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A three-phase nonequilibrium dynamic model for catalytic distillation

Yongqiang Xu, Yuxiang Zheng, Flora T.T. Ng*, Garry L. Rempel

Department of Chemical Engineering, University of Waterloo, Waterloo, Ont., Canada N2L 3G1

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Abstract

A detailed three-phase nonequilibrium (NEQ) dynamic model for simulating batch and continuous catalytic distillation (CD) processes has been developed. In this model, both molar and energy holdups in liquid and vapour phases are taken into account. Multicomponent mass transfer and heat transfer between vapour and liquid phases as well as between liquid and solid (catalyst) phases are described by the Maxwell–Stefan equations. The resulting differential and algebra equations in this model are implemented in gPROMS and C++. The simulation results are in good agreement with the experimental data obtained from the batch and continuous CD processes for the production of diacetone alcohol (DAA) using Amberlite IRA-900 as a catalyst. Sensitivity analysis on the mass transfer and kinetics using the three-phase NEQ dynamic model indicates that the formation of DAA is controlled by solid–liquid mass transfer, whereas the formation of mesityl oxide is kinetically controlled under the simulation conditions.

Keywords: Catalytic distillation; Dynamic simulation; Nonequilibrium modelling; Mass transfer; Diacetone alcohol

1. Introduction

Catalytic distillation (CD) is a unit operation combining a heterogeneous catalysed reaction and distillation together and has many advantages, such as increasing product conversion and selectivity, saving energy by utilizing the reaction heat and prolonging catalyst lifetime by avoiding the formation of hot spots because the catalyst is surrounded by the boiling liquid in the CD reaction zone (Ng and Rempel, 2003; Podrebarac et al., 1997a). Most of the CD processes at present are continuous processes used for producing large quantities of chemicals. However, there are also literature reports on batch CD processes (Podrebarac et al., 1998a; Schneider et al., 2001).

A dynamic model, which can be used to simulate batch CD processes and step changes of operating variables as well as start up and shutdown procedures in the continuous CD processes, is needed for a better understanding of the complex behaviour of the CD column. However, most of the existing dynamic models are based on the equilibrium (EQ) assumptions between vapour and liquid phases (Abufares and Douglas, 1995; Sneesby et al., 1998). In the EQ model, the concept of stage efficiency or height equivalent to a theoretical plate (HETP) is generally introduced. However, the estimation of stage efficiency or HETP is very difficult for a CD process.

Recently, a number of publications on two-phase nonequilibrium dynamic models have been presented. A two-phase nonequilibrium (NEQ) dynamic model was developed by Kooijman and Taylor (1995) for the simulation of distillation processes which was based on the Maxwell–Stefan theory. Kreul et al. (1999) also reported a two-phase dynamic NEQ model for simulating batch distillation columns. The dynamic distillation models were further extended to simulate the CD columns by including the reaction terms (Kreul et al., 1998; Schneider et al., 2001). Recently, Baur et al. (2000, 2001) developed a dynamic NEQ cell model for CD columns in which the use of multiple well-mixed cells in the liquid and vapour flow directions accounted for staging in either fluid phase. A comparison of the dynamic EQ and

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* Corresponding author. Tel.: +1 519 888 4567x3979; fax: +1 519 746 4979.

E-mail address: fttng@cape.uwaterloo.ca (F.T.T. Ng).

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NEQ models was given by Peng et al. (2003). However, all of these pseudo-homogeneous (two-phase) dynamic models do not consider the mass and heat transfer between the liquid phase and external catalyst surface.

In our laboratory, Huang et al. (1998, 2000) reported a three-phase NEQ model (MECRES equations) for a steady-state CD process where the empirical overall vapour–liquid and liquid–solid mass transfer coefficients were used. Recently, Zheng et al. (2001, 2003a,b) refined this MECRES model by taking into account the mass and heat transfer among phases according to the Maxwell–Stefan theory. It was validated by comparison with the experimental data obtained for the CD processes of the aldol condensation of acetone (Zheng et al., 2001) and the synthesis of ethyl cellosolve (Zheng et al., 2003a). This model is also effective for design and can be used to provide the optimal design and operation parameters of a CD process (Zheng et al., 2003b). A CD process is more complex than a homogeneous reactive distillation process due to the existence of the heterogeneous reactions. In general, a three-phase NEQ model is more appropriate for the simulation of CD because there are concentration and temperature gradients between the liquid and solid phases in most reaction systems. Recently, we reported that a three-phase NEQ model is more appropriate for a CD process when the system is solid–liquid mass transfer controlled (Zheng et al., 2004).

However, there is no literature report on modelling a dynamic CD process by using a three-phase NEQ model. In this paper, a three-phase NEQ dynamic model is developed which accounts for mass and heat transfer between liquid and catalyst surface based on the Maxwell–Stefan theory. The model reaction in this paper is the aldol condensation of acetone to produce diacetone alcohol (DAA) using the Amberlite IRA-900 anion exchange resin as a catalyst (Podrebarac et al., 1998a). The catalyst was held within the fibreglass bags with approximately 1.5 cm in diameter inside the CD column, which has been described by Smith (1984). The aldol condensation is a consecutive reaction and DAA is an intermediate product which undergoes dehydration to produce mesityl oxide (MO) and water. The reaction scheme is provided in Eq. (1).

$$2\mathrm{Ac} = \mathrm{DAA} \rightarrow \mathrm{MO} + \mathrm{H_2O}. \tag{1}$$

DAA is a very useful solvent for cellulose acetate, nitrocellulose, vinyl chloride–vinyl acetate, and epoxy resins. DAA is also an intermediate product for manufacturing methyl isobutyl ketone (Podrebarac et al., 1998a). The reaction has an unfavourable equilibrium for the production of DAA. The equilibrium conversion at the normal boiling point of acetone, 54 °C, is only 4.3 wt%. However, the CD process was found to increase DAA conversion greatly by in situ removal of it from the reaction zone (Podrebarac et al., 1998a).

2. A three-phase NEQ dynamic model

A physical model of a typical NEQ section is shown in Fig. 1. The column is divided into a number of NEQ sections. The following assumptions are made in the model development:

1. The condenser and the reboiler are assumed to be at equilibrium.
2. Vapour–liquid equilibrium occurs at the vapour–liquid interface.
3. Perfect mixing for bulk phases.
4. No mass and energy holdups in the condenser, adjacent films, and solid phases.
5. Constant pressure along the CD column.
6. The catalyst particles are completely wetted with the liquid.

The mathematical equations for the three-phase NEQ dynamic CD model are described below.

2.1. Total condenser ($j = 1$)

For the total condenser, the mass balance is as follows at total reflux:

$$l_{i1} - v_{i,2} = 0, \quad i = 1, 2, \ldots, C \tag{2}$$

and temperature

$$T_1 = T_{\mathrm{bubble}}. \tag{3}$$

2.2. Nonequilibrium sections ($j = 2, \ldots, n-1$)

For the vapour phase:

Mass balance

$$\frac{\mathrm{d}M_{ij}^V}{\mathrm{d}t} = v_{ij} - v_{i,j+1} - f_{ij}^V + N_{ij}^V, \quad i = 1, 2, \ldots, C. \tag{4}$$

Heat balance

$$\frac{\mathrm{d}\sum_{i=1}^{C} M_{ij}^V H_j^V}{\mathrm{d}t} = \sum_{i=1}^{c} v_{ij} H_j^V - \sum_{i=1}^{c} v_{i,j+1} H_{j+1}^V - \sum_{i=1}^{c} f_{i,j} H_j^{VF} + e_j^V. \tag{5}$$

Mass transfer rate

$$N_{ij}^V = \sum_{k=1}^{c-1} k_{ikj}^V a_j \left(y_{kj} - y_{kj}^I \right) + y_{ij} \sum_{k=1}^{c} N_{kj}^V, \quad i = 1, 2, \ldots, C-1. \tag{6}$$

Heat transfer rate

$$e_j^V = h_j^V a_j \frac{\varepsilon_j^V}{\exp \varepsilon_j^V - 1} \left(T_j^V - T_j^I \right) + \sum_{k=1}^{c} N_{kj}^V H_{kj}^V. \tag{7}$$