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Gas Introduction by Permeation into Long Fluorinated Ethylene Propylene Capillaries with Slug Flow

Due to the density differences between gases and liquids, the gas supply often limits the conversion of gas-liquid reactions in slug flows. This paper investigates the permeation of reacting gas into an existing gas-liquid slug flow in fluorinated ethylene propylene capillaries of up to 40 m in length, representing a significant sizing-up of tube-in-tube reactors (maximum 4 m). The amount of gas introduced can be estimated with permeation coefficients given in the literature. Moreover, existing gas bubbles serve as reservoirs for the permeating gas, maintaining the advantageous slug flow pattern.

Keywords: Capillary reactors, Gas permeation, Multiphase systems, Segmented flows, Sizing-up

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Supporting Information available online

1 Introduction

Continuous-flow microreactors, such as capillaries, are attracting increasing attention due to their potential for increasing selectivities and space-time yields [1–3]. Firstly, these microreactors are approaching ideal plug flow reactor (PFR) behavior, which can be exploited for enhancing selectivity in consecutive reactions. Secondly, the small dimensions ensure substantial surface-to-volume ratios, intensifying heat transport. Extensive surface areas can be provided to improve the pertinent transport phenomena in multiphase systems, which are limited by interphase mass transfer. Segmented slug flow has been identified as a flow regime appropriate for multiphase systems, providing both large surface areas and intense mixing within its segments [4, 5].

These multiphase systems often contain gas-liquid reactions. However, due to the significant density differences between gases and liquids, the available molar amount of the reaction gas is often insufficient, which causes the gas to be quickly consumed and limits the reaction. This effect becomes more significant if the liquid reactant is provided in a high concentration or pure. In such cases, the physical property of gas permeation through polymers might be used to advantage by supplying the otherwise limiting reaction gas externally along the capillary.

In the literature, such concepts are also referred to as tube-in-tube reactors, which employ highly specialized polymers, such as Teflon AF 2400, exhibiting very high permeation coefficients [6–8]. In this reactor concept, reaction gases are usually fed externally over a distance of 0.5–4 m from an outer concentric gas-bearing tube through the internal capillary wall into the usually single-phase liquid reaction medium. This approach offers excellent mass transport for gas-liquid reactions (also in comparison to slug flow). In addition to permeation into single-phase liquid flows, utilizing a uniform slug flow pattern in the inner capillary can provide further benefits. For example, for short-residence time reactions like the aerobic dimerization of desmethoxycarpacine, Aka et al. [9] demonstrated that slug flow is more favorable than a tube-in-tube reactor for yield and reaction times under otherwise similar conditions. In this case, the slug flow showed better results due to the favorable PFR-like flow pattern and since there is no indication of mass flow limitations. This indicates that a combination of slug flow and wall permeation is promising.

To the authors' knowledge, only a few examples of using permeation to feed reaction gas in slug flow reactors have been presented in the literature. Rahman et al. [10] demonstrated a feed of CO in a < 1 m capillary in an existing liquid-liquid slug flow to provide constant flow conditions using a poly(dimethylsiloxane) membrane. This study observed no gas bubble formation due to the parameters used and the short capillary.

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Önal et al. [11] hydrogenated prenal to prenol with a homogenous ruthenium catalyst and investigated various reactor designs. Initially, Önal et al. [11] observed low conversion in a gas-liquid-liquid slug capillary flow compared to batch reactors, which was caused by a lack of hydrogen. By imposing an external hydrogen pressure on the polytetrafluoroethylene (PTFE) capillary used, permeation was meant to be exploited to overcome this deficit. However, the gas flow into the capillary via permeation was too low under the conditions selected (T, Δp, τ, L_{cap}[1)]) [12]. The influence of gas permeation on the stability of an existing slug flow is so far unknown. However, on paper, combining the advantageous slug flow with gas supply via permeation along the capillary would seem to open up an elegant technique of process intensification.

For long capillaries, conventional materials with lower permeation coefficients, such as fluorinated ethylene propylene (FEP) or PTFE, can also be employed since the gas flow per area is not required to be as large as for short capillaries using Teflon AF 2400. Elvira et al. [13] demonstrated the syntheses of ascaridole from α-terpinene with singlet oxygen by using oxygen permeation in a single-liquid flow through a FEP microcapillary film, which consists of multiple parallel capillaries. They observed an increase in the reaction rate at a high partial pressure of oxygen outside the microcapillary film. The results prove that permeation is feasible for FEP capillaries, despite the lower permeation coefficients and its benefit for reactions. The results indicate a dependence of the permeation flux on the partial pressure, which can be actively used to control the reaction performance. The utilization of FEP capillaries enables long capillaries for a multiphase tube-in-tube concept representing a scale-up approach in the sense of sizing up in length. With a long capillary and otherwise similar diameter, the volumetric throughput can be increased while keeping the same mean residence time [14].

In this communication, slug flow with gas addition via permeation is investigated. Gas permeation fluxes into long FEP capillaries (30–40 m) containing slug flow are determined, and the influence of gas bubble formation on the flow stability is examined. Both temperature and pressure differences between the inside and outside of the capillary are evaluated as appropriate control parameters, and their effects are compared with theoretical predictions.

2 Experimental Setup

For the investigation of permeation in a FEP capillary, the setup shown in Fig. 1 was used. The capillary is introduced after a slug generation part (K1, K2, bottom part) in a steel housing with serval modules (R1–R4). First, 1-hexanol, water, and nitrogen (later also hydrogen) are used to generate a gas-liquid-liquid slug flow. Then, between the modules, the capillary could be led out of the housing, and a camera can observe the resulting flow pattern. Within the steel housing, various gas atmospheres can be applied at controlled pressures and temperatures, allowing the examination of different conditions for permeation. To determine the volumetric permeation flow, a pneumatic trough is used to collect gas over liquid at the end of the capillary. The comparison with theoretical values considers the measured pressure drop and the incoming volumetric gas

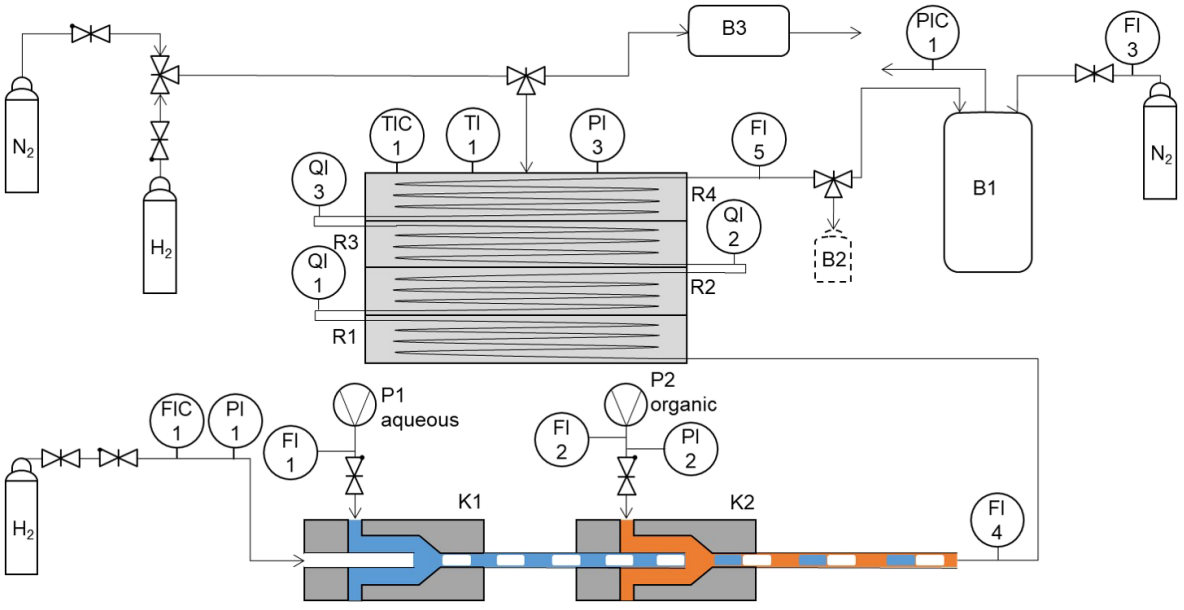

Figure 1. Schematic flow sheet of the capillary reactor. Bottom: slug flow generation with coaxial mixers. Middle: temperature-controlled capillary in a steel housing with outlets to sensors/sampling locations. Top, right: collection vessel. PI, pressure indicator; TI, temperature indicator; FI, flow indicator; QI, sampling port/camera observation; TIC, temperature indicator and controller; PIC, pressure indicator and controller.

1) List of symbols at the end of the paper.

flow at the inlet of the capillary. Further Information can be found in Sect. S1 of the Supporting Information (SI).

3 Results

First, the gas permeation of nitrogen into an existing liquid-liquid segmented flow was quantified, and the stability of the flow was evaluated. If the flow retains a stable and regular form, a liquid-liquid flow would be preferable over an initially gas-liquid-liquid slug flow, as this would simplify slug generation. The influence of the temperature and of the pressure difference was investigated.

The volumetric permeation flow is plotted versus the temperature at various external pressures in Fig. 2. This behavior is predicted by the theoretically calculated curves (dashed lines, calculation in Sect. S2 of the SI). The slightly higher experimental values may be due to the permeation data presented in the literature, which was established under more ideal conditions, and the FEP properties may vary depending on the supplier (different ratios of ethylene/propylene; degree of crystallinity).

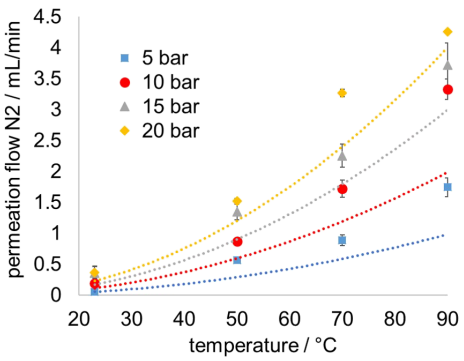

Figure 2. Permeated nitrogen volumetric flow rates versus temperature for different external pressures into a liquid-liquid slug flow. The same colors are used for the experimental and the corresponding theoretical values. L_{cap} = 40 m.

Although the total gas permeation is in an acceptable range, the slug flow is negatively affected. Fig. 3 shows the flow patterns at different distances downstream. While isolated tiny bubbles can be observed after 10 m, irregular larger gas agglomerates (about one larger gas agglomerate with several single gas bubbles per meter of capillary) can be observed at the end of the capillary. The formation of these irregular long agglomerates destroys the previously uniform slug flow. Without permeation, a stable slug flow was observed along the whole capillary.

Phenomenologically, the dissolved gas concentration in the liquid solvents increases until saturation is reached after a small gas bubble is formed. Further dissolved gas molecules have two possibilities: forming another bubble or affiliating with an existing bubble. Energetically, the latter option is more favorable since no additional surface energy is required to form a new phase interface. Thus, it is more likely that existing bubbles will be filled with the permeated dissolved gas rather than that new bubbles will be formed. Very long gas segments can then, in turn, break down into smaller gas bubbles due to shear

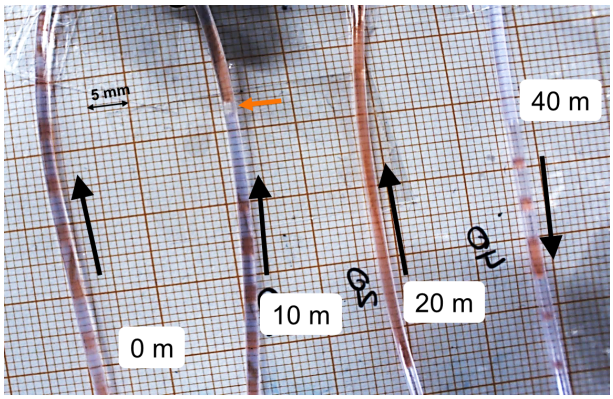

Figure 3. Flow patterns of a slug flow with nitrogen permeation after 0, 10, 20, and 40 m. After 10 m, the first single gas bubbles are visible (indicated by the orange arrow). Subsequently, the flow loses its regular structure. Red phase: hexanol (0.6 mL min^{-1}); blue phase: water (0.6 mL min^{-1}); clear phase: nitrogen. The black arrows indicate the flow direction of the respective capillary section. At T = 50 °C, Δp = 5 bar.

forces. Thus, gas agglomerates are formed as several single gas segments that appear to coalesce in the flow.

In a regular gas-liquid-liquid slug flow, the permeation fluxes of nitrogen are similar to those with the two-phase liquid-liquid flow and comparable to the theoretical values. Considering the flow pattern, a continuous and stable three-phase flow could be observed. The gas bubbles entering grow in size along the capillary to form long bubbles. In the process, all the gas bubbles become uniformly larger, and the advantageous slug flow is maintained. Hence, this flow pattern is able to counteract the irregular gas bubble formation in the liquid-liquid flow.

To enhance the permeation flux even further, hydrogen was used instead since, as a smaller molecule, it exhibits a higher permeation coefficient. In addition, hydrogen is particularly interesting as a reaction gas for practical applications.

Fig. 4 depicts the flow pattern at three locations along the capillary (at 0, 15, 35 m) in a gas-liquid-liquid slug flow with hydrogen permeation at different temperatures (23, 50 °C) influencing the gas flux and a pressure difference of 5 bar. In both cases, it can be seen that, despite the significant increase in the size of the gas bubbles, the liquid segments remain unaffected. However, for very high permeation fluxes (at 50 °C), it can be observed that the liquid segments become separated by a gas segment. This is unfavorable for systems with significant liquid-liquid mass transfer since, in this case, the liquid-liquid interface is no longer available. In actual applications, the permeation flow should therefore be adjusted to ensure that only a comparable amount of gas consumed by the reaction is fed.

4 Discussion and Outlook

Gas permeation is suitable with conventional polymer materials such as FEP to feed gases into segmented capillary flows. The measured gas flows are in agreement with theoretical estimation. It was found that a segmented slug flow with regular

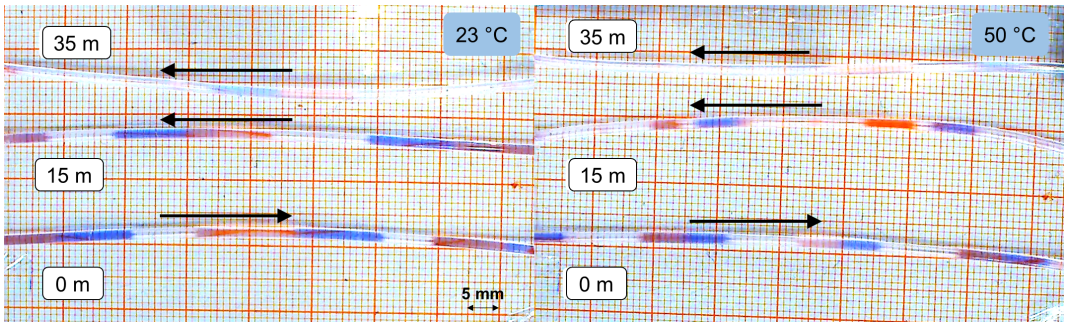

Figure 4. Flow patterns of a gas-liquid-liquid slug flow with hydrogen permeation after 0, 15, and 35 m. Red phase: hexanol (0.6 mL min^{-1}); blue phase: water (0.6 mL min^{-1}); clear phase: hydrogen (0.6 mL min^{-1} at the inlet). The black arrows indicate the flow direction. Left: T = 23 °C, Δp = 5 bar; right: T = 50 °C, Δp = 5 bar.

gas bubbles entering a capillary is advantageous since, in this case, the existing gas bubbles are uniformly filled, whereas the flow pattern without gas bubbles was affected by random gas bubble formation, thus losing the advantageous properties of the slug flow.

The technique presented can thus be used to apply gas-limited multiphase gas-consuming reactions to the operation of a segmented slug flow in capillaries, without the trade-off of lower conversions. Furthermore, since gas permeation can be exploited in both directions, it offers a wide range of further reaction options. For example, (consecutive) reactions can be regulated locally. In a tandem-catalyzed reaction system, for instance, hydrogenation could be performed selectively, excess hydrogen could be removed, and another reaction gas could be introduced for a subsequent reaction.

Compared to existing tube-in-tube reactors, which are limited in length, the presented system describes a sizing-up (increasing volumetric flow and capillary length). This enables reactions with slow kinetics and increases the capacity of such permeation-capillary systems. In Sect. S3 of the SI, a discussion with selection criteria for other gas-feeding methods like electrolysis or valves can be found.

Data Availability Statement

The data that support the findings of this study are available on request from the corresponding author. The data are not publicly available due to privacy or ethical restrictions.

Supporting Information

Supporting Information for this article can be found under DOI: https://doi.org/10.1002/ceat.202200557. This section includes references to primary literature relevant to this research [15–18].

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The authors have declared no conflict of interest.

Symbols used

L_{cap}	[m]	length of the capillary
p	[bar]	pressure
T	[°C]	temperature

Greek letter

τ	[h]	residence time

Abbreviations

FEP	fluorinated ethylene propylene
PFR	plug flow reactor
PTFE	polytetrafluoroethylene

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