**Modelling and optimization of a reactive distillation column to obtain high pure cyclohexanone in caprolactam production process.**

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**Highlights**

* 2-ciclohexen-1-one is easily removed using a reactive distillation.
* NaOH is used as catalyst in a reactive distillation to produce high pure cyclohexanone.
* The reactive distillation model is experimentally validated.
* A reactive distillation model is used to optimize the production of cyclohexanone.

**1. Introduction**

Cyclohexanone (CX-ONE) is the main compound used in the caprolactam production which is the monomer of nylon 6. The most common cyclohexanone production process starts oxidizing cyclohexane to produce a mixture of cyclohexanol, cyclohexanone and other organic impurities [1-3]. Cyclohexanone purification process involves three distillation columns and a reactor where the cyclohexanol is dehydrogenated to cyclohexanone. However, some of the organic impurities (formed either during cyclohexane oxidation or cyclohexanol dehydrogenation) cannot be removed by a standard distillation because their boiling point are close to cyclohexanone. One of those is 2-cyclohexen-1-one (CX-ENONE), it has drastic effects in the nylon fiber because it can produce a rubber during the polymerization. To reduce the amount of this impurity in the pure cyclohexanone a reactive distillation (RD) step has been proposed using NaOH. Sodium hydroxide promotes the condensation of the impurity and cyclohexanone yielding a dione compound [4]. Dione boiling point is higher than cyclohexanone and can be easily removed within the purification process. Nevertheless, the presence of alkali in the reaction medium also promotes the self-condensation of cyclohexanone, which is a non-desirable loss of cyclohexanone. In this work the RD process is modelled and optimised in order to select the operating conditions that guarantee the removal CX-ENONE with minimum losses of CX-ONE.

**2. Methods**

The RD column is modelled considering both the physical and chemical processes taking place in the column trays, condenser and reboiler. The RD model developed was validated using experimental data obtained at the laboratory-scale distillation packed column. The selfconstructed model was used to simulate and optimized the RD column operating at industrial-scale which ensure the minimal unit total cost (UTC), defined as the production cost of a unit of mass of pure cyclohexanone. A mixed non-linear programming problem (MINLP) was formulated and solved using the optimization algorithm which is available in gPROMS[5].

**3. Results and discussion**

To study the operating condition range and the UTC, different case studies were carried out. Those cases depend on the CX-ENONE amount which is presented in the pure CX-ONE stream within the range 5-15 mg/kg of impurity. The results are summarized in Table 1. They show the optimal operation conditions to obtain a high purity cyclohexanone product with the minimum unitary total cost.

**Table 1.**

|  |  |  |  |
| --- | --- | --- | --- |
| Parameter | Value | | |
| Case | 1 | 2 | 3 |
| , mg/kg | 15 | 10 | 5 |
| Pressure, bar | 0.12 | 0.10 | 0.09 |
| , %w:w | 99.56 | 99.83 | 99.85 |
| Reflux Rate | 2.52 | 2.42 | 2.36 |
| UTC, $/kgCX-ONE | 0.76 | 0.77 | 0.75 |
|  | 33.1 | 36.3 | 40.0 |
| Nstrip | 21 | 20 | 23 |
| Nrect | 19 | 19 | 20 |
| Ntrays | 41 | 40 | 44 |
| Number of reaction trays | 37 | 37 | 38 |
|  | 2.31 | 2.41 | 2.36 |

**4. Conclusions**

Following validation, the reactive distillation model was used to optimize conditions of operation. The objective function used was the minimization of the unitary total cost to produce a kg of pure cyclohexanone. The model was implemented as a MINLP problem which was solved using the optimiser within gPROMS. The optimal values of NaOH concentration, number of reaction stages, number of trays, pressure, and reflux rate were obtained. Using this information, other design and operation variables were obtained. The model is a powerful tool to study the design of the purification unit to produce high pure cyclohexanone in the caprolactam production process.

**References [Calibri 10]**

1. Jodra, L.G., et al., *Impurity content and quality definition of commercial epsilon-caprolactam.* Ind. Eng. Chem. Prod. Res. Dev., 1981. **20**(3): p. 562-566.

2. Burlone, D.A., et al., *A Method o Minimizing Aldehyde-Based Impurities in a Process Stream*. 2006.

3. Meier, H.P., E.J. Van, and E. Terweduwe, *Purification of cyclohexanone*. 1993, Bayer Antwerpen N.V., Belg. . p. 5 pp.

4. Wyatt, L., A.H. Benneker, and A.P.H. Schouteten, *Process for reducing the aldehyde concentration in a mixture comprising cyclohexanone and one or more aldehydes*. 2004, Koninklijke DSM N.V., Neth. . p. 8 pp.

5. Tanvir, M.S. and I.M. Mujtaba, *Optimisation of design and operation of MSF desalination process using MINLP technique in gPROMS.* Desalination, 2008. **222**(1): p. 419-430.