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► **To cite this version:**

Nathalie Di Miceli Raimondi, Sébastien Elgue, Laurent Prat, Patrick Cognet, Michel Cabassud. Optimisation of operating conditions in batch for more sustainable continuous process transposition. Chemical Product and Process Modeling, 2008, 3 (1), pp.0. hal-04468390

HAL Id: hal-04468390

<https://hal.science/hal-04468390>

Submitted on 20 Feb 2024

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Optimisation of operating conditions in batch for more sustainable continuous process transposition

N. Di Miceli, S. Elgue, L. Prat, P. Cognet, M. Cabassud

Abstract

Implementation of exothermic and fast reactions requires a perfect temperature control to avoid thermal runaway and in most cases to limit by-products production. In order to fit with the heat removal capacity of common devices, expensive strategies are currently used to slow down this kind of reactions in order to avoid a strong temperature increase such as reactants dilution. Within the concept of process intensification, industries could move towards more sustainable process by reducing technology constraints to the benefit of chemistry. For that purpose, a two-step methodology is implemented. The first step consists in the optimisation of the operating conditions only based on stoichio-chemical scheme and kinetic laws. This is carried out by adjusting temperature profile and feeding rate strategy in a batch operation. Then a design for a continuous process is proposed, trying to approach the optimal batch operating conditions. This methodology is applied to the linear alkylbenzene sulfonation.

Keywords: Optimisation, exothermic and fast reactions, process intensification.

1. Introduction

Fast and exothermic reactions are difficult to carry out at industrial scale because their processing requires a perfect temperature control. In conventional devices, the heat transfer capacity is often limited as shown in Table 1: while the jacketed batch reactor offers a very poor thermal efficiency, it is still used in many manufactures to carry out fast and exothermic reactions. In such reactors, the temperature control is insured by diluting the reactants, or by implementing a feeding strategy which generally does not favour the selectivity of the reactions and lead to an increase in the residence time. This procedure tends to adapt the chemistry to the technology constraints. In agreement with the concept of process intensification (Stankiewicz and Moulijn, 2000), the current trend is to adapt the technology to the chemistry. The emergence of highly efficient technologies in

terms of heat removal (heat exchanger reactors, microreactors) allows a better fitting of the technology with the chemical constraints.

Table 1. Heat exchange capability for different reactors (Ferrouillat et al., 2006).

Process	Compact multifunctional heat exchanger reactor	Tubular heat exchanger reactor	Batch reactor with outer heat exchanger	Jacketed batch reactor
Volumic area A (m^2/m^3)	800	400	10	2.5
Heat transfer coefficient U ($\text{W}/(\text{m}^2 \text{K})$)	5 000	500	1 000	400
Volumic thermal conductance UA ($\text{kW}/(\text{m}^3 \text{K})$)	4 000	200	10	1

This can be illustrated by the sulfonation, which is a key reaction in the detergent production. Sulfonates have a white colour and are mainly used as surfactants in laundry, while by-products are black: consequently, sulfonation manufacture aims at the purest product to satisfy consumers' requirements. Processes using gaseous sulfur trioxide (SO_3) as sulfonating agent are predominant since there are very versatile (a wide variety of feedstocks can be sulfonated or sulfated) and they produce high quality products with a purity of more than 95 % (Foster, 1997). Because by-products formation is mainly favoured by high temperature, temperature has to be perfectly controlled in the reactor. This makes the sulfonation processing complex since the main reaction and the secondary ones are very fast and exothermic. Moreover, the viscosity of the sulfonate solution is between 15 and 300 times higher than the feedstock one, leading to a drastic decrease in the local heat transfer coefficient of the liquid phase as the reaction proceeds. This reaction is generally carried out in a falling film reactor coupled with a cooling water jacket where the cooling area is around $3\,000 \text{ m}^2/\text{m}^3$ and the global heat transfer coefficient around $800 \text{ W}/(\text{m}^2 \text{K})$ (Chemithon annular falling film reactor, Ballestra multi-tube film sulfonator (Foster, 1997)). Therefore this technology is characterized by a high thermal efficiency ($2\,400 \text{ kW}/(\text{m}^3 \text{K})$). Nevertheless, this thermal efficiency added to the small thickness of the liquid are not sufficient to efficiently dissipate the heat generated by the reactions, the heat of reaction being of the order of -170 kJ per mole of sulfonate produced. Consequently, the increase in temperature is currently limited by diluting the gaseous reactant SO_3 with air (volumetric fraction in SO_3

between 3 % and 7 % (de Groot, 1991)). However, air needs to be dried before being in contact with SO_3 to avoid the formation of sulfuric acid which can corrode the process devices. Therefore, since an important flow rate of air is used, the air/ SO_3 process is highly energy consuming. In order to avoid air consumption, other reactor technologies have to be considered to enhance heat transfer between the reaction mixture and the cooling system.

In this article a methodology to adapt process designs to chemical constraints is presented, illustrated by the linear alkylbenzene (LAB) sulfonation with SO_3 . In order to suppress the impact of the transfer of SO_3 from the gas phase to the liquid mixture, this study focuses on LAB sulfonation with liquid SO_3 . This way, the present work concentrates only on the chemistry of the system. This methodology is developed in two steps: first, the optimal operating conditions are determined only considering the thermo-kinetic parameters of the reaction in batch conditions. Then a reactor design is proposed trying to approach the optimal operating conditions in a continuous reactor.

2. A fast and exothermic reaction: the LAB sulfonation

2.1. Reaction scheme

Since sulfonation is very fast, very few data on the reaction kinetic are available. Indeed, previous works used to model this process assuming the kinetic rate instantaneous compared to the rate of SO_3 mass transfer from the gas phase to the organic medium (Johnson and Crynes, 1974; Davis et al., 1979). This approach has notably been validated in falling film reactors by Talens-Alesson (1999). However, this work aims to propose a method of process design optimisation to the benefit of the chemistry. For that purpose, chemical kinetic is the only contribution that we consider in this work to model the sulfonation process. As illustrated in Figure 1, a reaction scheme is proposed to simulate and optimise the LAB sulfonation, inspired from Roberts's works (2003):

- (1) The first reaction R1 allows the production of a small amount of pyrosulfonic acid (Pyro) required to prime the main mechanism of sulfonation.
- (2) The main mechanism of the LAB sulfonation is composed of two reactions (R2 and R3) and leads to the formation of the desired product: the linear alkylbenzene sulfonate (LAS).
- (3) Numerous competitive side reactions were suggested by Roberts (2003); to simplify the simulation of the sulfonation, only two side reactions have been considered: the production of the linear alkyl benzene sulfonate anhydride LASA (R4) and of the pyroanhydride LASP (R5). Both reactions also lead to the formation of sulphuric acid H_2SO_4 .

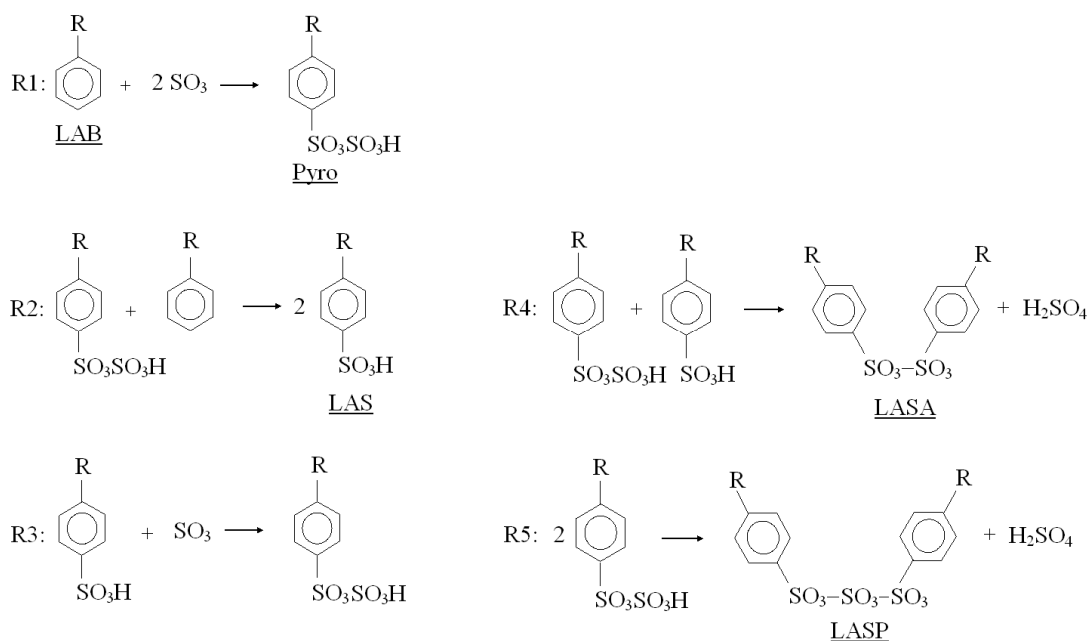


Figure 1. Reaction scheme proposed to model the LAB sulfonation.

This scheme suggests that both reactants should be introduced in the reactor in equimolar ratio. Indeed, in one hand an excess in SO₃ would favour the consumption of the desired product, LAS, to form pyrosulfonic acid through R3. On the other hand, an excess of LAB does not seem to influence the selectivity of the sulfonation. Therefore, it would lead to a poor conversion of this reactant while the reaction scheme does not justify it.

2.2. Thermo-kinetic parameters

The thermo-kinetic parameters used to represent the LAB sulfonation are based on the following considerations (Table 2):

- (1) Roberts (2003) suggested to represent the self-priming reaction R1 as first order in LAB and second order in SO₃. For the other reactions, we assumed that the order of the reactions could be deduced from the stoichiometric coefficients of each reactant as described in Table 2.
- (2) The rate constant k can be written in term of Arrhenius law. Roberts estimated the pre-exponential factor k_0 regarding to the number of reactant molecules and product in agreement with the kinetic theory of gases (Frost and Pearson, 1953). For instance, R2 being a reaction in which two reacting molecules form

- two product molecules, he proposed a pre-exponential factor of 10^{11} L/(mol s). The same assumption allows the estimation of k_0 for reactions R4 and R5. For reactions where two reacting molecules form one product molecule such as R3, Roberts suggested a pre-exponential value of 10^8 L/(mol s). Finally, for the self-priming reaction R1 which is a third-order reaction, he estimated k_0 around 10^4 L²/(mol² s).
- (3) Roberts gave 54 300 J/mol as the estimated activation energy of R2 (production of LAS from LAB and the pyrosulfonic acid). Then, he suggested that the activation energy of R3 should be very low since the chemical mechanism to form the pyrosulfonic acid from LAS and SO₃ might be rather “facile”. Therefore, we arbitrary set activation energy lower than the main sulfonation reaction one. Finally, Roberts estimated the activation energy of the self-priming reaction R1 by considering the enthalpy of formation of the probable intermediate products that lead to the formation of the pyrosulfonic acid from LAB and SO₃. He assumed it ranged from 8 500 J/mol to 12 500 J/mol.
 - (4) By-products production is favoured by high temperature; therefore the activation energy of the side reactions R4 and R5 must be higher than the others. We considered that E_a of R4 and R5 were 20 % higher than the one estimated for R2.
 - (5) Roberts estimated the enthalpies of reaction for the main reactions from the enthalpies of formation of the different products by means of calculations of molecular orbital energies.
 - (6) The reaction enthalpies of the side reactions should be very small assuming that these data can be deduced from the dissociation enthalpies of the broken and formed bonds during the reaction. In both R4 and R5, two bonds Sulphur – Oxygen are broken and then formed.

Table 2. Thermo-kinetic parameters used to model the LAB sulfonation.

Reaction	Reaction rate r (mol/(L s))	Pre-exponential factor k_0	Activation energy E_a (J/mol)	Reaction enthalpy ΔH (kJ/mol)
R1	$k c_{LAB} c_{SO_3}^2$	10^4 L ² /(mol ² s)	10 500	-70
R2	$k c_{LAB} c_{Pyro}$	10^{11} L/(mol s)	54 300	-140
R3	$k c_{LAS} c_{SO_3}$	10^8 L/(mol s)	45 000	-70
R4	$k c_{LAS} c_{Pyro}$	10^{11} L/(mol s)	65 000	0
R5	$k c_{Pyro}^2$	10^{11} L/(mol s)	65 000	0

3. Operating conditions optimisation

3.1. Description of the optimiser Optibatch

Optibatch (License INPT, 1998) is a software developed for the optimisation of operating conditions in a batch or semi-batch reactor only based on the chemistry of a process (no mass transfer considerations). The objective of this tool is to optimise a criterion defined in terms of yield, selectivity, time of reaction, ..., while taking into account different constraints specified by the operator: technology and/or safety constraints, productivity and/or selectivity constraints. The evolution over time of the variables that describe the reactor state such as temperature and composition is calculated by integrating mass and energy balances in respect with constraints. To solve the problem, the residence time t is divided into a finite number of intervals n_{int} equals to 5 in this work. The optimisation algorithm allows the determination of the $(n_{\text{int}} + 1)$ temperatures at each bond of each interval. The temperature profile is then assumed to be linear in each interval:

$$T = T_{j-1} + (t - t_{j-1}) \cdot \left(\frac{T_j - T_{j-1}}{t_j - t_{j-1}} \right) \quad \text{with } 1 < j < (n_{\text{int}} + 1) \quad (1)$$

For the feeding profile, the program determines the mass that should be introduced in each interval. The flow rate is then obtained by assuming it remains constant over each interval. Garcia et al. (1995) described in more details the numerical formulation of the problem and validated the method with general examples of reaction schemes (consecutive-competitive and parallel reactions).

In the present work, the criterion to be optimised is the final amount ratio of LAS x_{LAS} using pure reactants (LAB and liquid SO_3). In our study, the molecule of LAB is composed of a radical R of molecular formula $\text{C}_{12}\text{H}_{25}$ (dodecylbenzene). The residence time is set to one second. The operating conditions to be defined are the temperature profile in the reactor and the SO_3 feeding profile ($c_{\text{SO}_3} = 10.6 \text{ mol/L}$). We decided to feed the reactor with SO_3 rather than LAB since an excess of SO_3 would dramatically affect the selectivity of the sulfonation regarding the reaction scheme considered in this study (Figure 1). Therefore, at initial time, the reactor contains only LAB ($c_{\text{LAB}} = 3.46 \text{ mol/L}$). It is assumed that SO_3 is totally and instantaneously mixed in the organic matter. The physico-chemical properties of the mixture in terms of density and heat capacity are supposed constant during the reaction, calculated at the initial time. Finally, the temperature in the reactor is constrained: it must not be lower than $25 \text{ }^\circ\text{C}$ and higher than $150 \text{ }^\circ\text{C}$ to maintain the solution in liquid phase (molecules that contain long carbon chain may freeze at $20\text{--}25 \text{ }^\circ\text{C}$; the decomposition temperature of the products is arbitrary set to $150 \text{ }^\circ\text{C}$).

3.2. Optimisation results

First, we determined the optimal operating conditions for a discontinuous operation (batch or semi-batch) without constraining the heat removal capability of the reactor. This optimisation supposes that the temperature in the reactor can be perfectly controlled whatever the heat that needs to be removed or provided to the reactive system. The result of the optimisation computation is a semi-batch reactor at minimum temperature to achieve 95% of the final amount of LAS, which corresponds to a residence time of 0.4 s (Figure 2 **Erreur ! Source du renvoi introuvable.**). Then a higher conversion is reached with an increase of the temperature ($x_{LAS} = 92.06\%$). As expected, the total amount of SO_3 introduced in the reactor is in equimolar ratio with the initial amount of LAB.

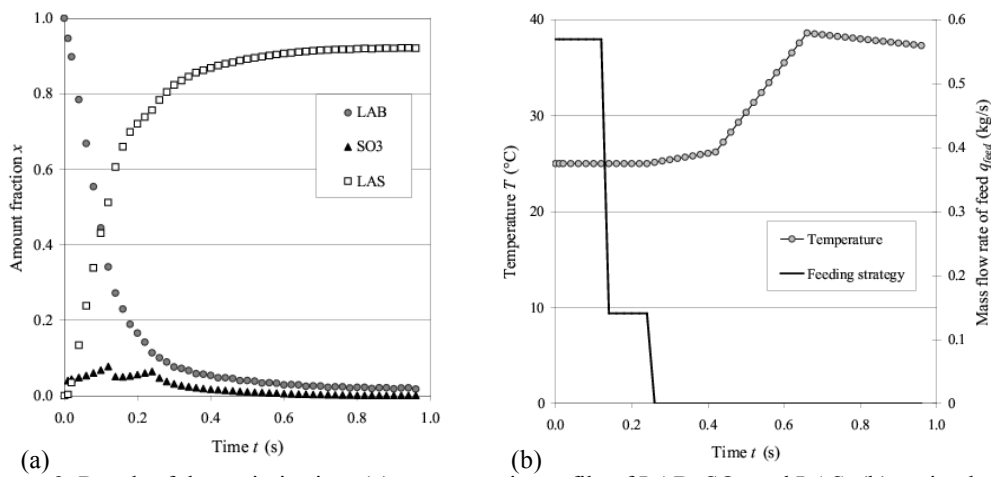


Figure 2. Result of the optimisation: (a) amount ratio profile of LAB, SO_3 and LAS; (b) optimal temperature and feeding profiles obtained for the production of one mole of LAS.

However, this simulation shows that a lot of heat needs to be removed from the reactor in a hundred seconds to reach such a conversion as illustrated on Figure 3 ($2 \cdot 10^6$ kW/m³ of reactor). It corresponds to the heat flow rate produced by the reaction since the temperature of the mixture is constant during this period.

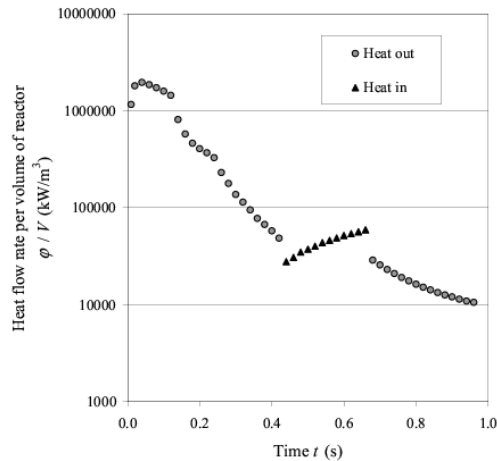


Figure 3. Optimal heat flow rate per volume of reactor.

We can compare the maximal heat flow rate necessary to optimise the sulfonation with the thermal powers of different devices:

- (1) Considering a new concept of continuous heat exchanger reactor, the “open plate reactor” designed by Alfa Laval Vicarb (OPR), Prat et al. (2005) and Benaissa (2006) proved its high thermal efficiency (heat transfer coefficient up to $2500 \text{ W}/(\text{m}^2 \text{ K})$ for a volumic area of $240 \text{ m}^2/\text{m}^3$). With this reactor of 0.4 L, they decreased the temperature of hot water of $45 \text{ }^\circ\text{C}$ by exchange with cold water ($15 \text{ }^\circ\text{C}$). Therefore, this device can be characterized by a thermal power of $9\,000 \text{ kW}/\text{m}^3$ which is very far from the $2 \cdot 10^6 \text{ kW}/\text{m}^3$ of reactor required to obtain maximal conversion.
- (2) To approach so high thermal power, micro-heat exchangers seem to be appropriate apparatus to carry out the reaction since they offer a high exchange area for a very small reactive volume. Indeed, McGovern et al. (2006) calculated that microreactors can offer an area per volume unit ratio of more than $20\,000 \text{ m}^2/\text{m}^3$ compared to roughly $500 \text{ m}^2/\text{m}^3$ for usual device. Schubert et al. (2001) obtained thermal powers up to 20 kW with microstructured devices having 1 cm^3 active volume, i.e. up to $2 \cdot 10^7 \text{ kW}/\text{m}^3$.

The previous results shows that technology constraints to carry out the sulfonation reaction can be reduced to the benefit of the chemistry (use of pure reactants) by using highly efficient devices in terms of thermal power such as microreactors. Optimal operating conditions were determined in semi-batch reactor (temperature and feeding profiles): the transposition to continuous operation is now required to fit with the use of miniaturised structures.

4. Process design optimisation for a continuous operation

4.1. Geometry of the reactor

The previous part demonstrates that sulfonation manufacture is strongly constrained by the capability of the reactor to dissipate the heat generated by the reactions. Since micro-heat exchangers are considered as highly efficient apparatus (Qu et al., 2000; Gao et al., 2002; Gamrat et al., 2005), sulfonation is simulated in a microchannel coupled with a cooling system as illustrated in Figure 4: the cooling of the reactive media is insured by thermal exchange with an utility fluid that flows around the process channel. The simulated structure is in steel and the size of the channels and the walls between the process and the utility channels are given in Table 3. This geometry is inspired by a microstructured reactor designed by the Forschungszentrum Karlsruhe (FZK, Germany), where the process passage consists of 20 foils with 34 microchannels of such geometry. The length of the reactor is estimated from the desired residence time which is set to one second to compare the results of the simulations with those obtained with Optibatch. The channel has roughly $25\,000\text{ m}^2/\text{m}^3$ of volumic area.

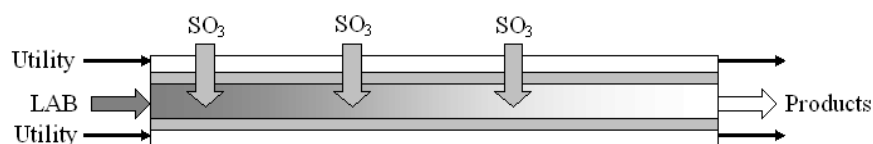


Figure 4. Scheme of the microchannel used for the simulation of the LAB sulfonation in a continuous reactor.

Table 3. Geometric characteristics of the simulated microchannel.

	Process channel	Utility channel	Wall
Length L (mm)	33	33	33
Depth d (μm)	110	55	90
Width w (μm)	320	320	320

The inlet flow rates are estimated so that the fluid velocity in the channel is around 3 cm/s. Pure LAB is introduced at the inlet of the reactor ($c_{\text{LAB}} = 3.46\text{ mol/L}$) while SO_3 is injected at several points in the main channel to approach the semi-batch reactor behaviour ($c_{\text{SO}_3} = 10.6\text{ mol/L}$). In order to approach the results obtained with Optibatch, the total amount of SO_3 injected is in equi-molar ratio with the LAB introduced at the inlet of the channel. The cooling fluid is water, with a volume flow rate that is approximately twice the process fluid one. In such conditions, the temperature of the utility fluid remains roughly constant. It

assumes that no heat is exchanged with the ambient environment, at room temperature. Table 4 summarizes the properties of the inlet streams.

Table 4. Properties of the inlet streams in the simulated microchannel.

	Process channel	Injections	Utility channels
Entity	LAB	SO ₃	water
Flow rate q_V ($\mu\text{L/s}$)	1.11	0.16 (in total)	1.39 (per channel)
Temperature T ($^{\circ}\text{C}$)	25	25	25
Pressure p (bar)	5	5	5

Different multi-injection strategies are compared in terms of final amount of LAS.

4.2. Simulator description

The simulator is based on the integration of a dynamic model. It has been described and validated by Elgue et al. (2006) through the simulation of sodium thiosulfate oxidation in the OPR. The different parts of the reactor (process and utility channels) are represented by series of perfectly stirred tank reactors called cells. Since mixing is supposed to be very fast compared to the reaction time, we considered that the flow in the channel can be represented by a perfect plug flow, which is equivalent to a serie of a high number of stirred tanks, set to 100 in this work. The modeling of a cell is based on the resolution of mass and energy balances and constraint equations (geometrical characteristic of the reactor, physical properties of the fluids...). This resolution allows the calculation of the parameters characterizing the flows: temperature, flow rates, composition, pressure....

The balance equations and the correlations used to model the system require the estimation of the physical properties of each fluid. For that purpose, the model implemented has been linked to a commercial thermodynamic and equilibrium database: Bibphy32 (Prosim ®). The local heat transfer coefficients on the utility and process sides are calculated considering that Nusselt number is constant in microchannels, equal to 2.181 (Shen et al., 2006).

The mathematical model that represents the operation is an extremely complex model due to the number and also the type of equations that it involves: differential and algebraic equations (global and component mass balances, energy balances within the process and utility fluids, pressure balance, ...). The resolution of the model calls for a specific strategy and solving method. The system is solved using a global approach (i.e. simultaneous treatment of all equations with no discrimination according to the type of equation) by means of

the specifically designed solving tool based on the Gear method: DISCo (Sargousse et al., 1999).

4.3. Results and discussions

Results of the simulations done with different injection configurations are summed up in Table 5. Figure 5 shows that the more numerous the injection points are, the best the yield of LAS is. However, the number of injection channels of the optimal device will be limited by manufacture constraint. Figure 6 illustrates that the injections should occur during 0.4 seconds in terms of residence time: these results fit with those previously obtained despite the discretisation of feeding.

Table 5. Result of the simulations with different multi-injection strategies (residence time=1s).

Injections	Hot spot	Yield of LAS
1 in 0.4 seconds	123.64°C	86.91 %
4 in 0.4 seconds	53.15°C	92.37 %
10 in 0.4 seconds	43.85°C	92.62 %
10 in 0.65 seconds	40.99°C	92.08 %
10 in 0.9 seconds	40.04°C	91.11 %
10 in 0.2 seconds	51.08°C	92.50 %

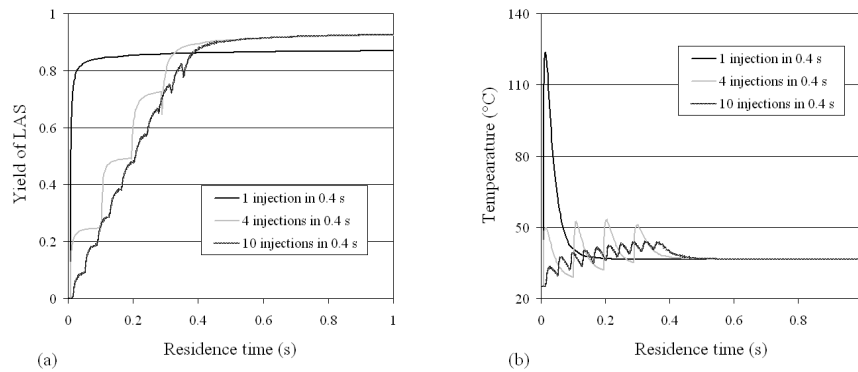


Figure 5. Comparison between different process designs varying the number of injections in 0.4 s: (a) yield of LAS profile; (b) temperature profile.

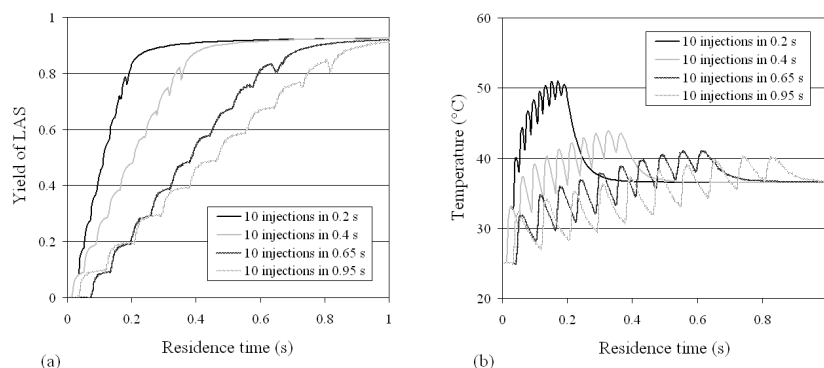


Figure 6. Comparison between different process designs varying the space interval between the injections: (a) yield of LAS profile; (b) temperature profile.

5. Conclusion

The methodology presented aims to optimise a process design in two steps according to the process intensification principle. First, the optimal operating conditions are determined in a batch or semi-batch reactor only considering kinetic and thermal constraints. The second step consists in defining an optimal geometry, suggested by the results previously obtained, to carry out the reaction in a continuous reactor. All the parameters that could influence the optimisation have not been thoroughly studied (utility flow rate, channel dimensions, wall properties) but this work aims to demonstrate the capability of such a methodology of optimisation, and the performances of the associated tools we used.

In the case of the LAB sulfonation the application of this methodology reveals that the reaction should be carried out in a micro-exchanger. Indeed this technology allows a good heat removal and so a good temperature control while implementing a multi-injections strategy of pure SO_3 in the process channels. Mixing limitations have not been brought up in this study but Hessel et al. (2005) reviewed numerous ways to enhance mixing in micro-device. Kockmann et al. (2006) tested different mixers based on successions of T-mixers and obtained a characteristic mixing time between 0.1 and 10 ms depending on the Reynolds number in the channel. For reaction processing, additionally to mixing elements, the size of the main and injection channels could be designed in order to create turbulences where the fluids get in contact. The reactants flow rates could also have a major effect on mixing and should be properly chosen to obtain a mixing time very small compared to the characteristic reaction time.

Notation

A	Volumic area (m^2/m^3)
c	Concentration (mol/L)
d	Depth (m)
E_a	Activation energy (J/(mol K))
k	Rate constant ($\text{L}^i/(\text{mol}^i \text{ s})$) where i depends on the reaction rate law
k_0	Pre-exponential factor ($\text{L}^i/(\text{mol}^i \text{ s})$)
L	Length (m)
n_{int}	Number of intervals for the discretisation of the residence time
p	Pressure (bar)
q_{feed}	Mass flow rate of feed (kg/s)
q_V	Volume flow rate (m^3/s)
r	Reaction rate (mol/(L s))
t	Residence time (s)
T	Temperature ($^{\circ}\text{C}$)
U	Heat transfer coefficient ($\text{W}/(\text{m}^2 \text{ K})$)
V	Volume of the reactor (m^3)
w	Width (m)
x	Amount ratio

Greek letters

ΔH	Enthalpy of reaction (J/mol)
Φ	Heat flow rate (W)

Abbreviations

DISCo	Do Integrate by a Software Component
FZK	Forschungszentrum Karlsruhe
INPT	Institut National Polytechnique de Toulouse
LAB	Linear AlkylBenzene
LAS	Linear Alkylbenzene Sulfonate
LASA	Linear Alkylbenzene Sulfonate Anhydride
LASP	Linear Alkylbenzene sulfonate Pyroanhydride
Pyro	Pyrosulfonic acid
OPR	Open Plate Reactor

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