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HEAT TRANSFER LIMITATIONS OF GAS-LIQUID EXOTHERMIC REACTIONS IN MICROCHANNELS

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ABSTRACT

Chemical reactions in gas-liquid systems are often occurring and embrace many issues, especially the contacting of the gas and liquid stream and generation of gas bubbles. Continuous mixing and generation of a large interface between the phases is very important for maintaining and intensifying a chemical reaction between the two phases. The generated heat from the chemical reaction has to be removed very quickly from the flowing stream, which is also a challenging task. Recent applications of microreactors at Lonza Ltd. are described with gas-liquid mass transfer and highly exothermic chemical reactions. The proper description and understanding of convective flow, heat transfer and reaction kinetics are essential for the successful application of microstructured devices.

INTRODUCTION

Microchannels can handle exothermic chemical reactions due to their superior heat and mass transfer characteristics, and excellent mixing conditions. This was demonstrated for homogeneous liquid [1] or gaseous systems [2] as well as for heterogeneous gas-liquid-solid systems [3, 4]. While homogeneous systems are well described, multiphase transport phenomena with chemical reactions in microchannels are still a wide and very active area in research. In the recently published *Handbook of Micro Process Engineering* [5] already the first chapter deals with multiphase flow phenomena in microchannels [6]. Additional four chapters describe 2-phase flow, mixing [7] and mass transfer, while chemical reactions have a review chapter [8] as well as nine chapters in total with liquid-liquid and gas-liquid systems. Emulsions and particle formation are described in six chapters. From this it can be clearly seen that multiphase flow and chemical reactions are a wide and thriving field in academic research and industrial application of microchannel devices.

Conventional technological and current development for multiphase reactions is summarized by Stitt in a comprehensive review [9]. Typical equipment comprises trickle bed reactors, bubble columns, and jet loop reactors. Major purpose of these devices is to provide large fluid interface, where the reaction takes place. In case of exothermic reactions, the heat has to be removed from the reactor to allow safe operation or avoid side product formation. However, to combine both in one single device is a challenging task. Here, microreactors can offer both high mechanical energy dissipation for phase dispersion and high surface-to-volume ratio for excellent heat transfer. The state-of-the-art of multiphase flow, transport, and transformation are reviewed by Günther and Jensen [10], Doku et al. [11], Hessel et al. [12] as well Kashid and Kiwi-Minsker [13] for chemical reactions. One can distinguish stabilized or regular interface from irregular, dispersed interfaces. The first comprises falling film microreactors, microstructured post reactors, or Taylor bubble flow in capillaries. The latter case describes irregular interfacial structure between phases due to complex flow, winding channel geometry, nozzle flow [14], or high flow rates. Most of the studies in literature deal with the first case because the phenomena are easier to describe. One of the few cases of the beneficial application of irregular interface structure is used in dispersed flow for polymerization reaction [15].

This contribution describes chemical reactions in gas-liquid systems with the goal of high throughput, high conversion, yield, and selectivity. Contacting of the gas and liquid streams is described to generate fine gas bubbles with high surface. Another issue is to achieve a proper dispersion along the channel length to counteract coalescence. Continuous mixing and generation of a large interface between the phases is very important for maintaining and intensifying mass transfer with chemical reaction between the two phases. The generated heat from the chemical reaction has to be removed very quickly from the flowing stream, otherwise unwanted side reactions may occur. Recent applications of microreactors at Lonza Ltd. are described with gas-liquid mass transfer and highly exothermic chemical reactions. The proper understanding of main reaction and side reactions is essential for the successful application of microstructured devices in fine-chemical and pharmaceutical production.

NOMENCLATURE

Bo	Bond number, -
Ca	capillary number, -
d	characteristic length, m
d_h	hydraulic diameter, m
g	gravitation constant, m s^{-2}
Re	Reynolds number, -
We	Weber number, -
w	flow velocity, m s^{-1}

Greek Symbols

η	dynamic viscosity, kg m^{-1} s^{-1}
ρ	density, kg m^{-3}
σ	surface tension, N m^{-1}

GAS-LIQUID FLOW REGIMES

In microchannel flow, the surface effects become more and more important and can be the dominant force in comparison to gravity, viscous, or inertial forces. Dimensionless numbers are ratios of forces and indicate the regime, in which the system is operating and which forces are dominant. The gravity related to surface forces is expressed by the Bond number.

$$\mathrm{Bo} = \frac{(\rho_L - \rho_G)\, g\, d^2}{\sigma} \tag{1}$$

The discussed systems here are relatively small, where the gravity plays no role anymore. This means, for example, that the orientation of the equipment setup has no influence on flow phenomena and bubble generation. Only for very low flow rates of less than 1 mL/min, gas bubble agglomeration at higher channel points has been observed. The momentum force in relation to viscous fluid forces is expressed by the Reynolds number.

$$\mathrm{Re} = \frac{w\, \rho\, d_h}{\eta} \tag{2}$$

With high flow rates of more than 10 mL/min, high flow velocities are associated, and inertia forces are dominant in complex channel flow. Vortices are generated in bends and curves, which assist bubble breakup. Surface tension gets more important for smaller dimensions. The momentum force in relation to surface tension force is expressed with the capillary number.

$$\mathrm{Ca} = \frac{\eta\, w}{\sigma} \tag{3}$$

For Ca < 1, surface tension is the dominant effect, which is the case in the discussed systems. However, due to the high flow velocity, surface tension does not control the flow, but mainly the bubble generation and agglomeration. The product of capillary number and Reynolds number is called Weber number.

$$\mathrm{We} = \frac{\rho\, w^2\, d}{\sigma}, \tag{4}$$

This is the ratio of inertia to surface forces. In our investigations, the Weber number is always >1 indicating dominant inertial forces. Further correlations and a profound discussion can be found in [6, 7].

The flow regime is determined by channel shape and flow velocities of both phases. First contacting of gas and liquid phases are very important for bubble generation [16] as well as continuous mixing along the channel. This process determines bubble agglomeration and dispersion for new bubble generation.

Reactor device and channel shape

To visualize the flow patterns and reaction conditions, a microstructured plate device under view glass called the LabPlate reactor was developed at Lonza to enable process development under tiny flow rates. Conditions are similar to capillary chemistry with the advantage that the reaction zone can be inspected and viewed. This reactor is also an exceptional tool to develop new channel structures for gas-liquid or liquid-liquid reactions that will be later integrated in large-scale reactors.

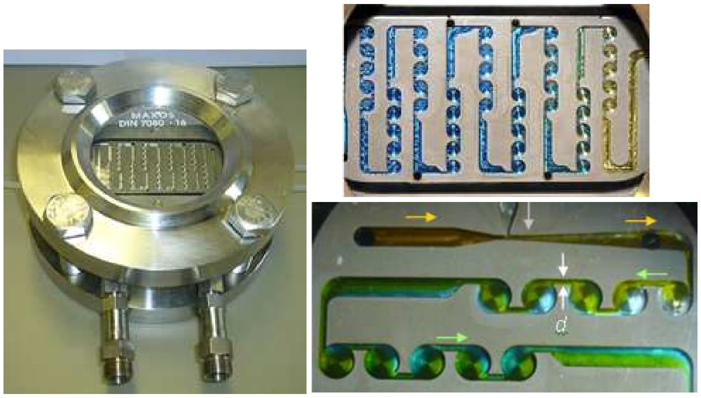


Fig. 1: Left: Lonza LabPlate reactor setup with view glass for optical access to microchannels, connectors for heat exchange medium pointing to the bottom; Top right: Microchannel arrangement with several injection possibilities; Bottom right: Channel detail with contacting, mixing and residence time channel elements.

Different test reactions and also process development of cryogenic reactions were already performed in this device, which gave valuable insight into the reaction dynamics. The investigated plate consists of entrance holes, the contacting nozzle with a width of 0.2 mm to generate small bubbles and serial mixing elements to maintain fine dispersion of the flow. After five tangential elements consisting of a nozzle channel with a width of 0.7 mm, a short straight channel with a width of 2 mm serves for larger volume for higher residence time of the fluids. The depth of the mixing channel is 1.5 mm. Only one single channel is used to control flow distribution, stoichiometry of the reagents, and pressure drop over the device.

Fluid dynamics and flow regimes

The above described plate with a microstructured channel was characterized with carbon dioxide (CO_2)-water flow concerning the flow regimes. In Figure 2, the flow patterns observed in the wide, straight channel are displayed for different flow rates and gas-liquid ratios.

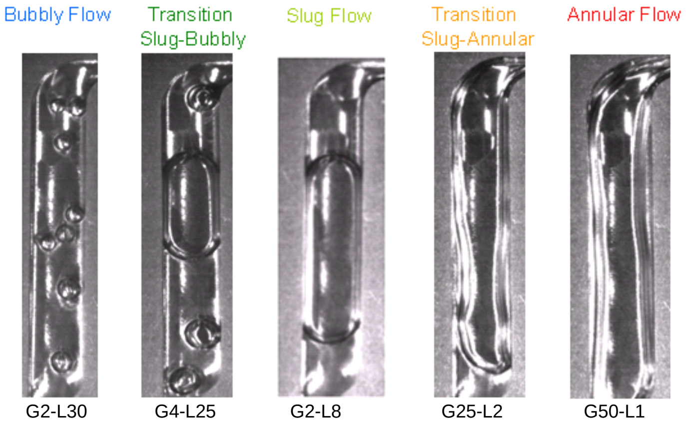


Fig. 2: Classification of CO_2-water flow regimes, the subscripts of the images indicate gas (G) and liquid (L) flow rate in mL/min and mLN/min.

Five different flow regimes can be distinguished and are displayed in Figure 3. The water flow rate in mL/min is displayed on the top axis and the gaseous CO_2 flow rate is displayed on the left side axis in mLN/min. The unit mLN/min gives the volumetric flow rate related to the standard state (273.15 K and 10^5 Pa of the gas) and can directly be correlated over the standard density (1.977 kg m^{-3} for CO_2) with the mass flow rate.

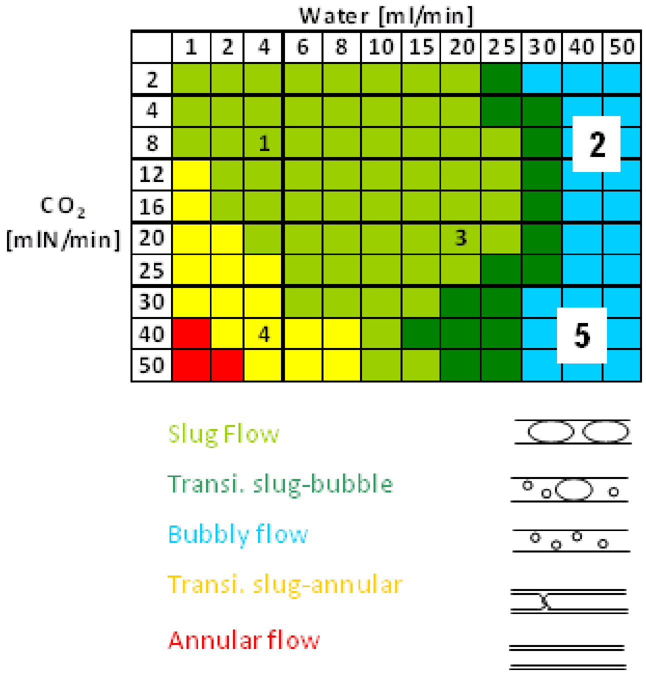


Fig. 3: Flow regimes in tangential mixing elements and short residence time channels. The numbers indicate points, where the mass transfer was measured, see text.

For low gas and liquid flow rates, slug flow was observed. For 10 mL/min, this flow regime is valid for all studied gas flow rates. Increasing gas flow rate leads to annular flow at low liquid flow rate (<10 mL/min). For all investigated gas flow rates, bubbly flow was reached for high liquid flow rates (> 40 mL/min). This flow map may differ from other flow maps in capillaries due to different geometry.

MASS TRANSFER FROM CO_2 REACTION

Together with the flow regimes, the mass transfer of the CO_2 absorbed in the aqueous phase was measured and correlated with the flow regime. More details of the measurement method can be found in [17]. The mass transfer coefficient is expressed by the k_La value to 0.16 s^{-1} for slug flow (1) with low flow rates and to 0.46 s^{-1} for bubbly flow (2). The numbers in brackets indicate the location in the flow regime map in Figure 3. Slug flow with higher flow rates (3) has a k_La value of 0.80 s^{-1}, while the annular flow with only high gas flow rates (4) possess a k_La value of 1.12 s^{-1}. The highest mass transfer coefficient was measured in bubbly flow (5) with 2.07 s^{-1}. This is comparable to the typical mass transfer coefficient in static mixers, which ranges from 0.1 to 2.5 s^{-1}. Other mass transfer equipment such as conventional bubble columns or stirred tanks only reach typical k_La-values [18] of 0.03 to 0.4 s^{-1}, while capillary micromixers with typical diameters of 100 µm or smaller can realize high values of 0.3 to 10 s^{-1}. The channels here are larger due to their optimization for high flow throughput. The investigated flow regimes and mass transfer range give guidance for the following experiments with gas-liquid chemical reaction.

LITHIATION OF ACETYLENE

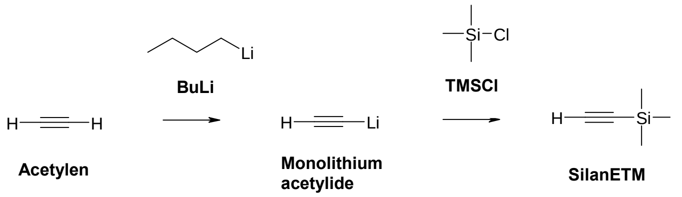
Lithiation is a prominent reaction class in organic chemistry to couple various moieties by first a lithium-proton exchange and a following lithium chloride formation while coupling the second moiety. In batch mode, this reaction is often performed under cryogenic conditions down to -100 °C and under strict exclusion of water and oxygen [19, 20], which form unwanted side products. In microreactors, the reaction temperature can often be boosted to higher level due to the excellent heat transfer avoiding hot spot formation [21]. Additionally, short and controlled residence time and rapid mixing can assist to increase the performance of complex chemical reactions.

In the following, a test reaction with lithiation of acetylene is described [19]. Acetylene (C_2H_2) is very reactive and is produced at Lonza in Visp, CH, on-site in a naphta cracker [22]. In microreactors lithiation is a well known reaction class [23] and already performed on industrial scale [24].

Reaction characteristics and kinetics

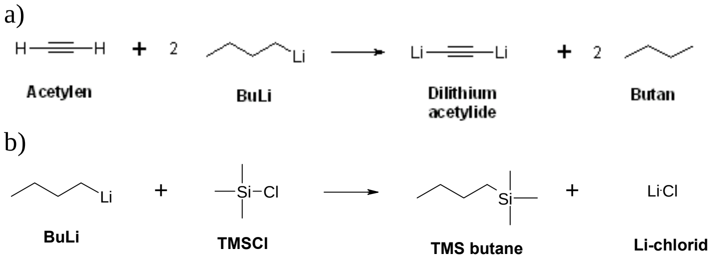
The aim of this study is to develop a continuous flow process to lithiate acetylene in a microreactor with high flow rates for good temperature control. Quantitatively, yield based on butyl lithium consumption should be optimized. A parameter optimization study is performed concerning reaction temperature *T*, pressure loss in the reactor Δp, and stoichiometry of the reagents.

Before starting the experiments, some safety measures concerning handling of acetylene and *n*-butyl lithium were addressed. Acetylene is stored in pressure cylinders solved in acetone to avoid decomposition [25]. Acetone does not trouble conventional applications such as welding, but might disturb the chemical application. We installed an activated carbon filter after the cylinder to remove traces of acetone. Acetylene can decompose to soot at pressure levels higher than 2.5 bar absolute with heat release. The pressure after the cylinder is limited to a threshold of 1.5 barg, and the maximum flow rate is restricted by a specially designed orifice. The gas containing tubes are connected to a nitrogen purge system exiting in the vent of the fume hood. A special risk assessment was performed to ensure safe operation of the test equipment in the lab.



Scheme 1: Lithiation of acetylene and quench with trimethylsilyl chloride (TMSCl) to stabilize monolithium acetylide.

Analytical methods with GC were developed to determine the mass fractions of product (monolithium acetylide, see Scheme 1) and by-products, see Scheme 2. Monolithium acetylide is unstable and is quenched directly after reaction with trimethylsilyl chloride (TMSCl).



Scheme 2: Side reactions [26] from lithiation and quench reaction:
a) Consecutive reaction to dilithium acetylide, b) parallel reaction during quench.

Detailed analysis of all reaction products and side products is very important to understand the reaction. A high molar ratio of butyl lithium to acetylene, high temperature above -25°C, and bad mixing leads to dilithium acetylide, an unwanted side product. Non-reacted butyl lithium reacts with TMSCl in the quench to trimetylsilyl butane, either by imperfect mixing or too short residence time in the microreactor.

Often batch experiments based on literature data are the first step into the reaction to test analytics and safety measures. A glass stirred vessel (500mL) was filled with tetrahydrofuran (THF purum, water-free) and cooled down to -75 °C. Gaseous acetone-free acetylene was bubbled into the vessel under vigorous stirring. After saturation, stoichiometric amount of *n*-butyl lithium was carefully dosed into the stirred vessel. After 2h reaction time, TMSCl solved in THF was fed into the vessel to quench the reaction. Yield of >93% with selectivity of S > 99% was obtained in the best results comparable to or better than literature data (Y > 90% [19]).

Continuous process in microreactor: homogeneous reaction

The first step from batch to continuous operation was the homogeneous reaction of acetylene solved in THF á priori from batch with *n*-butyl lithium. The reactor setup with two feed pumps is displayed in Figure 4. Acetylene is dissolved in THF at 20°C to saturation limit (approx. 3.5 w%) due to operating temperature of the pump (rotating piston pump, Ismatec). THF solution is mixed in a microstructured plate reactor with tangential mixing elements, d_{char} = 0.5 mm [27, 28] with *n*-butyl lithium (15 w% in hexane). A total flow rate of 30 mL/min and reactor temperature of -40 °C, a maximum yield of 98 % was achieved with stoichiometric mixing.

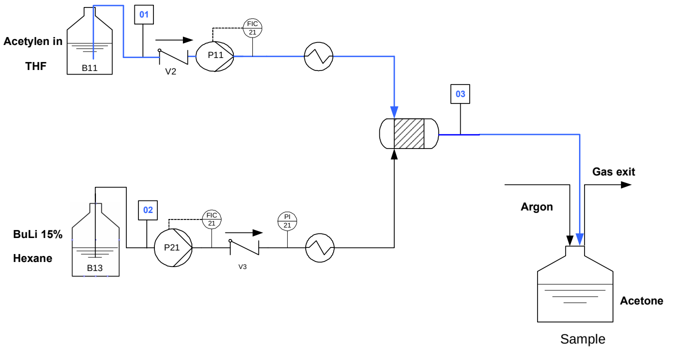


Fig. 4: Experimental setup for lithiation of dissolved acetylene in tetrahydrofuran (THF).

In comparison with batch, a similar yield was achieved, but with higher dilution in continuous process. The acetylene dissolution at 20 °C in THF is a great limitation of this process. Due to batch-wise acetylene dissolution, a continuous process is not practical.

Continuous process in microreactor: gas/liquid reaction

For fully continuous operation, acetylene is fed as gas to the microreactor and dissolved in THF, then mixed with *n*-butyl lithium. Acetylene limitation is now the maximum pressure of p_{max} = 1.5 barg, resulting in a maximum pressure loss in the microreactor of approx. $\Delta p_{reactor}$ < 1 bar. The experimental setup is shown in Figure 5. Two liquid feeds of THF and *n*-butyl lithium in hexane are pumped by rotating piston pumps and pre-cooled in tube coils plunged in ethanol bath cooled down to reactor temperature. Acetylene flow rate is controlled by mass flow controller and calibrated by weight balance under the pressure cylinder. The reactor is also cooled down, while the quench vessel at room temperature is purged by argon to avoid humidity and oxygen reacting with acetylene or *n*-butyl lithium.

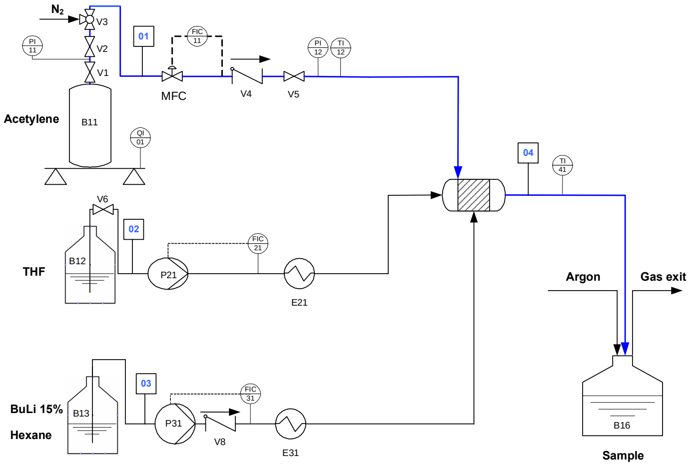
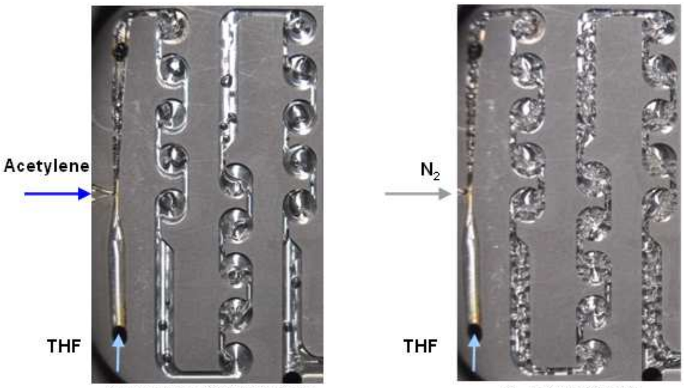


Fig. 5: Experimental setup for dissolution of gaseous acetylene in tetrahydrofuran (THF) and further lithiation of acetylene.

Here, the optimization goal is to identify and understand the bottleneck of acetylene dissolution in THF as well as to increase the reaction throughput. The first investigations were performed in the Lonza LabPlate reactor, already shown in Figure 1. The flow regime of acetylene dissolving in THF at -50 °C is shown in Figure 6 and compared with the flow regime of nitrogen with similar liquid flow rate, but less gas flow rate. The disappearing acetylene bubbles clearly indicate good dissolution along the channel. In contrary, nitrogen is sparsely soluble in THF, hence the bubble size and number are not changing along the channel.



Acetylene = 615 mlN/min
THF = 25 ml/min

N_2 = 50 mlN/min
THF = 25 ml/min

Fig. 6: Comparison of dissolution and flow patterns of acetylene in THF at -40 °C (left side) and nitrogen N_2 in THF. Please note the bad dissolution of nitrogen from the similar flow patterns along the mixing channel.

The three-feed reaction at -40 °C in the reactor is displayed in Figure 7. THF enters the reactor from the lower left side, acetylene from the middle left side and is dissolved rapidly. From the lower entrance in the middle, *n*-butyl lithium enters the reaction channel. Soon after starting *n*-butyl lithium feed, grey scale formation and precipitation was observed at the entry channel accompanied with sudden pressure loss increase over the reactor. After few minutes, the pumps must be stopped, because the pressure safety limit of acetylene was reached. The reason of precipitation was soon identified: hot spot formation at the entry with dilithium acetylide salt formation, which is already described in Scheme 2.

Please note the location of the precipitation along the channel from entry point to first mixing cylinder, but also approx. 2 to 3 mm upstream. The latter is caused by flow recirculation of the incoming flow in the bend and near wall flow and diffusion. The disappearance of scale formation in the first mixing cylinder indicates the limit of the hot spot downstream.

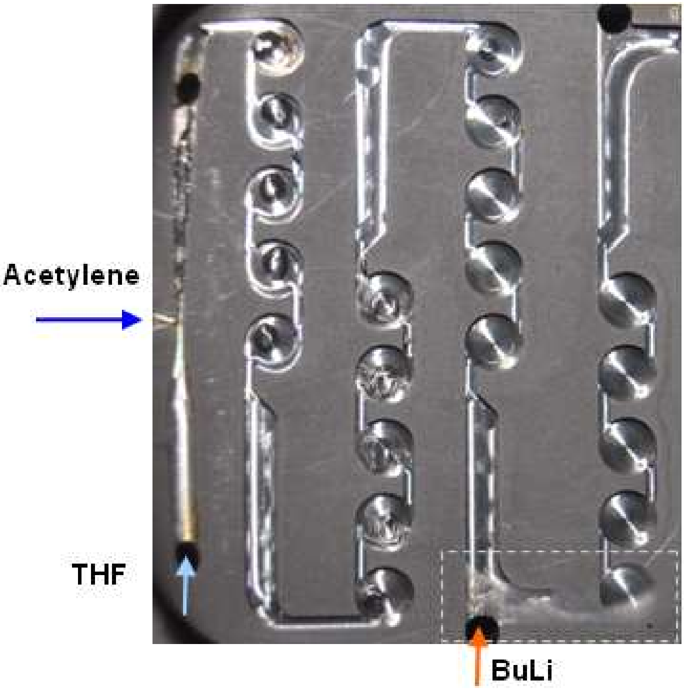


Fig.7: Dissolution of acetylene in THF and following lithiation by *n*-butyl lithium (BuLi). Solid formation is clearly to see due to side product formation at -40 °C.

Hot spot formation can be diminished by heat transfer enhancement in the reactor or less reaction heat being produced by lower temperature or lower concentration. The Lonza LabPlate reactor is cooled from the rear side, while the glass view plate thermally insulates the reactor plate. In the next step, the reaction was performed in a microstructured Hastelloy plate with several inlets and mixing channel segments, the so-called multi-injection plate, see Figure 8. Here, both sides of the plate are cooled, but size and shape of the mixing channel is similar.

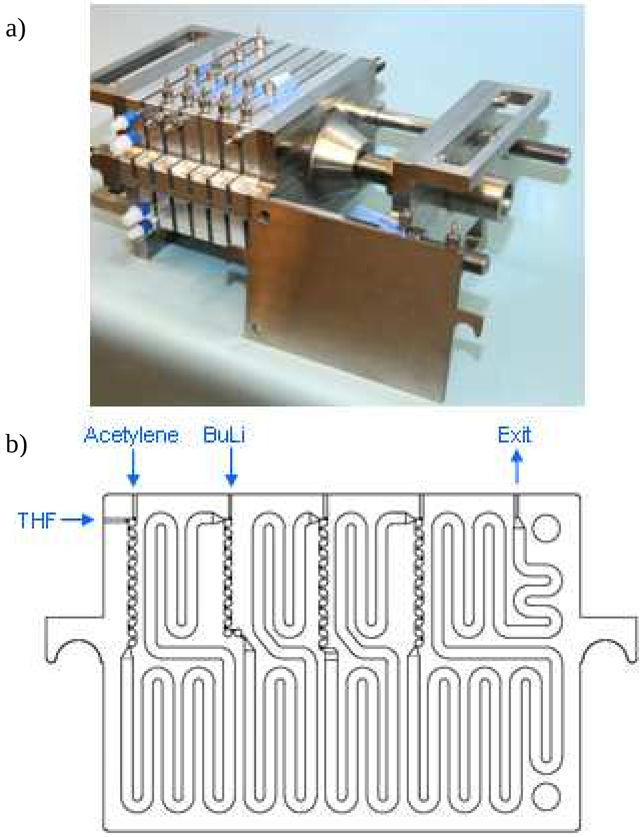


Fig. 8: Multi-injection plate to perform stepwise reactions.

Continuous-flow reaction in plate reactor

Lonza has developed a plate reactor stack (Figure 8 a), which contains microstructured reactor plates from Hastelloy (Figure 8 b) with channel arrangement) integrated between heat exchange plates made from aluminum. Through the heat exchange plates, thermal fluid can be pumped through in high excess leading to nearly constant temperature over the reactor stack. More details of the reactor setup can be found in [27, 29].

The three-feed setup, given in Figure 5, is implemented with the multi-injection plate. THF and *n*-butyl lithium solution are pre-cooled to the reaction temperature in other plates integrated in the reactor stack. THF and acetylene are entering the plate from top left side to dissolve acetylene, see Figure 8 b). After a residence time of few seconds, depending on the flow rate, *n*-butyl lithium enters the plate and both reagents are intensively mixed. A cooling fluid temperature of -40 °C and higher leads again to reactor plugging, due to hot spot formation. At -50 °C cooling fluid temperature, the hot spot temperature was apparently below -25 °C, no dilithium acetylide was formed, and no plugging was observed. Residence time had no influence in the investigated flow range, hence, dissolution and reaction are very fast. A maximum yield of 97 % was achieved at flow rates of THF and *n*-butyl lithium of 26.5 and 8 g/min, respectively. Molar ratio acetylene to *n*-butyl lithium was 1.2 for maximum yield, while the yield of monolithium acetylide was constantly decreasing for *n*-butyl lithium > 0.45 mol/L in total solution, see Figure 9. This is also a hint for hot spot formation and side product generation at higher *n*-butyl lithium concentrations.

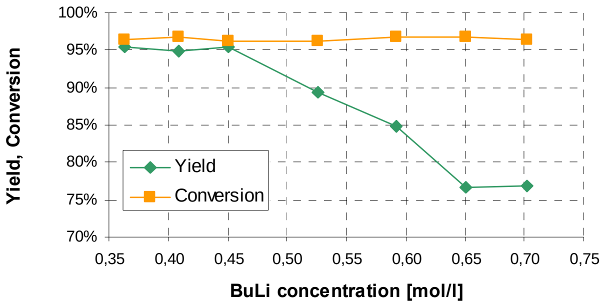


Fig.9: Conversion and yield of monolithiated acetylide as function of *n*-butyl lithium concentration.

Similar results for *n*-butyl lithium concentrations are mentioned in literature for batch reactions. A possible explanation is that monolithium acetylide is less stabilized by THF decreases if concentration of *n*-butyl lithium is above 0.5 mol/L. This implies a great limitation to the reaction throughput.

CONCLUSIONS

Gas-liquid reactions were investigated in microstructured reactors. Flow regimes of carbon dioxide, nitrogen, and acetylene were optically characterized and correlated with mass transfer coefficient for CO_2 in water. Results were used to design flow conditions for strongly exothermic gas-liquid reactions. Lithiation of acetylene was investigated as exothermic test reaction with critical side products. Batch experiments at -75 °C gave good yield, while same yield were achieved at -50 °C in microstructured continuous flow reactor with no reactor plugging from side product formation. Optimal conditions were 0.45 mol/L *n*-butyl lithium concentration and acetylene/*n*-butyl lithium ratio of 1.2. At higher reaction temperature, plugging was observed at entry of *n*-butyl lithium, probably due to double lithiation of acetylene and precipitating of this side product. Successful transfer of demanding batch reaction into continuous flow process was demonstrated with higher yield within microstructured reactor plate with enhanced heat transfer. The setup can be used as generator for activated acetylene for chemical synthesis. Major limitations are maximum feasible *n*-butyl lithium concentration and maximum acetylene pressure, both decreasing reactor throughput.

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