



# Hydrodynamics and kinetics in semi-batch stirred tank precipitation of L-glutamic acid based on pH shift with mineral acids

Ulla Ojaniemi <sup>a,\*</sup>, Johanna Puranen <sup>b</sup>, Mikko Manninen <sup>a</sup>, Elena Gorshkova <sup>a</sup>, Marjatta Louhi-Kultanen <sup>b,c</sup>

<sup>a</sup> VTT Technical Research Centre of Finland Oy, P.O. Box 1000, FI-02044 VTT, Finland

<sup>b</sup> Lappeenranta University of Technology, School of Engineering Science, P.O. Box 20, FI-53851 Lappeenranta, Finland

<sup>c</sup> Aalto University, School of Chemical Engineering, P.O. Box 16100, FI-00076 Aalto, Finland

## HIGHLIGHTS

- Precipitation of L-glutamic acid by acidification with two mineral acids is studied.
- The CFD model for semi-batch process with changing fluid volume is presented.
- Local concentrations and activities are important in the precipitation process.
- The two acids resulted in different pH evolution: separate kinetics is needed.

## ARTICLE INFO

### Article history:

Received 23 March 2017

Received in revised form 13 December 2017

Accepted 15 December 2017

Available online 16 December 2017

### Keywords:

Precipitation  
L-glutamic acid  
Hydrochloric acid  
Sulphuric acid  
CFD  
Size distribution

## ABSTRACT

The precipitation process of L-glutamic acid from monosodium glutamate solution through acidification is studied by using hydrochloric acid and sulphuric acid. Both experimental and modelling methods are applied. The experiments have been carried out with a single feed semi-batch process applying two acid feed rates and two rotational mixing speeds. The method for computational fluid dynamics (CFD) modelling of the semi-batch process with a changing fluid volume is presented. The precipitation process including nucleation and crystal growth is modelled with CFD by using the kinetics presented in the literature for hydrochloric acid. A model for agglomeration presented in the literature and Eddy Dissipation Concept for micromixing are applied in the case of a lower rotational speed and hydrochloric acid. The particle size distribution is modelled with the simple number density model and with Quadrature Method of Moments. Micromixing was found to have an insignificant effect, but when including the model for agglomeration, the particle size distribution was in better agreement with the experiments. However, pH evolution of the system was captured better without the agglomeration model, indicating that the kinetic model may not describe the precipitation accurately. The pH and saturation ratio  $S_{\alpha}$  were modelled based on thermodynamics. The significance of activities is highlighted in computing the thermodynamic equilibrium, and in precipitation kinetics. It was found that the applied acid had an effect on the chemical process, although the species concentrations were the same. The difference of the kinetic models between hydrochloric acid and sulphuric acid could be explained by the more complex dissociation of sulphuric acid. The greater computational ionic strength with sulphuric acid increased the nucleation rate, resulting in a difference in pH evolution in comparison with hydrochloric acid. Therefore, the kinetic parameters determined for the hydrochloric acid system are not applicable for other acid systems with different chemical compositions. For the modelling of the precipitating systems, more experimental work is needed for determining the kinetics.

© 2017 Elsevier Ltd. All rights reserved.

## 1. Introduction

Precipitation processes are applied widely in the production of fine chemicals. Precipitation from a solution includes several

sub-processes, namely nucleation, crystal growth and agglomeration. These fundamental mechanisms determine the final crystal size and size distribution. Typical particle sizes of precipitates range from a few nanometres to several micrometres. Supersaturation, the driving force for the nucleation and particle growth rate, is a transient and local quantity created by the chemical reactions of components in a mixture. Therefore, mixing and the consecutive

\* Corresponding author.

E-mail address: [ulla.ojaniemi@vtt.fi](mailto:ulla.ojaniemi@vtt.fi) (U. Ojaniemi).

## Nomenclature

$a$	specific surface area of particles per unit volume [ $\text{m}^2/\text{m}^3$ ]	$R_i$	source term of species $i$ [ $\text{kg}/\text{m}^3 \text{ s}$ ]
$A_p$	surface area of the particle [ $\text{m}^2$ ]	$Q_{feed}$	volumetric feed addition rate [ $\text{m}^3/\text{s}$ ]
$C_i$	molar concentration of species $i$ [ $\text{kmol}/\text{m}^3$ ]	$S_\alpha$	saturation ratio
$C^*(\alpha)$	solubility of $\alpha$ -form glutamate [ $\text{kmol}/\text{m}^3$ ]	$Sc$	Schmidt number ( $=\nu/D$ )
$C_I$	constant depending on the pumping capacity of the impeller	$\bar{u}$	local average velocity magnitude [ $\text{m}/\text{s}$ ]
$D$	diffusivity [ $\text{m}^2/\text{s}$ ]	$V$	liquid volume in the reactor [ $\text{m}^3$ ]
$D_{imp}$	impeller diameter [ $\text{m}$ ]	$V_p$	volume of the particle [ $\text{m}^3$ ]
$D_t$	turbulent diffusivity [ $\text{m}^2/\text{s}$ ]	$Y_i^0$	fine-scale mass fraction of species $i$ corresponding to chemical equilibrium
$E$	engulfment parameter [1/s]	$Y_i^0$	mass fraction of species $i$ in the surrounding fluid
$F$	shape factor ( $=A_p L/V_p$ )	$Y_i$	local average mass fraction of species $i$
$I$	ionic strength of the liquid [ $\text{kmol}/\text{m}^3$ ]	$z_i$	charge number of ion $i$
$k$	turbulent kinetic energy [ $\text{m}^2/\text{s}^2$ ]	$\alpha_v$	detectable volume fraction of newly formed solid phase
$k_{dzz}$	mass transfer coefficient [ $\text{m}/\text{s}$ ]	$\varepsilon$	energy dissipation [ $\text{m}^2/\text{s}^3$ ]
$k_a$	surface shape factor ( $=6$ for cubic shape)	$\rho_p$	density of the crystal [ $\text{kg}/\text{m}^3$ ]
$k_v$	volume shape factor ( $=1$ for cubic shape)	$\tau_C$	time scale for macromixing [s]
$K_{SP}$	solubility product [ $(\text{kmol}/\text{m}^3)^2$ ]	$\tau_D$	time scale for turbulent diffusion [s]
$L$	size of the particle [ $\text{m}$ ]	$\tau_E$	time scale for micromixing by engulfment [s]
$L_i$	size of particles in size interval $i$ [ $\text{m}$ ]	$\tau_G$	time scale for crystal growth [s]
$\Delta L$	interval of size $L_i$ [ $\text{m}$ ]	$\tau_{ind}$	induction time for the primary nucleation process [s]
$L_{ave}$	average size of the particle, $L_{30}$ [ $\text{m}$ ]	$\tau_N$	time scale for nucleation [s]
$L_{mean}$	average size of the particle, $L_{10}$ [ $\text{m}$ ]	$\tau_S$	time scale for mesomixing, dissipation of segregation in inertial-convective subrange [s]
$m_i$	$i$ -th moment	$\nu$	kinematic viscosity [ $\text{m}^2/\text{s}$ ]
$M_{Glu}$	molar mass of crystal ( $=147.13 \text{ g/mol}$ )	$\gamma_{\pm 1}$	activity coefficient
$n_i$	number of particles in size interval $i$ (-)	$\gamma$	length fraction of the fine scales
$N$	number density of nuclei [ $1/\text{m}^3$ ]		
	$N_{imp}$ stirring rate [1/s]		

build-up of supersaturation through the chemical reaction rate determine the size distribution of the precipitates. The kinetics of the precipitation mechanisms is of significant importance in designing and developing the precipitation processes. Further, characteristic time and eddy length analyses are needed for evaluating the significance of the turbulent mixing levels in the process.

The modelling of precipitation involves complex processes such as turbulence and mixing, in addition to the fundamental mechanisms of the precipitation process. At the same time, modelling is a practical way to study the effects of process conditions, such as stirring in the reactor. The range of models includes zonal or multi-block models (Zauner and Jones, 2000), computational fluid dynamics (CFD) with detailed flow prediction (Jaworski and Nienow, 2003; Vicum and Mazzotti, 2007; Rane et al., 2014), and process models with detailed population balances (Borissova et al., 2005; Schöll, 2006; Schöll et al., 2006; Lindenberg et al., 2008; Cheng et al., 2012). The chemical reaction is a molecular-level process affected essentially by the mixing on that scale, i.e. micromixing. Larger scale mixing mechanisms have indirect effects by changing the environment for local mixing. The levels of turbulent mixing of the processes has been studied e.g. by Baldyga and Pohorecki (1995) and Vicum et al. (2004).

We studied the precipitation process of L-glutamic acid (Glu,  $\text{C}_5\text{H}_9\text{NO}_4$ ) from a monosodium glutamate solution through acidification. The experiments were carried out in a single feed semi-batch mode by using hydrochloric acid or sulphuric acid for the pH shift. L-glutamic acid was chosen as the model compound because it is a relatively well-studied model compound and has an ability to form two monotropically related polymorphs (metastable  $\alpha$ -form and stable  $\beta$ -form) (Hirokawa, 1955). The polymorphs have different physical properties, including packing, thermodynamic, spectroscopic, kinetic, surface, and mechanical properties (Grant and Britain, 1999). The polymorphs can be dis-

criminated for example by X-ray powder diffraction. The prismatic  $\alpha$ -form is a favourable polymorph in comparison to the flake or needle-shaped  $\beta$ -form. From the measurements, pH was monitored as a function of time, and the concentration of the solid particles was measured at several time instants during the testing period, as well as in the end of the experiment.

In precipitation based on the pH shift, the used specific acidic or basic reactant is typically ignored and the focus is mainly on the pH change. In the present work, two mineral acids, hydrochloric acid and sulphuric acid, are used in the precipitation of L-glutamic acid. The kinetics for L-glutamic acid precipitation presented in the literature are measured for hydrochloric acid (Borissova et al., 2005; Schöll, 2006; Schöll et al., 2006). CFD simulation is a useful tool to investigate the applicability of the measured kinetics for precipitation with sulphuric acid. Sulphuric acid is thermodynamically a more complex acid, dissociating differently depending on the pH range. In this study, the precipitation process including nucleation, crystal growth and agglomeration, is modelled by using CFD, Ansys Fluent 16.0 (Fluent, 2015). Particle size distribution is modelled with the simple number density model and with QMOM (Quadrature Method of Moments), first presented by McGraw (1997).

CFD has been recently applied for modelling a wide range of precipitation processes. Leybros et al. (2012) applied CFD for modelling precipitation in a supercritical water synthesis reactor by using the class method for population balance. Cheng et al. (2012) also applied the class method for modelling the population balance combined with CFD. Pasquale et al. (2013) and Metzger and Kind, (2017) investigated the influence of mixing on fast precipitation processes by coupling CFD and the direct quadrature method of moments (DQMOM). To our knowledge, CFD simulation results have not been reported for semi-batch precipitation processes where significant volume changes occur.

Download English Version:

<https://daneshyari.com/en/article/6588716>

Download Persian Version:

<https://daneshyari.com/article/6588716>

[Daneshyari.com](https://daneshyari.com)