Structured porous milli-reactors for liquid-liquid chemical reactions

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Abstract:

Milli-scale reactors with an integrated micro-structure offer a promising scale-up approach for conventional micro-reactors. This study applies 3D printed structured porous milli-reactors to industrially-relevant liquid-liquid reactions. The underlying transport mechanisms are identified by quantifying interfacial heat and mass transfer. The structured reactors perform limited in Taylor flow compared to a packed-bed reactor due to limited interfacial mass transfer. However, in stratified flow, their productivity increases significantly at a fraction of the pressure drop of a packed-bed.

Keywords: biphasic reactions, heat transfer, mass transfer, scale-up, structured porous reactor

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1 Introduction

Process Intensification plays a vital role in the chemical industry as it increases process efficiency by identifying ways to overcome the limitations posed to transport phenomena of matter, momentum and energy with concurrent reduction in capital cost and environmental impact. Over the last decade, as a result of research on process intensification, several novel reactor concepts have been proposed to improve the efficiency of chemical processes, e.g. HiGee or spinning disc reactors [1], static mixers [2], multifunctional reactors like reactive distillation columns [3], membrane reactors [4]. Another groundbreaking approach is the miniaturization of chemical process equipment, i.e. micro-structured reactors. Micro-structured devices have several advantages over conventional reactors such as improved energy efficiency, safety, higher yield and improved process control [5-7]. Especially for heterogeneous reaction systems, packed-bed micro-reactors have been shown to achieve increased transport and reaction performance [8-10]. However, the efforts to design such miniaturized continuous systems often failed to achieve sufficiently large productivity. Therefore, scale-up is needed for operation at industrial scale, and one proposed approach is numbering up, which means operating individual devices in parallel. However, this approach presents challenges for the daily operation of these reactors due to difficulties like non-uniform fluid distribution in the parallel micro-structured devices. Therefore, this is not an economical viable solution for large-scale production [11]. Another approach is scale-up by increasing the characteristic dimensions resulting in milli-scale reactors [12-14]. These milli-scale reactors can also be integrated with micro-structures, which offers a promising scale-up approach as it combines their throughput with the advantages of micro-structured reactors. Examples include milli-scale packed-bed reactors, monolith reactors, and porous cellular structures. Milli-scale packed-bed reactors were successfully demonstrated for e.g. aerobic oxidation [15], Fischer–Tropsch synthesis [16], and Pd-catalyzed cross coupling reaction [17]. However, they are also susceptible to high pressure drops and channeling which limits their usage. Monolith reactors as catalyst supports are applied in industry for e.g. liquid phase hydrogenation [18],

nitro-aromatic hydrogenations [19], and toluene saturation [20]. However, the most widely used honeycomb monolith reactor provides only limited mass transfer in its radial direction [21]. Porous reactors (or open-cell metal foam reactors) have been shown to have superior heat transfer performance [22, 23]. Moreover, they offer a high specific surface area at lower pressure drop compared to conventional reactors which makes them ideal candidates to carry out chemical processes. Most of the investigated porous structures are random structures, making it difficult to maintain consistent performance within different replicated structures. Due to the advances in additive manufacturing techniques, detailed designs of micro-structured reactors can be manufactured in a variety of materials like plastics, aluminum, and stainless steel. Busse et al. [24] investigated the heat transfer performance of periodic open cell structures (POCS) in terms of material, morphology and wall coupling. They observed that at lower flow rates, POCS structures surpass packed-bed reactors with equivalent specific surface area due to high conductive heat transfer. Lammermann et al. [25] studied the gas-liquid distribution across POCS consisting of Kelvin and diamond shaped unit cells. It was observed that Kelvin cells promote inward liquid flow while diamond cells push the liquid towards the edges. Therefore, a hybrid cell design was proposed which leads to a uniform distribution of the two phases. Open-cell metal foams have been widely used as catalytic support for multiphase reactions [26]. Wan et al. [27] applied random porous metal structures (Ni, Al, and Cu) to perform a Fenton like aeration reaction (gas-liquid-solid reaction) for waste-water treatment, which compared favorably in terms of efficiency and cost with conventional approaches. Tourvieille et al. [28] observed an enhanced performance of metal foam reactors for the hydrogenation of α -methylstyrene over a Pd/Al₂O₃ catalyst compared to conventional fixed bed reactors.

In our previous work, Potdar et al. [29] have investigated in detail the effect of various design parameters of 6 different fibre-based structured porous reactors in relation with their interfacial mass transfer performance for liquid-liquid flow (stratified and Taylor flow (slug flow)). Optimum design parameters and structures have been identified which results in enhanced mass transfer depending on the two-phase flow pattern. The present study focuses on their application to industrially relevant liquid-liquid chemical reactions. Moreover, critical factors in the application of these reactors to biphasic chemical reactions are identified by evaluating interfacial mass transfer and heat transfer under identical operating conditions.

2 Experimental setup

2.1 Reactors

Two structured porous reactors were selected based on their superior performance in our previous investigation, namely; Insp1 (manufactured by Selective Laser Sintering (SLS) [30]) and Vito2 (manufactured by 3DFD technique [31]). The nomenclature of these reactors is based on the aforementioned study of the structured porous reactors [29]. The details of each design are summarized in Tab. 1 and Fig. 1 visualizes the design parameters. To quantitatively analyze the performance of the structured porous reactors, they are evaluated against conventional industrial reactors, i.e. a packed-bed reactor (PB1) and an empty tube (ET), both having an identical void volume as the porous reactors.

Figure 1. Two design parameters of the porous structures containing layered cylindrical fibres; (1) Orientation (2) Stacking arrangement. Orientation includes the rotation of the fibre layers with respect to the flow direction (z axis) ' θ ' and rotation perpendicular to the flow direction (x, y-plane) ' ϕ '. The stacking arrangement consists of two patterns '1-3-5' (fibres in consecutive layers are shifted by a third interfibre distance) and '1-3' (fibres in consecutive layers are shifted by a half interfibre distance)[29].

Table 1. Description of reactors evaluated for industrially relevant chemical reactions.

Name	Porosity (%)	Specific surface area* (m^{-1})	Void Volume (μL)	Description
Insp1 (SLS)	74	4160	449.6	$\theta = \pm 22.5^\circ$ in alternate stacks, $\phi = 45^\circ$ interfibre distance 500 μm
Vito2 (3DFD)	71	4715	448.3	Alternate stacking every 10 rows, $\phi = 0^\circ$ & $\theta = 0^\circ$, interfibre distance 1-3: 250 μm , interfibre distance 1-3-5: 500 μm
PB1	40	37895	453.6	Stainless steel spheres, particle size: 60-125 μm , tube I. D: 3.8 mm and length 10 cm
ET	100	0	419.6	Stainless steel tube with I.D.: 3.8 mm and length 3.7 cm

* Represents specific surface area of inserts excluding reactor walls.

2.2 Chemical reactions

We have selected two chemical schemes to evaluate the applicability of the structured porous reactors to industrially-relevant reactions, which are (1) a C-N cross coupling reaction and (2) the oxidation of a primary alcohol. The first reaction uses toluene and water as solvents, which forms Taylor flow at the considered length scale, while the second reaction takes place in a dichloromethane (DCM)-water system which forms stratified flow at the considered length scale.

2.2.1 Taylor flow: C-N cross coupling reaction

The product of the C-N cross coupling reaction (Fig. 2), aryl amines, represents an important class of intermediates for the pharmaceutical industry [32, 33]. Recent advances in the field of phase transfer catalysis enable to perform this reaction in a biphasic system, which eliminates reactor clogging due to the formation of insoluble salts [17]. However, in a biphasic system the reaction becomes interfacial mass transfer limited. This limitation can be overcome by implementing reactors that enhance interfacial mass and heat transfer for biphasic systems. Naber et al. [17] observed full conversion of

C-N cross coupling reactions in a packed-bed reactor in contrast to an empty tube which resulted in less than 20% of product yield at the same residence time.

Figure 2. C-N cross coupling reaction setup consisting of the reactor immersed in a silicon oil bath at 100 °C. At the inlet of the reactor three initial solutions were mixed using a T-connection. At the outlet of the reactor, the reaction is quenched by dilution and cooling by adding an excess amount of ethyl acetate and water.

2.2.1.1 Materials

The reagents 2-chloro anisole, ethyl-2-amino benzoate, biphenyl, tetra-butyl-ammonium bromide (TBAB), brett-Phos and allyl palladium chloride dimer ($(\text{AllylPdCl})_2$) were purchased from Sigma-Aldrich and used as received. Analytical grade toluene was purchased from Alfa Aesar. Additionally, KOH pellets and ethyl acetate were received from VWR Chemicals. Starting materials were prepared using the method reported by Naber et al. [17].

2.2.1.2 Procedure

Three starting solutions were prepared; solution 1 consisted of catalyst and pre-catalyst in toluene, solution 2 was composed of both reagents with phase transfer catalyst and internal standard dissolved also in toluene; solution 3 was the aqueous solution of the base. Details of the preparation of each starting solution are summarized in the Supporting Information (Sect. S.1).

Both organic solutions (solution 1 and 2) were filled in 5 ml glass syringes (Hamilton) respectively, while the aqueous solution (solution 3) was inserted in a 10 ml plastic syringe (Terumo). The flow was controlled by syringe pumps (PHD ULTRA, Harvard apparatus) such that the overall organic to aqueous flow ratio is maintained at 1:1.

The aqueous and organic phases were mixed in a T-junction before entering the reactor (Fig. 2). The reactor was immersed in a silicon oil bath at 100 °C and a backpressure regulator (20 psig) was added to its outlet. The reaction was terminated by simultaneously diluting and cooling the reaction mixture with an excess of ethyl acetate and water. Subsequently, the two phases were gravitationally separated, and the organic phase was further filtered to remove any solids. The product yield was measured by analyzing the organic phase with GC (PerkinElmer Auto-system; Column: CpSil 8CB (50 m x 0.32 mm ID x 0.39 μm)).

2.2.2 Stratified flow: Oxidation reaction

The selective oxidation of primary alcohols to aldehydes without any acid byproducts is highly relevant for industry [34]. Anelli et al. [35] developed an efficient and convenient method for the selective production of aldehydes by reacting alcohol and sodium hypochlorite (NaOCl) in a dichloromethane-water system at 0 °C in the presence of oxoammonium salt (4-methoxy TEMPO). As the oxidation reaction itself occurs in the organic phase [34], the overall reaction rate is limited by interfacial mass transfer.

2.2.2.1 Materials:

Dichloromethane (DCM), 1-nonanol, decane, KBr powder, and sodium thiosulfate were purchased from Sigma-Aldrich and used as received. 4-methoxy TEMPO and chlorine bleach were also purchased from Sigma-Aldrich and stored at a temperature between 4-8 °C. The concentration of bleach and sodium thiosulfate was regularly evaluated by iodometric titrations with a starch indicator.

2.2.2.2 Procedure:

The starting reagent solutions were prepared following the method reported by Anelli et al. [35]. The first syringe was filled with a 30 ml dichloromethane solution including 1-nonanol (0.4 M), decane (0.12 M) as internal standard, and the catalyst 4-methoxy TEMPO (0.004 M). The second syringe was filled with 0.5 M of aqueous KBr solution. The third solution was prepared just before the reaction by mixing 1.5 g of NaHCO₃ with 30 ml of 0.35 M aqueous NaOCl to attain a pH of 8.6 (third syringe). These three syringes were mounted on individual syringe pumps, to maintain the flow ratio of 25:2:36 (syringe 1: syringe 2: syringe 3).

The three solutions were mixed using a cross connector before entering the reactor (Fig. 3). The reactor was submerged in an ice bath maintained at 0 °C. At the outlet of the reactor, the reaction was quenched by neutralizing aqueous NaOCl (bleach) with an excess of sodium thiosulfate. The two phases were gravitationally separated and the organic phase was further analyzed by GC (PerkinElmer Auto-system; Column: CpSil 8CB (50 m x 0.32 mm ID x 0.39 µm)).

Figure 3. Oxidation reaction setup consisting of the reactor immersed in an ice bath. At the inlet of the reactor, three initial solutions are mixed using a cross connection. At the reactor outlet, the reaction is stopped by the neutralization of bleach with sodium thiosulfate.

2.3 Mass transfer

To evaluate the mass transfer performance for the toluene-water system (Taylor flow), the neutralization of trichloroacetic acid with sodium hydroxide is selected as model system. The organic phase consisted of a 0.6 M trichloroacetic acid (Sigma-Aldrich, ACS reagent, 99.0%) in toluene (Sigma-Aldrich, anhydrous, 99.8%). The aqueous phase was a 0.6 M sodium hydroxide (Fischer Scientific, sodium hydroxide pearls) solution in deionized water.

The mass transfer performance for stratified flow was evaluated by quantifying the extraction of succinic acid from n-butanol to water. Before each experiment, both phases were mutually saturated with each other, and 1 wt.-% of succinic acid was added to n-butanol. All chemicals were purchased from Sigma Aldrich and used as received.

The experimental setup used for the interfacial mass transfer measurements in both systems is depicted in Fig. 4. Two 30 mL syringes (Terumo) filled, respectively with aqueous and organic phase, were mounted on a syringe pump (Fusion 200, CHEMYX) which provided an equal flow rate for both phases. The total flow rate applied during the experiments ranges from 1-5 mL min⁻¹. Both phases were contacted through a T-connection before entering the reactor. The outlet of the reactor was connected to an in-house in-situ phase separator [36]. The organic phase was discarded as waste, while the aqueous phase was further analyzed by titration (using 0.1 N HCl with bromothymol blue as indicator for the water-toluene system, and 0.1 N NaOH solution with phenolphthalein as indicator for the n-butanol-water system). To ensure repeatability, experiments were performed three times for each reactor setup at every flow rate.

Figure 4. Liquid-Liquid mass transfer setup where the organic and aqueous phases are contacted in a T-connection before entering the reactor. At the reactor outlet the two phases are instantaneously phase separated using a membrane-based separator to collect the aqueous and organic phases [29].

Estimation of mass transfer coefficient:

The n-butanol water system is governed by the physical mass transfer of succinic acid between the two phases. As the two phases were mutually saturated, and the solubility of the solute is sufficiently low to assume constant properties of the second phase, the logarithmic mean driving force is applied to determine the overall volumetric mass transfer coefficient $k_L a$ according to,

$$k_L a = \frac{1}{\tau} \ln \left(\frac{C_{aq}^* - C_{aq,i}}{C_{aq}^* - C_{aq,o}} \right) \quad (1)$$

where C_{aq}^* is the equilibrium concentration of succinic acid in the aqueous phase, $C_{aq,i}$ is the inlet concentration of succinic acid in the aqueous phase, and $C_{aq,o}$ is the outlet concentration of succinic acid in the aqueous phase. τ denotes the average residence time which is calculated as

$$\tau = \frac{V_R}{Q_{aq} + Q_{org}} \quad (2)$$

where V_R is the reactor void volume, and Q_{aq} and Q_{org} represent the volumetric flow rate of the aqueous and organic phase respectively.

The toluene-water system represents a neutralization reaction controlled by interfacial mass transfer. As the reaction is instantaneous, the acid concentration in the aqueous phase close to the interphase is zero, which also means that the equilibrium concentration of the acid in the organic phase is zero [37]. Thus, the overall volumetric mass transfer coefficient is calculated as,

$$k_L a = \frac{1}{\tau} \ln \left(\frac{C_{org,i}}{C_{org,o}} \right) \quad (3)$$

where $C_{org,i}$ is the initial concentration of trichloroacetic acid in the organic phase, and $C_{org,o}$ is the outlet concentration of trichloroacetic acid in the organic phase. At the volumetric flow ratio of 1:1, $C_{org,o}$ is estimated from the trichloroacetic acid concentration in the aqueous phase ($C_{aq,o}$) as,

$$C_{org,o} = C_{org,i} - C_{aq,o} \quad (4)$$

2.4 Heat transfer

The experimental setup used for the evaluation of heat transfer in both systems is depicted in Fig. 5.

Figure 5. Liquid-liquid heat transfer setup where the reactor is encompassed by an aluminum block heated resistively with an electrical heating foil. The heating foil is controlled by a PID controller to achieve a constant reactor wall temperature. The data logger records K-type thermocouple readings at four locations: (1) Inlet liquid temperature $T_{f, in}$, (2) Inlet wall temperature $T_{w, in}$, (3) Outlet wall temperature $T_{w, out}$, (4) Outlet liquid temperature $T_{f, out}$.

The two phases were contacted using a T-connection, and before entering the reactor a K-type thermocouple is used to measure the inlet fluid temperature ($T_{f, in}$). The reactor itself was encompassed inside an aluminum block heated resistively with an electrical heating foil (5 Watt). The heating foil was controlled by a PID controller to achieve a constant reactor wall temperature. Three holes were drilled inside the aluminum block to measure the reactor wall temperature at three locations: (1) inlet wall temperature ($T_{w, in}$), (2) wall temperature in the middle of the reactor (connected to the PID controller) (3) outlet wall temperature ($T_{w, out}$). Furthermore, the aluminum block was insulated to avoid heat losses to the surrounding. The temperature of the biphasic flow leaving the reactor was also measured with a K-type thermocouple ($T_{f, out}$). To compare the heat transfer performance of the different reactors, the overall heat transfer coefficient is measured per unit reactor void volume.

Evaluation of overall heat transfer coefficient:

The overall heat transfer coefficient ($h_{overall}$) per reactor void volume V_R is calculated according to,

$$h_{overall} = \frac{mC_{p,avg} (T_{f,in} - T_{f,out})}{V_R(T_w - T_f)_{ln}} \quad (5)$$

where m is the total mass flux and $C_{p, avg}$ denotes the phase-averaged specific heat capacity.

3 Results

3.1 Taylor flow

The performance of reactors for C-N cross coupling reaction at different residence times is evaluated on the basis of the product yield which is calculated from GC analysis (Fig. 6a). For the investigated range of residence times, the packed-bed reactor (PB1) shows the highest yield of the desired product followed by the structured reactors; Vito2 and Insp1. Notably, the performance of both structured reactors is quite identical for all studied residence times. The lowest yield is observed for the empty tube (ET) case. The C-N cross coupling reaction between 2-chloro-anisole and ethyl-2-amino benzoate is relatively slow requiring a long residence time for high conversion. At these high residence times (low flow rates), the flow inside the structured reactors is not highly affected by the presence of the cylindrical fibres. This lack of structural influence hinders slug breakage inside the structured reactors and consequently induces mass transfer limitations. In contrast, even at high residence times, narrow chaotic paths inside packed-bed reactors result in slug breakage resulting in better mass transfer.

Figure 6. [a] GC yield for the C-N cross coupling reaction of 2-chloro anisole with ethyl-2-amino benzoate subject to residence time in the toluene-water system. [b] Interfacial mass transfer coefficient k_{La} for the chemical extraction of trichloroacetic acid from toluene to water at different residence times. [c] Overall heat transfer coefficient subject to the residence time for the structured reactors, packed-bed and empty tube. The measurements are performed for the toluene-water system, which establishes as Taylor flow in the empty tube.

These observations can be further supported by the results obtained from the mass transfer study for an instantaneous chemical reaction in the toluene-water system (Fig. 6b). For the structured reactors a mass transfer performance analogous to the C-N cross coupling reaction is observed. The largest k_{La} -value is found for the packed-bed (PB1) followed by the structured porous reactors Insp1 and Vito2. The lowest performance is observed for the empty tube (ET). These observations are also in line with the trends in the measured overall heat transfer coefficient (Fig. 6c). The largest value is found for the packed-bed reactor (PB1), followed by the structured porous reactors Insp1 and Vito2, with the lowest heat transfer performance for the empty tube (ET). The lower performance of Vito2 in contrast to Insp1 can be attributed to the manufacturing technique (3DFD), which doesn't allow printing of the reactor walls together with the porous structure. Consequently, the porous structure has to be inserted inside the stainless steel tube which results in non-uniform wall coupling. While the overall decrease in the heat transfer coefficient due to non-uniform wall coupling is limited [24], its effect is observed for the largest flow rates. Notably, with increasing residence time the heat transfer coefficients of the individual reactors converge, indicating that at residence times above 30 s the convective contribution to the overall heat transfer is limited, and the thermal behavior of all reactors is similar. Consequently, heat transfer has no significant role in determining the performance of the different reactors for the C-N cross coupling reaction as the residence time is in the range of 100 s - 600 s (Sect. S.2). For two phase systems, heat transfer is determined by the intrinsic properties of the two fluids, while the mass transfer is also governed by the solute properties that is being transferred between the two phases. Hence, heat and mass transfer limitations appear uncoupled for this particular case.

3.2 Stratified flow

The results of the oxidation of 1-nonanol are assessed in terms of GC yield of nonanal for the considered range of residence times (Fig. 7a). The highest yield is observed for both Vito2 and PB1 at

residence times exceeding 20 s. However, at lower residence times ($\tau < 20$ s), Vito2 surpasses the performance of the packed-bed. These results also coincide with the measured mass transfer coefficients using the n-butanol-water system (Fig. 7b), where Vito2 also prevails over PB1 at lower residence times ($\tau < 20$ s). Moreover, in the mass transfer study larger $k_L a$ -values are observed for the Insp1 structure compared to PB1 and Vito2. However, its performance declines for the oxidation reaction (DCM-water system) in comparison to Vito2 and PB1 reactors. This difference in performance of the Insp1 reactor can be explained by its geometry (Tab. 1), which is characterized by a strong radial asymmetry along its length due to its angular orientation ($\varphi = 45^\circ$, $\theta = \pm 22.5^\circ$) compared with Vito2 ($\varphi = 0^\circ$, $\theta = 0^\circ$) and PB1. Moreover, interfacial mass transport in stratified flow is also governed by the location and shape of the interface. For the extraction of succinic acid, the volumetric flow rate ratio of both phases was 1:1, while for the oxidation reaction the flow rate ratio between the organic and aqueous phase was kept at 25:38 to replicate conditions reported in literature [35]. This results in a different location of the interface inside the reactor for the two fluid systems. Due to the radial asymmetry in Insp1, the interface interacts with different geometrical features resulting in different interfacial transport. This behavior is not observed for the Vito2 reactor, which is symmetric in the radial direction. As the packed-bed has a random internal structure the location of the interface is not expected to influence the interfacial transport processes, which is also confirmed by our results. Another aspect to consider is that chemical reactions will generate local concentration fluctuations in the vicinity of the interface, which will also alter the observed mass transfer [38, 39]. For the stratified flow case, the lowest performance for both mass transfer and chemical reaction is observed for the empty tube (ET).

Figure 7. [a] GC yield for the oxidation of 1-nonanol in the DCM-water system subject to residence time. [b] Interfacial mass transfer coefficient $k_L a$ for the extraction of succinic acid from n-butanol to water at different residence times. [c] Overall heat transfer coefficient subject to the residence time for the structured reactors, packed-bed and empty tube. The measurements are performed for n-butanol-water system, which establishes as stratified flow in the empty tube. [d] GC yield of nonanol against pressure drop in the structured reactors, packed-bed and empty tube.

The measured overall heat transfer coefficient in stratified flow (Fig. 7c) shows similar trends as observed previously for Taylor flow. The largest heat transfer coefficient is observed for the packed-bed (PB1) followed by the structured porous reactors, Insp1 and Vito2, respectively. The lowest performance is observed for the empty tube (ET). However, a larger difference is observed between Insp1 and Vito2 in stratified flow compared to Taylor flow. In Taylor flow a thin film of water is covering the entire wall of the reactor, while in stratified flow approximately half of the reactor wall is covered by the organic phase, which has a lower heat conductivity. Together with the aforementioned non-uniform wall coupling, this can explain the lower heat transfer coefficients observed for Vito2. However, the effect of heat transfer on the oxidation reaction is expected to be limited. The temperature sensitivity of the reaction is mainly due to the instability of the oxoammonium salt when exceeding temperatures of 8 °C [34]. However, such a large change in temperature was not observed for any reactor in the biphasic heat transfer measurements.

To qualitatively evaluate the performance of the different reactors for the oxidation reaction, the observed yield is plotted against the measured pressure drop (Fig. 7d). It is observed that the yield in the Vito2 reactor, which is as high as the PB1, is obtained at two orders of magnitude lower pressure drop. At identical pressure drop, the Insp1 reactor is characterized by a lower yield compared to Vito2. Nevertheless, these results highlight that the structured porous reactors represent a viable alternative to a conventional packed-bed reactor for fast biphasic reactions.

4 Conclusions

Two structured porous reactors, Insp1 and Vito2, are applied to industrially relevant chemical reactions; (1) C-N cross coupling in toluene-water system (Taylor flow), (2) Oxidation of primary alcohols in DCM-water system (stratified flow). Moreover, the critical parameters governing the performance of structured reactors for chemical reactions are assessed based on their heat and mass transfer performance under identical operating conditions. For quantitative analysis the structured reactors are compared with conventional reactors, a packed-bed (PB1) and an empty tube (ET). For the C-N cross coupling reaction between 2-chloro anisole and ethyl-2-amino benzoate, it is observed that the packed-bed reactor (PB1) shows a better performance than the structured porous reactors Insp1 and Vito2. This better performance can be attributed to the enhanced mass transfer inside the packed-bed compared to Insp1 and Vito2. The heat transfer performance of both structured reactors is comparable to the packed-bed (PB1) and shows significant improvement over the empty tube (ET). However, due to the required long residence time of the chemical reaction, the thermal boundary layer inside the reactors is already well developed and thus has no influence on the relative performance of the different reactors.

For stratified flow, it is observed that geometrical structures at the interface play a vital role in determining interfacial mass transfer. The radially symmetric reactors, Vito2 and PB1, show superior performance for both the oxidation reaction and the observed interfacial mass transfer, where Vito2 surpasses the performance of PB1 at lower residence times. The radially asymmetric Insp1 reactor also performs well for the mass transfer study using the n-butanol-water system, but shows a lower yield for the chemical reaction in the DCM-water system due to variation in the location of interfacial boundary. Finally, analyzing the overall pressure drop reveals the potential of the Vito2 reactor, as it provides the same yield as the conventional packed-bed, but at two orders of magnitude lower pressure drop.

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6 Symbols

C_{aq}^*	$[mol\ L^{-1}]$	Equilibrium concentration
$C_{aq,i}$	$[mol\ L^{-1}]$	Inlet aqueous phase concentration
$C_{aq,o}$	$[mol\ L^{-1}]$	Outlet aqueous phase concentration
$C_{org,i}$	$[mol\ L^{-1}]$	Inlet organic phase concentration
$C_{org,o}$	$[mol\ L^{-1}]$	Outlet organic phase concentration
$C_{p,avg.}$	$[J\ kg^{-1}\ K^{-1}]$	Phase-averaged specific heat capacity
$h_{overall}$	$[W\ m^{-2}\ K^{-1}]$	Overall heat transfer coefficient
$k_L a$	$[s^{-1}]$	Interfacial mass transfer coefficient
m	$[kg\ s^{-1}]$	Total mass flux
Q_{aq}	$[ml\ s^{-1}]$	Volumetric flow rate of aqueous phase
Q_{org}	$[ml\ s^{-1}]$	Volumetric flow rate of organic phase
T_f	$[K]$	Fluid temperature
$T_{f,in}$	$[K]$	Inlet fluid temperature
$T_{f,out}$	$[K]$	Outlet fluid temperature
T_w	$[K]$	Wall temperature
V_R	$[ml]$	Reactor void volume

Greek letters

θ	$[^\circ]$	Rotation angle around z-axis
φ	$[^\circ]$	Rotation angle with respect to the x-y plane
τ	$[s]$	Residence time

Abbreviations

3DFD	3-dimensional fibre deposition
SLS	Selective laser sintering
DCM	Dichloromethane

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