ISCRE25 FLORENCE 2018
BRIDGING SCIENCE & TECHNOLOGY
The 25th International Symposium on Chemical Reaction Engineering
20-23 May 2018
Florence, Italy
www.aidic.it/iscre25

Design and scale-up of a pinched tube flow reactor for continuous di-nitration

Mrityunjay K. Sharma[1], Roopashree B. Acharya[2], Amol A. Kulkarni[3]*

Chem. Eng. Proc. Dev. Division, National Chemical Laboratory - PUNE

** aa.kulkarni@ncl.res.in*

Highlights

- A continuous process including inline extraction and separation is developed.
- Kinetics of di-nitration reaction are obtained for the reaction network.
- A model is developed for predicting reactor behavior at 2 kg/hr production.
- The simulations help to obtain the scale up strategy and operating conditions for this exothermic di-nitration reaction.

1. Introduction

Pendimethalin is widely used selective herbicide which is synthesized by di-nitration of aniline derivative **(fig. 1)**[1]. The conventional di-nitration involve mono nitration with low concentration nitric acid (50%) followed by high concentration nitric acid (69%) for second nitration[2]. Conventional methods of synthesis utilized large quantity of solvent at low temperature to avoid the risk (safety) and issues (heat and mass transfer) at large scale reducing the reaction rate with long reaction time. Selectivity is an issue in the di-nitration case owing to the dilute reaction conditions and long reaction time may lead to the oxidation of the product. One way to improve is to use the continuous flow synthesis technology to overcome the challenges in the conventional synthesis mode. Literature shows the synthesis of Pendimethalin in continuous flow mode with neat reagent in a single step with very low residence time[3]. However reaction kinetics for Pendimethalin synthesis are still unknown. Employing such an exothermic reaction at the larger scale in continuous mode is challenging. In light of this kinetics and scale up analysis was done for the 2kg/hr. production of Pendimethalin.

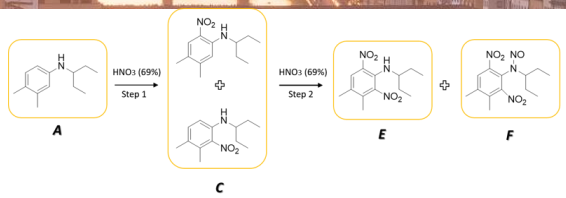
2. Methods

Determination of reaction kinetics: Reactions in the laboratory scale were done in 1/8" SS316 tube reactor with 10 ml volume having 5 outlets at equal distance along the reactor length. Experiments were performed at different temperatures (40 °C, 50 °C, 60 °C) and at different reactant concentrations (40%, 50%, 60%) at different residence times (1 – 5 min). Samples at the outlet was quenched in ice and extracted in EDC. Water wash was given to remove the traces of acid passed from sodium sulfate solution to remove traces of water. Two different analysis techniques were used where mono nitro product and di-nitro product was analyzed on GC and byproduct was analyzed on HPLC.

Reaction modeling and simulation: Second order isothermal reaction kinetic model was used for modeling a continuous flow reactor. The measured reaction kinetics were used for simulating temperature and concentration data in the reactor. A separate non-isothermal model was developed to explore the spatial hot spots that would help to decide the heat removal strategy along the reactor length. All the simulations were performed using MATLAB.

3. Results and discussion

Reaction rate constants were determined assuming second order rate equation which showed excellent fit when compared with the laboratory data. Model equations were solved **(fig. 1)** for prediction of reactor parameters for proposed production capacity for ¼'' pinch tubular reactor. The extent of dispersion was taken into account based on the dispersion coefficient values obtained experimentally. Simulations were done for 50 ml



N-(1-ethylpropyl)-3,4-dimethyl-aniline (A)

$$\frac{dCa}{dt} = -K1 * Ca * Cb$$

N-(1-ethylpropyl)-3,4-dimethyl-2-nitroaniline (C)

$$\frac{dCc}{dt} = K1 * Ca * Cb - K2 * Cc * Cb - K3 * Cc * Cb$$

N-nitroso-N-(1-ethylpropyl)-3,4-dimethyl-2,6-dinitroaniline (F)

$$\frac{dCf}{dt} = K3 * Cc * Cb$$

Nitric Acid (B)

$$\frac{dCb}{dt} = -K1 * Ca * Cb - K2 * Cc * Cb - K3 * Cc * Cb$$

N-(1-ethylpropyl)-3,4-dimethyl-2,6-dinitroaniline (Pendimethalin) (E)

$$\frac{dCe}{dt} = K2 * Cc * Cb$$

Water (D)

$$\frac{dCd}{dt} = K1 * Ca * Cb + K2 * Cc * Cb + K3 * Cc * Cb$$

Figure 1. Reaction scheme, model equations.

reactor volume for different reaction temperatures. The observations show that 50 ml reactor is sufficient for 2kg/hr production capacity, however it is not suitable in terms of safety as the maximum temperature in the reactor is much above the adiabatic temperature limit (fig.2) and can lead to run-away situation. Initial simulations show that for safe scale up of the lab process it is not advisable to do the reaction based on the lab conditions and achieving complete energy balance along the reactor length is essential. A detailed analysis of operable steady state of the reactor is under progress.

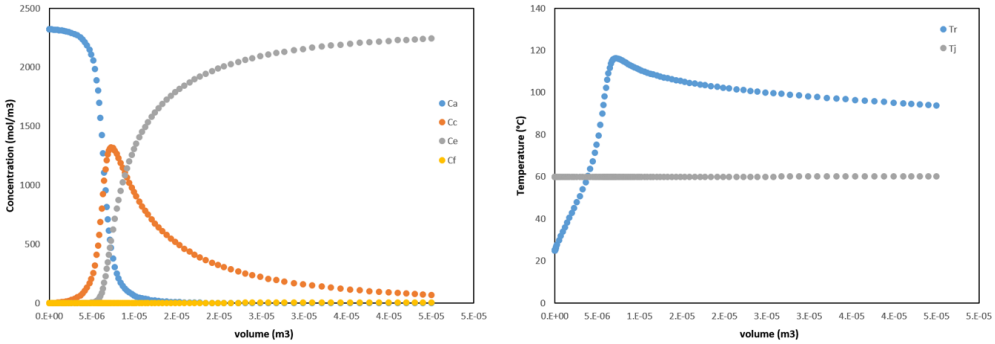


Figure 2. Simulation for 80% reactant concentration at 60°C jacket temperature

4. Conclusions

Reaction kinetics were determined for the highly exothermic di-nitration process for Pendimethalin synthesis. Model equations were formulated and were used for the prediction of reaction conditions for pilot scale operation. Investigations for safe operating conditions of pilot scale for different reactor volumes are in progress and will be presented from an operating pilot plant.

References

[1] S. Piutti, A. L. Marchand, B. Lagacherie, F. Martin-Laurent, Pest management science 2002, 58, 303-312.
[2] L. A. McDaniel, US4621157, 1986.
[3] Y. Chen, Y. Zhao, M. Han, C. Ye, M. Dang, G. Chen, Green Chemistry 2013, 15, 91-94.

Keywords
"Reaction kinetics; Modeling; scale up; pinch tube".