VALIDATING STIRRED TANK REACTOR MODELS FOR A LIQUID-LIQUID NITRATION

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Abstract

A model for stirred tank reactors where a heterogeneous pseudo-first order liquid-liquid nitration is carried out was developed. Adiabatic operation was considered, by-products formation was contemplated, as well as deviations from ideal flow. The model was confronted with industrial data showing good predictions of conversion and temperature at different levels of production. After validation the model was used to optimize production, targeting at reducing by-products formation. It showed that this could be achieved by particular combinations of inlet flow rates of both organic and aqueous phases, while lowering the temperature in the train of reactors. These findings were validated during a 54 h trial in the plant which confirmed 16% decrease in the total amount of by-products formed.

Keywords

Mathematical model, Optimization, Validation

Introduction

A long time elapsed since chemical reactors design and analysis started being based on mathematical models and precise methodologies. Chemical Engineering owes this to eminent engineers: N. Amundson, R. Aris and O. Levenspiel, to name a few. Nowadays mathematical models are widely used, and not only at design stage. In the chemical process industry daily operation relies on these instruments for diagnose of anomalous results. The planning of unusual operations and process optimization is hard to envisage without these very important tools.

Aromatic nitrations, carried out with isothermal or adiabatic technology, are heterogeneous liquid-liquid reactions involving simultaneous mass transfer, for which different mechanistic models are available. The film model (Whitman, 1923) confines mass transfer to a stagnant layer in the interface and has proved to be adequate for benzene nitration (Quadros et al., 2005). The rate of formation of byproducts is slightly higher in the adiabatic mononitrobenzene (MNB) technology and the mechanisms involved are yet not fully understood. Moreover physical and chemical properties of these nitrophenols are not available. The first generation adiabatic nitrators were stirred reactors (Guenkel, 2013), still in use after revamp. This fully supports the development of a mathematical model for a train of stirred reactors.

Model Development

The production of MNB in an adiabatic stirred nitrator proved to be adequately modeled in a simple way by the film model, assuming that the pseudo-first order reaction occurs in the stagnant film near the interface between the organic and aqueous phases (Quadros et al., 2005). As it is known that temperature influences by-products formation, an energy balance was considered in this study.

To overcome the lack of information on the rate of formation of 2,4- dinitrophenol (DNP) and trinitrophenol (TNP), the main process by-products, Nogueira (2015)

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used industrial data to develop prediction models. Given the range of operating conditions in the plant, these empirical models for DNP and TNP formation were chosen over others obtained in pilot plants, and available in the literature.

In a flow system non-uniform regions or bypassing influence the performance and should be assessed. Nogueira (2015) carried out residence time studies in order to develop a combined model to contemplate real flow in the liquid-liquid system.

The whole detailed model for the train of nitrators included the above mentioned modules. This is a strategy enabling an easy updating whenever changes are introduced in the plant, or a different production is envisaged.

Model Validation and Process Optimization

The MNB plant provided data used to validate the model and this was achieved for different productions in the range 61-106%. For the sake of confidentiality data were normalized. The model proved to estimate temperature with differences in the range 1-5%, depending on the nitrator position in the train. Very good results were also achieved for benzene percentage ($\%B_k$) in the last (k) nitrator. Nevertheless, the total amount of by-products was only predicted within a 14% error, with poorer results for DNP. This may be a consequence of using the PLS model beyond the range for the benzene/nitric acid inlet molar flow ratio.

Aiming at reducing nitrophenols (NPs) formation, the validated model was used to optimize the operating conditions while reaching different target MNB productions in the range 61-106%. The flow rate of nitric acid was set constant and its full conversion was imposed. GAMS 23.5 together with CONOPT library were used to solve the model. Two scenarios were assessed, with different constraints on maximum $\%B_k$ and a constraint on the maximum mixed acid (nitric and sulfuric acids) inlet flow rate. Excepting two MNB productions, 61 and 89%, the model optimum solution was very close to the maximum $\%B_k$. The temperature estimate for the last reactor ($T_k \approx 1.08$) was lower than in present operation, in agreement to what is known to reduce NPs formation (Nogueira, 2015). According to model results a 19% decrease in NPs was achieved.

The next step in this study was the validation of the model predictions in the plant for a 111% MNB production target. The aim was to confirm the influence of operating at $T_k \approx 1.08$ and $\%B_k \approx 0.20$ upon NPs reduction. In the first stage of the trial the inlet flow rates of benzene and mixed acid were gradually increased till reaching the values expected to lead to the target T_k and $\%B_k$. The plant was run under these conditions for about 48 h and in the following 4 hours the benzene flow rate was decreased. Ten outlet stream samples were collected during the trial. Figure 1 shows the percentage decrease achieved in the by-products concentration at the nitrators train outlet during this test. The magnitude of the decrease for TNP is 3 times higher than for DNP, and this good outcome should be valued also in terms of the properties and environmental footprint of these two nitrophenols. Moreover, although slightly lower than model predictions (19%) a 16% reduction in the total amount of nitrophenols formed was confirmed by the results in Figure 1.

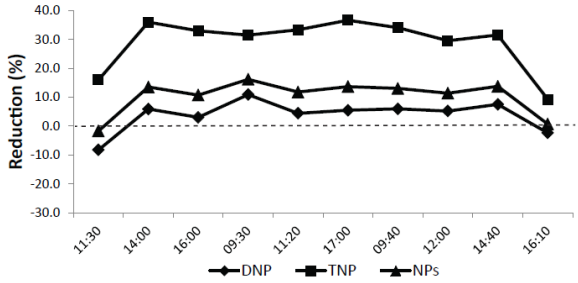

Figure 1. Decrease in by-products formation during the trial in the plant with optimum operating conditions

Conclusions

Currently, the software and the computers available allow using complex mathematical models as powerful instruments for improving operation in the chemical process industry. From now on, the model developed in this work may be used to improve yield and the environmental footprint of the plant, as it confirmed good prediction ability. Its modular design allows easy replacement of the contributing models, and may be easily adapted to other production processes

Acknowledgments

Financial support from Fundação para a Ciência e Tecnologia (FCT) for PhD grant SFRH/BDE/33907/2009, is gratefully acknowledged.

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