Intensification of a highly exothermic chlorination reaction using a combined experimental and simulation approach for fast operating conditions prediction

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A B S T R A C T

Process intensification and micro-structured reactor design can be relevant means to improve the safety of a process involving hazardous substances. This work deals with the intensification of a chlorination reaction usually performed in batch mode, using thionyl chloride ($SOCl_2$) to chlorinate a sterically hindered carboxylic acid dissolved in dimethylacetamide (DMAC). This chlorination reaction involves the exothermic formation of a species called Vilsmeier reagent, resulting from a reaction between $SOCl_2$ and DMAC. In order to intensify this process, a reaction scheme with kinetic and thermal data is identified in the first place. This model is then used to suggest how the chlorination reaction could be carried out in a continuous mode and under which optimal operating conditions it should be operated. Tests are then conducted using a lab-scale microreactor providing good mixing and heat exchange, resulting in better performances than the batch process, within seconds of residence time. Further tests are performed at larger scale using a pilot-scale microreactor, designed to achieve the same yield and quality performances as the lab-scale microreactor with a higher throughput, as long as residence time, ratio between reactants and temperature remain constant.

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1. Introduction

Process intensification has been subject to many works in the past few years, especially in the field of organic chemistry [1–4]. Indeed, flow reactor design, and more particularly microreactor design, has become a mean of intensifying chemical reaction processes by suggesting the appropriate equipment to reach the reaction's full chemical performance. This approach, that places the chemical reaction at the center of the design problem, can be opposed to the commonly-used approach that mainly consists in slowing down the operating conditions to fit chemical reaction into the limited capacities of batch equipment [5]. Flow reactors can be designed to fit mass and heat transfer requirements to improve reaction performances in a safer way, due to higher mixing performances, larger surface-to-volume ratios and larger heat and mass transfer coefficients [6,7]. Besides, microreactor design enables the use of techniques that enhance reaction performance, as ultrasounds or microwaves [8]. Hazardous chemicals can also be used in a safe way while highly exothermic reactions are carried out [9]. These reactions, when carried out in conventional reactors, are often limited by heat transfer, leading to thermal runaway, affecting product quality and process safety [10]. Microreactors, providing efficient thermal control and mixing performances while keeping a small reactive volume, have enabled safe syntheses of highly exothermic reactions like direct fluorination [11] or Grignard reaction [12] with significant yield improvement compared to batch processes.

The present work deals with the exothermic chlorination reaction of a sterically hindered carboxylic acid (R-COOH) dissolved in dimethylacetamide using thionyl chloride. Whereas this class of reactions is routinely used at industrial scale for synthesis of high-added value chemicals, no reference work describes these production processes or large-scale protocols. Many works deal with the synthesis route and chemical factors that impact the synthesis, but no results relative to the reaction kinetics are reported: thionyl chloride, phosphorus trichloride or phosphorus pentachloride may be used for such chlorination

Notations

A	Contact area (m^2)
A_i	Frequency factor of reaction i ($m^3 \, mol^{-1}$) reaction order$^{-1} \, s^{-1}$
C	Concentration ($mol \, m^{-3}$)
C_{pj}	Specific heat capacity of species j ($J \, kg^{-1} \, K^{-1}$)
d_{in}	Internal diameter (m)
d_{out}	External diameter (m)
e	Wall thickness (m)
E_{ai}	Activation energy of reaction i ($J \, mol^{-1}$)
E(t)	Residence time distribution, RTD (s^{-1})
F_j	Molar flow for species j ($mol \, s^{-1}$)
J	Adiabatic temperature elevation (K)
m_j	Mass of species j (kg)
n_0	Initial molar amount (mol)
N	Number of CSTRs (Continuous stirred tank reactors)
Nu	Nusselt number ($-$)
Pr	Prandtl number ($-$)
Q_j	Volumetric flow for species j ($m^3 \, s^{-1}$)
Q_r	Reaction heat release (W)
Re	Reynolds number ($-$)
RTD	Residence rime distribution
T	Temperature (K)
T_j	Jacket temperature (K)
T_R	Reactor temperature (K)
U	Overall heat exchange coefficient ($W \, m^{-2} \, K^{-1}$)
V	Volume (m^3)

Greek letters

α_{ij}	Reaction order for species j and reaction I ($-$)
Γ_R	Reactor heat capacity (J/K)
$\Delta_r H$	Reaction enthalpy ($J \, mol^{-1}$)
λ	Thermal conductivity ($W \, m^{-1} \, K^{-1}$)
ν_{ij}	Stoichiometric coefficient for species j and reaction i ($-$)
Π	Product
ρ	Density ($kg \, m^{-3}$)
σ	Variance (s)
Σ	Sum
τ	Average residence time (s)
τ_c	Characteristic time (s)
φ	Adiabatic ratio factor ($-$)

Superscripts

In	Inlet
M	Mixture
out	Outlet
w	Wall

Subscripts

amb	Ambient
j	Jacket
R	Reaction/reactor
0	Initial value (at time t = 0)

reactions, in solvent dimethylacetamide or dimethylformamide [13–21]. Dimethylacetamide (DMAC) is a dipolar, aprotic solvent with high solving power for high molecular-weight polymers. Therefore, it is known to be an efficient solvent, used in many organic syntheses [22]. Dimethylacetamide and thionyl chloride

are commonly used in chlorination reactions. Thionyl chloride ($SOCl_2$) reacts with dimethylacetamide to form a chlorinating agent called Vilsmeier reagent (an imidoyl chloride) [23,24]. Once the Vilsmeier reagent has been formed, it can either act as a chlorinating agent or be deactivated [24,25]. The thermal influence of the Vilsmeier complex has been studied for chlorination with phosphorus trichloride in dimethylformamide and the risk of thermal runaway has been demonstrated, indicating that the choice of the solvent is a key feature for these reactions [26]. The synthesis route studied in the present work involves toxic ($SOCl_2$) and CMR (carcinogenic, mutagenic and/or toxic for reproduction) substances (DMAC), undergoing a highly exothermic reaction [26,27]. This study therefore aims at finding a safer way to carry out the chlorination reaction than the conventional semi-batch mode, with high conversion and selectivity, and as little residual $SOCl_2$ as possible. Indeed, acyl chlorides are commonly used for further synthesis reactions, where final conversion can be affected by the presence of residual $SOCl_2$. The aim of the article is to develop, with little experimental data, a simplified reaction model, able to predict results in continuous intensified mode.

A classical intensification methodology involves a first reaction characterization, including detailed kinetic schemes, kinetic and thermal parameters. These kinetic and thermal data should enable the building of a phenomenological model, whose analysis allows the identification of process limitations. Simulations, in intensified conditions, should then help determining under which operating conditions the process can possibly be intensified. A final experimental validation should confirm the process intensification.

For such a methodology, the reaction characterization is an important step. Indeed, the key reactions that occur need to be identified and the corresponding reaction kinetic and thermal parameters need to be determined by fitting simulation results and experimental data. The more accurately heat- and mass-transfer data are estimated, the more reliable the prediction of the model is [28]. However, a clear identification of reactional paths is not always obvious, particularly in the case of multiple competitive and successive reactions, where some of the products are difficult to analyze or exhibit rapid apparition or disappearance times compared to the time required for their analyses.

The purpose of the present work is thus to show that identification and analysis of two limiting reaction schemes, that may not exactly represent the real and complex reaction scheme, also allows the intensification of a semi-batch process. Indeed, in this case, the rapid analysis of intermediate components is not possible, and only thermal acquisition allows monitoring the reactions. However, if multiple exo- or endothermic reactions induce temperature variations, the thermal signature does not make it possible to separate the contribution of each reaction on the overall heat release.

Such a methodology is applied to the reaction between $SOCl_2$ and RCOOH in DMAC, leading to the formation and subsequent degradation of the Vilsmeier complex. Since rapid analysis of the Vilsmeier reactant is not possible regarding its apparition and disappearance times, temperature acquisition only is used to follow the reactions evolutions. Two limiting cases, assuming the overall heat is released by the first (formation of reactant) or the second (disappearance of reactant) reaction are thus defined, while in reality the two reactions might be exo- or endothermic. It will be shown that this methodology allows the numerical identification of intensified conditions, which will be confirmed in a lab-scale and then in a pilot-scale device.

The reactions are performed, in conventional mode, in a semi-batch reactor that will be characterized in the first place. In this semi-batch reactor, the reaction between $SOCl_2$ and DMAC, forming the Vilsmeier reagent, will be studied and two limiting