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Modelling and Simulation of Operation for the TAEE Synthesis by Catalytic Distillation

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Abstract

Catalytic distillation (CD), involving reaction and separation in the same unit, is possible and beneficial when both volatility of reactants is close each other, but quite different from the volatility of products, and the conversion is limited by chemical equilibrium. Synthesis of tert-amyl-ethyl-ether (TAEE), additive for ecological gasoline, from ethanol and isoamylenes fits these conditions. The reaction takes place on the surface and/or in the pores of the catalyst grains (e.g. cationic exchange resin Amberlyst). In this contribution a model including kinetic effects for both mass transfer and chemical reaction is built and simulation is performed for specific conditions. Mass transfer kinetics is represented by Maxwell Stefan model (Taylor, 1993). Reaction kinetic model reported by Linnekoski (1997) is adopted. The CD column has in the reactive zone, Sulzer Katapak structured packing with Amberlyst 15 and has in the non-reactive zone Sulzer Mellapak. One-dimensional discrete model built for the space occupied by each phase in the structured packing, includes mass and heat balance, as well as kinetic model. The model is implemented in MATLAB. During model solving, HYSYS simulation environment calculates on-line the thermo-physical properties. Starting values are imported from simulation of a simplified model developed previously in HYSYS (Bozga et. al., 2003, p. 575, Ciornei, 2004). In this last work solution routine, based on Newton homotopy continuation was developed. Given column geometry, packing and feed characteristics CD column performance (conversion, product concentrations) is calculated. The results are presented as concentration and temperature profiles along the CD column. In future, column design and process optimisation, will be considered.

Keywords: catalytic distillation, TAEE, modelling and simulation, data transfer

1. Introduction

Oxygenated hydrocarbon compounds as tertiary ethers and alcohols play an important role in ecological gasoline formulation. Tertiary ethers were obtained treating with alcohols the olefins contained in FCC gasoline. First industrial scale process of this type

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was synthesis of MTBE (methyl tertiary-butyl ether). Then other tertiary ethers were considered e.g.: ETBE (ethyl-tertiary butyl ether), TAME (tert-amyl methyl ether) and TAEE (tert-amyl ethyl ether). This procedure reduces substantially the olefin content of gasoline. TAEE can be obtained industrially in two steps: reaction mixture passes firstly through a fixed bed pre-reactor when conversion of 45-50% is obtained. Then, the reaction is completed in the CD column. TAEE is separated as bottom product, whereas the other compounds are separated as top product. Process modelling and simulation is of great importance for operation, design and optimisation of CD. The process can be approximated reasonable considering MESH type model (Mass balance, vapour-liquid Equilibrium, mole fraction Summation and Heat balance equations) including as well kinetic model for chemical reaction (Bozga et. al., 2003, p. 575). Model simulation was performed combining different basic units of HYSYS flowsheet simulator. Performance of these models should be improved. ASPEN Custom Modeller (ACM) offers facilities for modelling. In this contribution, on-line combination between modelling capabilities of MATLAB and physical - chemical data availability in HYSYS is investigated.

2. MATLAB – HYSYS link

Good process evaluation depends of accurate physical-chemical data calculation. Considering the recognised quality of the property packages of HYSYS, we propose to use them to run MATLAB's CD model for TAEE synthesis. As MATLAB is widely used, we think to other extensions as control and optimisation. ActiveX technology is used. ActiveX (www.microsoft.com) technology is built on COM (Component Object Model). This can be used to create some interactions between software applications such as ActiveX documents, ActiveX automation and even OLE (Object Linking and Embedding). This technology allows using in one application the source code of other application or components of such application, keeping them invisible, protecting, in this manner, the intellectual property rights of developers. In our case this technology allows to use the thermodynamic packages of HYSYS in combination with process engineering models, as CD process simulation, written in MATLAB.
The problem of communication between HYSYS and MATLAB is solved building a software interface (a dll-file written in Visual Basic), dedicated to control data transfer, especially composition vectors from MATLAB to HYSYS. OLE capabilities of HYSYS offer a good opportunity to control, all internally defined functions, using Active X technology, by a compatible external application.

3. Thermodynamic and kinetic aspects

Main reactions for TAEE synthesis are presented below.

$$\underset{\text{ethanol}}{EtOH_{(liq)}} + \underset{\text{2-methyl-butene-1}}{2M1B_{(liq)}} \leftrightarrow \underset{\text{tert-amyl-ethyl ether}}{TAEE_{(liq)}} \qquad \text{(I)}$$

$$\underset{\text{ethanol}}{EtOH_{(liq)}} + \underset{\text{2-methyl-butene-2}}{2M2B_{(liq)}} \leftrightarrow \underset{\text{tert-amyl-ethyl ether}}{TAEE_{(liq)}} \qquad \text{(II)}$$

$$\underset{\text{2-methyl-butene-1}}{2M1B_{(liq)}} \leftrightarrow \underset{\text{2-methyl-butene-2}}{2M2B_{(liq)}} \qquad \text{(III)}$$

Keeping, for the reaction zone certain operating conditions, secondary reactions can be avoided (e.g. intermolecular dehydration of ethanol, isoamylenes hydrolysis). Thermodynamic model and kinetic model, for catalyst Amberlyst 15, are used as presented by (Linnekoski et. al., 1997, p. 310). As liquid phase is highly non-ideal, component activities are calculated with UNIQUAC model. Vapour phase is described with PRSV equation of state and liquid-vapour equilibrium is considered at interface.

4. Mathematical model

The CD column physical model has three zones (see Figure 1). Rectifying and stripping zones contain Mellapak structured packing. The reactive zone contains Katapak catalytic packing. In Figure 2, discretised physical model of each zone is presented. Mathematical model of the CD column accounts MERQ equations (Mass balance, Energy balance, Rate of reaction, mass transfer, summation eQuations) and phase equilibrium at the vapour-liquid interface). For multicomponent interphase mass transfer, Maxwell-Stefan (Taylor et al., 1993) model is adopted. These equations are written for discrete slices resulted from the decomposition of each column zone. Pseudohomogeneous model for each phase, as well as generalised interphase multicomponent mass transfer given by film theory, are considered.

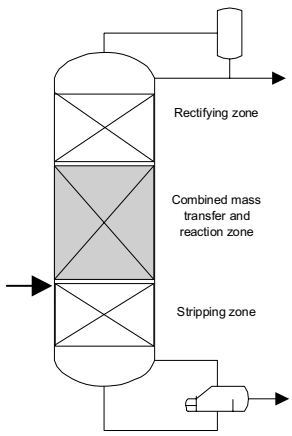

Figure 1 CD column structure

The mathematical model equations are presented below :

liquid phase mass balance :

$$L_{k-1} + N_k^L + F_k^L - L_k + \sum_i \sum_j \nu_{j,i} R_{j,k} \varepsilon_k = 0$$

$$L_{k-1}\, x_{k-1,i} + N_{k,i}^L + F_k^L\, x_{k,i}^F - L_k\, x_{k,i} + \sum_j \nu_{j,i} R_{j,k} \varepsilon_k = 0$$

liquid phase heat balance:

$$\left(N_k^L - L_k\right) h_k^L + L_{k-1}\, h_{k-1}^L + F_k^L\, h_{F,k}^L = 0$$

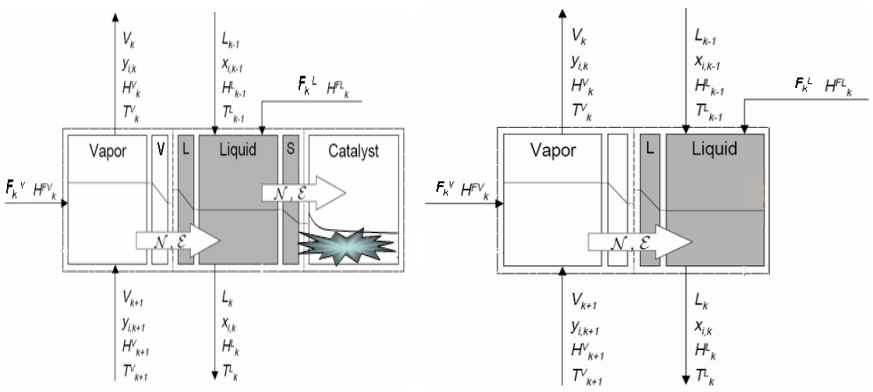

Figure 2 CD column physical model (a: reactive zone, b: non-reactive zone)

vapour phase mass balance:

$$V_k + N_k^V - V_{k+1} - F_k^V = 0\,, \qquad V_k\, y_{k,i} + N_{k,i}^L - V_{k+1}\, y_{k,i+1} - F_k^V\, y_{k,i}^F = 0$$

vapour phase heat balance:

$$\left(V_k + N_k^V\right) H_k^V - V_{k+1}\, H_{k+1}^V - F_k^V\, H_{F,k}^V = 0$$

equations containing Maxwell-Stefan model:

$$N_{k,i}^V - A^I\, J_{k,i}^V - y_{k,i}\, N_k^V = 0 \qquad N_{k,i}^L - A^I\, J_{k,i}^L - x_{k,i}\, N_i^L = 0$$

equilibrium equations: $y_{k,i}^I = K_{k,i}^I\, x_{k,i}^I$,

summation equations:

$$N_k^V - \sum_k N_{k,i}^V = 0 \qquad N_k^L - \sum_i N_{k,i}^L = 0 \qquad 1 - \sum_i y_{k,i}^I = 0 \qquad 1 - \sum_i x_{k,i}^I = 0$$

continuity equations: $N_{k,i}^V - N_{k,i}^L = 0$

where L liquid flowrate, V vapour flowrate, N interfacial flowrate, F feed flowrate, R reaction rate, x liquid molar fraction, y vapour molar fraction, A interfacial area, H vapour enthalpy, h liquid enthalpy, K equilibrium constant and T – temperature.

Condenser and reboiler models are described in (Ciornei, 2004). The model has 6c + 7 equations for each slice. Four slices in rectifying zone, two in reactive zone and seven in stripping zone are considered. The overall system has 1716 equations. The high non-linearity of the system of equations imposed a robust numerical method, Newton homotopy continuation (Wen-Jing, 1987, p. 887). The model neglects internal diffusion in solid phase, as catalyst grains are considered to be less than 1 mm diameter.

In this paper, the initial solution for the numerical algorithm is produced considering a MESH type model (Bozga et al, 2003, p. 575).

5. Results and discussions

CD column feed represents effluent of the pre-reactor. It contains more than seventeen C4-C6 hydrocarbons. Some characteristics are given (see Table 1). TAEE composition results from chemical equilibrium, in respect to the isoamylene composition, reported to operating conditions of the pre-reactor.

Table 1 Feed stream characteristics

Temperature ^{0}C	74
Pressure (kPa)	650
Mass flow (kg/h)	176.73
Composition	
C4 (2 components)	0.0331
C5 (8 components)	0.6901
2Methyl-1 Butene	0.0089
2Methyl- 2 Butene	0.0824
C6 and others (6 components)	0.0016
Ethanol	0.0736
TAEE	0.1103

The conversion of the isoamylenes is 44% whereas the excess of ethanol is 1.13 molar. Geometric data corresponding to a pilot plant: 0.15 m diameter, 2.3 m rectifying zone packing height, 1.95 m reactive zone height, 3.86 m stripping zone height are considered. Heat duties for condenser (86 kW) and reboiler (108 kW) are column specifications. Operating pressure in reboiler is 6.5 bar. This pressure allows getting less than 94^{0}C in the reactive zone, as a condition to protect catalyst activity.

These values were estimated simulating the MESH model type with HYSYS to obtain high isoamylene conversion. Taking into account the feed composition and the volatility of TAEE, the feed in the CD column was introduced below the reaction zone. The

Table 2 Results of the CD model simulation

		Distillate drum	Reaction zone	Reboiler
Temperature, ^{0}C		88	91.5-94	173
Composition, wt fraction	2M1B	0.0100	0.0125*	0.000021
	2M2B	0.0925	0.1020*	0.000481
	EtOH	0.0772	0.1420*	0.044000
	TAEE	0.0060	0.0820*	0.953000

TAEE rate: 36.97 kg/h; * composition in liquid phase at reaction zone exit

simulation results with MATLAB are given in Table 2. The calculated reflux ratio was 6.1. Figure 3 represents temperature profile in the column. Composition profiles of reactive species are presented in Figure 4 for the liquid phase.

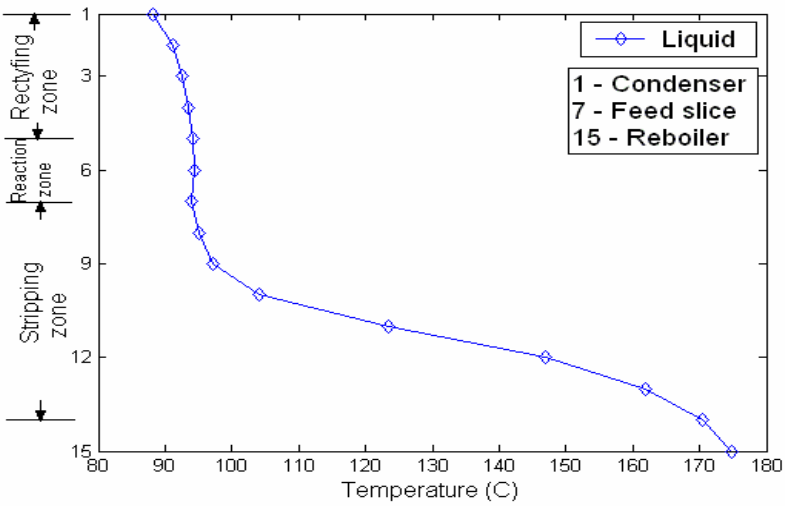

Figure 3 CD column temperature profile

Temperature profile is quite smooth in the rectifying and reaction zones. Maximum temperature for protecting catalyst life is observed. In stripping zone the temperature profile is very steep, corresponding to separation of very different boiling point components (amylenes, hydrocarbons, TAEE).

The composition profile for amylenes presents constant quite values in the rectifying and reaction zones corresponding to the necessities of the chemical reaction. Ethanol has a strong variation, exhibiting a maximum to the middle of the stripping zone as a source for the reactive zone. TAEE is progressively concentrating in the CD column bottoms due to low volatility.

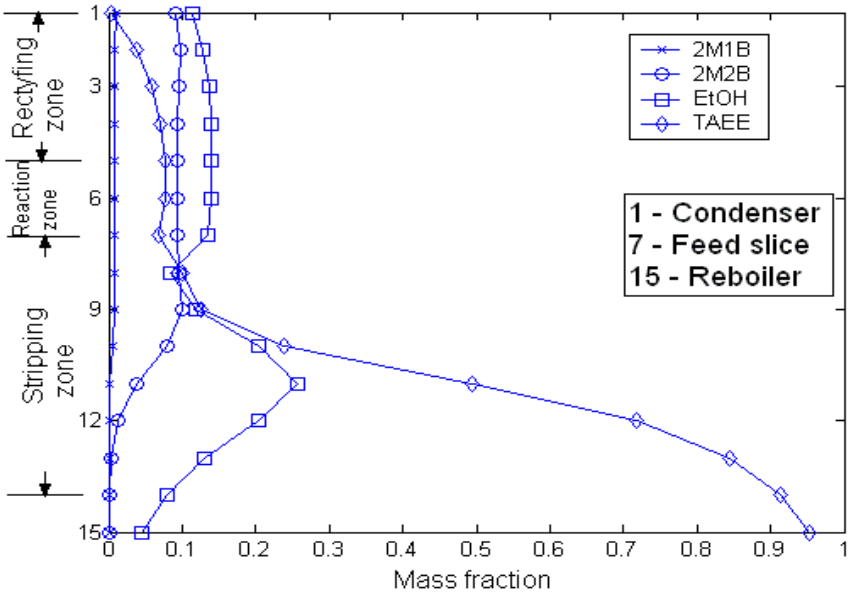

Figure 4. CD-Column liquid phase composition profiles

6. Conclusions

This paper presents an original approach to solve CD problems combining on-line model solving power of MATLAB with accuracy of thermo-physical data of HYSYS using ActiveX technology. In this context a complex model was possible to be built (considering both mass transfer and chemical reaction rate effects). CD column operation and geometric characteristics were specific to a TAEE synthesis pilot plant. The results of simulation encourage us to foreseen application of this technique to setup methodologies for design, operation and on-line optimisation of TAEE synthesis.

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