Intensification of zinc dithionite production: from a batch to a mesofluidic reactor.

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Highlights

- Development of a continuous milli pilot reactor with solid particles.
- Parametric adjustment of kinetics.
- Design and operating conditions optimization.

1. Introduction

Zinc dithionite (ZnS_2O_4) is an intermediate in the production of sodium dithionite ($Na_2S_2O_4$), a product mainly used as a bleaching agent (textiles, paper). The industrial process involves the attack, in aqueous solution, of zinc particles by SO_2 in an open batch stirred tank reactor. Its effectiveness is limited by the parasitic reactions that lead to the decomposition of zinc dithionite (ZnS_2O_4) into zinc sulfite ($ZnSO_3$), which becomes predominant if the temperature exceeds a certain T_{ref} threshold.
The synthesis reaction is an oxidoreduction reaction, described as followed:

$$Zn + 2\,SO_2 \rightarrow ZnS_2O_4$$

As this reaction is exothermic (ΔH = -234 kJ/mol), regulating the temperature in the reactor requires the SO_2 feed to be staggered over time. In this way, it enables the reactor's heat exchange system (double jacket + coil) to extract the heat released by the reaction and maintain the temperature inside the reactor at its optimum level, below T_{ref}. However, staggering the SO_2 feed has the effect of significantly extending the duration of the $Zn2S_2O_4$ synthesis operation and therefore limiting the productivity of the overall $Na_2S_2O_4$ production process.

The aim of the project is to intensify the process by running it continuously through an intensified reactor. The main challenges are linked to the presence of liquid and solid phases, which must be distributed and circulated within the reactor, while controlling the residence time in the reactor in order to optimize the yield and selectivity of the nominal reaction. A review of the literature shows that, in the case of continuous processes involving solid particles, efforts at intensification come up against the difficulty of ensuring intimate mixing of the reactants and avoiding plugging of the installation. [1]

2. Methods

A pilot reactor has been designed to evaluate the potential and limitations of a continuous process. To improve process performance, this pilot reactor is a mesofluidic tubular type of ¼-inch outlet diameter and a range of length from 0.5 m to 2.5 m operating at 12 atm. Considering the flows of the slurry and liquid SO_2, the residence time in the reactor varies from 2.5 to 12.5 seconds. This reactor has a high surface/volume ratio and the enhanced heat exchange performance allows for maintaining the reactor temperature within an optimal range, even if significant heat is released by the reaction. It could therefore be possible to supply all the SO_2 required for the synthesis reaction from the reactor inlet, without penalizing selectivity. [2] Continuous operation also eliminates shutdown phases and help to intensify the process.

A numerical model of the reactor, considering plug flow, reaction kinetics and thermal phenomena, is simultaneously being developed on MATLAB. At this stage, the rates of reactions are still to be confirmed. Fitting of kinetic parameters of pseudo-first-order reactions is ongoing by comparison of model predictions with experimental results such as estimated concentrations_from IR spectroscopy and temperatures.

3. Results and discussion

IR absorbances profiles measured at the reactor exit for different steady-state operating conditions are shown on Figure 1a. At present, the experimental results are still qualitative. IR peaks must be calibrated to allow estimation of the exit product concentrations. However, the (relative) peak heights at a wavenumber of 1051 cm^{-1} on the absorbance profiles already give an estimate of the distribution between the different zinc dithionite concentrations at the reactor outlet.

Figure 1b shows the simulated profiles of zinc conversion (red) and of temperature (blue) in the reactor. The kinetic parameters used for this simulation are raw guesses, fitted on the basis of the temperature measured at the reactor outlet (L = 1.75 m) for a single operating condition. The agreement is fair as the measured temperature equals 32°C, while the computed value equals 31.2°C.

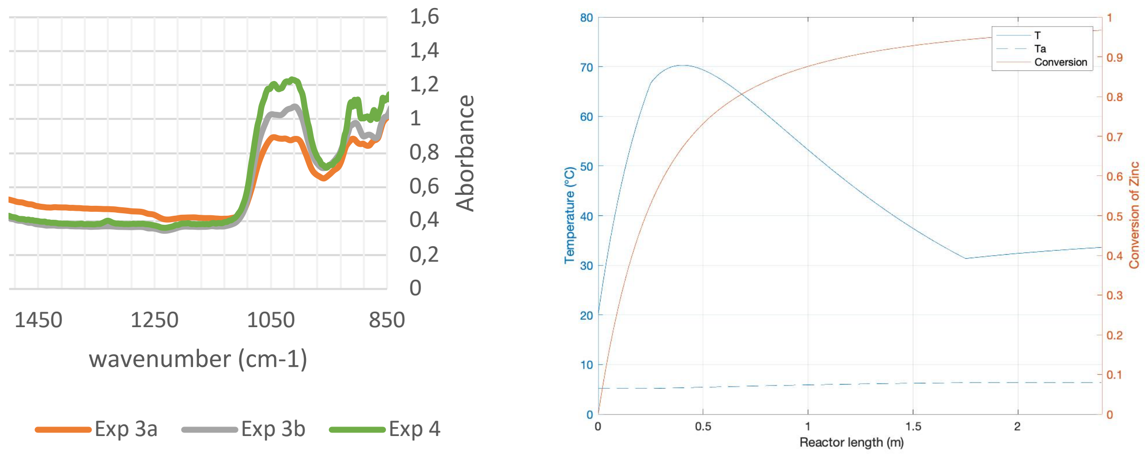

Figure 1. (a) IR absorbances of 3 experiments (b) MATLAB simulation curves for a given experiment case.

4. Conclusions

The utilization of a mesofluidic tubular pilot reactor seems to hold promise for intensifying the process as continuous processing eliminates downtime and reduces the residence time from approximately an hour to about ten seconds. Transitioning to a mesofluidic reactor with a high surface-to-volume ratio facilitates efficient heat transfer. Consequently, there is no longer a need to stage the SO_2 feed to control the reaction temperature and, thus, the selectivity towards the key product.

Our ongoing research employs MATLAB to refine pseudo-first-order kinetic parameters, utilizing experimental data from IR spectrometers. More experiments in different conditions must be made to refine the model but it seems to be able to match the experimental values after optimization.

References

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Keywords

Intensification; milli; reactor; multiphase