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Process alternatives for methyl acetate conversion using reactive distillation. 1. Hydrolysis

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Abstract

In a polyvinyl alcohol (PVA) plant, reaction stoichiometry indicates that equal molar of methyl acetate is generated for every mole of PVA produced. This work explores an alternative to convert methyl acetate back to acetic acid (raw materials of PVA plant), methyl acetate (MeAc) hydrolysis. The design and control of methyl acetate hydrolysis using reactive distillation is studied. Because of the small chemical equilibrium constant (~ 0.013) and unfavorable boiling point ranking (MeAc being the lightest boiler), the reactive distillation exhibits the following characteristics: (1) total reflux operation and (2) excess reactant (water) design. The proposed flowsheet consists of one reactive distillation column with a reactive reflux drum, two separation columns, and one water-rich recycle stream. A systematic design procedure is used to generate the flowsheet based on the total annual cost (TAC). Two dominate design variables are: recycle flow rate (for the degree of excess in water) and the overhead impurity level of acetic acid in the product column (to avoid tangent pinch). Finally, the operability of the hydrolysis plant is evaluated. A plantwide control structure is developed followed by process identification and controller tuning. The results show that reasonable control performance can be achieved using simple temperature control for feed flow and feed composition disturbances. © 2007 Elsevier Ltd. All rights reserved.

Keywords: Reactive distillation; Methyl acetate; Hydrolysis; Process design; Process control

1. Introduction

Large amount of methyl acetate (MeAc) is produced as byproduct in the production of polyvinyl alcohol (PVA), around 1.68 times of the PVA product by weight. One approach is to hydrolyze MeAc back to acetic acid (HAc) and methanol (MeOH), raw materials for the PVA plant. The conventional hydrolysis process consists of a reactor and four distillation columns (Fuchigami, 1990). The hydrolysis reaction is carried out in a fixed bed reactor catalyzed by ion exchange resin. Because of the small equilibrium constant, ($K_{eq} \sim 0.04$), the one-pass conversion is relatively low and it results in large recycle flows. This subsequently leads to high energy demand for the conventional process. It is not likely to enhance the conversion or to reduce energy consumption by changing the molar feed ratio of H₂O/MeAc (FR_{H₂O/MeAc}).

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Reactive distillation is an attractive alternative for reaction/separation processes and it gives clear advantages for systems with small equilibrium constant (Kaymak and Luyben, 2004). The number of papers in this field has grown rapidly in recent years for process design (Doherty and Buzad, 1992; Okasinski and Doherty, 1998), steady-state behavior description (Barbosa and Doherty, 1988; Al-Arfaj and Luyben, 2000a, b; Chen et al., 2000; Tang et al., 2005), and dynamics and control (Sneesby et al., 1999; Al-Arfaj and Luyben, 2000a, b; Luyben et al., 2004; Hung et al., 2006). For process systems studied, related papers and patents in hydrolysis are much less than that of esterification reactions (Sundmacher and Kienle, 2003). Fuchigami (1990) proposes a reactive distillation configuration with total reflux on the top with bottoms product withdrawal for the hydrolysis process. The catalyst consists of ion exchange resin and polyethylene powder. With a feed ratio greater than 8, i.e., $FR_{H_2O/MeAc} = F_{H_2O}/F_{MeAc} = 8.2$, a near complete conversion ($\sim 99\%$) can be achieved. Also note that the reactive zone is placed in the mid-section of the column. Kim and Roh (1998), followed the work of Fuchigami, study

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Table 1 Different process configurations from literature with corresponding conversion (X)



the hydrolysis using reactive distillation, but azeotrope feed of MeAc/MeOH is considered. Almost complete conversion, \sim 99.9%, can be obtained with much higher water to methanol feed ratio, $FR_{H_2O/MeAc} = 15$. Using the same total reflux configuration, Xiao et al. (2001) investigated the effect of three operating variables, feed ratio of H₂O to MeAc (FR_{H₂O/MeAc}), recycle flow rate, and catalyst holdup, to the overall conversion. They also concluded that near 100% conversion of MeAc can be achieved by increasing the feed ratio. In an experimental work, Han et al. (1997) add a pre-reactor to the reactive distillation configuration with sieve-type tray installed in the reactive zone. However, products are withdrawn from both top and bottoms of the column, a one-feed-two-product RD column. With a feed ratio of unity, the overall conversion, including the pre-reactor and RD column, is only 50%. Wang et al. (2001), following the configuration of Han et al. (1997), change the operating condition by increasing the molar feed ratio of H₂O/MeAc and the reflux ratio. The conversion of the limiting reactant, (MeAc), is improved, from 50% to 72%. Lee (2002) proposes a configuration which is similar to a distillation column plus a side-reactor. The reflux drum of the distillation column is replaced by a fix bed reactor while the column is operated with total reflux. With an excess of water, almost complete conversion of MeAc ($\sim 99.8\%$) can be obtained and trace amount of MeAc is detected in the column base. Different ion exchange catalysts and feed compositions were also tested in Lee (2002). Table 1 summarizes different process configuration with conversions reported. Hoyme and Holcomb (2003) carry out the hydrolysis reaction in a high-pressure (10 atm) reactive distillation column. They observed that the methanol dehydration side reaction is significant, under such a high reaction temperature as a result of high operating pressure and, the overhead product is dimethyl ether, instead of methanol. For reaction kinetics, literature review shows that much of the research focuses on the esterification reaction and much less is found for the hydrolysis

reaction. Nevertheless, two groups, Song et al. (1998) and Pöpken et al. (2000), have studied the MeAc esterification and hydrolysis reaction catalyzed by Amberlyst 15 ion exchange resin with various initial reactant compositions. Pilot plant test of hydrolysis reaction was carried out in a RD column by Pöpken et al. (2001). Based on the experimental data and simulation results, the authors concluded that the adsorption-based kinetic model is more reliable than the pseudo-homogeneous one for hydrolysis reaction.

At the process design level, literature survey shows four possible configurations for MeAc hydrolysis (Table 1). However, the competitiveness of these four flowsheets in Table 1 is not clear and, yet, is an improved design possible? The objective of this work is to find a process configuration for MeAc hydrolysis using a mixed MeAc and MeOH feed with the composition MeAc/MeOH (60/40) close to the binary azeotrope. Next, the control aspect of the RD process will be explored. This paper is organized as follows. Section 2 explores process characteristic which includes reaction kinetics and phase equilibria. Conceptual design and systematic design procedure are studied in Section 3. The dynamics and control of the plantwide RD system is examined in Section 4 followed by the conclusion.

2. Reaction kinetics and phase equilibrium

2.1. Reaction kinetics

The hydrolysis of methyl acetate is a reversible reaction with the following expression:

$$MeAc + H_2O \iff HAc + MeOH.$$
 (1)

The reaction kinetics is given in Pöpken et al. (2000) with Amberlyst 15 ion exchange resin as catalyst. The

adsorption-based model can be written as

$$\mathcal{R} = m_{\text{cat}} \times \frac{k_f a'_{\text{MeAc}} a'_{\text{H}_2\text{O}} - k_r a'_{\text{HAc}} a'_{\text{MeOH}}}{\left(a'_{\text{MeAc}} + a'_{\text{H}_2\text{O}} + a'_{\text{HAc}} + a'_{\text{MeOH}}\right)^2}, \quad a'_i = \frac{K_i a_i}{M_i},$$

$$K_{\text{MeAc}} = 4.15, \quad K_{\text{H}_2\text{O}} = 5.24, \quad K_{\text{HAc}} = 3.15,$$

$$K_{\text{MeOH}} = 5.64,$$

$$k_f = 6.127 \times 10^5 \exp\left(\frac{-63\,730}{RT}\right),$$

$$k_r = 8.498 \times 10^6 \exp\left(\frac{-60\,470}{RT}\right).$$
(2)

The overall reaction rate \mathcal{R} has the unit of kilomole per second (kmol/s) and a_i is the activity, m_{cat} is the catalyst weight in kilograms, K_i is the adsorption equilibrium constant, M_i is the molecular weight of component *i*. The parameters k_f and k_r are forward and reverse rate constants with units of kmol/kg_{cat}/s and the activation energy in kilojoule per mole with temperature in Kelvin. An important characteristic in MeAc hydrolysis is extremely low equilibrium constant. This model gives an equilibrium constant of 0.013 (i.e., $K_{eq} = 0.013$) at 50 °C which is far below unity. Notice that water has a stronger uptake into the catalyst than methyl acetate as can be seen from the values of K_i/M_i . If we make water as the excess reactant, the molar ratio of H₂O/MeAc at the surface of the catalyst should be greater than that in the bulk. Thus, the adsorption-based kinetics model is more appropriate than the pseudo-homogeneous one. At each reactive section (i.e., reactive tray and reactive reflux drum), we assume the catalyst occupies half of the holdup volume. A bulk catalyst density of 770 kg/m^3 is used to convert into a volume-based rate equation for Aspen Plus reaction setup.

2.2. Phase equilibrium

For the reactive distillation modeling, it is essential to capture the nonideal vapor–liquid equilibrium (VLE), especially for good prediction of azeotropes and liquid–liquid (LL) envelops whenever two-liquid zone exists. The UNIQUAC (Abrams and Prausnitz, 1975) model is used for VLE calculation in the quaternary system and model parameters are taken from by Pöpken et al. (2000). We also take the vapor phase dimerization (for acetic acid) into account using Hayden–O'Conell second virial coefficient (Hayden and O'Connell, 1975) model and the model parameters are Aspen Plus built-in values.

The phase behavior gives two distinct features. The first is the existence of binary azeotropes: (1) methyl acetate and methanol form a minimum-boiling azeotrope with the composition of 65.9 mol% methyl acetate at 53.7 °C, and (2) methyl acetate and water forms minimum-boiling azeotrope with the composition of 89.0 mol% at 56.4 °C. Both are predicted at atmospheric pressure. Thus, the order of the normal boiling point temperature for pure components and azeotropes is:

 $HAc > H_2O > MeOH > MeAc > MeAc/H_2O > MeAc/MeOH$ 118 °C 100 °C 64.5 °C 57.5 °C 56.4 °C 53.6 °C



Fig. 1. Vapor–liquid equilibrium of acetic acid (HAc) and water ($\rm H_2O$) system and the tangent pinch indicated by the dashed line.

In theory, if one consumes all the light reactant (MeAc), the lightest pure component, toward the top of a single reactive distillation column, relatively pure light product (MeOH) can be obtained (Tung and Yu, 2007). However, the light product (MeOH) is a saddle MeAc-MeOH-H₂O ternary residue curve map (RCM) diagram (Tang et al., 2005). With a low equilibrium constant ($K_{\rm eq} \sim 0.013$), it is not likely to obtain high purity MeOH product under the "neat" operation. Thus, total reflux design (e.g., Fuchigami, 1990) with upper section reactive zone seems to be a reasonable choice, especially one of the reactants being the lightest pure component. Moreover, the removal of the light product (MeOH), heavy product (HAc), and excess reactant (H₂O) from the bottoms of the column is also relatively easy. The second feature in the VLE is related to the downstream separation columns. Fig. 1 shows the binary VLE diagram for water-acetic acid system. It shows a tangent pinch point existing near the pure water end. This implies that a near complete removal of acetic acid from water will require excessive large reflux ratio, high reboiler duty. In terms of process design, this means recycling a certain portion of the heavy product (HAc) back to the RD may be acceptable as far as the energy consumption is concerned. Thus, the purity level of acetic acid at the top of acetic acid dehydration column should be investigated in the design of entire plant.

3. Steady state design

3.1. Process flowsheet

Reaction kinetics and phase equilibria reveal that, for a near complete conversion of methyl acetate, the reactive distillation systems possess the following characteristics. First, the "neat" design is not favorable because of the small equilibrium constant, i.e., ($K_{eq} \sim 0.013$). Second, from reaction perspective,



Fig. 2. Process flowsheet of MeAc hydrolysis system and design parameters indicated in italics.

we should make water as the excess reactant as explained earlier based on the adsorption-based kinetics. This implies that we make the heavy reactant (H_2O) in excess. Third, from phase equilibrium perspective, it is favorable to withdraw the products as well as excess reactant from the bottoms of the reactive distillation column for the ease of separation (avoid azeotropes). Thus, a total reflux operation with product withdrawal from the bottoms of reactive column is, indeed, a good candidate for this hydrolysis reaction. It is also clear that the reactive zone should be placed at where the reactant is most abundant, upper section of the column. Because the reflux drum has a large holdup with significant amount of MeAc (limiting reactant), it is made reactive by placing catalyst inside. Therefore, we have a reactive distillation column under total reflux operation with reactive zone placed at the upper section of the column, including a reactive reflux drum, as shown in Fig. 2. For the subsequent separation for the ternary mixture, the indirect sequence is adapted here. Therefore, the entire process consists of one reactive distillation column, two distillation columns with one recycle stream. The hydrolysis reaction takes place in the RD column with total reflux operation. There are three feeds into the RD column: fresh water feed (50 kmol/h), water-rich recycle stream from bottom of the 3rd column (methanol product column), and the fresh feed with a composition close to the binary azeotrope, i.e., 60 mol% methyl acetate and 40 mol% methanol, and a flow rate of 83.33 kmol/h. The two feeds, rich in water, are fed into the reflux drum. The third feed stream is the light reactant (MeAc) which is fed to the lower section of the RD column.

The following design specifications are made for the reactive distillation column. Five minutes residence time is assumed for the reactive reflux drum and half of the holdup volume is packed with catalyst. For reactive trays, we assume that the catalyst occupies half of the tray holdup volume. The tray holdup is determined by the column diameter which is sized using the Tray Sizing Utility in Aspen Plus by assuming a weir height of 10 cm. The conversion of methyl acetate is set to 98.7% by adjusting the reboiler duty. The bottoms product of the RD column is fed into acetic dehydration column, namely the 2nd column, with the product, 99 mol% acetic acid, taken from the bottoms. The overhead product, mostly methanol and water, of the 2nd column enters the recycle column, namely the 3rd



Fig. 3. Effects of design variables on TAC in the reactive column with perturbation from nominal steady state ($F_R = 240 \text{ kmol/h}$ and $x_{D2,\text{HAC}} = 0.13$): (A) number of reactive trays and number of trays in the stripping section and (B) feed tray locations.

column, for further purification. High-purity methanol, 99 mol%, is withdrawn from the column top and water-rich bottoms flow is recycled back to the reflux drum of the RD column. The impurity level, methanol at the bottoms of the 3rd column, is set to 0.1 mol% for the recycle stream.

3.2. Design procedure

Once the conceptual design is completed and specifications are given, we can proceed with the preliminary design. The objective is to minimize total annual cost (TAC) by adjusting the design parameters, e.g., tray numbers in each section, feed location in the column, etc. The TAC is defined as (Douglas, 1988):

$$TAC = operating cost + \frac{capital cost}{payback year}.$$
 (3)



Fig. 4. Effects of total number of trays and feed tray location on TAC with perturbation from nominal steady state (F_R =240 kmol/h and $x_{D2,HAC}$ =0.13 for: (A) 2nd column, (B) 3rd column.

Here, a payback of 3 years is used. The operating cost includes the costs of steam, cooling water, and catalysts. The capital cost comprises the costs of the column, trays, and heat exchangers. Cost models and corresponding values are given in Appendix A and a catalyst life of 3 months is assumed.

In the flowsheet, obvious design parameters are shown in italics in Fig. 2. They are: the number of reactive and stripping trays (N_{rxn} and N_S), water and acetate feed tray location (NF_{H2O} and NF_{MeAc}) of the RD column, the total number of trays and feed tray location of the 2nd column (N_{T2} and NF₂) and the 3rd column (N_{T3} and NF₃). In addition to tray numbers and feed locations in each columns, there are two important design variables (Yi and Luyben, 1997): recycle flow rate (F_R) and the overhead acetic acid impurity in the 2nd column ($X_{D2,HAc}$) as mentioned earlier. The former means the degree of excess water into the RD column. An increase in F_R favors the hydrolysis reaction at the expense of a higher recycle



Fig. 5. Effects of recycle flow rate (F_R) on TAC of the entire plant, RD column, and distillation columns with perturbation from nominal steady-state ($x_{D2,HAC} = 0.13$).



Fig. 6. Effects of the overhead acetic acid impurity of the 2nd column $(X_{D2,HAc})$ on TAC.

cost (energy for subsequent separation). The latter comes from the tangent pinch behavior between acetic acid and water. A higher product recovery, a small $X_{D2,HAc}$ value in the second column, prevents the product recycled back to the RD column, but a much larger energy consumption is needed as a result of the tangent pinch. Thus, a tradeoff between the reaction (RD cost) and separation (cost of 2nd column) should be made and $X_{D2,HAc}$ is also an important design variable.

We have identified 10 design variables above, and a systematic design procedure is devised for the flowsheet generation (Chiang et al., 2002; Tang et al., 2005). All the simulations are carried out in Aspen Plus using the RADFRAC module with FORTRAN subroutines for the activity-based reaction kinetics. Given the production rate and product specifications, the



Fig. 7. Optimized process flowsheet "indirect" separation sequence for the hydrolysis system.

Table 2						
Steady-state operating parameters	and total	annual	cost (TAC) for Me	Ac hydrolysis	process

Column	RD column	2nd column	3rd column
Total no. of trays	29	15	27
No. of trays in reactive section $(N_{\rm rxn})$	18		
No. of trays in stripping section (N_S)	11	14	11
Reactive trays	12–29		
Acetate feed tray (NF _{MeAc})	6		
Water feed tray (NF_{H_2O})	30		
Feed tray		14	11
Catalyst in reflux drum (m ³)	3.03		
Catalyst in each tray/sum (m ³)	0.11/1.98		
Acetate/water feed flow rate (kmol/h)	83.33/50		
Recycle flowrate (kmol/h) (F_R)	240		
Top product flow rate (kmol/h)		323.50	83.50
XD			
m.f. of acid	0.108	0.130	0.000
m.f. of alcohol	0.106	0.256	0.990
m.f. of acetate	0.391	0.00198	0.00766
m.f. of water	0.395	0.612	0.00234
Bottom product flow rate (kmol/h)	373.33	49.83	240
X _B			
m.f. of acid	0.245	0.990	0.175
m.f. of alcohol	0.222	3.922×10^{-7}	0.00100
m.f. of acetate	0.00171	0.000	0.000
m.f. of water	0.531	0.010	0.824
Condenser duty (kW)	-4036.42	-3862.52	-2010.94
Reboiler duty (kW)	4140.85	3779.98	2116.60
Column diameter (m)	1.75	1.80	1.05
Condenser heat transfer area (m ²)	500.34	199.28	215.43
Reboiler heat transfer area (m ²)	342.62	312.76	175.13
Damköhler number (Da)	3.68		
TAC of RD column (\$1000/year)	841.08	654.49	409.89
Total capital cost (\$1000/year)		973.51	
Column/trays/heat exchanger		328.37/57.26/587.88	
Total operating cost (\$1000/year)		931.95	
Catalyst/energy		119.12/812.83	
TAC (\$1000/year) (50 kmol/h)		1905.46	



Fig. 8. Composition and temperature profiles in the reactive column.

design steps are

- (1) Guess a specification of acetic acid in distillate of 2nd column (e.g., $X_{D2,HAc} = 0.01$).
- (2) Guess the recycle flow rate (F_R) (e.g., $F_R = 100 \text{ kmol/h}$).
- (3) Guess a number of reactive trays (N_{rxn}) .
- (4) Guess a tray number in the stripping section (N_S) .
- (5) Guess the heavy reactant feed (NF_{H_2O}) and guess the light reactant feed (NF_{MeAc}).
- (6) Change the heat input (Q_R) until the reaction conversion is achieved.
- (7) Go back to (5) and change N_S until the TAC is minimized.
- (8) Go back to (4) and vary $N_{\rm rxn}$ until the TAC is minimized.
- (9) Go back to (3) and find the feed locations ($\rm NF_{H_2O}$ and $\rm NF_{MeAc})$ until the TAC is minimized.
- (10) Pick a total number of trays in the 2nd column (N_{T2}) .
- (11) Guess a feed location in the 2nd column (NF₂) and change the reflux flow (R) and heat input (Q_R) until the product specification is met.
- (12) Go back to (10) and change NF_2 until the TAC is minimized.
- (13) Go back to (9) and vary N_{T2} until the TAC is minimized.
- (14) Pick a total number of trays in the 3rd column (N_{T3}) .
- (15) Guess a feed location in the 3rd column (NF₃) and then change the reflux flow (R) and heat input (Q_R) until the product specification is met.
- (16) Go back to (14) and change NF₃ until the TAC is minimized.
- (17) Go back to (13) and vary N_{T3} until the TAC is minimized.



Fig. 9. (A) The column with reactive reflux drum with 5.01 m^3 catalyst loading and (B) the effect of reboiler duty (Q_R) on the conversion of MeAc (the red dashed line for nominal heat input and solid line for heat duty for desired conversion).

- (18) Go back to (2) and change F_R until the TAC is minimized.
- (19) Go back to (1) and find $X_{D2,HAc}$ until the TAC is minimized.

These steps may seem excessive, but the procedure is set up in such a way (i.e., fixed specifications for all product streams) that the design of each column is decoupled. For example, steps (3)-(8), (9)-(12), and (13)-(16) are the design steps for the RD, the 2nd column, and the 3rd column, respectively, given a recycle flow rate and composition.

3.3. Results

For the RD column, Fig. 3 shows that the number of trays in the stripping section (N_S) to the TAC is more sensitive than that of the number of reactive trays (N_{rxn}) . The reason for that is: almost ~ 70% of the total conversion occurs in the reactive reflux drum as a result of the large amount of catalyst and high reactant concentration. Subsequently, N_{rxn} has little effect on the TAC. There are 18 reactive trays and 11 stripping trays in the RD column. Fig. 3 also reveals that water should be introduced into the reactive reflux drum (denoted as 30th tray) and the light reactant (mixture MeAc/MeOH below the azeotropic





Fig. 10. Plantwide control of the hydrolysis plant.

composition) should be introduced into the stripping section (below the reactive zone in the 6th tray). This is also expected because the light reactant (MeAc) is lighter than MeOH and a certain degree of purification is helpful for the reactant composition in the reactive zone. Note that the tray number is counted from the bottom-up. Fig. 4 shows how the effects of total numbers of trays and feed tray locations in the separation section (2nd and 3rd columns) to the TAC. Because of having large amount of water, the optimal feed tray is placed in the upper section of the column. The 2nd column has 15 trays with $NF_2 = 14$. The 3rd column has a total 27 trays with the feed introduced to the lower section of the column, i.e., $NF_3 = 11$. For the recycle flow rate (F_R) , Fig. 5 shows a minimum in TAC occurs when the recycle flow take the value of 240 kmol/h. The tradeoff comes from the RD cost and the separation column costs. The RD cost decreases as the recycle flow increases as the result of a higher reactant concentration, but the cost of subsequent separation also increases for a higher flow rate (Fig. 5). That implies the feed ratio (FR_{H2O/MeAc}) is the dominant design variable and the TAC minimum corresponds to $FR_{H_2O/MeAc} = 4.95$. Fig. 6 shows the overhead composition (impurity) of acetic acid of the distillate of 2nd column $(X_{D2,HAc})$ has significant impact on the TAC. As shown in Fig. 1, the tangent pinch point toward the pure water end makes the complete removal of HAc from the recycle stream difficult. Thus, we have a tradeoff between reactant composition (mixed with product HAc) and separation cost. As the $X_{D2,HAc}$ approaches 0.13, the energy intensive separation (tangent pinch) can be mitigated and, however, a further increase in the purity leads to a rapid increase in the TAC as a result of unfavorable reactant composition. In summary, for the plantwide design of the hydrolysis plant, two dominant design variables are identified, F_R and $X_{D2,HAc}$. The optimized flowsheet can be obtained by carefully adjusting these design

parameters as shown in Fig. 7. Table 2 summarizes design parameters and corresponding costs.

3.4. Discussion

Because of the small equilibrium constant, near complete conversion of the limiting reactant (MeAc) leads to a relative large boilup-to-fresh feed (3.25 = 432/133) ratio. Fig. 8 shows the composition profile in the RD column and the vertical dashed line indicates the lower limit of the reactive zone with the feeds introduced on tray 6 and the reflux drum, respectively. The profiles in Fig. 8 indicate that fairly large (\sim 40%) and constant reactant concentrations of both reactants, MeAc and H₂O, throughout the reactive zone. This facilitates the forward reaction for a system with small equilibrium constant. The reflux drum is packed with 3.03 m³ catalyst which results in $\sim 70\%$ of the total conversion (R_i/R_{tot} as indicated by shaded area in Fig. 8). The rest of the catalyst holdup (on reactive trays) sums up to 1.98 m³ (by volume) which accounts for the remaining 30% of the total conversion. A final note is that the introduction of the mixed MeAc/MeOH feed below the reactive zone indeed prevents the product MeOH from entering the reactive zone as indicated by the profiles between the lower feed tray and bottoms of the reactive zone.

The total reflux configuration in Fig. 7 seems to be a viable choice to overcome systems with a small chemical equilibrium constant. However, it is also observed that most of the conversion occurs in the reactive reflux drum. The question then becomes: can we further simplify the process flowsheet by removing all the catalyst from reactive trays and putting them into the reflux drum? That is: we have a total of 5.01 m^3 catalyst ($3.03 + 1.98 = 5.01 \text{ m}^3$) placed in the reflux drum while making the upper section of the RD column non-reactive



Fig. 11. Sensitivities of trays temperature for $\pm 0.01\%$ changes in the manipulated variable: (A) RD column, (B) 2nd column, and (C) 3rd column.

Fig. 9A. Using the same total number of tray, feed conditions, and the same reboiler duty, the results show that the conversion drops to 83.4% as compared to 98.7% of the proposed one (indicated by the dashed line in Fig. 9B). Moreover, in order to achieve the desired conversion (98.7%), the reboiler should be doubled (solid line in Fig. 9B). This clearly shows that, despite

having insignificant contribution to the total conversion, the reactive trays are essential for a near complete conversion of the limiting reactant. This is especially true of chemical systems with a small equilibrium constant.

The second question is: what will happen if pure methyl acetate is used instead of mixed MeAc/MeOH feed (60/40)? Certainly, this will require pre-processing of the azeotropic mixture using, for example, pressure swing to break the azeotrope. However, the purified MeAc reactive distillation system only gives a 12% reduction (from \$1,905,468 to \$1,681,250) in the TAC as compared to the mixed 60/40 mixed MeAc/MeOH feed. The reduction is almost equally distributed between the capital cost and the operating cost. A noticeable difference in the process flowsheet is that the pure MeAc should be introduced into the reactive reflux drum, instead of tray 6 for the mixed MeAc/MeOH feed.

Before leaving this section, we would like to explore alternative separation sequence on the design of this hydrolysis plant. Fig. 7 shows that we have an "indirect" separation sequence for the mixture of methanol, water, and acetic acid. The "direct" separation is examined. The result shows that these two sequences differ by less than 10% in TAC for the two distillation columns and the "indirect" sequence in Fig. 7 is more favorable in terms of capital as well as operating costs. Appendix B gives the optimized process flowsheet for the hydrolysis plant with direct separation sequence.

4. Process dynamics and control

Plantwide control of processes with reactive distillation column and separation columns is less common as compared to the control of reactive distillation columns and plantwide control of reactor/separator (Luyben et al., 1998; Wu and Yu, 1996). Al-Arfaj and Luyben (2004) develop control scheme for the "pseudo-neat" TAME process (one RD with two columns) using temperature control and effective control performance can be obtained. In this work, temperatures are used to infer the product composition as well as degree of conversion. As pointed out by Al-Arfaj and Luyben (2000a, b), two fresh feeds cannot be adjusted using simple ratio control. One of the feed should be under feedback control to maintain stoichiometric balance. Following these principles, a control structure is developed for the hydrolysis plant (Fig. 10).

- (1) Control a tray temperature of reactive distillation by changing the reboiler duty to meet the desired conversion.
- (2) Control a tray temperature of the 2nd column by adjusting reboiler duty to maintain the product (HAc) purity and control a tray temperature of the 3rd column by changing the reflux ratio to maintain product (MeOH) purity.
- (3) Ratio the fresh feed of MeAc/MeOH mixture to the recycle flow (F_R) . Note that this mixed MeAc/MeOH feed is the throughput manipulator.
- (4) Maintain the 3rd column base inventory by adjusting the fresh water feed.
- (5) Fix the reflux ratio in the 2nd column and maintain the boilup ratio in the 3rd column.



Fig. 12. Sequences of relay feedback tests for the hydrolysis plant.

- (6) Control the top and bottoms holdups in the reactive distillation column by changing the reflux flow rate and bottoms flow rate, respectively.
- (7) Control the top and bottom holdups of the 2nd column by manipulating the distillate flow rate and bottoms flow rate, respectively.
- (8) Control the top holdup of the 3rd column by changing the distillate flow rate.

This is a relatively simple control structure where the stoichiometric balance is maintained by adjusting the fresh water feed flow rate via column base level control as mentioned in step (4), avoid accumulation or depletion of water in the system. Also note that the reason the base level of the 3rd column can be controlled using the fresh water feed is that, the total recycle rate is under flow control, i.e., the sum of bottoms flow and fresh feed is fixed. The next step is to achieve composition control by identifying the temperature control trays in all three columns. The objective is to infer conversion in the RD column, the bottoms HAc composition in the 2nd column, and the overhead MeOH composition in the 3rd column. Sensitivity analyses are performed for $\pm 0.01\%$ variations in the corresponding manipulated variables. Because of small perturbations, the temperature responses are quite linear as shown

Table 3Tuning parameters of temperature control

CV	MV	Tuning parameter
$T_{1,4}$ $T_{2,5}$ $T_{3,15}$	$ \begin{array}{c} Q_{R_1} \\ Q_{R_2} \\ RR_3 \end{array} $	$K_{C,1} = 04.24, \tau_{I,1} = 10.32$ (min) $K_{C,2} = 14.62, \tau_{I,2} = 06.96$ (min) $K_{C,3} = 20.10, \tau_{I,3} = 12.00$ (min)

in Fig. 11. The temperature control points are tray 4, tray 5 and tray 15 for the RD column, 2nd column, and 3rd column, respectively. Performing dynamic simulation using Aspen Dynamics, a third-order 0.5 min time lag is assumed for temperature measurement (Luyben et al., 1998). Liquid level is controlled using proportional-only controller. Proportional-integral controllers are used for flow, pressure, and temperature controls. Relay feedback tests (Shen and Yu, 1994) are performed on the temperature loops to find the ultimate gains (K_u) and ultimate period (P_u) of each temperature control loop followed by the Tyreus–Luyben settings (Luyben et al., 1998) and a simple version is: $K_c = K_u/3$ and $\tau_I = 2P_u$. The multifunctional nature of the reactive distillation complicates already very nonlinear natures of either reaction or separation, in addition to recycle structure of the process. To mitigate the interaction arisen from



Fig. 13. Temperature control performance for (A) ±20% production rate changes and (B) ±5% (mf) acetate feed composition changes.

recycle, the autotuning starts from the column right after the RD column (the 2nd column), to the 3rd column, and then back to the RD column as shown in Fig. 12. The sequential tuning procedure converges faster this way (Shen and Yu, 1994). Controller settings for all three loops are summarized in Table 3.

The plantwide control is tested for feed flow and composition disturbances. Fig. 13A shows that fast and symmetric responses can be obtained for $\pm 20\%$ feed flow changes. The temperature control trays $(T_{1,4}, T_{2,5}, \text{ and } T_{3,15})$ and product compositions ($X_{B2,HAc}$ and $X_{D3,MeOH}$) settle in less than 5 h. The recycle flow to the fresh feed ratio loop calls for a large recycle flow as the production rate increases. This affects the base holdup in the 3rd column and subsequently leads to a large overshoot in the water feed flow rate initially (Fig. 13A). It can also be seen that with temperature control, steady-state errors exist for both product compositions, by a factor of 0.5%error for 20% production rate changes. Nonetheless, reasonable control performance can be obtained using simple temperature for production rate variations. On the contrary, the feed composition disturbances are more difficult to handle. It takes almost twice the time span (~ 10 h) to settle the transient responses. However, the steady-state offsets in the product composition are much smaller as compared to the flow disturbances. Despite having relatively symmetric responses for temperatures, compositions ($X_{B1,MeAc}$ and $X_{D3,MeOH}$) exhibit nonlinear behavior (Fig. 13B).

5. Conclusion

In this work, design and control of methyl acetate hydrolysis plant is explored. The low chemical equilibrium constant and unfavorable boiling point ranking of the reactant (MeAc is the lightest pure component) lead to a new process configuration which is an improved version of existing ones. Next, a systematic design procedure is proposed to complete the preliminary design based on the total annual cost (TAC). Two dominate design variables are identified and they are: recycle flow rate (F_R) and the overhead impurity of acetic acid $(X_{D2,HAc})$ in the HAc dehydration column (i.e., the 2nd column in our notation). Quantitative comparison is made between the proposed one and a literature example (the hybrid system of Lee, 2002) and the results show that 50% energy saving can be obtained in the reactive distillation column alone. Finally, the operability of the proposed process flowsheet is tested for feed flow and feed composition disturbances. The results show that reasonable control performance can be obtained using simple temperature control scheme.

Notation

a_i	activity coefficient for each component <i>i</i>
Da	Damköhler number
F_d	factor for design type
F_m	factor for radiant tube material
F_p	factor for design pressure
F_R	recycle flow rate

FR _{H2} O/MeAc	feed ratio of total water flow to total methyl acetate flow
HAc	acetic acid
k f	forward rate constant
kr	backward rate constant
K	controller gain
K _i	adsorption equilibrium constants for each com-
1	ponent <i>i</i>
Kea	equilibrium constant for the hydrolysis reaction
K_{μ}	ultimate gain
$m_{\rm cat}$	catalyst weight
MeAc	methyl acetate
MeOH	methanol
Mi	molecular weight of component <i>i</i>
N _{rxn}	number of trays in the reactive section
N_S	number of trays in the stripping section
N_{T2}	total number of trays in the 2nd column
N_{T3}	total number of trays in the 3rd column
NF_{H_2O}	water feed location
NF _{MeAc}	acetate feed location
NF ₂	feed location in the 2nd column
NF ₃	feed location in the 3rd column
P_u	ultimate frequency
Q_R	reboiler duty
R	reaction rate
R_i	reaction on tray <i>i</i>
R _{tot}	total reaction in the column
Т	reaction temperature
TAC	total annual cost
X_B	liquid mole fraction in the bottom product
X_D	liquid mole fraction in the distillate
$X_{D2, HAc}$	the overhead specification of acetic acid in the
	2nd column

Greek letter

 τ_I integral time

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Appendix A. TAC calculation

The evaluation of equipments follows the procedure of Douglas (1988) and specific equations of Elliott and Luyben (1996), Chiang et al. (2002), and Tang et al. (2005). A payback period of 3-year is assumed and a M&S index of 1108.1 (the year of 2002) is applied in the calculation. Materials of construction are stainless steel. The equipment is sized as follows:

(1) Reboiler heat transfer area (A_R)

$$A_R(\text{ft}^2) = \frac{Q_R}{U_R \cdot \Delta T_R},\tag{A.1}$$

where Q_R (Btu/h) is the reboiler duty, the overall heattransfer coefficient U_R is assumed 250 Btu/(h*ft²), and the temperature driving force ΔT_R (F) in the reboiler depends on the steam.

(2) Condenser heat transfer area (A_C)

$$A_C(\mathrm{ft}^2) = \frac{Q_C}{U_C \cdot \Delta T_C},\tag{A.2}$$

where Q_C (Btu/h) is the condenser duty, the overall heattransfer coefficient U_C is assumed 150 Btu/(h * ft²), and the log-mean temperature driving force ΔT_C (F) depends on the dew points and bubble points for a total condenser. (3) Column length (L_C)

$$L_C(\mathrm{ft}) = 2.4N_T,\tag{A.3}$$

where N_T is the total number of trays.

The capital and operating costs are calculated according to

(1) Column cost

Column cost [\$]

$$=\frac{M\&S}{280}(101.9D_C^{1.066}L_C^{0.802}(2.18+F_C)),\tag{A.4}$$

where $F_C = F_m F_p = 3.67$.

(2) Tray cost

Tray cost
$$[\$] = \frac{M\&S}{280} (4.7D_C^{1.55}L_CF_C),$$
 (A.5)

where $F_C = F_s + F_t + F_m = 1 + 1.8 + 1.7$. (3) Heat exchanger cost

Heat exchanger cost
$$[\$] = \frac{M\&S}{280} (A^{0.65} (2.29 + F_C)),$$
(A.6)

where $F_C = (F_d + F_p)F_m = (1.35 + 0) \times 3.75$ for the reboiler and $F_C = (F_d + F_p)F_m = (1 + 0) \times 3.75$ for the condenser.

(4) Steam cost

steam cost [\$/year] =
$$\frac{\$2.28}{1000 \text{ lb}} \times \left(\frac{Q_H}{947.0}\right) \left(\$150\frac{\text{h}}{\text{year}}\right)$$

for RD column, (A.7)
steam cost [\$/year] = $\frac{\$3.00}{1000 \text{ lb}} \times \left(\frac{Q_H}{905.5}\right) \left(\$150\frac{\text{h}}{\text{year}}\right)$
for 2nd column, (A.8)
steam cost [\$/year] = $\frac{\$2.45}{1000 \text{ lb}} \times \left(\frac{Q_H}{934.7}\right) \left(\$150\frac{\text{h}}{\text{year}}\right)$

for 3rd column.

(5) Cooling water cost

Cooling water cost
$$\left[\frac{\$}{\text{year}}\right]$$

= $\frac{\$0.03}{1000 \text{ gal}} \left(\frac{1 \text{ gal}}{8.34 \text{ lb}}\right) \left(\frac{Q_C}{30}\right) \left(\$150\frac{\text{h}}{\text{year}}\right).$ (A.10)

(A.9)

(6) Catalyst cost (assuming a catalyst life of 3 months)

Catalyst cost [\$] = catalyst loading [lb]
$$\times 3.5 \frac{\text{\$}}{\text{lb}}$$
. (A.11)

Appendix B. Process flowsheet for the hydrolysis plant with the "direct" separation sequence

In the flowsheet, we use the same RD column and explore the effect of separation sequencing on the total annual cost. Thus, we have the same inlet and outlet streams for the "direct" separation sequence. The design parameters become: the total number of trays and feed tray location of the 2nd column (N_{T2} & NF₂) and the 3rd column (N_{T3} & NF₃). Given the production rate and product specifications, the design steps are

(1) Pick a total number of trays in the 2nd column (N_{T2}) .



Fig. B1. Effects of total number of trays and feed tray location on TAC for the direct separation sequence with perturbation from nominal steady state for: (A) 2nd column, (B) 3rd column.



Fig. B2. Optimized process flowsheet with the "direct" separation sequence for the hydrolysis system.

Table B1 Comparison of TAC with "direct" and "indirect" separation sequences

Sequence	Indirect	Direct
N _{T2}	15	28
NF ₂	14	15
TAC ^{2nd column} (\$1000/year)	654.49	463.5
N _{T3}	27	19
NF ₃	11	15
TAC ^{3rd column} (\$1000/year)	409.9	684.6
TAC ^{2nd} column + TAC ^{3rd} column	1064.4	1148.1

- (2) Guess a feed location in the 2nd column (NF₂) and change the reflux flow (R) and heat input (Q_R) until the product specification is met.
- (3) Go back to (2) and change NF_2 until the TAC is minimized.
- (4) Go back to (1) and vary N_{T2} until the TAC is minimized.
- (5) Pick a total number of trays in the 3rd column (N_{T3}) .
- (6) Guess a feed location in the 3rd column (NF₃) and then change the reflux flow (R) and heat input (Q_R) until the product specification is met.
- (7) Go back to (6) and change NF_3 until the TAC is minimized.
- (8) Go back to (5) and vary N_{T3} until the TAC is minimized.

Fig. B1 shows how the effects of total number of trays and feed tray locations in the separation section (2nd and 3rd columns) to the TAC. The 2nd column has 19 trays with NF₂ = 15. The 3rd column has a total 28 trays with the feed introduced to the middle section of the column, i.e., NF₃ = 15. The optimized flowsheet can be obtained by adjusting these design parameters and the result is given in Fig. B2. Table B1 summarizes design parameters and corresponding TAC for the distillation columns for these two, "indirect" and "direct", separation sequences.

References

- Abrams, D.S., Prausnitz, J.M., 1975. Statistical thermodynamics of liquid mixture: a new expression for the excess Gibbs energy of partly or completely miscible system. A.I.Ch.E. Journal 21, 116.
- Al-Arfaj, M.A., Luyben, W.L., 2000a. Effect of number of fractionating trays on reactive distillation performance. A.I.Ch.E. Journal 46 (12), 2417.
- Al-Arfaj, M.A., Luyben, W.L., 2000b. Comparison of alternative control structures for an ideal two-product reactive distillation column. Industrial & Engineering Chemistry Research 39 (9), 3298.
- Al-Arfaj, M., Luyben, W.L., 2004. Plantwide control for TAME production using reactive distillation. A.I.Ch.E. Journal 50 (7), 1462.
- Barbosa, D., Doherty, M.F., 1988. Simple distillation of homogeneous reactive mixtures. Chemical Engineering Science 43 (3), 541.
- Chen, F., Huss, R.S., Malone, M.F., Doherty, M.F., 2000. Simulation of kinetic effects in reactive distillation. Computers & Chemical Engineering 24 (11), 2457.
- Chiang, S.F., Kuo, C.L., Yu, C.C., Wong, D.S.H., 2002. Design alternatives for the amyl acetate process: coupled reactor/column and reactive distillation. Industrial & Engineering Chemistry Research 41, 3233.
- Doherty, M.F., Buzad, G., 1992. Reactive distillation by design. Trans. IChemE 70 (A5), 448.
- Douglas, J.M., 1988. Conceptual Design of Chemical Process. McGraw-Hill, New York, USA.
- Elliott, T.R., Luyben, W.L., 1996. Quantitative assessment of controllability during the design of a ternary system with two recycle streams. Industrial & Engineering Chemistry Research 35, 3470.
- Fuchigami, Y., 1990. Hydrolysis of methyl acetate in distillation column packed with reactive packing of ion exchange resin. Journal of Chemical Engineering of Japan 23 (3), 354.
- Han, S.J., Jin, Y., Yu, Z.Q., 1997. Application of a fluidized reaction distillation column for hydrolysis of methyl acetate. Chemical Engineering Journal 66 (3), 227.
- Hayden, J.G., O'Connell, J.P., 1975. A generalized method for predicting second virial coefficients. Industrial & Engineering Chemistry Process Design and Development 14, 209.
- Hoyme, C.A., Holcomb, E.F., 2003. Reactive distillation process for hydrolysis of esters. US Patent 6518465.
- Hung, S.B., Lee, M.J., Tang, Y.T., Chen, Y.W., Lai, I.K., Hung, W.J., Huang, H.P., Yu, C.C., 2006. Control of different reactive distillation configurations. A.I.Ch.E. Journal 52 (4), 1423.
- Kaymak, D.B., Luyben, W.L., 2004. Quantitative comparison of reactive distillation with conventional multiunit reactor/column/recycle systems for different chemical equilibrium constants. Industrial & Engineering Chemistry Research 43 (10), 2493.

- Kim, K.J., Roh, H.D., 1998. Reactive distillation process and equipment for the production of acetic acid and methanol from methyl acetate hydrolysis. US Patent 5770770.
- Lee, M.M., 2002. Method and apparatus for hydrolyzing methyl acetate. US Patent 20020183549A1.
- Luyben, W.L., Tyreus, B.D., Luyben, M.L., 1998. Plantwide Process Control. McGraw-Hill, New York.
- Luyben, W.L., Pszalgowski, K.M., Schaefer, M.R., Siddons, C., 2004. Design and control of conventional and reactive distillation processes for the production of butyl acetate. Industrial & Engineering Chemistry Research 43 (25), 8014.
- Okasinski, M.J., Doherty, M.F., 1998. Design method for kinetically controlled, staged reactive distillation columns. Industrial & Engineering Chemistry Research 37 (7), 2821.
- Pöpken, T., Götze, L., Gmehling, J., 2000. Reaction kinetics and chemical equilibrium of homogeneously and heterogneously catalyzed acetic acid esterification with methanol and methyl acetate hydrolysis. Industrial & Engineering Chemistry Research 39 (7), 2601.
- Pöpken, T., Steinigeweg, S., Gmehling, J., 2001. Synthesis and hydrolysis of methyl acetate by reactive distillation using structured catalytic packings: experiments and simulation. Industrial & Engineering Chemistry Research 40 (6), 1566.
- Shen, S.H., Yu, C.C., 1994. Use of relay-feedback test for automatic tuning of multivariable systems. A.I.Ch.E. Journal 40, 627.
- Sneesby, M.G., Tade, M.O., Smith, T.N., 1999. Two-point control of a reactive distillation for composition and conversion. Journal of Process Control 9 (1), 19.

- Song, W., Venimadhavan, G., Manning, J.M., Malone, M.F., Doherty, M.F., 1998. Measurement of residue curve maps and heterogeneous kinetics in methyl acetate synthesis. Industrial & Engineering Chemistry Research 37 (5), 1917.
- Sundmacher, K., Kienle, A., 2003. Reactive Distillation. Wiley-VCH, Weinheim.
- Tang, Y.T., Chen, Y.W., Huang, H.P., Yu, C.C., Hung, S.B., Lee, M.J., 2005. Design of reactive distillations for acetic acid esterification. A.I.Ch.E. Journal 51 (6), 1683.
- Tung, S.T., Yu, C.C., 2007. Effects of relative volatility ranking to the design of reactive distillation columns. A.I.Ch.E. Journal 53 (5), 1278–1297.
- Wang, J., Ge, X., Wang, Z., Jin, Y., 2001. Experimental studies on the catalytic distillation for hydrolysis of methyl acetate. Chemical Engineering & Technology 24 (2), 155.
- Wu, K.L., Yu, C.C., 1996. Reactor/separator processes with recycle: 1. Candidate control structure for operability. Computers & Chemical Engineering 20 (11), 1291.
- Xiao, J., Liu, J., Li, J., Jiang, X., Zhang, Z., 2001. Increase MeOAc conversion in PVA production by replacing the fixed bed reactor with a catalytic distillation column. Chemical Engineering Science 56 (23), 6553.
- Yi, C.K., Luyben, W.L., 1997. Design and control of coupled reactor/column systems—part 3. A reactor/stripper with two columns and recycle. Computers & Chemical Engineering 21, 69.