Application of column and pulsating flow reactors in the valorization of glycerol through hydrochlorination

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Highlights

- Glycerol can be efficiently valorized to chlorohydrins in continuous column reactors
- A detailed kinetic model, mass transfer model and flow model was developed for column reactors
- Plug flow pattern can be approached by shifting from conventional bubble column reactors to pulsating flow reactors with varying diameters
- Pulsating flow improves the conversion of glycerol because of higher Péclet number

1. Introduction

In the development of new, green process technology it is important to shift to the use of continuous reactors, which provide clear benefits compared to batch processes. One of the important raw materials in green technology is glycerol, which is obtained as a stoichiometric co-product from the production of biodiesel (fatty acid methyl esters). Glycerol valorization by hydrochlorination with HCl was performed in continuous co-current bubble column and pulsating flow column reactors (Figure 1). Acetic acid was used as a homogeneous catalyst. The influence of liquid flow rate, gas flow rate, reaction temperature and catalyst concentration was thoroughly investigated by a large set of experiments. Residence time distributions and high-speed camera images were used to characterize the flow inside the reactors.

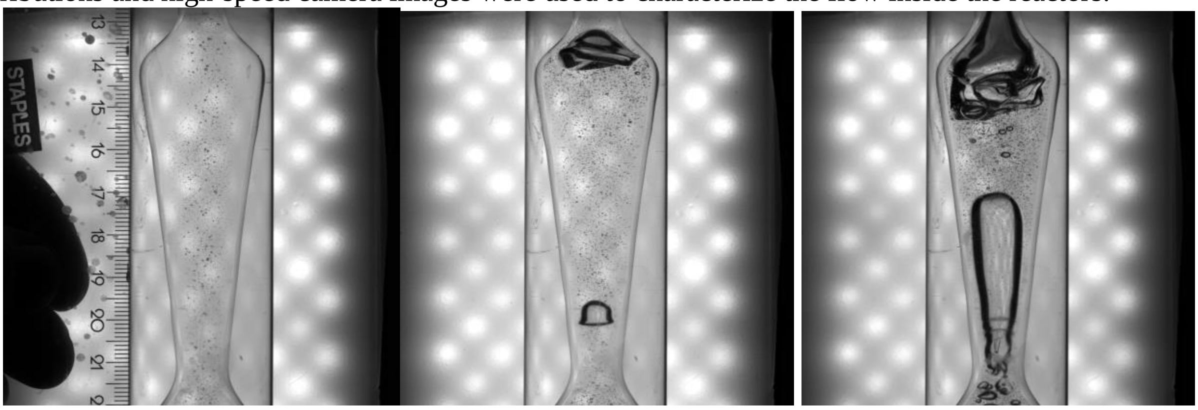

Figure 1. Gas and liquid flow in a compartment of the pulsating flow column reactor.

The following kinetic model was used for the chemical process: hydrochlorination of glycerol (A) to α-chlorohydrin,

$$r_3 = \frac{k_3' c_A c_{CAT} c_{HCl}^2 (c_{CAT} + \kappa')}{c_{CAT} c_W + \alpha_{HCl} c_{HCl} + \alpha_W c_W}$$

and hydrochlorination of α-chlorohydrin to αγ-chlorohydrin,

$$r_7 = \frac{k_7' c_\alpha c_{CAT} c_{HCl}^2}{c_{CAT} c_W + (\gamma' c_W + \delta') c_{HCl}}$$

where k_3' and k_7' are rate parameters, while c_A, c_{CAT}, c_{HCL}, c_W denote the concentrations of glycerol, catalyst (acetic acid), dissolved HCl, and water, respectively. The rate parameters obtained in a previous work of our group were used in the simulation of the bubble column and pulsating flow reactors.

2. Results and discussion

Glycerol was fed, together with acetic acid (homogeneous catalyst), continuously to the isothermally operated columns concurrently with gaseous HCl. Interesting fluid dynamics was observed, similar to vertical tubular absorbers. A very interesting phenomenon was observed: the flow pattern changed inside the column reactor because of the consumption of HCl in the chemical reactions. At the inlet, a churn-turbulent regime was observed, where gas bubbles were large and intense mixing took place. Past this zone, the bubbles were pretty small and finely dispersed. As the gas flow was increased above a certain level, the churn-turbulent zone expanded and Taylor bubbles started emerging from it, characterizing the establishment of the slug flow regime. The flow behaviour was confirmed by high-speed camera images shown in Figure 2.

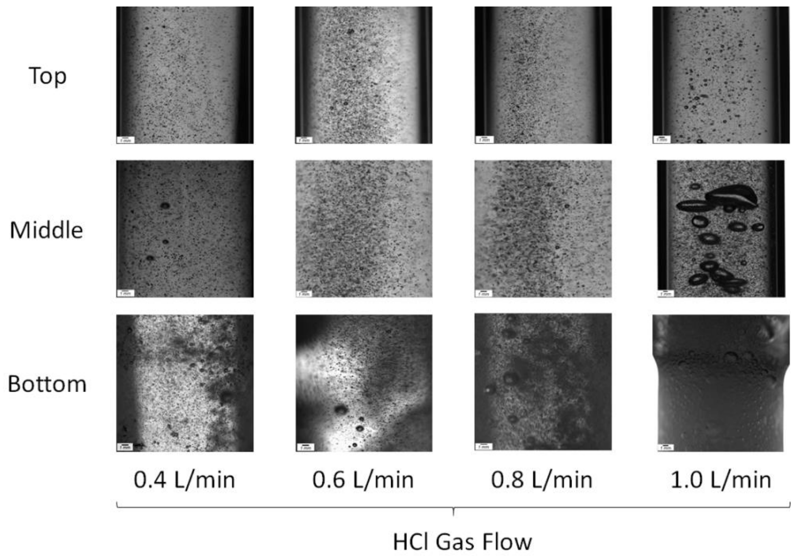

Figure 2. Hydrodynamics in different positions of the column reactor: change of the flow pattern.

The hydrochlorination process in the continuous pulsating flow column was modelled mathematically by using the cell model with backflow concept. The backmixing effects between the cells (axial dispersion) were described by backmixing flows which were calculated separately for each phase. It is argued that the cell model describes the hydrodynamics well for this kind of variable cross-section reactor consisting of a series of identical mixing elements. The transient mass balance equations for HCl in gas and liquid phases, as well as those of glycerol, chlorohydrins and water in liquid phase were solved numerically from the mass balance equations of the cell model. To characterize the liquid-phase flow pattern more precisely, the Péclet number was evaluated experimentally by separate tracer measurements. The unknown model parameters were fitted to experimental data by minimizing the squared difference between the measured and simulated concentrations.

3. Conclusions

Bubble column and pulsed flow column reactors were developed and characterized for glycerol valorization via homogeneously catalyzed hydrochlorination. By shifting from bubble column to pulsating flow column, the conditions of plug flow were approached and the glycerol conversion was clearly improved. The observations were confirmed by chemical analysis and measurement of the Péclet number. A detailed mathematical model, a cell model was developed for the bubble column reactor and the pulsating flow reactor. The model described successfully the behaviour of the continuous reactors.

Keywords
"Column reactor", "Pulsating flow reactor", "Flow visualization", "Cell model"