CHEMICAL ENGINEERING TRANSACTIONS
VOL. 69, 2018

A publication of
AIDIC
The Italian Association
of Chemical Engineering
Online at www.aidic.it/cet

Guest Editors: Elisabetta Brunazzi, Eva Sorensen
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ISBN 978-88-95608-66-2; **ISSN** 2283-9216
DOI: 10.3303/CET1869097

Novel Dual-Effect Side Reactive Distillation for Improving Energy Efficiency of Methyl Acetate Hydrolysis Process

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In a polyvinyl alcohol (PVA) plant, reaction stoichiometry indicates that equal molar of methyl acetate (MA) is generated for every mole of PVA produced. One possible way is to convert MA back to acetic acid and methanol, which are raw materials of PVA plant, using MA hydrolysis. Tough environmental regulations, intense competition, and expensive fossil energy use have prompted efforts to retrofit the existing hydrolysis processes to reduce their energy requirements. Thus, in this paper, a novel dual-effect side stream reactive distillation was proposed to reduce the energy requirements. The design and optimization procedures using the response surface methodology, which can handle both structure and operating variables simultaneously, were employed for retrofit design with particular emphasis on simple and efficient efforts. This was found to be a simple and effective optimization methodology for a complex system. The simulation work was performed using simulator Aspen Plus V8.6. Furthermore, carbon dioxide (CO_2) emissions were considered and calculated when retrofitting an existing MA process to the proposed sequence. As a result, the proposed retrofitted sequence resulted in operating cost savings of 54% compared to the existing sequence. The short payback period of 2 months and reduced CO_2 emissions of up to 52% showed that the proposed sequence is an attractive option for retrofitting in industrial implementation. This sequence can be also employed for grass-root designs.

1. Introduction

Reactive distillation is one of the most attractive proven configurations of process intensification, in which the reaction and distillation occur at the same time and in the same location (Long et al., 2016). Compared to conventional reaction-distillation sequences, the so-called reactive distillation processes enable higher reactant conversion, product selectivity, as well as lower energy, water, and solvent consumption, leading to reduced investment and operating costs (Keller, 2014). Some of these benefits are realized by using the reaction to improve separation (e.g., overcoming azeotropes, reacting away contaminants, avoiding or eliminating difficult separations) while others are realized by using separation to improve reactions (e.g., enhancing overall rates, overcoming reaction equilibrium limitations, improving selectivity, removing catalyst poisons)—with the maximum effect being achieved when both aspects are important (Kiss, 2013).

Large amount of methyl acetate (MA) is produced as by-product in the production of polyvinyl alcohol (PVA), around 1.68 times as the PVA product by weight (Lin et al., 2008). One approach is to hydrolyse MA back to acetic acid (HAc) and methanol (MeOH), which are raw materials for the PVA plant. Because the MA hydrolysis reaction is reversible and the reaction equilibrium constant is relatively small, high energy is required in the conventional process. Reactive distillation is a favourable alternative for the advantages compared to the conventional fixed-bed process: (a) lower capital investment, (b) lower energy consumption, and (c) higher product yields (Xie et al., 2014). A total reflux operation with product withdrawal from the bottom of the reactive distillation column was selected as a good candidate for this hydrolysis reaction (Lee et al., 2010).

However, due to high operating cost, a novel dual-effect side stream reactive distillation (DESSRC) was proposed to reduce the energy requirements significantly in this paper. The design and optimization procedures using the response surface methodology, which can handle both structure and operating variables simultaneously, were employed for retrofit design with particular emphasis on simple and efficient efforts.

Please cite this article as: Nguyen L., Lee M., 2018, Novel dual-effect side reactive distillation for improving energy efficiency of methyl acetate hydrolysis process, Chemical Engineering Transactions, 69, 577-582 DOI: 10.3303/CET1869097

Furthermore, carbon dioxide (CO_2) emissions were considered and calculated when retrofitting an existing MA process to the proposed sequence.

2. Existing process

2.1 Phase equilibrium

There are four components in the studied system including two reactants: MA and water (H2O); and two products, HAc and MeOH. The UNIQUAC-HOC property method that uses the Hayden–O'Connell equation of state as the vapor phase model and UNIQUAC for the liquid phase was used for the prediction of the vapor–liquid equilibrium (VLE) of these simulations. Dimerization affects VLE, vapor phase properties, such as enthalpy and density, and liquid phase properties, such as enthalpy. The Hayden–O'Connell equation reliably predicts the solvation of polar compounds and dimerization in the vapor phase that occurs with mixtures containing carboxylic acids (Aspen Technology, 2009). The parameters for the UNIQUAC and HOC models are listed in Tables 1 and 2, respectively (Lee et al., 2010).

Table 1: UNIQUAC model parameters

(i,j)	a_{ij} (K)	a_{ji} (K)	b_{ij} (K)	b_{ji} (K)	c_{ij} (K^{-1})	c_{ji} (K^{-1})
(1,2)	-0.9704	2.0346	-390.26	-65.245	0.003061	-0.003157
(1,3)	0.4364	-1.1162	62.19	-81.848	-0.0002724	0.001331
(1,4)	0.05101	0.2936	-422.38	98.120	0.0002402	0.00007674
(2,3)	0.7101	-0.7248	-62.97	-326.20	-0.001167	0.002355
(2,4)	-3.1453	2.0585	575.68	-219.04	0.006071	-0.007015
(3,4)	-0.01014	-0.9630	-593.70	265.83	0.002161	-0.0002013

1: HAc; 2: MeOH; 3: MA; 4: H_2O. UNIQUAC model:

$$\ln\gamma_i = \ln\frac{\phi_i}{x_i} + \frac{z}{2}q_i\ln\frac{\theta_i}{\phi_i} + l_i - \frac{\phi_i}{x_i}\sum_{j=1}^{nc}x_j l_j + q_i^{'}\left[1 - \ln\left(\sum_{j=1}^{nc}\theta_j^{'}\tau_{ji}\right) - \sum_{j=1}^{nc}\frac{\theta_j^{'}\tau_{ij}}{\theta_k^{'}\tau_{kj}}\right)\right]$$

Where $\phi_i = \dfrac{r_i x_i}{\sum_{k=1}^{nc} r_k x_k};\ \theta_i = \dfrac{q_i x_i}{\sum_{k=1}^{nc} q_k x_k};\ \theta_i^{'} = \dfrac{q_i^{'} x_i}{\sum_{k=1}^{nc} q_k^{'} x_k}$

and $\tau_{ij} = a_{ij} + \dfrac{b_{ij}}{T} + c_{ij}T;\ l_i = \dfrac{z}{2}(r_i - q_i) - (r_i - 1);\ z = 10$

Table 2: Hayden and O'Connell association parameters

Component	HAc	MeOH	MA	H_2O
HAc	4.50	2.50	2.00	2.50
MeOH	2.50	1.63	1.30	1.55
MA	2.00	1.30	0.85	1.30
H_2O	2.50	1.55	1.30	1.70

2.2 Reaction kinetic

The hydrolysis of MA is an endothermic reversible reaction, which is shown below:

$$\text{MA} + H_2O \Leftrightarrow \text{HAc} + \text{MeOH} \qquad (1)$$

The reaction kinetic with Amberlyst 15 ion exchange resin as catalyst of above reaction was found in Popken et al. (2000). It was found that the adsorption-based model fits the experimental data better. The information of this kinetic model based on activity are shown below (Lin et al., 2008):

$$
\begin{aligned}
&R = m_{cat} \times \frac{k_f a'_{\mathrm{MA}} a'_{\mathrm{H_2O}} - k_r a'_{\mathrm{HAc}} a'_{\mathrm{MeOH}}}{(a'_{\mathrm{MA}} + a'_{\mathrm{H_2O}} + a'_{\mathrm{HAc}} + a'_{\mathrm{MeOH}})^2}; a'_i = \frac{K_i a_i}{M_i} \\
&K_{\mathrm{MA}} = 4.15; K_{\mathrm{H_2O}} = 5.24; K_{\mathrm{HAc}} = 3.15; K_{\mathrm{MeOH}} = 5.64 \\
&k_f = 6.127 \times 10^5 \exp\left(\frac{-63730}{RT}\right) \\
&k_r = 8.498 \times 10^6 \exp\left(\frac{-60470}{RT}\right)
\end{aligned}
\tag{2}
$$

The overall reaction rate 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 MA 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 (Lin et al., 2008). At each reactive section (i.e., reactive tray and reactive reflux drum), the catalyst was assumed 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. The simulation work was performed using simulator Aspen Plus V8.6.

2.3 Existing process description and analysis

There are two binary azeotropes in the system: (1) MA and MeOH form a minimum-boiling azeotrope with the composition of 65.9 mol% MA at 53.7 °C, and (2) MA and H_2O forms minimum-boiling azeotrope with the composition of 89.0 mol% MA at 56.4 °C (Lin et al., 2008). At atmospheric pressure, 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

It is found that, although one product (HAc) is the heavy-boiler, however, the other product is in the middle of the boiling point ranking. Thus, it is more difficult to come up with the overall design flowsheet. With a low equilibrium constant (Keq ~ 0.013), it is not likely to obtain high purity MeOH product under the "neat" operation (Lin et al., 2008). Besides, the reaction section should be located at where the reactant is dominant. Note that the reflux drum has a large holdup with substantial amount of MA. Therefore, total reflux design (Fuchigami, 1990) with upper section reactive zone seems to be a reasonable choice, especially one of the reactants being the lightest pure component. Furthermore, locating the reaction section in the top section can employ the internal heat integration, which utilizes the heat of reaction to separation. In particular, owing to endothermic reaction, the reaction section should be considered to location in the top section. Lee et al. (2010) proposed the overall design flowsheet as in Figure 1.

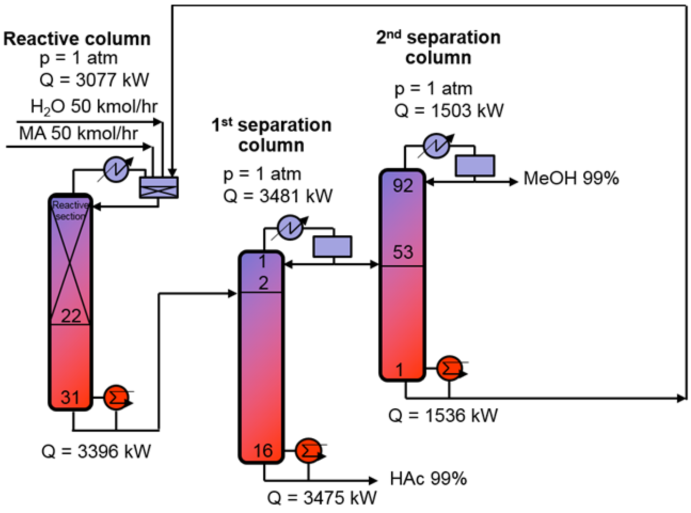

Figure 1: Simplified flow sheet illustrating the existing MA hydrolysis process.

The overall flowsheet includes a reactive distillation column and two other columns for purification of AA and MeOH. The two fresh feeds are all entered into the reflux drum of the reactive distillation column under total reflux operation with the upper section of this column all as reaction section. All products and the excess water are all withdrawn from the column bottoms to downstream separation system consisting of two columns. Because there is negligible MA in this feed stream to the downstream system, the separation should be easy because of no azeotrope in the ternary system of HAc, H_2O, and MeOH. The bottom of the second separation column is designed to avoid tangent pinch at the pure water end; thus, it contains mostly water with some acetic acid component. This stream is designed to be recycled back to the reactive distillation column. This process allows a high MA conversion avoiding the recycling of azeoptropic mixtures, which are otherwise formed in large quantities.

3. Proposed configuration

Because distillation is a separation process requiring large energy consumption and capital investment, distillation retrofit projects are performed more often than the grass-roots projects (Gadalla et al., 2003). In this paper, the retrofit purpose was performed to improve the energy efficiency in the MA hydrolysis process with the following assumptions: all columns are already fully used; the highest performance internals are already employed in all existing distillation columns; all products are kept constant in terms of recovery and purity in retrofit design.

3.1 Side stream reactive distillation column

Figure 2 presents the composition profiles of ($MeOH+H_2O$) and HAc in the existing reactive distillation. The composition of intermediate components (MeOH and H_2O) in the first column increases below the reactive section. On the other hand, moving further down the column, the composition of these intermediate components decreases again as the composition of the less-volatile component (HAc) increases. Therefore, the composition of intermediate components reaches a peak only to be remixed. This remixing that occurs in the reactive column is a source of inefficiency in the separation.

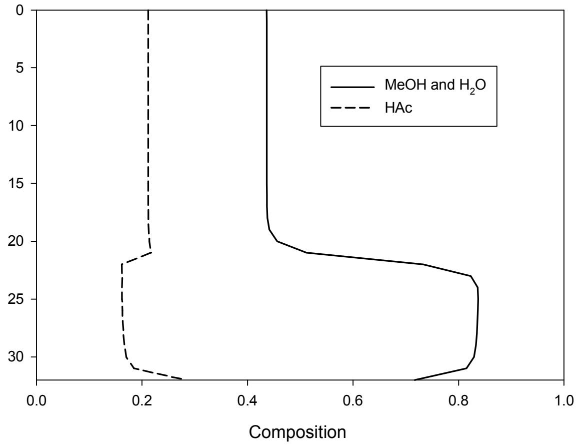

Figure 2: Composition profile

In that case, side-stream reactive column (SSRC), in which the intermediate component is withdrawn by a side draw (Figure 3), is considered to more energetically favorable alternative to avoid this phenomenon, possibly leading to substantial energy consumption in the existing sequence. In particular, the reactive column can be retrofitted to a SSRC, and then the side liquid stream also is fed into the first separation column. This can generate the multi-feed streams for the next column in a most efficient way by fully utilizing the advantages of SSRC. Moreover, the next column can take an advantage of improved separation efficiency from the prefractionated multi-feed streams. Note that to optimize the retrofitted SSRC, the flow rate and location of the side liquid stream are varied. The side stream is normally withdrawn at the tray where composition of intermediate components reaches the peak of the composition profile. Moreover, the location of that stream in the first separation column also need to be optimized so that its composition is matched to the feed tray composition in that column to reduce the mixing effect. The response surface methodology was used to optimize the proposed configuration. The operating cost saving generated from this arrangement was

14.2%, which was comparable to the performance of the existing arrangement. The modification is simple but effective.

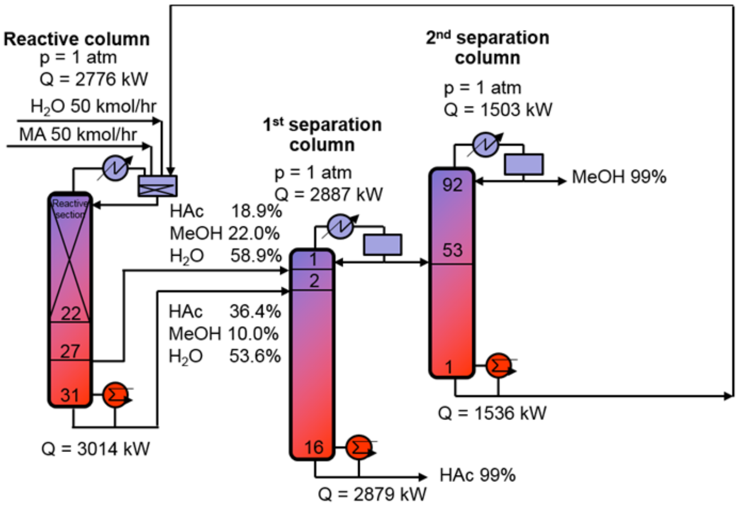

Figure 3: Simplified flow sheet illustrating the retrofitted process with SSRC.

3.2 Dual effect side stream reactive distillation column

A dual-effect distillation system allows a significant reduction in energy consumption, since the condensers and reboilers of different columns can be integrated thermally. Here this method is utilized to improve the performance of the existing system. The overhead vapor of the first separation column was used as a heat source to the reboiler of the SSRC (shown in Figure 4), which forms DESSRC congiguration. In this case, the pressure of the first separation column was set by the bubble point pressure of the overhead distillate at a temperature 10°C higher than the bottom temperature of the SSRC. The saving in operating cost obtained from the retrofitted DESSRC configuration is calculated as 54% when compared to that of the current sequence. The prices of cooling water and low-pressure steam used in this study correspond to 0.35 \$/GJ and 13.28 \$/GJ, respectively (Turton et al., 2012).

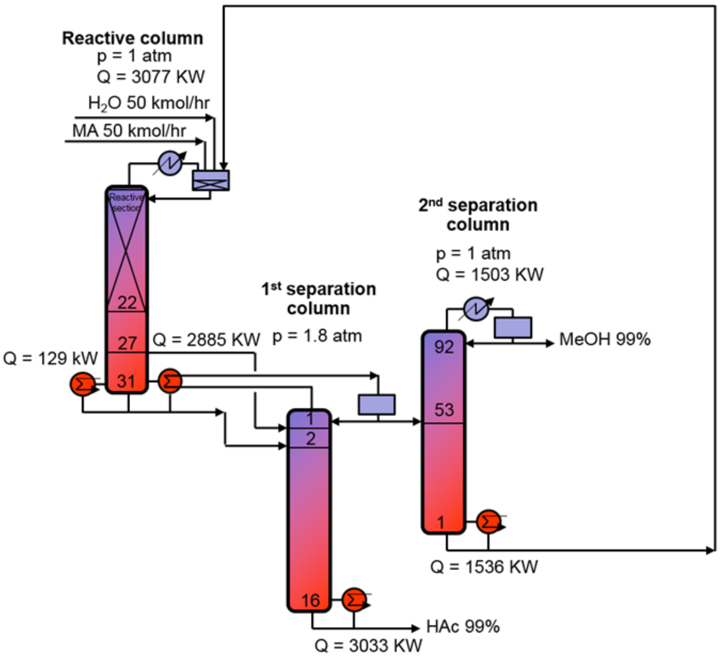

Figure 4: Simplified flow sheet illustrating the retrofitted process with DESSRC.

With the proposed DESSRC sequence, the simple payback period corresponds to 2 months. This payback period is economically attractive because of high energy costs saving and the re-use of most of the existing equipment. This sequence can be applied not only for retrofit design but also for grass-root designs. The decrease in CO_2 emissions that is linked to the lower energy requirement is another key advantage with respect to the retrofit of existing sequence. A method proposed by Gadalla et al. (2005) was employed to estimate the CO_2 emissions. The CO_2 emissions are substantially reduced when using the proposed sequence. Specifically, a saving of 52% in the CO_2 emission was achieved. The value of the CO_2 emission saving is slightly smaller than that of the reboiler duty saving because the higher temperature steam is needed in the first separation column.

4. Conclusions

This paper proposed a novel SSRC allowing to generate multi-feed streams for retrofitting the MA hydrolysis process. This SSRC was then integrated efficiently using duel-effect concept. After a preliminary design, the proposed configuration was then optimized and implemented simply and efficiently by the response surface methodology using Aspen Plus and Minitab. This was found to be a simple and effective optimization methodology for a complex system. The use of SSRC can have many benefits, such as decreasing the energy requirement in the reactive distillation and the first separation column and reducing CO_2 emissions. Notably, the retrofitted DESSRC sequence resulted in operating cost and CO_2 emissions savings of 54% and 52%, respectively, compared to the existing sequence.

Acknowledgments

This work was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education (2018R1A2B6001566), Priority Research Centers Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education (2014R1A6A1031189), and the R&D Center for Reduction of Non-CO_2 Greenhouse Gases (201700240008) funded by the Ministry of Environment as a ‘Global Top Environment R&D Program’.

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