Catalytic distillation for the synthesis of tert-butyl alcohol with structured catalytic packing

Zhigang Lei *, Yang Yang, Qunsheng Li, Biaohua Chen

State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Box 35, Beijing 100029, China

ARTICLE INFO

ABSTRACT

The catalytic distillation for the synthesis of tert-butyl alcohol (TBA) with hydration of isobutene from a C4 mixture was proposed, in which a new-type BH structured catalytic packing was employed in the reaction section of catalytic distillation column. The reaction kinetics over an ion-exchange resin embedded with and without catalyst bag has been determined in a batch stirred reactor, respectively. The kinetic equation and effective factor of the structured catalytic bag were incorporated into the mathematical model of a catalytic distillation column. On this basis, the operating performance of catalytic distillation column was investigated, and it was found that in the improved process the total isobutene conversion increased from 60% to 67.7%, and the total heat duty on reboilers per amount of TBA decreased by 4.72%.

1. Introduction

Tert-butyl alcohol (TBA) production is of much interest because it is an important oxygenated octane enhancer [RON (research octane number) = 109, MON (motor octane number) = 91] as alternative to other toxic lead additives in gasoline. In general, TBA is obtained from the direct hydration of isobutene (IB) contained in the refinery C4 mixture [1–4]. The synthesis reaction takes place in the liquid phase, and is expressed as

$$IB + H_2O \underset{k_2}{\overset{k_1}{\rightleftharpoons}} TBA \tag{1}$$

which is catalyzed by solid acid, exothermic, reversible and highly selective toward the desired product. In order to derive a high conversion of isobutene, water is often excessive.

The original process for producing TBA in industry is shown in Fig. 1, which consists of mixer (1), fixed-bed reactor (2), C4 column (3) and TBA column (4). However, it is known that this hydration reaction is equilibrium-controlled, and up to 70% isobutene conversion is reached at most in a fixed-bed reactor (2). Note that the original C4 column (3) is composed of three sections. Therefore, an improved process is proposed in this work, where the middle distillation section of the original C4 column (3) is replaced by the reaction section and thus the original C4 column (3) becomes catalytic distillation column. The equilibrium-controlled

conversion limitation is eliminated by continuous removal of TBA from the reaction section in the catalytic distillation column (3).

Catalytic distillation column is a kind of multifunctional reactor [5–8], combining chemical reaction and distillation separation in one single process unit. However, how to design the hardware containing catalyst is crucial for catalytic distillation. Structured catalysts and reactors appear to be one of the most significant and promising developments in the field of catalytic distillation. Structured catalysts can considerably improve the process performance, minimize side reaction, and reduce recycle costs and energy requirements [9]. There are various types of structured catalysts [10–13], including monoliths, open cross-flow structures, foams, catalytic membranes and many others. However, the catalytic distillation operates in the countercurrent mode of contact at the cost of restricted column capacity. In this case the open cross-flow structures are favorable because they cannot only fill a large amount of catalyst, but also enable in situ separation of catalyst particles from reaction products, thus becoming a highly selective reaction-separation system.

In this work a new-type structured catalytic packing made by BUCT was adopted, which is assembled with two-layer corrugated wire gauze sheets of the type of BH structured packing serving as separation function and porous metal catalyst bags containing an acidic ion-exchange resin (supplied by Qilu Petrochemical Corporation) serving as reaction function in alternative sequence (see Fig. 2). The BH structured packing is different from commercially available types of KATAPAK in that is that it has a low ratio of height to diameter, one two-layer corrugated wire gauze sheet of "X" or "Y" type between two neighboring porous metal catalyst bags, and high
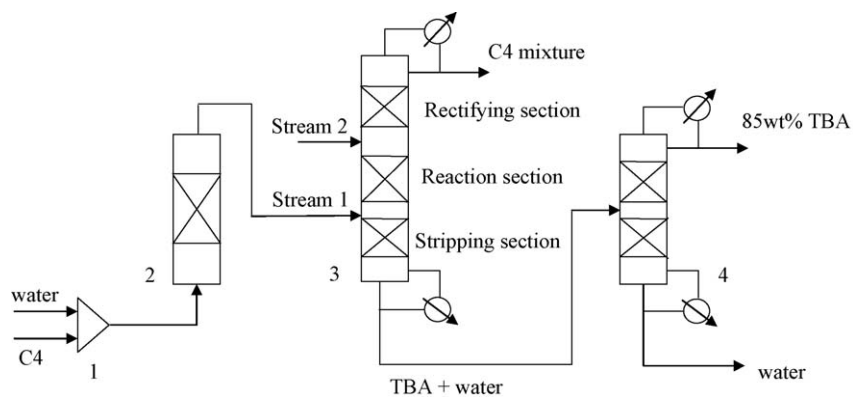
Fig. 1. Flowsheet of the process for producing TBA: 1, mixer; 2, fixed-bed hydration reactor; 3, C4 column (called catalytic distillation column in the improved process where the reaction section is filled with structured catalytic packings); 4, TBA column.
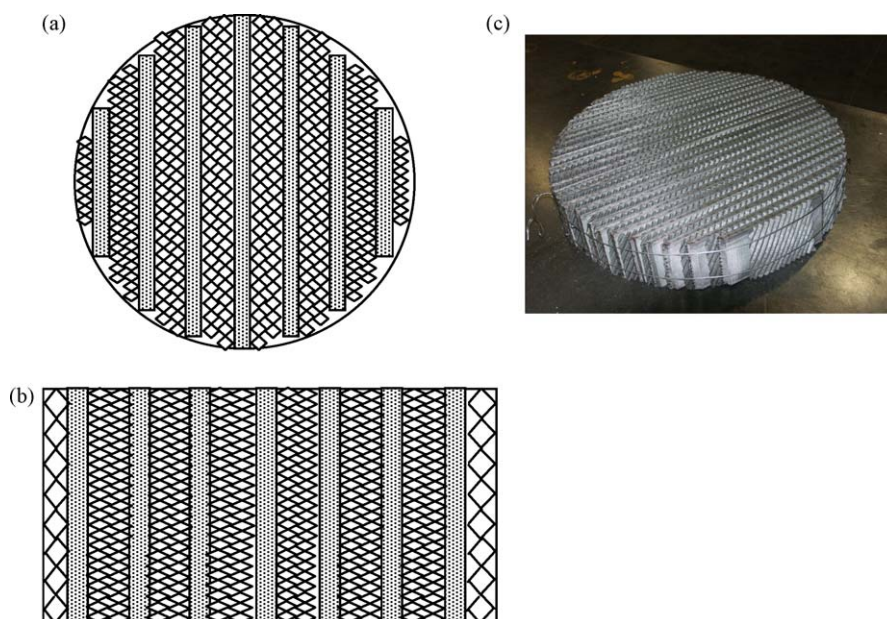

Fig. 2. Schematic representation of structured catalytic packing made by BUCT: (a) cross-section; (b) side view; (c) actual photography.

effective factor of porous metal catalyst bags. The corrugation direction at the cross-section of neighboring structured catalytic packings is crisscross each other and they are installed in the reaction section of catalytic distillation column (3) in the improved process. So focus of this work is given to determine the reaction kinetics over ion-exchange resin embedded with and without catalyst bag, and investigate the operating performance of catalytic distillation column so as to increase the conversion of isobutene and decrease the energy consumption per amount of TBA.

2. Reaction mechanism

There are three kinds of reaction mechanism for hydration of isobutene [14–18], i.e. LH1 (one site), LH2 (two sites) and the mechanism proposed by Petrus et al. The first two follows a Langmuir–Hinshelwood-type mechanism with different active sites, and the latter is based on the steady-state hypothesis for carbonium ion. In this work the LH2 reaction mechanism was adopted since it is assumed that both isobutene and water adsorb on the active sites. However, the polarity of water is stronger than olefins, and thus water adsorbs more preferentially than olefins. This assumption is consistent with that of liquid phase synthesis of methyl tert-butyl ether (MTBE) from methanol and isobutene [19].

The reaction rate can be expressed as follows:

$$r = r_+ - r_- = k\left(\frac{a_{IB}}{a_{H_2O}} - \frac{1}{K_a}\frac{a_{TBA}}{a_{H_2O}^2}\right) \tag{2}$$

where $k = k_+(K_{S,IB}/K_{S,H_2O})$, and $K_a = (k_+K_{S,H_2O}K_{S,IB}/k_-K_{S,TBA})$. r is the reaction rate of forward (+) and reverse (−) reactions, k is the rate constant of forward (+) and reverse (−) reactions, a ($a = x\gamma$) is the activity in the liquid phase, x is the mole fraction, γ is the activity coefficient, K_S is the equilibrium sorption constant. Chemical equilibrium constant K_a can be obtained from the Gibbs free energy change $\Delta_r G$ for the reaction:

$$K_a = \exp\left(-\frac{\Delta_r G}{RT}\right) \tag{3}$$

3. Experimental

3.1. Materials

A commercial cation-exchange resin catalyst with ionic form of H^+, bulk density 515.5 kg/m³ and average particle size diameter of 0.45 mm was used in the kinetic experiments. The catalyst is a kind

of macroporous sulfonic acid ion-exchange resin which acts as acidic catalytic sites. The ion-exchange resin was dried over night at 333–343 K in an oven drier to remove adsorbed water so as to determine the dry weight before use. TBA (purchased from Beijing Yi Li Fine Chemicals Limited Company, 99.99%) and deionized water were used as received.

3.2. Sample analysis

The gas chromatograph (GC 4000A Series) equipped with a Porapak-Q column and TCD detector was used to analyze the composition of the mixture from reactor. The carrier gas was hydrogen flowing at 30 cm^3 min^{-1}, and the operating conditions were as follows: the detector and column temperatures at 150 °C, and the injector temperature at 180 °C.

3.3. Kinetic measurement

The kinetics of hydration of isobutene (forward reaction) is difficult to be directly measured at high pressure. Therefore, we decide to measure the kinetics of dehydration of TBA (reverse reaction) at normal pressure and then deduce the kinetics of hydration of isobutene (forward reaction) in terms of chemical equilibrium constant. Liquid phase catalytic dehydration of TBA was performed in a 250 ml three-necked glass reactor equipped with two-bladed Teflon impellers and a condenser. The stirrer speed was 600 rpm in all experiments, at which speed the influence of external diffusion is eliminated. For each run, 12 g catalyst and 120 ml TBA solution were charged into the reactor, which was then heated to a selected temperature in the range of 333–348 K by a water bath. The reaction kinetics of dehydration of TBA over ion-exchange resin embedded with and without catalytic bags can be been determined in a batch stirred reactor.

4. Mathematical model

Experimentally determined reaction kinetic data were used to develop the model for catalytic distillation column. The rigorous equilibrium stage (EQ) model has been established to simulate catalytic distillation column. The equations that model EQs are known as the MESHR equations [20,21], into which the kinetic equation for structured catalytic packing is incorporated. MESHR is an acronym referring to the different types of equations. The M equations are the mass balance, E the phase equilibrium relations, S the summation equations, H the enthalpy balance, and R the reaction rate equations. The predictive UNIFAC model [22] is used for description of liquid phase non-ideality. The calculated results by this model were compared with the data from actual plant of Qilu Petrochemical Corporation without catalytic distillation column. It was found that both agree well.

5. Results and discussion

The chemical equilibrium constant K_a could be calculated by Eq. (3) where Gibbs free energy change $\Delta_r G$ for the reaction was obtained from the process simulation program (i.e. ASPEN PLUS). Therefore, K_a is deduced from linear fitting of T^{-1} and $\ln K_a$.

$$K_a = \exp\left(3971.6\frac{1}{T/K} - 9.9463\right) \tag{4}$$

where the correlation constant R^2 for the regression is 0.9997.

The kinetic data for dehydration of TBA measured in this work at four temperatures at normal pressure with and without catalyst bag are shown in Fig. 3. The dehydration rate of TBA increases with increasing temperatures. The product, isobutene, is volatile to
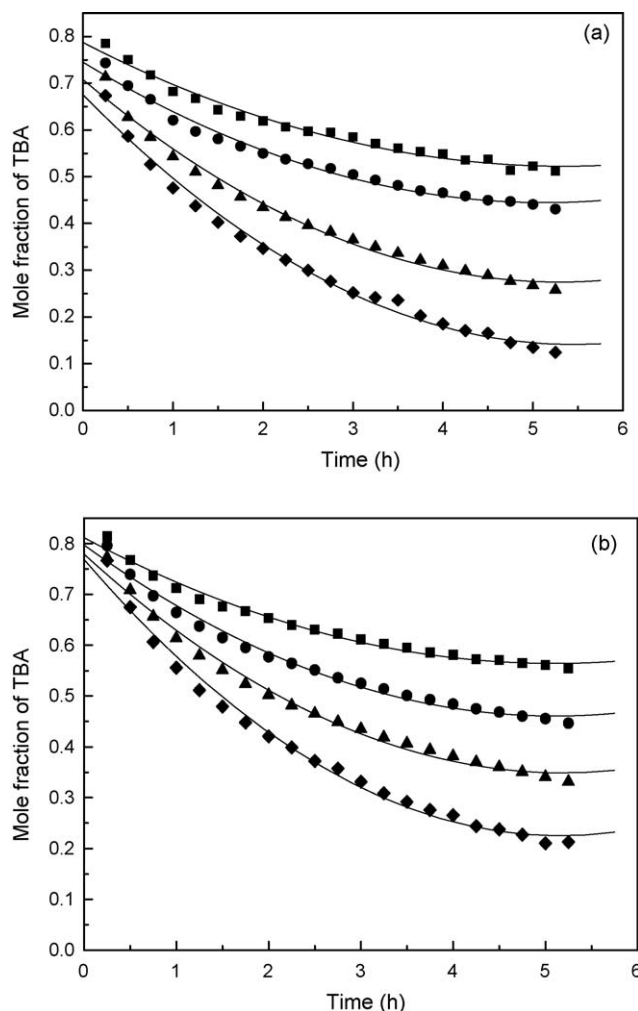
Fig. 3. Change of TBA composition with reaction time at different temperatures without (a) and with (b) catalyst bag: ■, 333 K; ●, 338 K; ▲, 343 K; □, 348 K.

leave from the reaction system continuously once it is produced so that the reverse reaction, i.e. hydration of isobutene, is prohibited. The rate equations were obtained after correlating the experimental data by the linear regression (see Fig. 4). Therefore, for dehydration of TBA without catalyst bag, the rate equation is

$$r_- = 9.739 \times 10^{10}\exp\left(\frac{-10576}{T}\right)\frac{a_{TBA}}{a_{H_2O}^2} \tag{5}$$
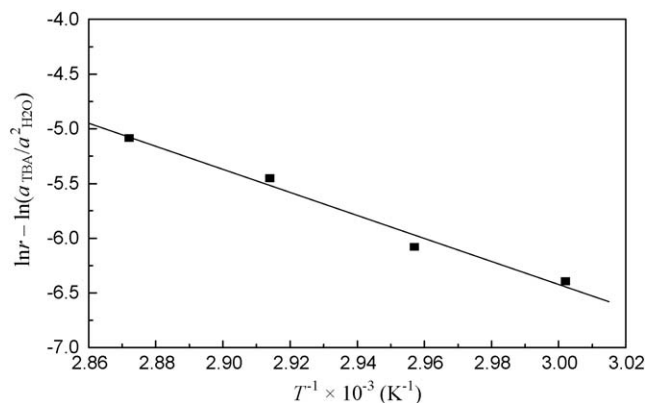
Fig. 4. Reaction rate as a linear function of inverse temperature in the kinetic measurement.

In terms of chemical equilibrium principle, the corresponding rate equation for hydration of isobutene is

$$r_+ = 4.667 \times 10^6 \exp\left(-\frac{6604.4}{T}\right) \frac{a_{IB}}{a_{H_2O}} \quad (6)$$

The reaction rate r is defined as the decrease or increase of TBA in the unit of $mol\,h^{-1}\,kg^{-1}$(cat.), the activity $a_i = x_i\gamma_i$, and the activity coefficient γ_i is derived from UNIFAC method.

The effectiveness factor of catalyst bag is defined as the ratio between the reaction rates with and without catalyst bag in the absence of external diffusion [23]:

$$\eta = \frac{r_r}{r_w} \quad (7)$$

where r_r is the reaction rate with catalyst bag, and r_w is the reaction rate without catalyst bag in the case of catalyst completely immersed. From Fig. 3b, for dehydration of TBA with catalyst bag, the rate equation is

$$r_- = 8.9403 \times 10^{11} \exp\left(\frac{-11,377}{T}\right) \frac{a_{TBA}}{a_{H_2O}^2} \quad (8)$$

Therefore, from Eqs. (6) and (8), the effective factor η of catalyst bag is

$$\eta = \exp\left(-\frac{801}{T} + 2.217\right).$$

In the simulation of improved process, the operating parameters come from the actual plant and are optimized as given in Table 1. Isobutene in the reaction mixture from fixed-bed reactor (2) is further converted into TBA in catalytic distillation column (3). The amount of catalyst required on each plate in reaction section is 32.7 kg for a production scale of 3000 tons TBA/year on the basis of kinetic data and apparatus size.

Operating pressure in catalytic distillation column can strongly affect reaction rates, cooling and heating sources by changing the column temperature profile. Fig. 5 shows the dependence of reaction section temperature on column pressure in the range of 0.4–0.7 MPa. As the column pressure increases, the column temperature increases, which enhances the reaction rates. At the same time, the temperatures of both cooling and heating
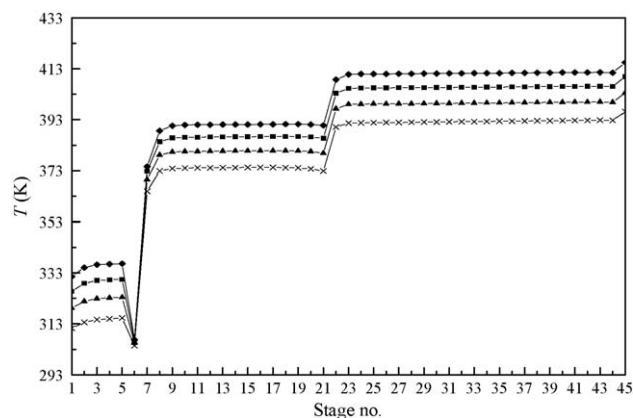

Fig. 5. Relationship between column pressure and column temperature: the stage no. is counted from the top to bottom including the stages of condenser and reboiler; □, 0.7 MPa; ■, 0.6 MPa; ▲, 0.5 MPa; ×, 0.4 MPa.

sources at the top and bottom of catalytic distillation column also increase.

Fig. 6 shows the distributions of temperature, composition in the liquid and vapor phases along the catalytic distillation column when operated under the conditions in Table 1. TBA and water were collected as the bottom product, and the residual C4 mixture were collected as the top product. The profiles of composition in the liquid and vapor phases exhibit the similar trend except that in the stripping section the composition curves of TBA and water in the vapor phase do not intersect due to a little high difference between the boiling points of TBA and water. In addition, there is an abrupt change of temperature near the stage no. 43, which

Table 1
Optimum operating parameters in the catalytic distillation column using structured catalytic packing.

|	Feed stream 1	Feed stream 2
Temperature	368 K	323 K
Pressure	1.5 MPa	0.8 MPa
Flow rate	5049.44 kg/h	640 kg/h
Feed composition (wt%)		
Water	66.77	100
TBA	6.40	
Isobutene	3.23	
Propane	0.38	
Isobutane	0.97	
N-butane	17.13	
N-butene	0.91	
trans-2-Butene	1.47	
cis-2-Butene	2.70	
Catalytic distillation column		
Total stages	45	
Rectification stages	1–5	
Reaction stages	6–22	
Stripping stages	23–45	
Feed stage	6, 22	
Catalyst loading	32.73 kg/stage	
Column pressure	0.7 MPa	
Reflux ratio	2.1 (mass ratio)	
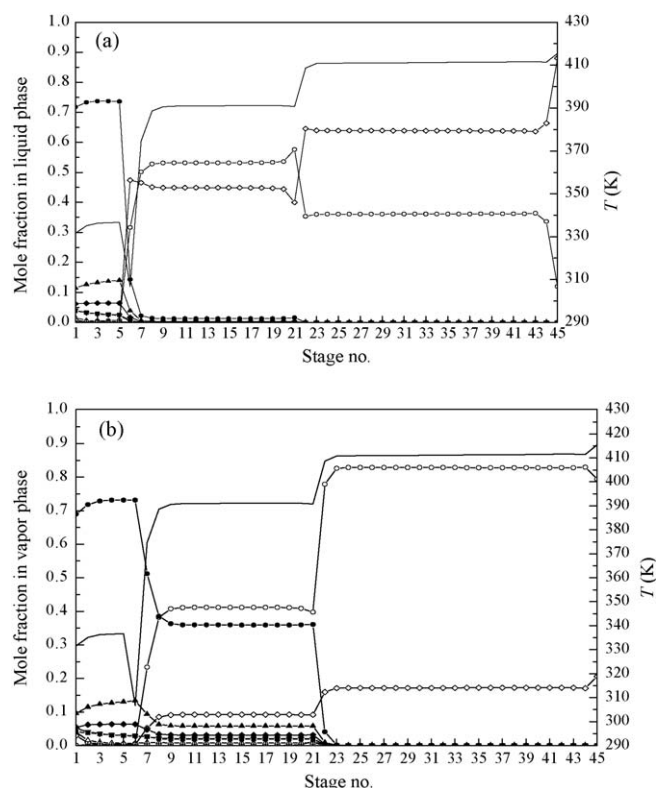
Fig. 6. Profiles of liquid composition (a), vapor composition (b) and temperature along the catalytic distillation column: the stage no. is counted from the top to bottom including the stages of condenser and reboiler; ○, TBA; □, IB; ◇, water; △, Propane; ▽, isobutane; ●, N-butane; ■, 1-butene; ◆, trans-2-butene; ▲, cis-2-butene; −, temperature.

Table 2
Comparison of the energy consumption between the original and improved processes.

Heat duty	Equipment	Original process	Improved process
Heat duty (MJ/h)	Fixed-bed reactor (2)	768	768
Heat duty on condensers (MJ/h)	C4 column (3)	1461.5	1634.4
	TBA column (4)	875	992.4
	Total	2336.5	2626.8
Heat duty on reboilers (MJ/h)	C4 column (3)	1992.5	2122.3
	TBA column (4)	1051.7	1161.6
	Total	3044.2	3283.9
Total heat duty per product on condensers (kJ/kg)	–	6180	6140
Total heat duty per product on reboilers (kJ/kg)	–	8050	7670

means that it is a sensitive plate and should be paid more attention in the design and control of catalytic distillation column.

Comparison of the energy consumption between the original and improved processes is given in Table 2. It can be seen that compared with the heat duty in the original process, the total heat duty on condensers per product in the improved process does not show significant change. However, the total heat duty on reboilers per product decreases by 4.72%. The reason is attributed to two aspects: one is that hydration of isobutene is an exothermic reaction, and the reaction heat is given off for distillation; the other is that more amount of TBA is produced in the catalytic distillation column, which leads to the further decrease of heat duty on reboilers per product. On the other hand, when the quality of product at the top of TBA column reaches 85.0 wt%, the quantity of product increases from 321.3 kg/h (corresponding to isobutene conversion 60.0%) to 364.1 kg/h (corresponding to isobutene conversion 67.7%).

6. Conclusions

An improved process was proposed in this work, in which the original C4 column is replaced by a catalytic distillation column. A new-type structured catalytic packing made by BUCT was installed in the reaction section of catalytic distillation column. It is expected that this kind of structured catalyst can intensify the coupling of reaction and separation, resulting in high energy efficiency and product quality.

Reaction kinetics of hydration of isobutene for the synthesis of TBA over a commercial cation-exchange resin catalyst has been measured, and kinetic equations with and without catalyst bag were established by using a Langmuir–Hinshelwood-type mechanism (LH2). The equilibrium stage (EQ) model was used to investigate the operating performance of catalytic distillation column, having a total 45 stages and 17 stages in reaction section, and operating at 0.70 MPa. It was found that in the improved process energy efficiency, product quality and quantity were all increased. However, it should be mentioned that there is no extra streams and equipments added based on the original process. The only change is that the traditional structured distillation packings in the middle section of original C4 column are replaced by structured catalytic packings. That is to say, the technology of structured catalysts is convenient to be implemented in the actual industrial plant.

References

[1] H. Beuther, T.P. Kobylinski, Am. Chem. Soc. Div. Pet. Chem. 27 (1982) 880.
[2] D.A. O'Sullivan, Chem. Eng. News 63 (1985) 10.
[3] E. Velo, L. Puigjaner, F. Recasens, Ind. Eng. Chem. Res. 27 (1998) 2224.
[4] C.M. Zhang, A.A. Adesina, M.S. Wainwright, Chem. Eng. Process. 43 (2004) 533.
[5] D.W. Agar, Chem. Eng. Sci. 54 (1999) 1299.
[6] Z.G. Lei, C.Y. Li, J.W. Li, B.H. Chen, Sep. Purif. Technol. 34 (2004) 265.
[7] Z.G. Lei, C.Y. Li, B.H. Chen, E.Q. Wang, J.C. Zhang, Chem. Eng. J. 93 (2003) 191.
[8] Z.G. Lei, J.F. Yang, J.J. Gao, B.H. Chen, C.Y. Li, Chem. Eng. Sci. 62 (2007) 7320.
[9] A.I. Stankiewicz, J.A. Moulijn, Chem. Eng. Prog. 96 (2000) 22.
[10] J. Ellenberger, R. Krishna, Chem. Eng. Sci. 54 (1999) 1399.
[11] S. Ratheesh, A. Kannan, Chem. Eng. J. 104 (2004) 45.
[12] A. Górak, A. Hoffmann, AIChE J. 47 (2001) 1067.
[13] K.K. Sirkar, P.V. Shanbhag, A.S. Kovvali, Ind. Eng. Chem. Res. 38 (1999) 3715.
[14] E.L. Purlee, R.W. Taft, C.A. DeFazzio, J. Am. Chem. Soc. 77 (1995) 837.
[15] V.J. Nowlan, T.T. Tidwell, Acc. Chem. Res. 10 (1977) 252.
[16] L. Petrus, R.W. De Roo, E.J. Stamhuis, G.E.H. Joosten, Chem. Eng. Sci. 39 (1984) 433.
[17] L. Petrus, R.W. De Roo, E.J. Stamhuis, G.E.H. Joosten, Chem. Eng. Sci. 41 (1986) 217.
[18] B.C. Gates, W. Rodriguez, J. Catal. 31 (1973) 27.
[19] A. Rehfinger, U. Hoffmann, Chem. Eng. Sci. 45 (1990) 1605.
[20] R. Taylor, R. Krishna, Chem. Eng. Sci. 55 (2000) 5183.
[21] Z.G. Lei, B.H. Chen, Z.W. Ding, Special Distillation Processes, Elsevier, Amsterdam, 2005, p. 178.
[22] Z.G. Lei, B.H. Chen, C.Y. Li, H. Liu, Chem. Rev. 108 (2008) 1419.
[23] G.R. Wang, W.J. Qin, J. Chem. Ind. Eng. (China) 43 (1992) 184.