VARIABLE AREA BUBBLE COLUMN FOR THE CHLORINATION OF GLYCEROL WITH HCL: A REACTION ENGINEERING AND MODELING APPROACH

J. Ibáñez Abad a*, D. Mondal a, P. Tolvanen a, A. Laari b and T. Salmi a
a Åbo Akademi, PCC/Chemical Engineering, –Turku/Åbo, FI 20500, Finland
b Lappeenranta University of Technology, Skinnarilankatu 34, 53850 Lappeenranta, Finland

Abstract

The chlorination of glycerol with HCl gas was investigated in a variable area pulsed flow reactor. The hydrodynamics of the reactor was studied combining reaction tests, residence time distribution experiments and automated analysis of high-speed video recordings. This innovative reactor geometry presents a higher per volume productivity when compared to a traditional bubble column, thanks to a 4.5x increase of the Péclet number and a 60% augmented range of operationally stable gas velocities. The experimental data were employed for the development of a fully transient gas-liquid reactor model. The model accounts for the dynamic behavior of both phases, describing the changes in the liquid flow rate and density due to the dilution of HCl and the gas phase holdup over time and axial position, affording an excellent description of the experimental data.

Keywords
Gas-liquid Reactor, Bubble Column, Transient Modeling, Digital Image Analysis

Introduction

For bubble column reactors, the gas phase can be generally regarded to be close to plug flow, whereas the degree of backmixing is higher in the liquid phase (Deckwer et al. 1974). For most cases of chemical kinetics, plug flow is a more efficient flow pattern than backmixing and thus, the development of reactor technologies that show closer to plug flow hydrodynamics is key in the design of efficient gas-liquid synthesis processes.

Recently, Araujo Filho et al. studied the chlorination of glycerol in a laboratory-scale bubble column (de Araujo Filho et al. 2016). Non-trivial flow patterns were observed as a function of time and axial position, related to the rapid HCl uptake and its impact in the liquid phase properties and dynamics (i.e. changes in density and flow rate). The authors proposed a transient hydrodynamic model based on the well-known axial dispersion model. Two main challenges could be identified from the work presented by de Araujo et al. First, the stoichiometry of the reaction requires of a high gas-to-liquid flow ratio, which presented several drawbacks: (i) gas flow rates above 1.0 L·min⁻¹ caused operation instability due the liquid being flushed out of the column and (ii) the high gas velocity caused severe mixing in the liquid phase. Second, the model proposed presents a somewhat simplistic picture of the reactor hydrodynamics, considering the gas holdup and the axial dispersion to be constant in time and position, disagreeing with the experimental observations.

In this work we aim to surmount the above-mentioned challenges by proposing an innovative reactor geometry (i.e. a variable area bubble-column reactor; see Figure 1) and an advanced transient hydrodynamic model.

* To whom all correspondence should be addressed
**Reactor performance and hydrodynamics**

A plausible solution to decrease the liquid-phase backmixing is provided in Figure 1, a variable area bubble column. The column is divided into 10 compartments, whose mutual interaction is hindered by gas bubbles residing in the narrow sections. This reactor geometry increased the axial Pécelt number from 4.5 for the traditional bubble-column (de Araujo Filho et al. 2016) up to 18 (Figure 1-right). Furthermore, the wider sections serve as a reservoir for liquid when operating at high gas flow rates and avoid the flushing of the column. A stable operation could be maintained with HCl flow rates up to 1.6 L·min⁻¹, representing a 60% increase relative to the traditional bubble column and boosting the glycerol conversion.

**Modeling approach**

The kinetic expressions derived by de Araujo et al. (de Araujo Filho et al. 2014) were implemented in a transient axial dispersion model. The liquid flow rate is time and position dependent, and is calculated considering the HCl uptake and the changes in density. The gas flow rate (V) and gas hold up (εg) are related according to Equation 1:

\[ \dot{V} = \alpha \cdot \epsilon_g^\beta \]  
(1)

where \( \alpha \) and \( \beta \) are obtained by fitting against the experimental data. Similarly, the liquid axial dispersion (\( D_{al} \)) is calculated from Equation 2 (adapted from Deckwer et al. 1974):

\[ D_{al} = \gamma \cdot \dot{V}^\delta + D_{al0} \]  
(2)

where \( D_{al0} \) is the liquid axial dispersion in absence of gas flow and \( \gamma \) and \( \delta \) are fitted constants. Finally, the liquid phase mass balances are calculated using Equation 3:

\[ \frac{\partial (\epsilon_i C_j)}{\partial t} = - \frac{\partial (u_i C_j)}{\partial z} + \frac{\partial^2 (\epsilon_i C_j D_{al})}{\partial z^2} + N_{Lj} a_s + \epsilon_i \tau_j \]  
(3)

where \( u_i \) is the liquid superficial velocity, \( N_{Lj} a_s \) is the gas-liquid mass transfer rate and \( \tau_j \) is the reaction rate. The temperature profiles in the reactor were experimentally determined and considered in the model. The system of PDEs was solved using the Isoda algorithm included in Julia DiffEq (Rackaukas and Nie 2017). The model parameters could be univocally and precisely estimated using an optimization approach, affording an excellent description of the experimental data (Figure 2).

**Conclusions**

The performance of a variable diameter reactor has been studied for the chlorination of glycerol. Compared to a traditional bubble column, an increase of 4.5x of the Pécelt number was observed. Furthermore, the possibility of operating at higher gas spatial velocities boosted the glycerol conversion. Overall, the productivity was essentially enhanced and the variable diameter reactor has proven to be a promising technology for gas-liquid reactions requiring high gas-to-liquid ratios.

Finally, a transient hydrodynamic model has been proposed, accounting for the non-trivial evolution of the gas hold-up, liquid phase density and flow rate. The analysis of high-speed recordings allowed to gather meaningful information of the hydrodynamics and was employed for the fitting of the empirical expressions relating the relevant parameters.

**Figure 1.** (left) Variable area reactor schema and high-speed images at varying HCl flowrate. (right) Example of a residence time distribution step-tracer experiment

**Figure 2.** Computed vs experimental data parity plot

**Acknowledgments**

This work is part of the activities of the Johan Gadolin Process Chemistry Center (PCC).

**References**