \((Sh_i)\) through an expression proposed by Comiti et al.\(^{[21]}\) at each longitudinal position of the channel:

\[
Sh_i = 3.66 + 0.101 \left( 1 + \frac{\pi(1 - \epsilon)}{4\epsilon} (\tau - 1) \right)
\]

\[
\times \left( 1 + \frac{\epsilon}{\tau^2} Sc^3 \exp \left( - \frac{1 - \epsilon}{3\epsilon} \sqrt{\tau Y X_{ew}} \right) \right) \left( X_{ew} \right)^{11} \frac{1}{48} Sc^{1/3}
\]

\[
k_{c,i} = \frac{Sh_i D_i}{D_p}
\]

The equation is valid for laminar and turbulent flow at \(0.03 < Re < 10^5\). \( \tau \) represents tortuosity, which is the ratio of the actual length of the flow path to the straight-line distance between the ends of the flow path, and is therefore \( \pi/2 \) for spherical particles. \( Y \) is the particle aspect ratio, defined in the direction normal to the flow, and is equal to 1 for spheres. \( X_{ew} \) is the dimensionless wall energetic criterion, which can be calculated for porous media

\[
X_{ew} = 64 Re^2 (1 + 1.21 \times 10^{-2} Re)
\]

The Reynolds number, for fluid flow in a packed bed of approximately spherical particles, is:

\[
Re = \frac{\rho V_s D_p}{\eta (1 - \epsilon)}
\]

where \( V_s \) is the superficial velocity of the flow.

The diffusion coefficients of binary gas mixtures were calculated with a diffusion
volume correlation method, developed by Fuller et al. [22]:

\[ D_{AB} = \frac{10^{-7}T^{1.75}(1/M_A + 1/M_B)^{1/2}}{P \left( \sum_{A} v_j \right)^{1/8} + \left( \sum_{B} v_j \right)^{1/8}} \]

in which case \( D_{AB} \) is in the units of \( \text{cm}^2 \text{s}^{-1} \), \( P \) is the pressure in atm, and \( v_j \) is a special atomic diffusion volume parameter, provided in the reference for each constitutive atom of the gas.

Sherwood values measured in the work of Bruno Tidona et al. [17] were compared to the correlation of Wakao and Funazkri [23]

\[ Sh = 2 + 1.1Re_0^{0.6}Sc^{1/3} \]

which can be applied in a large range of Reynolds number: \( 3<Re<10000 \)

and the correlation of Gnielinski [24]

\[ Sh_{Gn} = f_ε [2 + \sqrt{Sh_1^2 + Sh_2^2}] \]

with

\[ Sh_1 = 0.664Re^{1/2}Sc^{1/3} \]

\[ Sh_2 = \frac{0.037Re^{0.8}Sc}{1 + 2.443Re^{-0.1}(Sc^{2/3} - 1)} \]

\[ Re = \frac{Re_0}{ε} \]

and

\[ f_ε = 1 + 1.5(1 - ε) \]

Thoenes and Kramers, 1958, determined mass transfer coefficients in packed beds of spheres with flowing liquid and gas. A distinction is made between laminar, turbulent and stagnant contributions, which appear in this order: [25]

\[ Sh = \left( 1.26Re^{1/3}Sc^{1/3} \right) + \left( 0.054Re^{0.8}Sc^{0.4} \right) + 0.8Re^{0.2} \]

They have also proposed the correlation following for packed-bed reactors [69,76]:

\[ Sh = \frac{(1 - ε_b)^{1/2}}{ε_b}Re^{1/2}Sc^{1/3} \]

It is a semi-empirical correlation widely used for predicting the mass transfer coefficients in packed beds with \( 40 < Re_\mu/(1-ε_b) < 4000 \) and \( 0.25 < ε_b < 0.5 \).

Yoshida et al. [26] proposed these correlations to represent the Sherwood number in heterogeneous gas-solid packed bed reactor in terms of \( j \)-factor:[27]

\[ J_m = \frac{0.91}{Re^{0.51}\Psi} \quad Re < 50 \]
The effectiveness factor was calculated from the concentration profiles inside the particle with the equations.\cite{11}

\[ \eta_{e,i} = \frac{\sum_{x=1}^{M} (r_{i,x}) V_{x}}{r_{i,S} V_{p}} \]

The analysis based on the Damkohler number was first applied for each reaction to reveal the reaction rate at which particle diffusion started to influence the process. A general Damkohler number definition for power-law kinetics, namely

\[ \Lambda_{i,j} = \frac{v_{i,j} k_{j} C_{i,S} e^{a} C_{B_j,S}^{b_j}}{(D_{e,i} / R^2) C_{i,S}} \]

was used for this analysis.

where

- \( R \) characteristic mean radius of catalyst particles (m)
- \( r_{i,S} \) the total reaction rate of component i at the particle surface (mol/L.s)
- \( r_{i,x} \) the total reaction rate of component i at step x (mol/L.s)
- \( V_{p} \) particle volume (m\(^3\))
- \( V_{x} \) volume of the xth element of a particle (m\(^3\))
- \( v_{i,j} \) the stoichiometric coefficient of component i in reaction j
- \( b_j \) kinetic power-law parameter of reaction j
- \( D_{e,i} \) effective diffusivity of compound i (m\(^2\)/s)

The intraparticle transport rates in packed beds were modeled using the following effectiveness factor equations:\cite{76}

\[ \eta = \frac{1}{\Phi} (\coth(3\Phi) - 1/3\Phi) \]

where

\[ \Phi = \left( \frac{\phi_{p} d_{p}}{6} \right) \sqrt{\frac{k_{r} \rho_{c}}{D_{e}}} \]
To determine whether the pore diffusion limits the reaction rate, the Weisz modulus is calculated\(^{[13][19]}\)

\[
\Phi = a_c^{-1} \frac{n + 1}{2} \frac{(-r_{obs})}{D_{eff} C_{As}}
\]

where the specific surface area \((a_c)\) is

\[
a_c = \frac{6}{\varepsilon_{CALB,p} (d_p + 2\delta)}
\]

and the fraction of the particle containing enzyme is

\[
\varepsilon_{CALB,p} = 1 - \frac{d_p^3}{(d_p + 2\delta)^3}
\]

If \(\Phi > 3\) reaction is diffusion limited, whereas for \(\Phi < 0.1\), reaction is kinetically limited.

The following table represents the summary of correlation of mass transfer:

<table>
<thead>
<tr>
<th>Author and reference</th>
<th>Correlation</th>
<th>Explication</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ivana Denčić et al. [13]</td>
<td>(\varepsilon J_d = \frac{1.043}{Re^{0.82}} + \frac{0.95}{Re^{0.46}})</td>
<td>Re = (\frac{\rho u (d_p + 2\delta)}{\mu \varepsilon}) For 0.03 &lt; Re &lt; 10(^5)</td>
</tr>
<tr>
<td>Comiti et al. [21]</td>
<td>(Sh_i = 3.66 + 0.101 \left( 1 + \frac{\pi(1-\varepsilon)}{4\varepsilon} (\tau - 1) \times \left( 1 + \frac{\varepsilon}{\tau^2} Sc^2 \exp \left( \frac{1-\varepsilon}{3\varepsilon} \sqrt{\frac{Sc}{Sc^2 + 1}} \right) \right) \right) Xe_w^{1/2} Sc^{1/3} )</td>
<td>For 3 &lt; Re &lt; 10(^4)</td>
</tr>
<tr>
<td>Wakao and Funazkri [23]</td>
<td>(Sh = 2 + 1.1 Re_0^{0.6} Sc^{1/3})</td>
<td>(Sh_1 = 0.664 Re^{1/2} Sc^{1/3})</td>
</tr>
<tr>
<td>Thoenes and Kramers [25]</td>
<td>(Sh = (1.26 Re^{1/3} Sc^{1/3}) + (0.054 Re^{0.8} Sc^{0.4}) + 0.8 Re^{0.2})</td>
<td>(Sh_2 = \frac{0.037 Re^{0.8} Sc}{1 + 2.443 Re^{-0.1} (Sc^{2/3} - 1)}) 40 &lt; Re(_p)/((1-\varepsilon_b) &lt; 4000 and 0.25 &lt; \varepsilon_b &lt; 0.5)</td>
</tr>
<tr>
<td>Thoenes and Kramers [69,76]</td>
<td>(Sh = \left( \frac{1 - \varepsilon_b}{\varepsilon_b} \right)^{1/2} Re^{1/2} Sc^{1/3})</td>
<td>50 &lt; Re &lt; 1000</td>
</tr>
<tr>
<td>Yoshida et al. [26]</td>
<td>(J_m = \frac{0.91}{Re^{0.51}} \Psi)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(J_m = \frac{0.61}{Re^{0.41}} \Psi)</td>
<td></td>
</tr>
</tbody>
</table>

46
2.2.2  Heat transfer

The wall heat transfer coefficient is commonly defined as the sum of a flow-dependent and a flow-independent heat transfer coefficient:

\[ \alpha_w = \alpha_w^0 + \alpha_w^f \]

In correlations, \( \alpha_w \) is usually expressed in the form of a dimensionless Nusselt number \( N_u \):

\[ N_u = \frac{\alpha_w d_p^0}{\lambda_f} \]

A correlation for the heat transfer coefficient at the wall at low Reynolds number (\( Re < 20 \)) is given by

\[ \frac{h_w d_p}{\lambda_g} = \frac{h_w^0 d_p}{\lambda_g} + \alpha_w (Pr Re) \]

where \( h_w^0 \) is the heat transfer coefficient at \( Re = 0 \); \( \alpha_w \) = mass velocity in the direction of heat transfer near the wall surface=mass velocity based on area of the empty tube in the direction of fluid flow.

For packed beds, Yagi and Kunii\[^{10}\][\(^{28}\)] reported

\[ \alpha_w = 0.054 \]

It can be seen from the above equations that the heat transfer coefficient at the wall at low Peclet number (\( Pe = Re Pr \)) will be equal to that of a stagnant gas. For packed beds Yagi and Kunii reported that the Nusselt number at the wall in a stagnant gas (\( N_u^0_w = h_w^0 d_p = \lambda_g \)) ranged from 1.2–8.

Wall heat transfer coefficient is calculated using the correlation reported by Peters et al.\[^{15}\][\(^{29}\)].

\[ N_u = 5.1 \left( \frac{d_0}{d_i} \right)^{0.26} Re_p^{0.45} Pr_p^{0.33} \]

In the approach of Dixon and Cresswell, 1979, the effective wall heat transfer coefficient is closely related to the effective thermal conductivity. The full expression of the wall heat transfer coefficient is rather extensive and contains parameters as the fluid-to-particle heat transfer coefficient and a solid-Biot number\[^{25}\]

\[ Bi_s = \frac{\alpha_w s R_t / \lambda_f^0}{\lambda_f / \lambda_f} \]

\[ N_u = \frac{8 \beta}{N} + Nu_w^f (1 + \beta \frac{Pe_r^f}{Pe_h^f}) \]

\[ \beta = \frac{\lambda_f / \lambda_f}{8 N_s + \frac{Bi_s}{Bi_s} + 4} \]
\[ N_s = \frac{1.5(1 - \varepsilon)N^2}{\frac{\lambda_r}{\lambda_f} \left( \frac{1}{\mathrm{Nu}_p} + \frac{0.1}{\lambda_s/\lambda_f} \right)} \]

Instead of this correlation, the authors recommend to correlate the wall heat transfer coefficient to the effective radial thermal conductivity of the bed in terms of the Biot number:

\[ \mathrm{Bi} = \frac{\alpha_w R_t}{\lambda_{e,r}} = 1.5 N Re^{-0.25} \]

The use of correlations of \(\alpha_w\) in terms of the Biot number is to be preferred to the commonly used expressions for the wall Nusselt number.

### 2.2.3 Pressure drop

Generally, the pressure drop for spherical packing in a packed bed reactor was calculated with the Ergun equation\[30\]

\[ \frac{dP}{dx} = -\frac{G}{\rho D_p} \left( \frac{1 - \varepsilon}{\varepsilon} \right) \left( \frac{150(1 - \varepsilon)\eta}{D_p} + 1.75G \right) \]

which takes into account the characteristics of the packing (void fraction \(\varepsilon\), particle diameter \(D_p\)), the characteristics of fluid properties (viscosity \(\eta\), density \(\rho\)), and the characteristics of the operating parameters (mass velocity \(G\)).\[14\]

Momentum equation which shows the pressure distribution in the packed-bed reactor was described by the Tallmadge who proposed an extension of Ergun’s equation\[30\] under higher Reynolds numbers,\[15\][31]

\[ \frac{dp}{dz} = -f \frac{\rho u^2}{dp} \]

\[ f = \left( \frac{1 - v}{v^3} \right) \left[ 1.75 + \frac{4.2(1 - v)}{Re^{1/6}} \right] \]

### 3 Wall-Coated microreactors and macro-monolithinc reactors

Multichannel reactors with catalytically active walls were proposed in order to avoid high-pressure drop in packed-bed microreactors. Wall-coated microreactors can
substantially minimize the mass transfer resistance and ensure smooth inflow of reagents without leading to any adverse pressure drop or blockage of microchannels. Besides, well-defined flow geometries are observed in wall-coated microreactors, which contribute to predicting the fluid dynamics, and the heat and mass transfer properties inside the reactor.

In spite of good flow-through properties observed in this method, in general, the catalyst loading is lower compared to the other two approaches, owing to a monolayer/thin film of the catalyst supported on the inner walls of a microreactor. In order to overcome this shortfall, different methodologies such as tethering of polymer brushes and deposition of inorganic porous material on the microchannel surface to increase the catalyst loading were adopted. [8]

Microchannels with reactive walls can be found in many applications in the fields of energy generation, environmental protection, synthesis of fine chemicals and bio-transformations. The behavior of these heterogeneous systems is mainly determined by the following mechanisms: convection in single phase channel flow, diffusion towards the walls and inside the coating, and reaction in the catalyst. [42]

Monolith catalysts were first developed in the 1970s for treating automotive exhaust gas. The monolith, which is fabricated on ceramic supports in a honeycomb arrangement, often consists of a matrix of uniformly parallel channels with inside dimensions of roughly 1−2 mm. The surface of each channel is usually covered with a porous washcoat containing the catalyst. Therefore, the traditional macro-monolith can be regarded as the multi-microchannel reactors with catalytic walls.

\[8\]

In this part, the modeling of both the wall-coated microreactors and macro-monolithic reactors will be presented.

### 3.1 Research status of wall-coated microreactor modeling

O. Gorke et P. Pfeifer[32] have demonstrated the successful application of a wall-coated microchannel reactor to produce hydrogen by ethanol reforming.
Microchannels coated with Rh/CeO₂ catalyst were used at residence times of 9–42 ms. Reaction temperatures were 350–660 °C. The model and experiments were in good agreement for a wide range of ethanol and water partial pressures, steam to carbon ratios, and temperatures.

<table>
<thead>
<tr>
<th>Channel width</th>
<th>200 μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Channel height</td>
<td>200 μm</td>
</tr>
<tr>
<td>Fin width</td>
<td>100 μm</td>
</tr>
<tr>
<td>Channels per foil</td>
<td>100</td>
</tr>
<tr>
<td>Length of foil</td>
<td>80 mm</td>
</tr>
<tr>
<td>Width of foil</td>
<td>40 mm</td>
</tr>
<tr>
<td>Number of foils</td>
<td>9</td>
</tr>
<tr>
<td>Height of stack</td>
<td>2.7 mm</td>
</tr>
<tr>
<td>Channel volume of stack</td>
<td>2,880 mm³</td>
</tr>
<tr>
<td>Coated surface of stack</td>
<td>43,200 mm²</td>
</tr>
</tbody>
</table>

Figure 43  Geometry data of the microstructured body[32]

M.H. Akbari et al. [33][34] have presented a numerical investigation of catalytic autothermal reforming (ATR) of methane in a surface microreactor. A three-dimensional ATR reactor model is developed to simulate the flow and surface reactions in a microchannel of square cross-section. A four-reaction mechanism is implemented to simulate the surface reactions on a Ni/Al₂O₃ catalyst, and a global mechanism is used to model gas-phase methane oxidation.
Four major reactions are considered in the present model. These reactions are listed as follows:

(1) The exothermic total combustion of methane,

\[ \text{R1 : CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}, \quad \Delta H_{298} = -802 \text{kJ/mol} \]

(2) The endothermic steam reforming of methane to carbon monoxide,

\[ \text{R2 : CH}_4 + \text{H}_2\text{O} \leftrightarrow \text{CO} + 3\text{H}_2, \quad \Delta H_{298} = 206 \text{kJ/mol} \]

(3) The water–gas shift reaction,

\[ \text{R3 : CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2, \quad \Delta H_{298} = -41 \text{kJ/mol} \]

(4) The steam reforming of methane directly to carbon dioxide.

\[ \text{R4 : CH}_4 + 2\text{H}_2\text{O} \leftrightarrow \text{CO}_2 + 4\text{H}_2, \quad \Delta H_{298} = 165 \text{kJ/mol} \]

In their another research about the methanol reforming and oxidation in wash-coated microreactors, a microreactor consisting of two parallel channels is numerically simulated where methanol steam reforming takes place in one channel, and the required heat is supplied by methanol oxidation in the other channel.\[^{34}\]
Rob J. Berger and Freek Kapteijn have investigated the study of the radial mass transport limitation on the conversion in a coated-wall reactor empty\cite{35} and filled with inert particles \cite{36} (Fig. 47). A criterion for the maximum allowable conversion with a less than 5% deviation in the rate constant has been developed, which is a function of the modified Peclet number ($\text{Pe}'$), the reaction order ($n$), and two constants $a$ and $b$ that depend on the reactor geometry: $X_{\text{CWR}} < b/(a + n\text{Pe}')$. The simulations were carried out using Athena Visual Studio 10.0 and Comsol Multiphysics 3.2 for several reactor geometries (round, square, annular, rectangular, and triangular channels) and reaction orders. They concluded that, after filling the empty volume with particles, and preferentially relatively large particles, up to $d_{\text{particle}}/d_{\text{tube}} = 0.4$, is beneficial for the reactor performance and relaxes the criterion for plug-flow behavior. The correlation is generally applicable for gases and, with some precautions, also for liquid applications.

Ozgur Yasar Caglar et al.\cite{37} have investigated the detailed modeling of a wall-coated catalytic multi-channel microreactor, to lance the steam reforming (SR) of glycerol, by-product of biodiesel synthesis, and design an adiabatic microchannel reformer that can be integrated into a biodiesel production plant with an annual capacity of $4 \times 10^3$ m$^3$/year. Simulations made on a 2D unit cell are carried out using COMSOL Multiphysics™ software. The results show that the microchannel architecture enables fast and uniform transfer of the sensible heat of the feed stream to the SiC catalyst layer.

$$C_3H_8O_3 + 3H_2O = 3CO_2 + 7H_2 \quad \Delta H^0 = 346.4 \text{ kJ/mol}$$
The microchannel reactor is composed of parallel groups of identical channels separated by the reactor wall. Each channel, which is rectangular in shape, has dimensions of $6.5 \times 10^{-4}$ m (Height) $\times 1 \times 10^{-2}$ m (Width) $\times 1 \times 10^{-1}$ m (Length), and 5 $10^{-5}$ m thick layers of Ni/CeO$_2$ catalyst are being coated onto opposite inner walls of each channel. They have also proposed that, to convert a minimum of 90% of the glycerol supplied by a biodiesel synthesis plant with an annual capacity of $4 \times 10^3$ m$^3$, we can use a multichannel reactor made of SiC consisting of 5400 micro-channels with a total volume of $10^{-2}$ m$^3$ and a total catalyst amount of 1kg.

Ali Fazeli and Mohsen Behnam$^{[39]}$ have studied the hydrogen production from steam reforming of methanol on Cu/ZnO/Al$_2$O$_3$ catalyst for fuel cell application in a wall-coated microchannel reactor by CFD approach. In this study, straight and zigzag geometry was compared, and the effect of zigzag geometry on heat transfer, hydrogen concentration, carbon monoxide selectivity and methanol conversion has been studied.

Figure 48  Description of the parallel microchannel reactor configuration (a) and the characteristic unit cell (b) $^{[37]}$

Figure 49  Schematic figure of zigzag and straight geometry of catalytic wall coated microchannel reactor for converting methanol to hydrogen $^{[39]}$
The results of modeling show that zigzag has more H₂ selectivity and less CO selectivity than straight microreactor. CO is a by-product that is a poison for fuel cells. Also zigzag microreactor has more methanol conversion and low temperature than straight one. So it release less unconverted methanol and is better for insulation because of lower temperature. Zigzag geometry can improve mass transfer in laminar fluid flow regimes and increase the heat transfer.

A pseudo-2-dimensional model developed by Niket S. Kaisare et al.⁴⁰ is used for modeling a multifunctional microreactor for hydrogen generation by coupling ammonia decomposition on a Ru/Alumina catalyst with catalytic propane combustion on Pt/Alumina in concurrent operation mode. Stable, self-sustained device operation was found to be feasible at millisecond (or even submillisecond) contact times. A simple operating strategy to dial in the desirable power is proposed, which ensures high thermal efficiency, wall isothermicity, and high conversions.
The plates separating the two channels are 5 cm long and 750 μm thick. The gap sizes of the combustion and the ammonia channels are 300 and 200 μm, respectively. Owing to the symmetry of the device, only two half-channels and one separating wall are modeled. The reactor is modeled using a pseudo-2D model (also called 1D heterogeneous model), which involves conservation equations in the axial direction (of each channel and the separating wall) and a lumped parameter description of transverse heat and mass transfer in each channel (between the bulk gas and the wall). The main feature of the pseudo-2D model is that the transverse heat and mass transfer correlations were chosen based on 2D computational fluid dynamics (CFD) models.

João P. Lopes et al. have studied the operating regimes and mass transfer in in wall-coated microreactors, such as regime mapping and the role of the intermediate region, interplay between channel and catalyst operating regimes and the operation of a perfusive catalytic membrane with nonlinear kinetics. The applicability of mass transfer models with finite wall kinetics, the effect of nonlinear and inhibited kinetics on operating regimes, the analytical description of boundaries for overall and localized controlling regimes etc. have been discussed in detail.
They have proposed the design parameters in a microchannel reactor\cite{41}. It is possible to reduce the design of an isothermal coated microchannel to four independent dimensionless parameters:

i) the Graetz number (including the operation flow rate and the channel length, which normalizes the axial distance z and appears in the aspect ratio $\alpha = a/L$),

$$\frac{aPem_z}{z} = \frac{a^2 \langle u \rangle}{zLD}$$

$a$: channel transverse characteristic length (radius of a circular channel, slit half width spacing), m

$P_{em}$: mass Peclet number, $a<u>/D$, $<u>$ average fluid velocity in the channel, m/s

$D$: bulk channel diffusivity, m$^2$/s

$L$: length of the channel, m

ii) the inlet Damkohler number (with the characteristic radius of the channel $a$ and reaction rate referred to the inlet concentration and temperature per fluid-solid interface area, $R_{surf}$),

$$Da_{in} = \frac{a R_{surf}(c_{in})}{D c_{in}}$$

$Da_{in}$: inlet channel Damkohler number, $a$ and reaction rate referred to the inlet concentration, mol/m$^3$

$R_{surf}$: reaction rate per fluid-solid interface area, m$^{-1}$

$c_{in}$: inlet channel concentration, mol/m$^3$

iii) a ‘diffusion ratio’ (where the diffusivities and length scales of both domains are compared),

$$\Delta = \frac{D_{eff}a}{t_w D}$$

$D_{eff}$: effective diffusivity in the catalytic coating, m$^2$/s

$t_w$: washcoat characteristic thickness, m

iv) and a parameter related to the catalyst geometry, namely the ratio between the volume, surface and thickness of the coating:

$$\nu = \frac{V_{cat}}{t_w S_{surf}}$$

$S_{surf}$: area of the channel-coating interface

The geometry of the channel cross-section is accounted for using a shape factor $S$ (equals 1 for circular channel, 0 for slit). A parameter related with channel shape and flow profile also appears:

$$\sigma_c = \frac{u_{max}}{\langle u \rangle} (S + 1)$$

It can be interpreted as the ratio between the maximum and the actual flow rate in channels with the same wall area $S_{surf}$ and transverse characteristic dimension $a$ (equals 1 for plug-flow between parallel plates).

The Graetz number can be related directly to the dimensionless pressure drop (Euler number) by the Darcy–Weisbache quation in laminar conditions (with the geometry dependent friction factor coefficient $C_0 = f_0 Re$ and Schmidt number $S_c = v/D$):
\[
\Delta P = \frac{S + 1}{2} C_D Sc - \frac{z}{\alpha Pe_m}
\]

### 3.2 Summary of wall-coated microreactor modeling

#### 3.2.1 Mass transfer

**Mass transfer in the boundary layer**
When modifying the well-known criterion of Mears to wall coated microreactors, there is no influence of the mass transfer in the boundary layer on the reaction rate, if the following inequality is fulfilled:[32]

\[
\frac{r(V_C/O_C)}{k_g c} < 0.05
\]

The right side of the inequality, which is normally 0.15 for spherical catalyst particles, is substituted by 0.05 for a generalized geometry of a catalyst (with substitution to volume and surface of catalyst). \(V_C\) and \(O_C\) denotes the volume and geometric surface of the catalyst, \(k_g\) represents the outer mass transfer coefficient from the gaseous phase through the boundary layer to the catalyst layer. It can be calculated as:

\[
k_g = 1.66 Re^{0.49} Sc^{0.33} \frac{D_{12}}{b}
\]

\(D_{12}\) (m\(^2\) s\(^{-1}\)) as binary diffusion coefficient and \(b\) as boundary layer thickness, which corresponds to half the hydrodynamic diameter in the case of the microchannel.

**Mass transfer in the catalyst layer (pore diffusion)**
To estimate the influence of pore diffusion, the so-called Weisz–Prater criterion[44] is normally applied. If this criterion is fulfilled, there is no influence of mass transfer in the catalyst layer. For the microchannel reactor the criterion can be adapted to:

\[
\Psi = \frac{L_c^2 r}{D_p c} < 0.1
\]

In the study of O. Gorke et P. Pfeifer[32], the characteristic length \(L_c = V_C/O_C\) equal the volume of catalyst divided by the geometric surface area of the catalyst layer, the effective reaction rate is \(r_{C_2H_5OH}\), the inlet concentration of ethanol is \(c_{C_2H_5OH}\) and the diffusion coefficient \(D_p\) can be calculated as follows:

\[
D_p = \frac{\varepsilon_p d_p}{\tau_k 3} \sqrt{\frac{8RT}{\pi M}}
\]

The binary diffusion coefficients can be estimated based on the Fullere Schettlerle Giddings (FSG) equation. Reid et al. [38][45] evaluated the different binary diffusivity estimation methods and recommend the FSG equation based on the smallest error.
\[ D_{ij} = \frac{0.000143T^{1.75}(\frac{1}{M_i} + \frac{1}{M_j})^{1/2}}{P_{atm}[\sum v_i^{1/3} + \sum v_j^{1/3}]} \]

where \( D_{ij} \) the binary diffusivity of species \( i \) in \( j \), \( M \) the molecular weight of species \( i \) and \( j \), \( v \) the atomic diffusion volume of species \( i \) and \( j \).

The effective diffusion coefficients appearing in the species conservation equations for the porous catalyst layer are calculated using the Bruggeman correlation, which accounts for the effect of porous matrix on gas phase mass transport \cite{46}

\[ D_{ij,eff} = D_{ij} \varepsilon^{1.5} \]

Serge Corbel et al.\cite{47} have used the Sherwood followed a law of the type:

\[ \text{Sh} = \frac{d_h}{L} + Re^\alpha Sc^\beta \]

with \( d_h \) the hydraulic diameter, \( L \) the length of the microchannel, \( Re \) the Reynolds number and \( Sc \) the Schmidt number. The coefficients \( \alpha \) and \( \beta \) were determined by linearization, and the values are determined from the slope and intercept point, respectively.

J.P. Lopes et al. have studied the regimes in wall-coated reactors and have proposed many correlations about the mass transfer. \cite{41-43}

For the Sherwood number (Shah and London(1978)):

\[ Sh_1 = \frac{\lambda^2}{\sigma_c} \]
\[ Sh_2 = M(\alpha Pe_{m,max}/z)^{1/3} \]

where \( M \) the numerical coefficient, \( Pe_{m} \) mass Peclet number, \( \alpha Pe_{m,max}/z \) the Graetz number evaluated with maximum velocity

the correlation proposed:

\[ Sh = [Sh_1^n + Sh_2^n]^{1/n} \]

\( n=4 \) for laminar flow

The inlet Damkohler number(with the characteristic radius of the channel \( a \) and reaction rate referred to the inlet concentration and temperature per fluid-solid interface area, \( R_{surf} \), \( c_{in} \) : inlet channel concentration, \( \text{mol/m}^3 \))

\[ Da_{in} = \frac{a \hat{R}_{surf}(\hat{c}_{in})}{D \hat{c}_{in}} \]
Table 3  Limits of $\theta$ (degree of mass transfer control) and $\eta$ \cite{48}\cite{49}

<table>
<thead>
<tr>
<th>Domain</th>
<th>Kinetic regime ($Da&gt;0$)</th>
<th>Diffusional regime ($Da&gt;&gt;\infty$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>External (channel)</td>
<td>$\theta = \frac{Da}{S_{\text{h0}}+Da}$</td>
<td>$\theta = \frac{Da}{S_{\text{h0}}+Da}$</td>
</tr>
<tr>
<td>Plug flow</td>
<td>$S_{\text{h0}} = \frac{(S + 7)(S + 5)}{5(S + 17)}$</td>
<td>$S_{\text{h0}} = \frac{\lambda_{\text{g}}}{S + 1 \ u_{\text{max}}} \langle u \rangle$</td>
</tr>
<tr>
<td>Laminar flow</td>
<td>$S_{\text{h0}} = \frac{\sqrt{\pi}}{2} \sqrt{\frac{\alpha \rho_{\text{e_m}}}{z}}$</td>
<td>$S_{\text{h0}} = \frac{1}{\sqrt{\pi}} \sqrt{\frac{\alpha \rho_{\text{e_m}}}{z}}$</td>
</tr>
<tr>
<td>Internal (catalyst coating)</td>
<td>$\eta = 1 - \Phi^2 A + O(\Phi^3)$</td>
<td>$\eta = \frac{1}{4v} + \frac{v-1}{v} \frac{1}{\Phi^2} + O(\Phi^{-3})$</td>
</tr>
</tbody>
</table>

Geometrical parameters

- $S = \frac{a_{\text{surf}}}{V_{\text{ch}}} - 1$, $A = \nu/3$ (thin coatings)
- $\nu = \frac{V_{\text{cat}}}{S_{\text{surf}}t_{\text{w}}} = 1 + \frac{\varepsilon \sigma}{2}$ ($\sigma=1$ for an annular washcoat)

### 3.2.2 Heat transfer

According to Anderson et al.\cite{32}\cite{50}, the outer heat transfer resistance in the boundary layer can be neglected by similar assumptions than for mass transfer. The inequality has been adapted to microreactors in the same way as the Mears criterion and it should be checked for our experiments since there is no main heat flux to a cooling media:

$$\frac{(-\Delta H_R) r_{\text{C}_2\text{H}_5\text{OH}C}}{\alpha_g T_R} \left( \frac{E_A}{RT_R} \right) < 0.05$$

$H_R$ (kJ/mol) indicates the reaction enthalpy and $E_A$ the activation energy of the reaction studied, $\alpha_g$ ($W \text{ m}^{-2} \text{ K}^{-1}$) represents the coefficient for heat transfer through the gaseous boundary layer. The heat transfer coefficient can be calculated by use of the hydrodynamic diameter of the channel:

$$\alpha_g = \frac{Nu \lambda_{\text{g}}}{d_h}$$

The heat conductivity $\lambda_{\text{g}}$ of the gas mixture can be deduced from kinetic gas theory.

The Nusselt number $Nu$ needed for the description of the heat transfer can be calculated as follows\cite{51}
3.2.3 Pressure drop

Rob J. Berger et al.\cite{36} have used the pressure drop equation from Ergun:

\[
\frac{\partial P}{\partial z} = -f_1 u(r) - f_2 (u(r))^2 + \frac{\mu_{F,\text{eff}}}{r} \frac{\partial}{\partial r} \left( r \frac{\partial u(r)}{\partial r} \right)
\]

\[
f_1 = 150 \left( 1 - \epsilon_b(r) \right)^2 \frac{\mu_F}{d_p^2}
\]

\[
f_2 = 1.75 \left( 1 - \epsilon_b(r) \right) \frac{\rho_F}{(\epsilon_b(r))^3} d_p
\]

\[
\mu_{F,\text{eff}} = 2 \epsilon^{0.002 R} \mu_F
\]

\[
Re_p = \frac{\rho_F u_0 d_p}{\mu_F}
\]

J. P. Lopes et al.\cite{41} have proposed the dimensionless pressure drop (Euler number) in laminar conditions:

\[
\Delta P = \frac{\Delta \dot{p}}{(1/2) \dot{\rho} \langle u \rangle^2} = \frac{S + 1}{2} C_D Sc \frac{z}{\alpha Pe_m}
\]

\[
\frac{\alpha Pe_m}{z} = \frac{a^2 \langle u \rangle}{2LD}
\]

\[
C_D = f_D Re
\]

\[
Sc = \frac{v}{D}
\]

\[
v = \frac{V_{cet}}{t_w S_{surf}}.
\]

\(f_D\): Darcy’s friction factor

S channel’s shape factor

Madhvanand N. Kashid et al.\cite{52} have proposed that the pressure drop through wall coated open channels with laminar flow can be given by the Hagen-Poiseuille equation. The geometric factor depends on the H/W ratio of rectangular channels.
\[ \Delta p = 32\zeta \frac{\mu u}{d_t^2} L_t \]

\[ \zeta = 0.8735 + 0.6265 \exp(-3.636 \frac{H}{W}) \]

3.3 Research status of macro-monolithic reactor modeling

N. Moazami et al.\textsuperscript{[55]} have developed a numerical two-phase one-dimensional mathematical model of a single channel catalytic monolith reactor. The new method used to solve the equations was the combination of the Euler’s method and central finite difference method. The advantage of this combined method is that the percentage error produced by the program code was negligible. In this model, it was assumed that the reactions only occur on the surface of catalyst. The temperatures and the concentrations of each species of interests (i.e. \( \text{H}_2, \text{CO}_2, \text{CO}, \) and \( \text{C}_{16}\text{H}_{34} \)) were obtained in both the gas phase and at the wall. The general autothermal reaction is as follows:

\[ \text{C}_n\text{H}_m + n\text{H}_2\text{O} + \left( \frac{m}{2} \right) \text{O}_2 \rightarrow n\text{CO}_2 + \left( \frac{m}{2} + n \right)\text{H}_2 \quad \Delta H < 0 \]

Fig. 53 shows all transport mechanisms, including mass and heat transfer, that were applied to the present model.

Figure 53 A single channel monolith reactor, and developed mole and energy balance equations in the gas and solid phases, considering heat and mass transfer; and reaction equation\textsuperscript{[55]}
Achim K. Heibel et al.\cite{57} have investigated the effects of structural and geometrical characteristics of wash-coated monolith catalysts on the NONO$_2$/NH$_3$ selective catalytic reduction (SCR) activity over the same Cu-exchanged zeolite system coated onto honeycomb cordierite substrates with different cell densities, lengths, washcoat loads, and channel shapes. The SCR process for mobile applications can be summarized by the following main reactions:

\[
4\text{NH}_3 + 4\text{NO} + \text{O}_2 \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O} \quad \text{(standard SCR)}
\]

\[
2\text{NH}_3 + \text{NO} + \text{NO}_2 \rightarrow 2\text{N}_2 + 3\text{H}_2\text{O} \quad \text{(fast SCR)}
\]

\[
8\text{NH}_3 + 6\text{NO}_2 \rightarrow 7\text{N}_2 + 12\text{H}_2\text{O} \quad \text{(NO}_2\text{ SCR)}
\]

The reactor was a stainless steel tube that contained a steel sample holder with a square internal cross section. Typical sizes of the tested monolith catalyst samples were approximately 8 mm × 8 mm × 50 mm. To ensure feed gas pre-mixing, upstream of the catalyst, the reactor was filled with quartz particles (3-5 mm in diameter), followed by a screen containing zirconium balls (1.6 mm in diameter).

Karthik Ramanathan et al.\cite{58} have studied in a one-dimensional two-phase model is used to derive an analytical light-off criterion for a straight channeled catalytic monolith with washcoat, in which the flow is laminar. For the case of high solid conductivity, they present an analytical expression for the transient time at which the monolith shifts from the kinetically controlled to the mass transfer controlled regime. They also determine the influence of various parameters such as the washcoat thickness, channel dimensions, catalyst loading and initial solid temperature on this transient time and the cumulative emissions.

Their researches have been used in many studies of reaction mechanism with catalytic monoliths and development of model, for example in a recent paper Sachi Shrestha et al.\cite{59} have used the equations of K.Ramanathan to develop the model of selective ammonia oxidation on multi-functional washcoated monolith Catalysts.

Alireza Behroozosarand and Ali Nakhaei Pour\cite{61} have compared the Langmuire-Hinshelwood kinetic and microkinetic models for dry reforming (DR) process in a monolith reactor.

\[
\text{CH}_4 + \text{CO}_2 \leftrightarrow 2\text{H}_2 + 2\text{CO}
\]
The effect of six key parameters Microchannel wall temperature, microchannel pressure, CH₄/CO₂, hydrogen, carbon monoxide, and steam concentration in feed stream on DR of a microchannel reactor was studied. The catalytic reaction takes place at the surface of microchannel wall.

According to results, it seems that provided C code for Langmuire-Hinshelwood Kinetic model of DR suggests more rational and appropriate responses than microkinetic model.

### 3.4 Summary of macro-monolithic microreactor modeling

#### 3.4.1 Mass transfer

N. Moazami et al.⁵⁵ have used the correlation of Sherwood number:

\[
S_h = \frac{1.013 \times 10^{-2} \rho_g^{1.75} \left( \frac{1}{M_i} + \frac{1}{M_j} \right)^{1/2}}{P \left[ \left( \sum v_k \right)_i^{1/3} + \left( \sum v_k \right)_j^{1/3} \right]^2}
\]

\[
k_{m,i} = \frac{D_T}{M_i \text{ average molar mass of a mixture kg mol}^{-1}}
\]
\( k_t \) thermal conductivity of fluid, \( \text{J m}^{-1} \text{s}^{-1} \text{K}^{-1} \)

\( D_t \) tube diameter, m

\( \nu_k \) diffusional volume coefficient, dimensionless

Achim K. Heibel et al.\(^{[57]}\) have adopted the following correlation to estimate the gas-solid mass-transfer coefficients in monolith channels\(^{[64]}\):

\[
Sh = Sh_\infty + 8.827 \left[ 1000 \left( \frac{zL}{d_h \text{ScRe}} \right) \right]^{-0.545} e^{-48.2 \left( \frac{zL}{d_h \text{ScRe}} \right)}
\]

with \( Sh_\infty \) asymptotic Sherwood number, \( d_h \) hydraulic diameter of monolith channel, \( L \) the monolith length, \( z \) dimensionless axial coordinate.

To test the sensitivity of the model simulations to external mass transfer, a different correlation was tentatively applied to evaluate the Sherwood numbers. In the past, the Votruba correlation\(^{[65]}\),

\[
Sh = 0.705 \left[ \frac{Re}{L} \right]^{0.43} S_c^{0.56}
\]

has been claimed to provide a good description of gas/solid mass transfer in SCR honeycomb catalysts.

For the case of fully developed laminar flow, the following expressions describe the local mass transfer\(^{[58]}\)

\[
Sh_{\Omega}(x) = \frac{k_c(x) R_{\Omega}}{D_m} = \begin{cases} 
0.82 \left( \frac{R_{\Omega}^2 \bar{u}}{xD_m} \right)^{1/3}, & 0 < \frac{R_{\Omega}^2 \bar{u}}{xD_m} \left( \frac{3.28}{Sh_{H,\infty}} \right)^3 \\
Sh_{H,\infty}/4, & x \geq \frac{R_{\Omega}^2 \bar{u}}{xD_m} \left( \frac{3.28}{Sh_{H,\infty}} \right)^3
\end{cases}
\]

When the velocity field is also developing along with concentration and thermal boundary layers, the following expressions give the local Sherwood number:

\[
Sh_{\Omega}(x) = \begin{cases} 
0.35 \left( \frac{R_{\Omega}^2 \bar{u}}{Sc^{1/6} xD_m} \right)^{1/2}, & 0 < \frac{R_{\Omega}^2 \bar{u}}{D_m Sc^{1/3}} \left( \frac{1.4}{Sh_{H,\infty}} \right)^2 \\
Sh_{H,\infty}/4, & x \geq \frac{R_{\Omega}^2 \bar{u}}{D_m Sc^{1/3}} \left( \frac{1.4}{Sh_{H,\infty}} \right)^2
\end{cases}
\]

with \( R_{\Omega} \) one-half the channel hydraulic radius, \( \bar{u} \) average fluid velocity in the channel.

In the research of Sachi Shrestha et al.\(^{[59]}\), the mass transfer coefficient (\( k_{me,j} \)) of species \( j \) is calculated using the following relation:

\[
k_{me,j} = \frac{Sh_e D_{f,j}}{4R_{\Omega}^2}
\]

where \( D_{f,j} \) is diffusivity of the gas species \( j \) in the fluid phase and was calculated as a function of temperature using the Lennard-Jones formulation. The relation between \( D_f \) and temperature can be found in Shakya et al.\(^{[60]}\). \( Sh_e \) is a position independent
external Sherwood number for a square channel. The axial variation of $Sh_e$ along the monolith length can be estimated using the relation developed by Ramanathan et al.\cite{58} which accounts for the developing velocity and concentration boundary layers:

$$z = \frac{\langle u \rangle R_e^2}{D_{f,j}} \frac{1}{Sc^3} \left( \frac{1.4}{Sh_e} \right)$$

Here $Sc$ is the fluid Schmidt number.

Shaibal Roy et al.\cite{66} have summarized the correlations for liquid–solid mass transfer and gas-liquid mass transfer in monolithic reactors.

Table 4  Correlations of mass transfer in monolithic reactors summarized by Shaibal Roy et al.

<table>
<thead>
<tr>
<th>Author (Year)</th>
<th>Liquid–Solid Mass Transfer</th>
<th>Gas–Liquid Mass Transfer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Haitziatou et al. (1982)</td>
<td>$Sh = 3.51 \left( \frac{ReSc}{\gamma} \right)^{0.14} \beta^{-0.09}$ with $\gamma = \frac{L}{u_id}$ and $\beta = \frac{L}{u_id}$</td>
<td>$Sh = 0.41 \sqrt{ReSc}$</td>
</tr>
<tr>
<td>Irandoust et al. (1988a)</td>
<td>$Sh = 1.5 \times 10^{-7} (Re)^{1.84} (Sc)^{0.17} (\alpha)^{-2.338}$ with $\alpha = \frac{d}{L_e}$</td>
<td>$1 \leq Re \leq 400; \left( \frac{Sh - 1}{Sc^{0.5}} \right) = \left[ 1 + \left( \frac{1}{ReSc} \right)^{1.09} \right] Re^{0.41}$</td>
</tr>
<tr>
<td>Irandoust et al. (1992)</td>
<td>$k_{GFT} = \left[ \left( 1 - \frac{\epsilon_1}{\epsilon_0} UCL_e - 0.150 UCL_e L_e \right)^{0.59} \right]^{0.5}$</td>
<td>$k_{GFT} = \left[ \left( 1 - \frac{\epsilon_1}{\epsilon_0} UCL_e - 0.150 UCL_e L_e \right)^{0.59} \right]^{0.5}$</td>
</tr>
<tr>
<td>Bercic et al. (1997)</td>
<td>$k_{GFT} = \left[ \left( 1 - \frac{\epsilon_1}{\epsilon_0} UCL_e - 0.150 UCL_e L_e \right)^{0.59} \right]^{0.5}$</td>
<td>$k_{GFT} = \left[ \left( 1 - \frac{\epsilon_1}{\epsilon_0} UCL_e - 0.150 UCL_e L_e \right)^{0.59} \right]^{0.5}$</td>
</tr>
<tr>
<td>Heiszwoolf et al. (1999)</td>
<td>$Sh = 3.66 \left[ 1 + 0.152 \left( \frac{\Psi_e}{ReSc} \right)^{0.65} \right]^{0.4}$</td>
<td>$Sh = 1.04 + \frac{L}{L_e} \left( 1 + 0.047 \frac{L}{L_e} \right)$ with $\frac{L}{L_e} \leq 1.0$</td>
</tr>
<tr>
<td>Lebens et al. (1999a)</td>
<td>$Sh = 20 \left[ 1 + 0.003 \left( \frac{\Psi_e}{ReSc} \right)^{-0.7} \right]^{0.45}$</td>
<td>$Sh = 1.04 + \frac{L}{L_e} \left( 1 + 0.047 \frac{L}{L_e} \right)$ with $\frac{L}{L_e} \leq 1.0$</td>
</tr>
</tbody>
</table>

Leonardo Giani et al.\cite{67} have adopted the correlation of Hawthorn et al.\cite{68} to calculate the Sherwood number of a monolithic reactor:

$$Sh = 2.977 \left[ 1 + 0.095 \left( \frac{Re}{\epsilon} \right) Sc \left( \frac{d}{L} \right) \right]^{0.45}$$

In the study of Ranjeeth R. Kalluri et al.\cite{69} and Sabrina Wahid et al.\cite{71}, the correlation proposed by Tronconi and Forzatti\cite{70,72} for the mass transfer in square...
channel monoliths was employed:

\[
\text{Sh} = 2.967 + 8.827 \times \left(\frac{1000}{Gz}\right)^{-0.545} \exp\left(\frac{48.2}{Gz}\right)
\]

The correlations of mass transfer in macro-monolithic reactor in addition to the summary of Shaibal Roy et al. (Table 4) can be summarized as below (Table 5):

<table>
<thead>
<tr>
<th>Author and reference</th>
<th>Correlation</th>
</tr>
</thead>
</table>
| N. Moazami et al. [55] | \[
\text{k}_{m,i} = \frac{1.013 \times 10^{-2} T_g^{1.75} \left(\frac{1}{M_i} + \frac{1}{M_f}\right)^{1/2}}{p \left[\sum v_i \nu_i^{1/3} + \left(\sum v_i \nu_i\right)^{1/3}\right]^2}
\] |
| Achim K. Heibel et al. [57] | \[
\text{Sh} = \text{Sh}_\infty + 8.827 \left[1000 \left(\frac{zL}{d_h \text{ScRe}}\right)\right]^{-0.545} e^{-48.2 \left(\frac{zL}{d_h \text{ScRe}}\right)}
\] |
| Votruba correlation [65] | \[
\text{Sh}_{\Omega}(x) = \frac{k_c(x)R_B}{D_m} = \begin{cases} 0.82 \left(\frac{R_B}{xD_m}\right)^{1/3}, & 0 < x < \frac{R_B}{xD_m} \left(\frac{3.28}{\text{Sh}_{H,\infty}}\right)^3 \\ \frac{\text{Sh}_{H,\infty}}{4}, & x \geq \frac{R_B}{xD_m} \left(\frac{3.28}{\text{Sh}_{H,\infty}}\right)^3 \end{cases}
\] |
| Karthik Ramanathan et al. [58] | \[
\text{Sh}_{\Omega}(x) = \begin{cases} 0.35 \left(\frac{R_B}{xD_m}\right)^{1/2}, & 0 < x < \frac{R_B}{D_m} \left(\frac{1}{\text{Sh}_{H,\infty}}\right)^2 \\ \frac{\text{Sh}_{H,\infty}}{4}, & x \geq \frac{R_B}{D_m} \left(\frac{1}{\text{Sh}_{H,\infty}}\right)^2 \end{cases}
\] |
| Sachi Shrestha et al. [59] | \[
\text{k}_{me,j} = \frac{\text{Sh}_c D_{f,j}}{4R_{21}}
\] |
| Leonardo Giani et al. [67] | \[
\text{Sh} = 2.977 \left[1 + 0.095 \left(\frac{\text{Re}}{\epsilon}\right) \text{Sc} \left(\frac{d}{L}\right)^{0.45}\right]
\] |
| Tronconi and Forzatti [70][72] | \[
\text{Sh} = 2.967 + 8.827 \times \left(\frac{1000}{Gz}\right)^{-0.545} \exp\left(\frac{48.2}{Gz}\right)
\] |

### 3.4.2 Heat transfer

The heat transfer coefficient was illustrated from the values of the Sherwood Nusselt numbers \[^{[55]}\]

\[
h = \frac{\text{Nuk}_f}{D_T}
\]

Thermal conductivity of fluid was calculated based on its value for C_{18}H_{34}, which varied with gas phase temperature and it was similar to the correlation done by Mukhamedzyanov et al. \[^{[73]}\]

\[
k_f = 1 \times (10^{-13}) T_g^4 - 3 \times (10^{-10}) T_g^3 + 3 \times (10^{-7}) T_g^2 - 0.0003 T_g + 0.2164
\]
For the case of fully developed laminar flow, the following expressions describe the local heat transfer:\(^{58}\)

\[
Nu(x) = \frac{h(x) \rho_f c_p R}{k_f} \\
= \begin{cases} 
0.82 \left( \frac{R_\infty \rho_f c_p \mu_f}{\mu_f} \right)^{1/3}, & 0 < x < \frac{R_\infty \rho_f c_p \mu_f}{k_f} \left( \frac{3.28}{Nu_{H, \infty}} \right)^3, \\
\frac{Nu_{H, \infty}}{4}, & x \geq \frac{R_\infty \rho_f c_p \mu_f}{k_f} \left( \frac{3.28}{Nu_{H, \infty}} \right)^3.
\end{cases}
\]

When the velocity field is also developing along with concentration and thermal boundary layers, the following expressions give the local Nusselt number:\(^{58}\)

\[
Nu(x) = \begin{cases} 
0.35 \left( \frac{R_\infty \rho_f c_p \mu_f}{\mu_f} \right)^{1/2}, & 0 < x < \frac{R_\infty \rho_f c_p \mu_f}{k_f} \left( \frac{1.4}{Nu_{H, \infty}} \right), \\
\frac{Nu_{H, \infty}}{4}, & x \geq \frac{R_\infty \rho_f c_p \mu_f}{k_f} \left( \frac{1.4}{Nu_{H, \infty}} \right)^2.
\end{cases}
\]

Bird R.B. et al.\(^{74}\) have proposed the monolith correlation for Nu in their classic book:

\[
Nu = 2.9(1 + 0.095Re \ Pr (d/L))^{0.45}
\]

### 3.4.3 Pressure drop

The pressure drop through the monolith is primarily caused by factors such as

1. the wall friction,
2. the acceleration of gas phase,
3. the orifice effect at the entry region and between the monolith stacks
4. pressure drop caused by the gas–liquid distributor.

Mewes et al. (1999) also considered the pressure drop attributed to aeration of liquid slugs, which depends on the number of bubbles formed in the liquid slugs. If we assume the phases moving along the monolith channel to be incompressible, the pressure drop caused by the acceleration can be neglected.\(^{66}\) Table flowing lists the pressure drop correlations reported by researchers working in the field of monolith.
Table 6  Pressure drop correlations of monolithic reactors summarized by Mewes et al.\cite{Mewes1999}

<table>
<thead>
<tr>
<th>Author</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Satterfield et al. (1977)</td>
<td>$\Delta P = \Delta P_J + \Delta P_{or} - g \rho u L \varepsilon_L$</td>
</tr>
<tr>
<td>Grolman et al. (1996)</td>
<td>$\Delta P = \Delta P_{TP} + \Delta P_G$</td>
</tr>
<tr>
<td>Mewes et al. (1999)</td>
<td>$\Delta P = \frac{N(V_{out} - V_{in})}{2} \varepsilon_L \rho_L \Delta L$</td>
</tr>
<tr>
<td></td>
<td>$\Delta P_{TP} = \frac{64}{Re_{TP}} \frac{L}{d} \frac{1}{2} \rho_L (u_L + u_T) \Delta L$</td>
</tr>
<tr>
<td></td>
<td>$\Delta P_G = C u_G$ with $C = 45,000 , \text{Pa s}^{-1} , \text{m}$</td>
</tr>
<tr>
<td>Heiszewolf et al. (2001a)</td>
<td>$f_{TP} Re_L = (f Re)_E \left[ 1 + 0.065 \left( \frac{L}{d Re_L} \right)^{-0.66} \right]$</td>
</tr>
<tr>
<td>Heiszewolf et al. (2001a)</td>
<td>$\Delta P = -f_{TP} \frac{1}{2} \rho_L u_T^2 d + \varepsilon_L \rho_L u_T$</td>
</tr>
<tr>
<td></td>
<td>$f_{TP} = \frac{F}{Re_{TP}}$ with $F = 18$ (200 cpsi, OFA = 0.74)</td>
</tr>
<tr>
<td></td>
<td>$f_{TP} = \frac{F}{Re_{TP}}$ with $F = 22$ (400 cpsi, OFA = 0.75)</td>
</tr>
<tr>
<td></td>
<td>$f_{TP} = \frac{F}{Re_{TP}}$ with $F = 28$ (600 cpsi, OFA = 0.79)</td>
</tr>
<tr>
<td></td>
<td>Pseudo-homogeneous model: $f_{TP} Re_L = \text{const}$</td>
</tr>
<tr>
<td>Lebens et al. (1999)</td>
<td>$\nabla (\mu_i \nabla U_{ij}) = \frac{dp}{dz} + g \rho_i$</td>
</tr>
<tr>
<td></td>
<td>with $i = G, L$</td>
</tr>
</tbody>
</table>

Besides, Leonardo Giani et al.\cite{Giani1999} have used the friction factor:

$$f = \frac{14.23}{\varepsilon Re}$$

$$\frac{\Delta P}{L} = \left( 2 \frac{f}{d} \right) \rho u^2$$

to calculate the pressure drop of their monolithic reactor.

In the research of Ranjeeth R. Kalluri et al.\cite{Kalluri2000}, the friction factors for monoliths were estimated using the following correlations\cite{Kalluri2000}:

$$f = \frac{13}{\varepsilon_b Re_{ch}}$$ for $\frac{Re_{ch}}{\varepsilon_b} < 1000$

$$f = \left( \frac{0.03}{\varepsilon_b} \right)^{0.18} Re_{ch}^{0.12}$$ for $\frac{Re_{ch}}{\varepsilon_b} > 1000$.
Sabrina Wahid et al.\textsuperscript{[71]} have considered the same friction factor correlation.

## 4 Monolithic Microreactors

Monolithic microreactors here are reactors with micro-monolith inside. Different with the mature macro-monolith technology, the micro-monolith is a rather new field, which is mainly used in continuous processes of fine chemical production with macropores of typically 2 to 10 μm.

![Micro-monolith (left a,b)\textsuperscript{[54]} and macro-monolith (right)\textsuperscript{[40]}](image)

A monolithic material is usually composed of a solitary mass of structured polymeric or inorganic material filled with interconnected pores that are both large flow-through pores and smaller meso- or micropores. In general, the geometric surface of the microchannels is not sufficient for performing catalytic reactions. Therefore, it is necessary to increase the specific surface area by chemical treatment of the channel walls or by applying reasonably thick porous coatings, as monolith. The porous layer formed can be catalytically active or serve as a support for a catalytic phase. And the most common catalytic microreactors used consist of packed-bed columns randomly filled with catalytic bodies in the form of grains with particle sizes in the range 50–100 mm. The use of such reactors may present several drawbacks as mentioned in part 2, among them the formation of stagnation zones, hot-spot formation and broad distributions of residence time, which may result in low process efficiency and selectivity due to poorly controlled fluid dynamics. In contrast, monolithic structures are the best structured material known to overcome these drawbacks. They have a high void volume and a large geometric surface area. This results in a low pressure drop during the passage of a gas or a fluid, a large contact area of the reagent or the catalyst with the fluid, a great tolerance to high flow rates, efficient mass transfer through their large and small pores allowing higher back pressures and a high productivities.\textsuperscript{[8,53,54]}

Although this approach possesses a number of advantages over the packed-bed and wall-coated approach, in a few cases drawbacks like pore clogging, non-uniformity of radial permeability, and reduced accessibility of the catalytic sites buried deeply inside the micropores of the monolith, are observed.\textsuperscript{[8]}
4.1 Micro-monolithic microreactor modeling

The performance study of micro-monolithic microreactor is reported in many papers.

Valerio Chirol et al.\textsuperscript{[62]} have investigated a chiral organocatalytic polymer-based monolithic reactor. Organocatalyzed cycloadditions between cyclopentadiene and cinnamic aldehyde were performed under continuous-flow conditions; by optimizing the experimental set up, excellent enantioselectivities (90% ee at 25 °C) and high productivities (higher than 330) were obtained, thus showing that a catalytic reactor may work efficiently to continuously produce enantiomerically enriched compounds. The monolithic organocatalyst was prepared inside a standard HPLC column (0.46 cm i.d. ×15 cm, 2.49 mL total volume).

The use of a catalytic monolithic reactor led to less waste materials and better use of a valuable chiral catalyst in comparison with alternative batch and continuous-flow process intensification schemes. They have compared some results obtained in the organocatalyzed cycloaddition performed with supported catalysts in batch or under continuous-flow conditions, with two different columns (packed-bed and monolithic reactors). The results show that the monolithic reactor performs better than batch reactor and packed bed reactor.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Conditions\textsuperscript{a}</th>
<th>Salt</th>
<th>Time (h)</th>
<th>Productivity\textsuperscript{b}</th>
<th>TON\textsuperscript{c}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Batch</td>
<td>TFA</td>
<td>48</td>
<td>59</td>
<td>2.8</td>
</tr>
<tr>
<td>2</td>
<td>Batch</td>
<td>TFA</td>
<td>120</td>
<td>31</td>
<td>3.8</td>
</tr>
<tr>
<td>3</td>
<td>Batch</td>
<td>HBF\textsubscript{4}</td>
<td>120</td>
<td>46</td>
<td>5.6</td>
</tr>
<tr>
<td>4\textsuperscript{d}</td>
<td>Monolithic flow</td>
<td>TFA</td>
<td>120</td>
<td>38</td>
<td>4.6</td>
</tr>
<tr>
<td>5\textsuperscript{d}</td>
<td>Monolithic flow</td>
<td>HBF\textsubscript{4}</td>
<td>120</td>
<td>37</td>
<td>4.4</td>
</tr>
<tr>
<td>6\textsuperscript{d}</td>
<td>Monolithic flow</td>
<td>HBF\textsubscript{4}</td>
<td>24</td>
<td>338</td>
<td>8.1</td>
</tr>
<tr>
<td>7\textsuperscript{d}</td>
<td>Packed bed flow</td>
<td>HBF\textsubscript{4}</td>
<td>24</td>
<td>120</td>
<td>4.4</td>
</tr>
</tbody>
</table>

Figure 57 Batch vs. continuous-flow reactions, with different columns
\textsuperscript{a} Reactions run at 25 °C; \textsuperscript{b} Productivity is measured in mmol(product) h\textsuperscript{-1} mmol(catalyst)\textsuperscript{-1} \times \textsuperscript{10}\textsuperscript{3}; \textsuperscript{c} Turn over number is measured in mmol(product) mmol (catalyst)\textsuperscript{-1}; \textsuperscript{d} Flow rate 2 μL min\textsuperscript{-1}; \textsuperscript{e} Flow rate 18.8 μL min\textsuperscript{-1}; \textsuperscript{f} Flow rate 7.7 μL min\textsuperscript{-1}\textsuperscript{[62]}

As far as we know, however, chiral organocatalysts immobilized onto a monolithic support are completely unknown; moreover, only a few examples of chiral organocatalysts employed under continuous-flow conditions were reported.

Noemi Linares et al.\textsuperscript{[63]} have immobilized Pd nanoparticles by a green procedure onto unconventional dual porosity titania monoliths. The material is used in catalytic continuous-flow hydrogenation reactions showing excellent efficiency, selectivity, and durability.
Figure 58  Images of the bimodal TiO$_2$ monolith with well-defined macroporosity: (a, b) optical; (c) X-ray tomography; (d), SEM.$^{[63]}$

Figure 59  Catalytic Hydrogenations over Pd@TiO$_2$ Monoliths

The hydrogenation reaction of 1 was used to evaluate the productivity of the novel Pd@TiO$_2$ monolith catalyst and to compare it with that of the corresponding packed-bed and batch (stirred tank) systems and of the parent SiO$_2$ monolith, under similar reaction conditions. Representative results are reported in Fig.59 in terms of both turnover frequency (TOF = mol$_{\text{product}}$/mol$_{\text{Pd}}$ × h) and space-to-time yield (STY = kg$_{\text{product}}$/liter$_{\text{reactor}}$ volume × h). Compared to the packed-bed system, the productivity of the monolith was about 50% higher in terms of TOF and about 4
times higher when referred to the reactor volume. These findings highlight the superiority of the monolithic reactor with respect of packed-bed and batch design.

However, the modeling study of micro-monolithic microreactor is rare. There isn’t related research on the kinetic of reactor, such as mass transfer and heat transfer. But there is another catalytic microreactor called foams microreactor, who has a similar structure as the micro-monolithic microreactor. Open-celled foams are three-dimensional (3D) cellular materials made of interconnected solid struts, forming a network. The unit cell in a foam resembles a polyhedron with pentagonal or hexagonal faces that limit a spherical-like inner space. Each cell, defined by the hollow volume of the polyhedron, constitutes a pore. Therefore, we can use the modeling of foam to simulate that of micro-monolith.

![Figure 61 Foam structure and pore identification.](image)

In the work of Leonardo Giani et al.\textsuperscript{[67]}, foams with different cell sizes were coated with a thin layer of palladium-alumina and tested in a 9-mm inner diameter tubular reactor by performing the catalytic oxidation of CO at empty tube velocities in the range of 0.8-2.6 m/s. The coated foams exhibited sufficient catalytic activity to achieve mass-transfer-limited operation in the temperature range of 300-450 °C. Under such conditions, mass-transfer coefficients were determined according to a simple one-dimensional model of the test reactor.

Mass-transfer coefficients $k_m$ (given in units of m/s) were estimated from the CO conversions ($\eta$) measured under diffusion-controlled conditions, which represents the steady-state CO mass balance in the reactor, assuming isothermal plug flow behavior and irreversible reaction:

$$k_m = -\frac{\ln(1 - \eta)}{S_v V_0 / Q}$$

where $S_v$ is the specific area (given in units of $m^2/m^3$), $V_0$ is the reactor volume (given in units of $m^3$), and $Q$ is the volumetric flow (given in units of $m^3/s$).

The mass-transfer data obtained for all the tested foams could be fitted by a single
correlation, represented by the following equation:

\[ \text{Sh} = 1.1 \text{Re}^{0.43} \text{Sc}^{1/3} \]

It is worth emphasizing that this correlation closely resembles semi-theoretical literature correlations for heat transfer in flow across banks of tubes at low Reynolds numbers, e.g., the Nusselt number is \( \text{Nu} = 0.9 \text{Re}^{0.4} \text{Pr}^{1/3} \) for \( 10 < \text{Re} < 100 \). (\( \text{Pr} \) denotes the Prandtl number.)

Many authors have studied pressure drop across foam structures. In accordance with the approach adopted for mass transfer in this work, analysis of the pressure drop measurements was also based on the analogy with pressure drop across banks of tubes. Considering an array of cylinders, the pressure drop experienced by the cross flow is proportional to the number of tube rows \( (N_T) \) and can be expressed as

\[ \Delta P = N_T x f' \left[ \rho \left( \frac{u_{\text{max}}^2}{2} \right) \right] \]

They have also proposed that the pressure drop in foams, packed beds of pellets, or monoliths can be described by the following general equation, where \( f \) is a friction factor and \( d \) is the characteristic length, specific for each support:

\[ \frac{\Delta P}{L} = \left( \frac{2f}{d} \right) \rho u^2 \]

Then they have compared metal foams with other structures that are traditionally used as catalyst supports for environmental applications, such as packed beds of pellets and honeycomb monoliths. In such applications, very high conversions must be typically achieved under diffusion-controlled conditions, to secure the required abatement efficiency while keeping the pressure drop as low as possible, to avoid undue energy losses. Accordingly, a tradeoff between mass transfer and pressure drop performances must be pursued.

<table>
<thead>
<tr>
<th>Characteristic dimension</th>
<th>pellets</th>
<th>foams</th>
<th>honeycombs</th>
</tr>
</thead>
<tbody>
<tr>
<td>relationship with ( S_T ) and ( \epsilon )</td>
<td>( d_p S_T = 6(1 - \epsilon) )</td>
<td>( d_p S_T = 4(1 - \epsilon) )</td>
<td>( d_p S_T = 4\epsilon )</td>
</tr>
<tr>
<td>friction factor</td>
<td>( 2f = \frac{1 - \epsilon}{\epsilon^2} \left[ 1.75 + 150 \left( \frac{1 - \epsilon}{\text{Re}} \right) \right] )</td>
<td>( f = \left( 0.87 + \frac{13.86}{\text{Re}} \right) \left( 1 - G(\epsilon) \right) \frac{G(\epsilon) - 1}{4} )</td>
<td>( f = \frac{14.25}{d \text{Re}} )</td>
</tr>
<tr>
<td>mass-transfer coefficient</td>
<td>( \text{Sh} = a \text{Re}^{0.43} \text{Sc}^{1/3} )</td>
<td>( \text{Sh} = 1.1 \text{Re}^{0.43} \text{Sc}^{1/3} )</td>
<td>( \text{Sh} = 2.977 \left[ 1 + 0.095 \left( \frac{\text{Re}}{\epsilon} \right) S_0 \left( \frac{d}{L} \right) \right]^{0.43} )</td>
</tr>
</tbody>
</table>

Figure 62 Expressions Adopted in the Calculation of the Tradeoff Index\(^{[67]} \)

The tradeoff analysis between pressure drop and mass transfer performances indicates that metal foams exhibit marked advantages over packed beds but behave slightly worse than honeycomb monoliths as catalyst supports for fast reactions. On the other hand, in fast diffusion-limited processes, where pressure drop is of less concern, metallic foams can achieve conversions equivalent to honeycombs with significant reductions of the reactor size\(^{[67]} \).
5 Other Microreactors:

5.1 Membrane microreactors

Membrane microreactors (MMRs) utilize a membrane to create two compartments in which the gas and the liquid flow separately. Thus, an excellent gas–liquid contact is established between the two phases and the interfacial area between them is maximized. An interesting advantage of membrane microreactors is the opportunity to fine-tune the flow rates of the gas and the liquid phase independently while maintaining the well-defined interfacial area. The selective product removal may achieve supra-equilibrium conversions and improve product purity, whereas the selective addition of a reactant may enhance product selectivity and achieve improved temperature control and safety by eliminating hot spots. In some cases, it is also helpful to prevent catalyst poisoning and deactivation by removing undesirable byproducts from the reaction zone. Hence it combines the advantages of both the membrane reactor and the microreactor, leading to greatly intensified production processes. It allows the reactor to work not only under optimum reaction conditions due to rapid mass and heat transfer rates but also at significantly lower operating temperature and/or using less catalyst than in conventional reactors.\cite{76,77}

Potential problems associated with these membrane microreactors are degradation of the membrane and breakthrough of the liquid phase from one channel to the other.\cite{76}

Xiaoyao Tan and K. Li\cite{77} have investigated the configurations and fabrication of MMRs. Then they have discussed the applications of MMRs in different reactions. Paris Chasanis et al.\cite{78} have studied the effect of miniaturization and inlet velocity variation on the performance of a membrane microreactor. The microreactor consists of a reaction channel, in which the water gas shift reaction takes place, and a permeate channel, in which the permeating hydrogen is swept away. These channels are separated by a selective palladium membrane. A 3D CFD model is developed to account for hydrodynamics, mass transfer, chemical reaction and permeation through the membrane.

\[
\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2 \uparrow, \quad \Delta H^\circ_k = -41.2\text{kJ/mol}
\]
By decreasing the reactor dimensions, the reactor performance significantly improves as a result of increasing catalyst and membrane surface per volume.

The impact of the reformate inlet velocity is found to be remarkable, whereas the sweep gas inlet velocity has a lower influence. However, in the velocity range under consideration, the achieved yields vary between 0.83 and 0.92 and the hydrogen recovery between 0.18 and 0.4. This indicates that the effect of sweep gas inlet velocity cannot be neglected and justifies the need to take both channels into consideration.

Jigar M.Jani et al. [79] have worked on a numerical model studying mass transport and heterogeneously catalyzed reactions in a porous membrane microreactor. The hydrogenation of nitrite over a Pd catalyst was used as a model reaction. The influence of liquid flow rates, initial nitrite concentration and catalytic membrane layer thickness (wetting thickness) on the conversion was studied. This study provides detailed understanding of the mass transfer taking place in membrane microreactors. It also provides routes towards optimized reactor configurations, which allows for more efficient catalyzed gas–liquid reaction processes.
The concept of the reactor has been successfully implemented for the hydrogenation of nitrites in water. The hydrogenation of nitrite ions ($\text{NO}_2^-$) over palladium (Pd) catalyst in aqueous phase is described as

$$2\text{NO}_2^- + 3\text{H}_2 \xrightarrow{\text{Pd}} \text{N}_2 + 2\text{OH}^- + 2\text{H}_2\text{O}$$

<table>
<thead>
<tr>
<th>Porous membrane microreactor</th>
<th>Specifications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fiber inner radius (mm)</td>
<td>Big fiber—1.4</td>
</tr>
<tr>
<td>Wetted membrane thickness ($\delta$) (µm)</td>
<td>Big fiber—40, 20, 10</td>
</tr>
<tr>
<td>Reactor length (m)</td>
<td>Small fiber—0.4</td>
</tr>
<tr>
<td>Inlet liquid flow rate (mL/min)</td>
<td>Small fiber—50</td>
</tr>
<tr>
<td>Initial nitrite concentration (mol/m$^3$)</td>
<td>0.1, 0.2, 0.3</td>
</tr>
<tr>
<td>Diffusion coefficient for nitrite–water (m$^2$/s)</td>
<td>0.217, 1.09, 2.17</td>
</tr>
<tr>
<td>Diffusion coefficient for hydrogen–water (m$^2$/s)</td>
<td>$1.5 \times 10^{-9}$</td>
</tr>
<tr>
<td>Membrane porosity</td>
<td>$4.8 \times 10^{-9}$</td>
</tr>
<tr>
<td>Membrane tortuosity</td>
<td>0.2</td>
</tr>
<tr>
<td>Catalyst area (m$^2$/g)</td>
<td>73</td>
</tr>
</tbody>
</table>

The rate of mass transfer to reaction boundaries is represented by the local Sherwood number $\text{Sh}(z)$. It can be used as an indicator for the efficiency of a reactant adsorbing on a catalytically active surface. It is defined as
\[ \text{Sh}(z) = - \frac{N(z)R}{[C_1(z) - C_{1,s}(z)|_{r=R}]D_l} \]

where \(N(z) \) (mol/m\(^2\) s) is the local flux to the surface, \(C_1(z) \) (mol/m\(^3\)) is the bulk concentration of the liquid reactant, and \(C_{1,s}(z) \) (mol/m\(^3\)) is the liquid reactant concentration at the inner surface of the microreactor (at \(r=R\)).

### 5.2 Microfibrous entrapped catalysts microreactor

Microfibrous entrapped catalysts (MFEC) and sorbents are a new class of microstructurized materials which have shown significant benefits in various heterogeneous catalysis and adsorption applications. Microfibrous entrapped ZnO/silica adsorbent beds have shown remarkable improvement in breakthrough times over packed beds in desulfurization of hydrogen reformate streams. Substantial improvements in conversion and selectivity have been reported with use of MFEC for preferential catalytic oxidation of CO in hydrogen reformate streams and low temperature oxidation of CO in air. Also, microfibrous entrapped activated carbon beds have shown significant benefits for VOC adsorption in various personal and collective protection applications. MFEC have smaller characteristic dimensions and remarkably different internal structures compared to conventional contacting systems. These distinct characteristics of MFEC lead to higher reaction rates and lower pressure drops. \([69][71]\)

Ranjeeth R. Kalluri et al.\([69]\) have prepared MFEC by entrapping small particles of γ-alumina (150–180 mm) in sinters-locked network of metal (SS-304) microfibers (8 and 12 mm). These materials are in the form of thin flexible sheets (0.5–2.0 mm) and have uniform structures of high and variable voidages.

Head-to-head theoretical comparisons of the performance efficiencies of flow-through pleated MFEC structures of various pleat factors (PF = face area of MFEC/cross-sectional area of the reactor) were made with packed bed reactors of various particle sizes (0.16–2.0 mm) and monolith reactors of various cpsi (100–900 cells per square inch). These comparisons showed that while packed beds produced high pressure drops, monoliths resulted in low fluid-solid mass transfer rates. On the other hand, MFEC structures with high PF (\(> =4\)) showed remarkable improvements in terms of conversion along with significant reduction in pressure drops and catalyst requirements compared to monoliths and packed beds. While small particles used in MFEC improved interphase and intraparticle mass transport rates, high voidages and ease of pleating helped lower the pressure drops in MFEC.
As mentioned before, the pressure gradient in packed beds, monoliths or MFEC can be described by the following general equation, where \( f \) is a friction factor and \( d_c \) is the characteristic length, specific for each reactor type.

\[
-\frac{\Delta P}{L} = \frac{2f}{d_c} \rho v_0^2
\]

The characteristic length\( (d_c) \) for packed-beds and MFEC is equal to the effective particle diameter \( (\varphi, d_p) \) whereas for monoliths it is equal to the channel diameter \( (d_{ch}) \). The friction factors and gas–solid mass transfer coefficients (or Sh) for each of the reactor geometries were estimated using specific correlations discussed below.

**Packed beds**

<table>
<thead>
<tr>
<th>Particle diameters, ( d_p ) (mm)</th>
<th>0.16, 0.5 and 2.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sphericity ( (\varphi_p) )</td>
<td>0.7</td>
</tr>
<tr>
<td>Void (vol.%)</td>
<td>40</td>
</tr>
<tr>
<td>Catalyst (vol.%)</td>
<td>60</td>
</tr>
</tbody>
</table>

Friction factors for packed beds were estimated using Ergun equation. The Sherwood number for packed beds were obtained using Thoenes–Kramers correlation\(^{[76]}\)
\[
Sh = \frac{(1 - \epsilon_b)^{1/2}}{\epsilon_b} Re_p^{1/2} Sc^{1/3}
\]

It is a semi-empirical correlation widely used for predicting the mass transfer coefficients in packed beds with \(40 < Re_p/(1-\epsilon_b) < 4000\) and \(0.25 < \epsilon_b < 0.5\). The \(Re_p\) and bed voidage for packed bed cases used in this study are within these limits. The intraparticle transport rates in packed beds were modeled using the following effectiveness factor equations:[76]

\[
\eta = \frac{1}{\Phi} \left( \coth(3\Phi) - \frac{1}{3\Phi} \right)
\]

where

\[
\Phi = \left( \frac{\varphi_p d_p}{6} \right) \sqrt{\frac{k_r \rho_c}{D_e}}
\]

For all the reactor geometries compared, the effective diffusivity \((De)\) of the ozone inside the catalyst support was obtained, with \(t_b = 2.5\) and \(\epsilon_b = 0.75\). These values of intraparticle tortuosity and porosity correspond to the \(\gamma\)-alumina used in the experiments.

**Monoliths**

<table>
<thead>
<tr>
<th>Cells per square inch (cpsi)</th>
<th>100</th>
<th>400</th>
<th>900</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wall thickness, (t_w) (0.001 in./(\mu m))</td>
<td>15/381</td>
<td>65/152</td>
<td>2/51</td>
</tr>
<tr>
<td>Catalyst washcoat thickness, (t_c) ((\mu m))</td>
<td>25</td>
<td>25</td>
<td>25</td>
</tr>
<tr>
<td>Channel dia., (d_h) (mm)</td>
<td>2.109</td>
<td>1.068</td>
<td>0.745</td>
</tr>
<tr>
<td>Void (vol.%)</td>
<td>68.94</td>
<td>70.67</td>
<td>77.56</td>
</tr>
<tr>
<td>Catalyst (vol.%)</td>
<td>3.31</td>
<td>6.77</td>
<td>10.75</td>
</tr>
<tr>
<td>Length, (l) (cm)</td>
<td>12.7</td>
<td>12.7</td>
<td>12.7</td>
</tr>
</tbody>
</table>

Figure 70  Properties of various monoliths used in the theoretical comparisons[69]

The friction factors for monoliths were estimated using the following correlations:[75]

\[
f = \begin{cases} 
\frac{13}{\epsilon_b Re_{ch}} & \text{for } Re_{ch} < 1000 \\
0.03 \epsilon_b^{0.88} Re_{ch}^{0.12} & \text{for } Re_{ch} \epsilon_b > 1000 
\end{cases}
\]

There are many empirical correlations and theoretical equations available in literature for predicting the fluid-phase mass transfer coefficients for monoliths. In this study the correlation proposed by Tronconi and Forzartti[70] for the mass transfer in square channel monoliths was employed.

\[
Sh = 2.967 + 8.827 \times \left( \frac{1000}{Gz} \right)^{-0.545} \exp\left( \frac{48.2}{Gz} \right)
\]

For the theoretical comparisons, the catalyst washcoat density was assumed to be the same as that of particle density of alumina support.
Fibers in MFEC resemble infinitely long cylinders with ridges on the surface. The shape factor for an infinitely long cylinder is 1.5. This was multiplied by a factor of 0.7 to account for the surface roughness due to the ridges on the fibers.

Pleat factor (PF), a term frequently used with MFEC systems, is defined as follows:

\[
PF = \frac{\text{(total face area of MFEC media)}}{\text{(cross-sectional area of the reactor)}}
\]

![Image](image.png)

Figure 71  MFEC cases and bed properties used in the theoretical and experimental comparisons. [69]

Figure 72  Schematic of MFEC reactors. (a) Plain design (PF = 1) and (b) pleated design (PF > 1) [69]
PF values for monoliths and packed beds are always equal to one, as they cannot be pleated. For estimating the friction factors in MFEC systems the porous-media permeability equation proposed by Cahela and Tatarchuk\cite{77} was used

\[
2f = \left\{ 72 \left[ \sum \frac{x_i \varphi_p d_p}{\varphi_i d_i} \right]^2 + x_{FD} \sum x_i \left( \frac{\varphi_p d_p}{\varphi_i d_i} \right)^2 \right\} \left( 1 - \varepsilon_b \right) \frac{1}{PF Re_p} \]

\[
+ 3 \frac{\tau_b}{\cos(\theta)} \frac{1}{PF^2} \left[ C_f + C_{FD} \frac{\varepsilon_b}{4} \right] \sum \left( \frac{x_i \varphi_p d_p}{\varphi_i d_i} \right)^2 \left( 1 - \varepsilon_b \right) \frac{\tau_b^2}{\varepsilon_b^3} \cos^2(\theta)
\]

To predict the Sh in MFEC, the following empirical equation proposed by Dwivedi and Upadhyay\cite{79} for gas–solid contacting in fixed beds was used:

\[
Sh = \frac{0.455 (Re_p \frac{PF}{PF})^{0.59} Sc^{0.33}}{\varepsilon_b}
\]

Theoines–Kramers correlation\cite{70}, used for packed beds, is not suitable for high voidage MFEC structures. The equation above could also be used for packed beds, in which case the mass transfer coefficients could differ (up to 20%) from the values obtained using Theoines–Kramers correlation (for packed bed). However, this difference in predicted mass transfer coefficients for packed beds, does not significantly affect the comparative analysis or trends obtained in this study.

Similarly, Sabrina Wahid et al.\cite{71} have made a head-to-head experimental performance comparisons for flow through pleated microfibrous structures (flat-, V-, and W-shaped) with wash-coated monolith of different cells per square inch (230 and 400). Microfibrous entrapped catalyst (MFEC) was prepared by entrapping support particles (γ-Al₂O₃, 150–250 μm diameter) into nickel microfibers.

![Figure 73](Image)

(a) Micrograph of (a) 150–250 μm Al₂O₃ entrapped in 8 μm sintered Ni fiber; (b) cylindrical Ni fiber with the ridges on the surface \cite{71}

The experimental studies showed that pleated MFEC (W-shaped) had shown significantly improved performance in VOC removal in terms of conversion and pressure drop than tested monolith for high face velocity system. The flexibility of pleating lowered the effective velocity inside the media that resulted lower pressure
drop and higher conversion. Furthermore, a reaction kinetic model was developed for pleated MFEC considering the Peffer’s model to substantiate the experimental results.

To predict the gas–solid mass-transfer coefficient in MFECs, the Peffers’s model was applied. which is applicable for low Re number and high Pe number. Peffer’s equation was specifically proposed for particulate beds operating in laminar flow conditions. The pleated formation and small characteristic dimension of the MFECs enhances the laminar behavior inside the media even though the inlet velocity is high. Another reason for applying this equation was because it considers the bed voidage. Most of the other semiempirical correlations widely used for estimating mass-transfer coefficients of packed beds are applicable for a limited voidage range.

\[ \text{Sh} = 1.26 \left( \frac{1 - \gamma}{W} \right)^{\frac{1}{3}} \left( \frac{Re_P \text{Sc}}{PF} \right)^{1/3} \]

For the pleated geometries compared in this study, the effective diffusivity of ethanol inside the catalyst support followed equation with the values of \( t_p = 3.0 \) and \( \varepsilon_p = 0.82 \). These values of intraparticle tortuosity and porosity resemble to the c-Al\(_2\)O\(_3\) particles used in the experiments.

\[ D_e = D_m \frac{\varepsilon_p}{t_p} \]

The molecular diffusivity (Dm) of ethanol in the air was estimated using Fuller’s method.

\[ D_{\text{m}} = \frac{0.00143 T^{1.75}}{PM_{AB} \left( \sum \nu_A + \sum \nu_B \right)^{0.7}} \]

<table>
<thead>
<tr>
<th>Numbers of pleat</th>
<th>1, 2, and 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness (mm)</td>
<td>3.6</td>
</tr>
<tr>
<td>Nominal fiber diameter, ( d_i ) (( \mu )m)</td>
<td>4, 8, and 12</td>
</tr>
<tr>
<td>Particle diameter, ( d_p ) (( \mu )m)</td>
<td>0.19</td>
</tr>
<tr>
<td>Catalyst particle sphericity, ( \varphi_p )</td>
<td>0.7</td>
</tr>
<tr>
<td>Fiber sphericity</td>
<td>1.05 (= 1.5 ( \times ) 0.7)</td>
</tr>
<tr>
<td>Catalyst (vol %)</td>
<td>11.1</td>
</tr>
<tr>
<td>Metal (vol %)</td>
<td>2.2</td>
</tr>
<tr>
<td>Void (vol %)</td>
<td>86.7</td>
</tr>
</tbody>
</table>

Figure 74 Properties of the MFEC

<table>
<thead>
<tr>
<th>Cells per square inch (CPSI)</th>
<th>230</th>
<th>400</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wall thickness, ( t_w ) (0.001 in./( \mu )m)</td>
<td>8/203</td>
<td>6.5/1.65</td>
</tr>
<tr>
<td>Catalyst washcoat thickness, ( t_c ) (( \mu )m)</td>
<td>12.5</td>
<td>12.5</td>
</tr>
<tr>
<td>Channel diameter, ( d_{ch} ) (mm)</td>
<td>1.422</td>
<td>1.054</td>
</tr>
<tr>
<td>Void (vol %)</td>
<td>72.13</td>
<td>68.89</td>
</tr>
<tr>
<td>Catalyst (vol %)</td>
<td>3.484</td>
<td>4.685</td>
</tr>
</tbody>
</table>

Figure 75 Properties of the Monolith

The bed properties and the pleat numbers of MFEC, and the structural properties of
monoliths, used in this study are listed in Fig. 74 and 75, respectively. A variable speed drive is used to control the system speed, which can reach over 30 m/s inlet velocity. Heaters as well as purging air are used to control the system temperature, which can be raised to as high as 473 K. The main reactor section is square shaped and has a dimension of 12.7 * 12.7 * 22.9 cm$^3$. The FEC formations were flat, V-shaped, W-shaped which correspond to the numbers of pleat 1, 2, and 4, respectively. The dimension of the monolith was 12.7 * 12.7 * 11.45 cm$^3$. Therefore, two monoliths were placed in series to make the length equal to MFEC structure.

<table>
<thead>
<tr>
<th>Correlation</th>
<th>Pleated MFEC</th>
<th>Wash-coated monolith</th>
</tr>
</thead>
<tbody>
<tr>
<td>Friction factor ($f$)</td>
<td>$f = Cr \times \left{ 72 \left[ \sum \frac{\mu_i \phi_i d_i}{\phi_i d_i} + \sum \phi_i \left( \frac{\mu_i}{\phi_i} \right)^2 \right] + \sum \phi_i \frac{d_i}{\phi_i} \left( \frac{1}{\mu_i} \right) \right} \left[ \frac{1}{\mu_i} \right] \frac{d_i}{\phi_i} \cos \theta$</td>
<td>$f_F = \frac{1}{\mu_i} \left( \frac{d_F}{\phi_i} \right)$ for $R_e_{\phi_i} &lt; 1000$ and $f_F = \frac{1}{\mu_i} \left( \frac{d_F}{\phi_i} \right)$ for $R_e_{\phi_i} &gt; 1000$</td>
</tr>
<tr>
<td>Mass Transfer ($Sh$)</td>
<td>$Sh = 1.26 \left( \frac{1}{\phi_i} \right) + \left( \frac{d_i}{\phi_i} \right)$</td>
<td>$Sh = 2.967 + 8.827 \left( \frac{1000}{Sh} \right)^{0.585} \exp \left( \frac{4}{Sh} \right)$</td>
</tr>
</tbody>
</table>

Figure 76  Friction Factor and Mass-Transfer Correlations Used in this Study for Pleated MFEC and Wash-Coated Monolith

Figure 77  Schematic diagram of various MFEC reactors

The pressure gradient occurring across monoliths and MFECs can be described by a general equation, as shown in

$$\frac{-\Delta P}{L} = \frac{1}{2} f \frac{\rho v_0^2}{d_c}$$

where $f$ is the friction factor and $d_c$ is the characteristic length, specific for each reactor type. The characteristic length ($d_c$) of MFECs is equal to the effective particle diameter whereas for monoliths, it is equal to the channel diameter ($d_{ch}$)
Experimental pressure drop occurring across different catalytic structures for various inlet velocities ($T = 473$ K).

The results showed that W-shaped MFEC exhibited improved performance than 230 CPSI and 400 CPSI monoliths. This increase in performance was the result of decreased effective velocity (inside the MFEC) due to the pleated formation. The decreased effective velocity lowered the pressure drop and increased the intralayer residence time which resulted better conversion. However, monoliths performed better relative to the MFECs of low pleat numbers because of the low resistance to flow and better conversion.

Pleated MFEC showed promising performance as it provided a large surface/volume ratio for the entrapped catalyst. This attribute facilitates the weight and volume demand of the air handling system in a limited space. Furthermore, microstructured reactor system provides the designer with the opportunity to “engineer the microfibrous properties of the media” to the desired intraparticle or intraparticle transport rates required to feed the embedded kinetics of the applications. The efforts were made to provide “second generation” structured reactor as compared to the conventional packed bed reactor and wash-coated monolith. As this study showed some remarkable advantages of pleated MFEC, further improvements of MFEC bed properties and compositions (Pleat numbers, voidage, catalyst loading, etc.) appear to be very promising.
6 Conclusions

The comparison of performance and the numerical modeling of different types of continuous-flow microreactors with supported catalysis such as packed-bed microreactors, wall-coated microreactors (macro-monolithic reactors), monolithic microreactors etc. have been presented. The advantages and disadvantages of them have been discussed and summarized below:

<table>
<thead>
<tr>
<th>Types of microreactors</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
</table>
| Packed-Bed Microreactors | High catalyst loading  
Easy characterization and quantification of the catalyst  
Large range of catalytic supports  
Easy fabrication | Uncontrolled fluid dynamics  
Heat transfer limitation  
Significant pressure drops developing along the microchannel  
Low process efficiency and selectivity |
| Wall-Coated Microreactors and macro-monolithic reactor | Reduction of the mass and heat transfer resistance  
Lower pressure drop than packed-bed microreactors  
Smooth inflow of reagents without adverse pressure drop or blockage of microchannels  
Well defined flow geometries | Lower catalyst loading  
Small specific surface area |
| Monolithic Microreactors | High void volume  
Large geometric surface area  
Low pressure drop  
Large contact area of the reagent or the catalyst with the fluid  
Great tolerance to high flow rates  
Efficient mass transfer  
High productivities | Pore clogging  
Non-uniformity of radial permeability  
Reduced accessibility of the catalytic sites buried deeply inside the micropores of the monolith |
| Membrane Microreactors | Supra-equilibrium conversion  
Great product purity and selectivity  
Improved temperature control and safety  
Avoidance of catalyst poisoning and deactivation | Degradation of the membrane  
Breakthrough of the liquid phase from one channel to the other |
| Microfibrous entrapped catalysts microreactor | Smaller characteristic dimensions and remarkably different internal structures  
High reaction rates and low pressure drops  
Reduction of catalyst requirements  
High interphase and intraparticle mass transport rate  
Large surface/volume ratio |
As for the numerical modeling of these microreactors, there are plenty of formulations and correlations proposed. We should choose suitable model and formulations according to our microreactors adopted and the properties of reactions.

The future work is the verification and comparison of these correlations with data obtained by our microreactor system, in order to choose the suitable modeling for our heterogeneous catalytic microreactors.

7 References

[3] Raweewan Klaewkla, Matthias Arend and Wolfgang F. Hoelderich, A Review of Mass Transfer Controlling the Reaction Rate in Heterogeneous Catalytic Systems, Chemical Technology and Heterogeneous Catalysis, University of Technology RWTH


[27] Tiziano Maffei, Fundamental assessment of gas to particle mass transfer in micro-channel packed bed reactors, thesis, 2013,


[37] Ozgur Yasar Caglar, C. Doga Demirhan, Ahmet K. Avci, Modeling and design of a microchannel reformer for efficient conversion of glycerol to hydrogen, international journal of hydrogen energy XXX (2014) 1-7


[63] Noemi Linares, Sarah Hartmann, Anne Galarneau, and Pierluigi Barbaro,
Continuous Partial Hydrogenation Reactions by Pd@unconventional Bimodal Porous Titania Monolith Catalysts, ACS Catal. 2012, 2, 2194–2198


IV  Experimental section

1  Model reaction

The reduction reaction of para-nitrophenol by palladium (Pd) catalyst has been chosen as the model reaction, which is simple, safe and fast.

\[ \text{NO}_2^- + 3\text{HCO}_2\text{H} \xrightarrow{\text{Catalyst}} \text{NH}_2^- + 3\text{CO}_2 + 2\text{H}_2\text{O} \]

Figure 79  Hydrogenation of p-nitrophenol with formic acid

p-Aminophenol is an important intermediate produced in the syntheses of various chemicals including dyes, pharmaceuticals, and anticorrosive lubricants. The catalytic hydrogenation of aromatic nitro compounds with H\(_2\) has been studied extensively in the presence of Pd, Pt, Ni, and Rh metals. Formic acid is another attractive H\(_2\) source because it is safe, easy to handle, and requires no high pressure equipment.

Rahat Javaid et al.\(^{(1)}\) have developed the hydrogenation of p-nitrophenol with formic acid in catalytic flow-through tubular reactors with Pd based catalysts. They have coated the inner surface of a metallic tube (i.d. 0.5 mm) with a Pd-based thin metallic layer by flow electroless plating. The reaction was conducted at ambient pressure. An aqueous solution containing p-nitrophenol (10 mM) and formic acid was fed into the tubular reactor (100 cm long with inner volume of 196 μL) at a constant flow rate (0.8 mL/min) controlled by a peristaltic pump. No side reaction occurred. The conversion of their experiment is 40% at 30°C and 58% at 40°C. The kinetic analysis of their experiment will be discussed in the following part.

2  Kinetic analysis of model reaction in the paper

2.1  Parameters:

In the study of Rahat Javaid et al., the parameters of the reactor are as follows:
Table 8  Parameters of Rahat Javaid et al.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Parameter</th>
<th>Unit</th>
<th>Dimension</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q</td>
<td>Flow rate</td>
<td>mL/min</td>
<td>0.8</td>
</tr>
<tr>
<td>D</td>
<td>Internal diameter</td>
<td>mm</td>
<td>0.5</td>
</tr>
<tr>
<td>L</td>
<td>Length</td>
<td>cm</td>
<td>100</td>
</tr>
<tr>
<td>V</td>
<td>Volume</td>
<td>mL</td>
<td>0.196</td>
</tr>
<tr>
<td>t&lt;sub&gt;s&lt;/sub&gt;</td>
<td>Residence time</td>
<td>s</td>
<td>14.7</td>
</tr>
<tr>
<td>T</td>
<td>Temperature</td>
<td>°C</td>
<td>30 – 40</td>
</tr>
<tr>
<td>m&lt;sub&gt;pd&lt;/sub&gt;</td>
<td>Palladium mass</td>
<td>mg</td>
<td>67.3</td>
</tr>
<tr>
<td>X</td>
<td>Conversion of A</td>
<td>%</td>
<td>40 – 100</td>
</tr>
<tr>
<td>C&lt;sub&gt;A&lt;/sub&gt;</td>
<td>Initial concentration of</td>
<td>mol/L</td>
<td>0.01</td>
</tr>
<tr>
<td>C&lt;sub&gt;B&lt;/sub&gt;</td>
<td>Initial concentration of</td>
<td>mol/L</td>
<td></td>
</tr>
<tr>
<td>ε</td>
<td>Void fraction (V&lt;sub&gt;f&lt;/sub&gt;/V, V&lt;sub&gt;f&lt;/sub&gt; is the</td>
<td>-</td>
<td>1</td>
</tr>
<tr>
<td>r</td>
<td>Volumetric reaction rate,</td>
<td>mol/(L&lt;sub&gt;f&lt;/sub&gt;.s)</td>
<td></td>
</tr>
<tr>
<td>k</td>
<td>Reaction rate constant on</td>
<td>L&lt;sub&gt;f&lt;/sub&gt;/(mol.s)</td>
<td></td>
</tr>
<tr>
<td>r'</td>
<td>Volumetric reaction rate,</td>
<td>mol/(g·s)</td>
<td></td>
</tr>
<tr>
<td>k'</td>
<td>Reaction rate constant on</td>
<td>L&lt;sup&gt;2&lt;/sup&gt;&lt;sub&gt;f&lt;/sub&gt;/(g·mol·s)</td>
<td></td>
</tr>
</tbody>
</table>

so \( t_s = \frac{V_f}{Q} = \varepsilon \frac{V}{Q} (s) \)

### 2.2 Relation of conversion rate – operating conditions

The packed bed reactor is supposed to be a perfect plug flow reactor:

![Flow diagram of reactor](image)

We assume that the flow rate and the temperature are constants. The balance of p-nitrophenol in \( dV \) is established as follows:
\[ Q C_A = Q(C_A + dC) + r \cdot \varepsilon \cdot dV \]  \hspace{1cm} (1)

\[ -Q \mathrm{d}C = r \cdot \varepsilon \cdot \mathrm{d}V \]  \hspace{1cm} (1')

\( r \), reaction rate based on the fluid volume.

Or, with \( r' \), the reaction rate based on the Pd mass:

\[ -Q \mathrm{d}C = r' \cdot \mathrm{d}m_{Pd} \]  \hspace{1cm} (2)

\[ \begin{array}{c}
\text{NO}_2 \\
\downarrow \\
\text{OH} \\
\text{Catalyst} \rightarrow \\
\text{NH}_2 \\
\downarrow \\
\text{OH} \\
+ 3\text{HCO}_2\text{H} \rightarrow \\
+ 3\text{CO}_2 + 2\text{H}_2\text{O}
\end{array} \]

For the hydrogenation of p-nitrophenol with formic acid, we suppose the reaction rate as:

\[ r = k C_A C_B \]
\[ r' = k' C_A C_B \]

We define the conversion rate of p-nitrophenol \( X \) as:

\[ X = \frac{C_A^0 - C_A}{C_A^0} \]

and the stoichiometric excess of formic acid \( M \) as:

\[ \frac{C_B^0}{3 \cdot C_A^0} = M \]

so we can get:

\[ C_A = C_A^0 (1 - X) \]
\[ C_B = (C_B^0 - 3 \cdot X \cdot C_A^0) = 3 \cdot C_A^0 (M - X) \]
\[ \mathrm{d}C = -C_A^0 \cdot \mathrm{d}X \]

In the study of Rahat Javaid et al., \( 1/3 < M < 10/3 \). It should be noted that if \( M < 1 \), there is a deficit of formic acid and \( X \) is limited \( X \leq M \).

So we have:

\[ r' = k' C_A C_B = 3 \cdot k' \cdot C_A^0^2 (1 - x)(M - x) \]

With the equation (2),

\[ Q \cdot C_A^0 \cdot \mathrm{d}X = 3 \cdot k' \cdot C_A^0^2 (1 - X)(M - X) \cdot \mathrm{d}m_{Pd} \]

\( If \; M=1: \)
\[
\frac{dX}{(1-X)^2} = \frac{3}{Q} k' \cdot C_A^0 \, dm_{pd} \\
\frac{X_f}{(1-X_f)} = \frac{3}{Q} k' \cdot C_A^0 \cdot m_{pd} = A
\]

So:
\[
X_f = \frac{A}{1+A}
\]

Or:
\[
k' = \frac{Q \cdot X_f}{3 \cdot C_A^0 \cdot m_{pd} \cdot (1-X_f)}
\]

If \(M \neq 1\):
\[
\frac{dX}{(1-X)(M-X)} = \frac{3}{Q} k' \cdot C_A^0 \, dm_{pd}
\]

As:
\[
\int \frac{dx}{(1-x)(M-x)} = \frac{1}{1-M} \ln \left( \frac{1-x}{M-x} \right) + C
\]

We get:
\[
\frac{1}{M-1} \ln \left( \frac{1-X_f/M}{1-X_f} \right) = \frac{3}{Q} k' \cdot C_A^0 m_{pd}
\]

So:
\[
k' = \frac{Q}{3(M-1) \cdot C_A^0 \cdot m_{pd}} \ln \left( \frac{1-X_f/M}{1-X_f} \right)
\]

Or, with \(B = \exp \left[ \frac{3(M-1)}{Q} k' \cdot C_A^0 m_{pd} \right] \):
\[
X_f = \frac{B-1}{B-1/M}
\]

### 2.3 Calculation of the reaction rate constant from Rahat Javaid et al. experimental data

The data from the article are:
- \(M = 10/3\)
- \(m_{pd} = 67.3\) mg
- \(C_A^0 = 0.01\) mol/L
- \(Q = 0.8\) mL/mn

when \(T = 30^\circ C, X_f = 0.40\) so \(k'_{(30^\circ C)} = 0.001084\) L^2/(gpd.mol.s)
when $T = 40^\circ C$, $X_f = 0.58$ so $k'(40^\circ C) = 0.001914 \text{ L}^2/(\text{g}_\text{Pd}.\text{mol.s})$

According to the Arrhenius equation:

$$k' = k'_0 e^{-E/RT}$$

where

- $k'_0$ the pre-exponential factor, $\text{L}^2/(\text{g}_\text{Pd}.\text{mol.s})$
- $E$ the activation energy, $\text{J/mol}$
- $R$ the gas constant $= 8.31 \text{ J/(mol K)}$

For that, we can calculate the activation energy $E$ and the pre-exponential factor $k_0$ in the study of Rahat Javaid. We can get:

$$E = 44818 \text{ J/mol}$$

### 3 UV–vis peaks analysis

The UV–vis absorption spectra of p-Nitrophenol and 4-aminophenol has been measured as follows:

![UV–vis absorption spectra](image)

**Figure 81** UV–vis absorption spectra of p-Nitrophenol(0.1mmol/L) and 4-aminophenol(0.1mmol/L)

In the figure above we could find that, in the range after about 330nm, there is only the absorption curve of p-nitrophenol. In order to confirm this range then to calculate the conversion rate of the reaction, we have ascertained the effective
absorption wavelength by measuring the UV–vis absorption spectra of p-Nitrophenol (NP), formic acid (AF) and 4-aminophenol (AP) calibration solution and calculating the response factor of each absorbance.

<table>
<thead>
<tr>
<th>Table 9</th>
<th>Concentration of calibration solution</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Concentration (mmol/L)</td>
</tr>
<tr>
<td></td>
<td>Series 1</td>
</tr>
<tr>
<td>NP</td>
<td>0.1</td>
</tr>
<tr>
<td>AF</td>
<td>0.3</td>
</tr>
<tr>
<td>AP</td>
<td></td>
</tr>
</tbody>
</table>

The response factor (RF) of p-Nitrophenol is calculated as follows:

\[
RF = \frac{\text{Absorbance}}{\text{Concentration of NP}}
\]

If in a certain range of absorption, the RF of different series remain the same, so we could choose this range as the effective absorption wavelength to calculate the conversion.

In the range of 313nm~370nm, the standard deviation of response factor is 0.01. So we can suppose that the conversion of the reaction can be calculated in the range of 313nm~370nm.
4 Experimental setup

The chemicals are listed as below:

Formic acid (>98%, ACROS ORGANICS)
p-Nitrophenol (99%, Fluke Chemie AG)
Palladium (5 wt% on alumina powder reduced, STREM CHEMICALS)
p-Aminophenol (>99%, Fluke Chemie AG)
Isopropanol (>99%, CARLO ERBA REAGENTS)
Distilled water

The scheme of the experimental setup is shown in Fig.83. The aqueous solution containing p-nitrophenol and formic acid is pumped by a micro flow pump (Thermo Fisher, Model ISO-3100SD) via the reservoir. The reactor investigated is a HPLC stainless steel tube, with the inner diameter of 4.47mm and volume of 0.64ml. The tube has sinter in both ends and is filled with palladium powder, with the average diameter of 70μm. The thermostatic bath(Huber, Ministat 230cc) is filled with silicone oil. The product is collected in a flacon and then analyzed by UV–vis spectroscopy (UVIKON 933, Kontron Instrument).

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Parameter</th>
<th>Unit</th>
<th>Dimension</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q</td>
<td>Flow rate</td>
<td>mL/min</td>
<td>0.5~2.5</td>
</tr>
<tr>
<td>D</td>
<td>Internal diameter</td>
<td>mm</td>
<td>4.47</td>
</tr>
<tr>
<td>L</td>
<td>Length</td>
<td>cm</td>
<td>40</td>
</tr>
<tr>
<td>V</td>
<td>Volume</td>
<td>mL</td>
<td>0.64</td>
</tr>
<tr>
<td>T</td>
<td>Temperature</td>
<td>°C</td>
<td>30 – 60</td>
</tr>
<tr>
<td>m&lt;sub&gt;cat&lt;/sub&gt;</td>
<td>Catalyst mass</td>
<td>mg</td>
<td>639.5</td>
</tr>
<tr>
<td>D&lt;sub&gt;cat&lt;/sub&gt;</td>
<td>Catalyst average diameter</td>
<td>mm</td>
<td>0.07</td>
</tr>
<tr>
<td>m&lt;sub&gt;pd&lt;/sub&gt;</td>
<td>Palladium mass</td>
<td>mg</td>
<td>32</td>
</tr>
</tbody>
</table>
5 Experimental results and discussion

Several series of experiments have been carried out. The experimental conditions and the conversions calculated by the UV-vis. measurement are summarized in the following table:

<table>
<thead>
<tr>
<th>Nb.</th>
<th>Date</th>
<th>C_{A^*}, mmol/L</th>
<th>C_{B^*}, mmol/L</th>
<th>T, °C</th>
<th>Q, mL/mn</th>
<th>observations</th>
<th>X</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1607</td>
<td>10</td>
<td>30</td>
<td>40</td>
<td>0.5</td>
<td>333-354nm</td>
<td>0.970</td>
</tr>
<tr>
<td>2</td>
<td>1707</td>
<td>10</td>
<td>30</td>
<td>30</td>
<td>0.5</td>
<td>335-357nm</td>
<td>0.957</td>
</tr>
<tr>
<td>3</td>
<td>1707</td>
<td>10</td>
<td>30</td>
<td>40</td>
<td>0.5</td>
<td>335-357nm</td>
<td>0.967</td>
</tr>
<tr>
<td>4</td>
<td>1707</td>
<td>10</td>
<td>30</td>
<td>50</td>
<td>0.5</td>
<td>335-357nm</td>
<td>0.967</td>
</tr>
<tr>
<td>5</td>
<td>1707</td>
<td>10</td>
<td>30</td>
<td>60</td>
<td>0.5</td>
<td>335-357nm</td>
<td>0.968</td>
</tr>
<tr>
<td>6</td>
<td>2007</td>
<td>10</td>
<td>30</td>
<td>30</td>
<td>1</td>
<td>334-347nm</td>
<td>0.955</td>
</tr>
<tr>
<td>7</td>
<td>2007</td>
<td>10</td>
<td>30</td>
<td>30</td>
<td>2</td>
<td>334-347nm</td>
<td>0.956</td>
</tr>
<tr>
<td>8</td>
<td>2007</td>
<td>10</td>
<td>30</td>
<td>30</td>
<td>2.5</td>
<td>334-347nm</td>
<td>0.956</td>
</tr>
<tr>
<td>9</td>
<td>2007</td>
<td>10</td>
<td>30</td>
<td>30</td>
<td>4</td>
<td>334-347nm</td>
<td>0.953</td>
</tr>
<tr>
<td>10</td>
<td>2107</td>
<td>1</td>
<td>3</td>
<td>30</td>
<td>1</td>
<td>333-348nm</td>
<td>0.925</td>
</tr>
<tr>
<td>11</td>
<td>2107</td>
<td>1</td>
<td>3</td>
<td>40</td>
<td>1</td>
<td>333-348nm</td>
<td>0.926</td>
</tr>
<tr>
<td>12</td>
<td>2207</td>
<td>0.1</td>
<td>0.3</td>
<td>30</td>
<td>1</td>
<td>313-346nm</td>
<td>0.059</td>
</tr>
<tr>
<td>13</td>
<td>2207</td>
<td>0.1</td>
<td>0.3</td>
<td>40</td>
<td>1</td>
<td>313-346nm</td>
<td>0.060</td>
</tr>
<tr>
<td>14</td>
<td>2707</td>
<td>0.1</td>
<td>0.3</td>
<td>30</td>
<td>0.5</td>
<td>300-314nm</td>
<td>0.076</td>
</tr>
<tr>
<td>15</td>
<td>2707</td>
<td>0.1</td>
<td>0.3</td>
<td>30</td>
<td>0.8</td>
<td>300-314nm</td>
<td>0.037</td>
</tr>
<tr>
<td>16</td>
<td>2707</td>
<td>0.1</td>
<td>0.3</td>
<td>30</td>
<td>1</td>
<td>300-314nm</td>
<td>0.035</td>
</tr>
<tr>
<td>17</td>
<td>2907</td>
<td>0.5</td>
<td>1.5</td>
<td>30</td>
<td>0.5</td>
<td>326-337nm</td>
<td>0.722</td>
</tr>
<tr>
<td>18</td>
<td>2907</td>
<td>0.5</td>
<td>1.5</td>
<td>30</td>
<td>0.8</td>
<td>326-337nm</td>
<td>0.722</td>
</tr>
<tr>
<td>19</td>
<td>2907</td>
<td>0.5</td>
<td>1.5</td>
<td>30</td>
<td>1</td>
<td>326-337nm</td>
<td>0.724</td>
</tr>
<tr>
<td>20</td>
<td>3007</td>
<td>0.2</td>
<td>0.6</td>
<td>30</td>
<td>1</td>
<td>316-339nm</td>
<td>0.286</td>
</tr>
<tr>
<td>21</td>
<td>3007</td>
<td>0.2</td>
<td>0.6</td>
<td>50</td>
<td>1</td>
<td>316-339nm</td>
<td>0.275</td>
</tr>
</tbody>
</table>

It should be noticed that when the concentration of p-nitrophenol is 10mmol/L, the conversion is always high and the flow rate and the reaction temperature have no influence on the conversion. The first experiment conditions were chosen according to the kinetics in the paper of R.Javid. Results indicate that our catalyst is more active. When we reduced the concentration from 10mmol/L to 1mmol/L and then to 0.1 mmol/L, the conversion varied a lot when the initial concentration is 0.1 mmol/L,
0.2 mmol/L and 0.5 mmol/L. Then the temperature and the flow rate have been changed to study the kinetic principle of our system.

In the experiment No.1 and 3, No.12 and 16, the operating conditions are the same, respectively. The conversion in the same operating conditions remains the same (with acceptable error), which verifies the repeatability of our experiments.

The composition and conversion of No.2 and 19 experiment have been also evaluated by using $^1$H NMR spectroscopy to validate the UV-vis. measurement. The spectroscopy (see Annex) indicates that there isn’t any by-product in the product collected.

Table 12 Conversion of $^1$H NMR spectroscopy and UV-vis. spectroscopy

<table>
<thead>
<tr>
<th>Nb</th>
<th>CA° , mmol/L</th>
<th>CB° , mmol/L</th>
<th>T, °C</th>
<th>Q, mL/mn</th>
<th>X(UV vis.)</th>
<th>X(NMR)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>10</td>
<td>30</td>
<td>30</td>
<td>0.5</td>
<td>0.957</td>
<td>~1</td>
</tr>
<tr>
<td>19</td>
<td>0.5</td>
<td>1.5</td>
<td>30</td>
<td>1</td>
<td>0.724</td>
<td>0.752</td>
</tr>
</tbody>
</table>

From Table 12 we can conclude that despite lack of precision, conversions calculated from the UV-vis. spectroscopy are valid.

### 5.1 Kinetic analysis

We assumed that the reaction has the second order kinetics. According to the equations obtained in IV 2.2, the rate coefficient $k$ of our experiments can be calculated as:

$$k = \frac{A Q}{3 C^0 A m_{Pd}}$$

with

$$A = \frac{X}{1 - X}$$

The reaction rate constant $k$ of our experiment can be calculated with equation (3):

Table 13 Reaction rate constant of experiment

<table>
<thead>
<tr>
<th>Nb</th>
<th>X</th>
<th>A</th>
<th>k(L²/(gPd.mol.s))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.970</td>
<td>32.33333333</td>
<td>0.280890742</td>
</tr>
<tr>
<td>2</td>
<td>0.957</td>
<td>22.29642813</td>
<td>0.193696709</td>
</tr>
<tr>
<td>3</td>
<td>0.967</td>
<td>29.53095185</td>
<td>0.256545494</td>
</tr>
<tr>
<td>4</td>
<td>0.967</td>
<td>29.05053155</td>
<td>0.252371919</td>
</tr>
<tr>
<td>5</td>
<td>0.968</td>
<td>30.34669557</td>
<td>0.263632139</td>
</tr>
<tr>
<td>6</td>
<td>0.955</td>
<td>21.22040445</td>
<td>0.368854217</td>
</tr>
<tr>
<td>7</td>
<td>0.956</td>
<td>21.49108809</td>
<td>0.746801775</td>
</tr>
</tbody>
</table>
Compared with the reaction rate constant in the paper of Rahat Javaid et al. \( k'(30^\circ \text{C}) = 0.001084 \text{ L}^2/(\text{g Pd.mol.s}) \) and \( k'(40^\circ \text{C}) = 0.001914 \text{ L}^2/(\text{g Pd.mol.s}) \), the reaction rate constant of our experiments are much larger, which indicates that the same reaction conducted in our packed bed microreactor is faster and more efficient, and the catalyst we used is much more active than that in the paper (Rahat Javaid et al.)

### 5.2 Mass transfer

The mass transfer has been introduced in the part of Introduction. The external mass transfer can be analyzed by the mass transfer coefficient \( k_0 \) (m/s), and the internal mass transfer can be analyzed by the effective diffusion coefficient \( D_{\text{eff}} \) (m\(^2\)/s).

**External mass transfer**

To obtain the mass transfer coefficient, the Reynolds number \( \text{Re} \), the diffusion coefficient \( D_m \) (m\(^2\)/s), the Schmidt number \( \text{Sc} \) and the Sherwood number \( \text{Sh} \) must be calculated as follows.

**The Reynolds number \( \text{Re} \):**

\[
\text{Re} = \frac{u D_{\text{cat}} \rho}{\mu}
\]

\( u \) (m/s) the superficial flow rate of the fluid,
\( D_{\text{cat}} \) (m) the catalyst average diameter,
\( \rho \) (g m\(^{-3}\)) the density of the fluid,
\( \mu \) (Pa.s) the viscosity of the fluid

\( D_m \) is the **mutual diffusion coefficient** of solute A at very low concentrations in solvent B. It exists many correlations to estimate the diffusion coefficient. A widely used correlation called Wilke-Chang\(^2\) estimation method is adopted here.
\[ D_m = \frac{7.4 \times 10^{-8}(\emptyset M_B)^{1/2}T}{\mu V_A^{0.6}} \]

\( M_B \) (g/mol) the molecular weight of solvent B, here is 18 g/mol,
\( \emptyset \) the association factor of solvent, for water \( \emptyset = 2.6 \),
\( T \) the temperature,
\( \mu \) (Pa.s) the viscosity of solvent
\( V_A \) (ml/mol) the molar volume of solute A at its normal boiling temperature, for p-nitrophenol, \( V_A = 151 \) ml/mol

**The Schmidt number Sc:**
\[ Sc = \frac{\mu}{(\rho \times D_m)} \]

**The Sherwood number Sh** can be estimated by a large number of correlations. We utilize the most widely used correlation here:
\[ Sh = 2 + 0.6 \text{Re}^{1/2}Sc^{1/3} \]

With \( Sh \), the mass transfer coefficient \( k_D \) can be estimate:
\[ k_D = Sh \times D_m/D_{cat} \]

For investigating the external mass diffusion, Mears proposed a criterion, **Mears’ criterion** \( f_E \), the ratio of the rate of reaction to the external diffusion rate. If this criterion is less than 0.05, it means that the external diffusion resistance is low and can be neglected.
\[ f_E = \frac{r_{exp}}{r_{diffusion}} = \frac{Q \times X/V}{k_D \times S_{cat}/V_{cat}} \]

where \( S_{cat} \) the external surface of catalyst and \( V_{cat} \) the volume of catalyst.

The related calculation results are listed in the following table:

<table>
<thead>
<tr>
<th>Nb</th>
<th>Re</th>
<th>( D_m ) (m²/s)</th>
<th>Sc</th>
<th>Sh</th>
<th>k_D (m/s)</th>
<th>f_E</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.03717</td>
<td>7.81126E-10</td>
<td>1280.20</td>
<td>3.26</td>
<td>3.63E-05</td>
<td>8.11E-09</td>
</tr>
<tr>
<td>2</td>
<td>0.03717</td>
<td>7.56182E-10</td>
<td>1322.43</td>
<td>3.27</td>
<td>3.53E-05</td>
<td>8.23E-09</td>
</tr>
<tr>
<td>3</td>
<td>0.03717</td>
<td>7.81126E-10</td>
<td>1280.20</td>
<td>3.26</td>
<td>3.63E-05</td>
<td>8.09E-09</td>
</tr>
<tr>
<td>4</td>
<td>0.03717</td>
<td>8.06076E-10</td>
<td>1240.59</td>
<td>3.24</td>
<td>3.73E-05</td>
<td>7.86E-09</td>
</tr>
<tr>
<td>5</td>
<td>0.03717</td>
<td>8.31014E-10</td>
<td>1203.35</td>
<td>3.23</td>
<td>3.84E-05</td>
<td>7.67E-09</td>
</tr>
<tr>
<td>6</td>
<td>0.07434</td>
<td>7.56182E-10</td>
<td>1322.43</td>
<td>3.80</td>
<td>4.10E-05</td>
<td>1.42E-08</td>
</tr>
<tr>
<td>7</td>
<td>0.14869</td>
<td>7.56182E-10</td>
<td>1322.43</td>
<td>4.54</td>
<td>4.90E-05</td>
<td>2.37E-08</td>
</tr>
<tr>
<td>8</td>
<td>0.18586</td>
<td>7.56182E-10</td>
<td>1322.43</td>
<td>4.84</td>
<td>5.23E-05</td>
<td>2.78E-08</td>
</tr>
<tr>
<td>9</td>
<td>0.29737</td>
<td>7.56182E-10</td>
<td>1322.43</td>
<td>5.59</td>
<td>6.04E-05</td>
<td>3.83E-08</td>
</tr>
<tr>
<td>10</td>
<td>0.07434</td>
<td>7.56182E-10</td>
<td>1322.43</td>
<td>3.80</td>
<td>4.10E-05</td>
<td>1.37E-08</td>
</tr>
<tr>
<td>11</td>
<td>0.07434</td>
<td>7.81126E-10</td>
<td>1280.20</td>
<td>3.78</td>
<td>4.21E-05</td>
<td>1.33E-08</td>
</tr>
</tbody>
</table>
In all the experiments, the Mears’ criterion $f_E << 0.05$. Therefore, the bulk diffusion can be neglected.

**Internal mass transfer**

The effective diffusion coefficient $D_{\text{eff}}$ is calculated by diffusion coefficient $D_m$, the porosity $\varepsilon$ and the tortuosity $\tau$:

$$D_E = D_m \cdot \varepsilon / \tau$$

The porosity $\varepsilon$ can be calculated by the correlation proposed by Tsotsas and Schlünder\(^3\) which were adapted from the empirical formula of Dixon\(^4\).

$$\varepsilon = 0.37 + \frac{0.05}{N} + \frac{0.5344}{N^2}$$

$$N = \frac{D}{D_{\text{cat}}}$$

We can get the porosity $\varepsilon = 0.371$

The tortuosity $\tau$ can be calculated by the correlation reported by Puncochar and Drahos\(^5\):

$$\tau = \frac{1}{\sqrt{\varepsilon}}$$

so $\tau = 1.64$

For investigation of internal mass diffusion effect inside the catalyst pellet, the Weisz-Prater criterion $\Theta_w$ is used to determine whether internal mass transfer is limiting the reaction.

$$\Theta_w = \frac{QX/V}{(S_{\text{cat}}/V_{\text{cat}})^2 D_E}$$

If $\Theta_w < 0.1$, the internal pore diffusion can be negligible.
From Table 15, the Weisz-Prater criterion is much smaller than 0.1, signifying that internal pore diffusion is also negligible.

5.3 Influence of concentration, flow rate and temperature

From the kinetic analysis of the reaction in the packed bed microreactor, we have the equation (3) based on the second order kinetics:

\[ A = 3kC_A^0 m_{pd}/Q \]

with

\[ A = \frac{X}{1 - X} \]

With this equation, the conversion \( X \) depends on the initial concentration of reactant, the flow rate and the mass of catalyst. Several series of experiments with different concentrations and flow rates have been conducted to analyze the influence of concentration and flow rate, then to verify the second order kinetics assumption.
Fig. 84 shows the linear fit of $A$ as the function of initial concentration $C_{NP0}$. When the flow rate $Q=1\text{ml/min}$, the linear function is $y=a_1 x + b_1$ with $a_1 = 2.08206$ and $b_1 = 0.44967$; when the flow rate $Q=0.5\text{ml/min}$, the linear function is $y=a_2 x + b_2$ with $a_2 = 4.2586$ and $b_2 = 0.05106$. The R square are 0.9939 and 0.9997, respectively, which means the linear correlation is strong. The temperature is $30^\circ\text{C}$ in both conditions.

With equation (3), we know that when $Q$ is 2 times larger, the slope of the linear function should be 2 times smaller. In our linear fit, $Q = 1\text{ml/min} = 2 \times 0.5\text{ml/min}$, then $a_1 = a_2 / 2$, which well corresponds the assumption. What’s more, the intercept $b_1$ and $b_2$ are close to 0. Therefore, we can conclude that influence of concentration on the conversion can well verify our second order kinetics assumption.

Furthermore, in equation (3), $A$ can be regarded as a function of $C_{NP0}/Q$ with the slope $3k m_{Pd}$ and intercept 0. It can be verified with the experiment results.

Figure 85 A and linear fit of $A$ as a function of $C_{NP}/Q$
Fig. 85 shows the linear fit of A as the function of $C_A^0/Q$. The linear function obtained is $y = a_3 x + b_3$ with $a_3 = 0.0758$ and $b_3 = 0.16725$.

In the assumption, $a_3' = 3k_{mpd} = 0.058395$, which is a little smaller than $a_3$ obtained by the linear fit. It’s probably due to the measurement error and bad precision of UV spectroscopy. For example, if the conversion calculated is $X = 0.95 \pm 0.03$, the $A = X/1 - X$ can vary between 11.5 and 49, which is a large gap.

To study the influence of flow rate and temperature on the conversion, the following tables have been summarized.

### Table 16 Influence of flow rate

<table>
<thead>
<tr>
<th>$C_{NP}^°$, mmol/L</th>
<th>$C_{AF}^°$, mmol/L</th>
<th>T, °C</th>
<th>Q, mL/mn</th>
<th>X</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>30</td>
<td>30</td>
<td>0.5</td>
<td>0.957</td>
</tr>
<tr>
<td>10</td>
<td>30</td>
<td>30</td>
<td>1</td>
<td>0.955</td>
</tr>
<tr>
<td>10</td>
<td>30</td>
<td>30</td>
<td>2</td>
<td>0.956</td>
</tr>
<tr>
<td>10</td>
<td>30</td>
<td>30</td>
<td>2.5</td>
<td>0.956</td>
</tr>
<tr>
<td>10</td>
<td>30</td>
<td>30</td>
<td>4</td>
<td>0.953</td>
</tr>
</tbody>
</table>

### Table 17 Influence of temperature

<table>
<thead>
<tr>
<th>$C_{NP}^°$, mmol/L</th>
<th>$C_{AF}^°$, mmol/L</th>
<th>T, °C</th>
<th>Q, mL/mn</th>
<th>X</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>30</td>
<td>30</td>
<td>0.5</td>
<td>0.957</td>
</tr>
<tr>
<td>10</td>
<td>30</td>
<td>40</td>
<td>0.5</td>
<td>0.967</td>
</tr>
<tr>
<td>10</td>
<td>30</td>
<td>50</td>
<td>0.5</td>
<td>0.967</td>
</tr>
<tr>
<td>10</td>
<td>30</td>
<td>60</td>
<td>0.5</td>
<td>0.968</td>
</tr>
</tbody>
</table>

In Table 16 and Table 17, the conversion X is almost constant when the flow rate and temperature vary. So it’s impossible to study the influence of Q and T. It’s perhaps because the reaction in such conditions is so fast and the catalyst is so active that the conversion is always high, the temperature and the flow rate haven little effect on the reaction process. Therefore, it’s necessary to decrease the reaction rate in the future work, by changing the catalyst for example.

### 6 Conclusions

The reduction reaction of para-nitrophenol was studied in a packed bed microreactor with palladium (Pd) powder catalyst. The reaction chosen is rapid and simple, and the experimental setup is easy to be carried out.
1. The UV-vis. spectroscopy was used to analyze the product. The conversion was validated by the \(^1\)H NMR, but the the accuracy is not enough. The repeatability of our experiments has also been verified. And \(^1\)H NMR spectroscopy proved that there is no by-product in our experiments.

2. The kinetic parameters has been calculated and studied. The reactor system is more efficient and the catalyst utilized is much more active than that in the paper published. The second order kinetics assumption was proposed and well verified by the study of strong influence of concentration on the conversion.

3. There is a non-workable part when the conversion X measured is too high (>0.95). And due to the bad precision of UV vis., the gap of A=X/1-X is large.

4. For a series of experiment No.17-19 and No.20-21, the flow rate Q and the temperature T have no influence on the conversion. This is difficult to understand.

5. The external and internal transport limitations have been studied. The bulk diffusion and the internal pore diffusion are both negligible.

6. The steady state of has been verified. The stabilization time is about 10 times longer than the residence time.

The future work will concentrate on increasing the precision of analytical method, utilize the gas chromatography for example, and decreasing the reaction rate, by changing the operating conditions or changing the catalyst.

7 References

V Conclusions

As the first part of thesis, the internship focus on the literature study and primary experiment. The objective of internship, is to know well the aim of the thesis (introduced in part I Introduction), to have a good grasp of basic concept of different heterogeneous catalytic microreactors, and chiral heterogeneous catalyst, and to attempt to carry out the primary experiments and then to analyze them.

This report presents two major sections of the internship: literature research section, which concentrate in the pilot and industrial application of microreactors and modeling studies of different types of heterogeneous catalytic microreactors; experimental section, which is carried out with a packed-bed microreactor and a fast and simple reaction: reduction reaction of para-nitrophenol by palladium (Pd) catalyst.

1. In the part of industrial application of microreactors, different types of pilot and industrial microreactors have been summarized. Different reactions that can be largely modified by microreactors have been presented. The microreactors can largely modify the current industrial reactor system, meanwhile improve the security and productivity efficiency of process. However, the ongoing developments in industry are not published, so that we can’t obtain whole information of different microreactors;

2. Three major types of heterogeneous catalytic microreactors have been introduced and compared. The modeling studies of them have been discussed in detail. Among the plentiful correlations of mass transfer, heat transfer and pressure drop, we should choose the corresponding correlations to different microreactors. Thus, the future work of this part will concentrate on the comparison of different correlations with the data got in our experiments.

3. A safe, simple and rapid model reaction has been chosen, and a simple packed-bed microreactor system has been set up. The kinetic parameters has been calculated and studied. The microreactor system is more efficient and the catalyst utilized is much more active than that in the paper published. The second order kinetics assumption has been proposed and well verified. But it still exists the lack of precision of analytical method. The following work is to modify analytical method and change the type of catalyst.

I have gained a lot during this internship. I have learned not only the knowledge of microreactors, but also the attitude and method of scientific research, which could help me to get well prepared for the following Phd thesis.

During the internship, there are other preparation works such as placing orders to
buy instruments, which takes a lot of time. These preparation works are boring but also important. As an old saying goes: Grinding a chopper will not delay the work of cutting firewood.
Annex

The $^1$H NMR spectroscopy of experiment Nb.2
The $^1$H NMR spectroscopy of experiment Nb.19