Novel structured porous reactors for the scale-up of liquid-liquid reactions

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Highlights

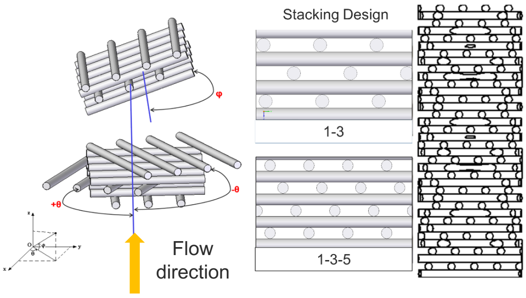
- Novel designed porous reactors for bi-phasic reactions are proposed.
- Design parameters for segmented and stratified flow are investigated.
- For stratified flow, increased yields at low overall pressure drops are observed.
- The developed reactors can be scaled-out from the micro- to the milli-scale.

1. Introduction

For biphasic transformations, packed beds represent a versatile reactor system to improve mixing and mass transfer. However, the main drawbacks limiting their use, especially for scale-up applications, is their large associated pressure drop, flow mal-distribution resulting in non-uniform contact time, and attrition of the small particles. An interesting alternative to overcome these drawbacks is the use of porous structures based on open cell metal foams, which combine the improved transport processes of the micro-scale with the throughput of milli-scale reactors [1]. For multiphase flow applications, open cell metal foams were primarily investigated for gas-liquid systems to study hydrodynamics and mass transfer in both co-current and counter-current operation in solid foam packings [2]. In our previous work, we have investigated liquid-liquid flow hydrodynamics and mass transfer in various structured and well-defined porous media similar to open cell foams [3]. We have found that depending on the fluid properties, different design parameters of the porous structures play a crucial role in determining the overall mass transfer performance. In general, it is observed that the porous reactors enhance slug breakup, resulting in lower mean slug lengths for both phases and an associated enhancement in surface renewal velocities. The designed porous milli-scale reactors provide enhanced mass transfer performance, with two orders of magnitude reduced energy dissipation compared to conventional milli-scale packed bed reactors.

2. Methods

In this study, we apply the designed porous milli-scale reactors for the amination reaction of aryl halides in the presence of a phase transfer catalyst (PTC) and to the oxidation of primary alcohols using Tempo. With these two systems, we are able to address segmented and stratified two-phase flows. The porous reactors are manufactured by either selective laser sintering (SLS) or 3-dimensional fibre deposition (3DFD). All structured porous reactors are made of stainless steel with an internal diameter of 3.4 mm. The base structure is shown in Fig. 1, and it consists of cylindrical fibres with an outer diameter of 250 μm in either a 1–3 or 1–3–5 stacking arrangement. Furthermore, additional rotations between fibre layers are introduced with respect to the mean flow direction (z-axis, angle θ) and with respect to the plane normal to the mean flow direction (x,y-plane, angle φ), see Fig. 1. The performance of the designed porous reactors is assessed by comparing with an equivalent void volume milli-scale packed bed reactor and an empty tube.



Name	Method	Porosity (%)	Specific surface area (m^2/m^3)	Void Volume (μL)	Description
Insp 1	SLS	74%	4160	449.6	$\theta=\pm 22.5^0$ in alternate stacks, $\varphi=45^0$ around x,y-axis Interfiber distance 500μm
Vito 2	3DFD	71%	4715	448.3	Alternate stacking after 10 rows $\varphi=0^0$ & $\theta=0^0$ Interfiber distance 1-3: 250μm, 1-3-5 : 500μm
PB 1	Packed bed	40%	37895	448.3	Stainless steel spheres, particle size: 60-125μm
ET	-	100%	1	419.6	Stainless steel tube with I.D.: 3.8mm and length 3.7cm

Figure 1. Geometric details of the investigated reactors.

3. Results and discussion

With respect to the amination of aryl halides, we observe increased yield for all porous reactors (compared with the empty tube), with full conversion achieved at a residence time of 8 min for the packed-bed. The designed porous reactors exhibit a lower conversion in comparison with the packed-bed, as due to their higher porosity a lower pore scale velocity is obtained, which is detrimental in increasing interfacial mass transfer for segmented flows. These observations are also confirmed when quantifying the k_La value, which is larger for the packed-bed. Advancing to the oxidation of primary alcohols using Tempo, which is a much faster reaction compared to aminations, we find that the designed novel reactors outperform the packed-bed. They are characterized by a larger reaction yield at similar residence times and a larger k_La value, both achieved at orders of magnitude smaller pressure drop compared to the packed-bed. In terms of internal design, the Vito2 reactor is most efficient at these high flow rates, indicating that the alternating stacking arrangement improves interfacial mass transfer in stratified flow.

4. Conclusions

In conclusion, we have applied the designed porous reactors to different biphasic reactions and have identified that they perform better (compared to a packed-bed) for fast reactions and for stratified flow cases. Furthermore, the structured porous reactors have great potential for scale-up applications. Firstly, their fixed wall contact (the surrounding tube is printed together with the porous structure) leads to superior heat transfer performance. Secondly, increasing the internal diameter of a tubular reactor will lead to stratified flow situations, for which especially the Vito2 reactor showed significant performance increase.

References

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Keywords
3D printing; porous reactors, biphasic reactions; scale-up