Production of High-purity Ethyl Acetate using reactive distillation:
Experimental Validation and Start-up procedure

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Abstract: The production of high-purity ethyl acetate (EtAc) using reactive distillation (RD) is studied experimentally in a pilot-scale plant. The objectives are two folds: (1) to validate the appropriateness of the type-II RD flowsheet, a complex two-column configuration with liquid phase split, developed by Tang et al. (2005) and (2) to provide a startup procedure for continuous operation. This pilot-scale plant consists of one RD column and a downstream stripper with a decanter in between. The two columns are equipped with temperature, flow, and level measurements and control is executed in a Delta-V process control computer. The alcohol feed is of industrial grade ethyl alcohol (95.5 wt%; below azeotropic composition) and the acid feed contains 99wt% of acetic acid with water as impurity. Very stringent specification on EtAc is required: 99.00 wt% EtAc with acetic acid less than 100 ppm. Five experimental runs were performed and the results show that, with a correct start-up procedure, high-purity acetate can be produced in a straightforward manner. *Copyright © 2007 IFAC*

Keywords: ethyl acetate, reactive distillation, startup, pilot plant test, esterification

1. INTRODUCTION

Ethyl acetate (EtAc) is an important organic solvent widely used in the chemical industry. One of the key issues in the production of acetates is the equilibrium limitation from the reversible reaction of acetic acid and alcohols. This motivates the use of reactive distillation (RD) to achieve high conversion. The reactive distillation is featured with its merits not only in promoting the reaction conversion, but also in reducing both the capital and operational costs as its multifunctional nature. The RD process appeared first in Keyes (1932) for the production of EtAc and became a new focus in 80's, since Eastman chemical company owned a commercial reactive distillation process for the production of methyl acetate. Later on, extensive researches on the RD process appeared in the literature. At the same time, successful commercial processes that apply reactive distillation are installed for producing various chemicals such as

methyl tert-butyl ether (MTBE), cumene, ethyl-benzene and 3-methyl-1-Butene, etc. In the work of Kenig et al. (2001), they studied by simulation and experiments on one single column with 80 bubble cup trays. Klöker et al. (2004) conducted experiments and simulation on two RD columns of different sizes. The common weakness in above two studies is the low chemical conversion in the RD column and the low EtAc concentration in the product. In this work, the pilot-scale plant was fed with near azeotropic alcohol and industrial grade acetic acid. Water is contained in both feed as impurities. This plant is equipped with inventory and quality control loops to maintain the specified mass and stoichiometric balances of the chemicals.

2. PHYSICAL PROPERTIES

In the EtAc system, the mixtures exhibit non-ideal phase behaviors. There are three minimum-boiling binary and one minimum-boiling ternary azeotrope in the system. Figure 1 shows the RCM diagrams of this EtAc-EtOH-H_2O system. In this diagram, significant two-liquid (LL) phase envelope is observed. The ternary minimum boiling azeotrope lies closely to the boundary of LL envelope. It is interesting to see that, in EtAc system, the tie lines slop toward pure water node and, consequently, relatively pure water can be recovered from the LL separation. This implies that a decanter is desirable to remove water. The alcohol studied in this work is ethanol (EtOH), and corresponding products is ethyl acetate (EtAc). The reactions are reversible:

For EtAc system:

$$EtOH + HAc \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} EtAc + H_2O$$
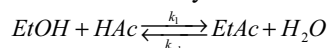
This is a solid acid catalyzed reaction with acidic ion-exchange resin (Amberlyst 35 wet; Rohm and Hass). In this work, the column base holdup is taken as 10 times of the tray holdup in the column. The flowsheet of this conceptual design is as shown in Figure 2. Steady-state simulations via the Aspen Plus show that this process yields high purity of EtAc as the products in the bottom of the stripper (the upper corner distillation region in Figure 1).
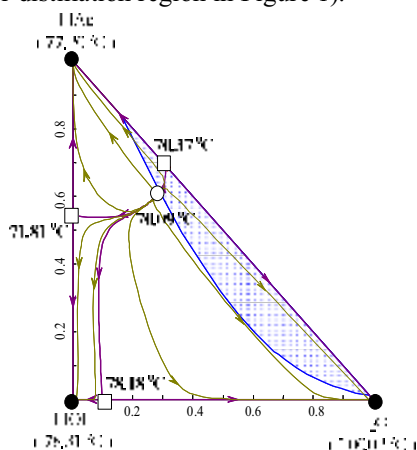

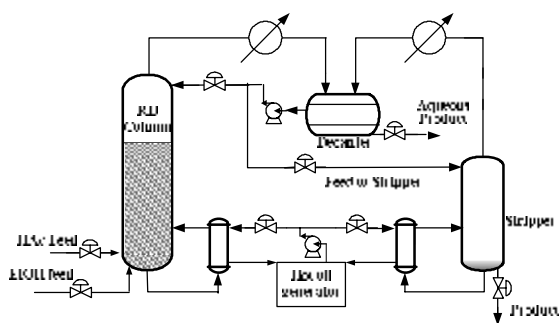Fig. 1. The RCM diagram of EtOH-EtAc-H_2O system.

Fig. 2. Process flowsheet of EtAc system.

3. PILOT PLANT

The experimental setup is shown in Figure 3 with a RD column in the middle, a stripper to the left, and a

decanter is placed in the lower left hand side. It was constructed with 316L stainless steel.

Fig 3. The experimental setup of reactive distillation system.

The rectifying section of the RD column and the stripper have a diameter of 55 mm and packed with structured packing. A special type of tray is used for the reactive tray, they are Jet Co-flow Packing Trays (JCPT) with two solid catalyst packings placed around the inner annular tube as shown in Fig.4.

Fig. 4. Jet Co-flow Packing Trays (JCPT) with Catalyst Package.

Each tray contains 88g wet Amberlyst 35 catalyst. In the RD column base, it is filled with 880g catalyst, 10 times to that of the catalyst weight in each tray. The rectifying section in the RD (Fig. 5A) and the stripper are filled with random packing (Figure 5B).

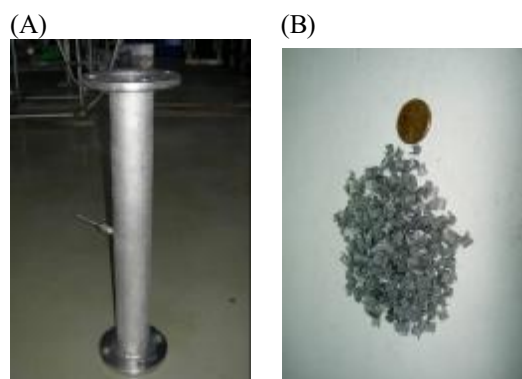(A)   (B)

Fig. 5. (A) rectifying section and stripper (1 m) with thermocouple nozzles, (B) random packing.

For measuring the temperature profiles in the two columns, thermocouples are installed on the stripper

and the RD column. In the stripper, the thermocouples are enumerated from top to bottom and are labeled with TI-101 to 106. Similarly, in the RD column, the thermocouples are numbered from top to bottom in the rectifying section (TI-201 to 207) as well as in in the reactive zone (TI-208 to 213). Another important device, decanter, it is used to separate organic and aqueous phases, and remove water after phase separation. The operation condition is under room temperature. The construction of decanter is shown in Figure 6.
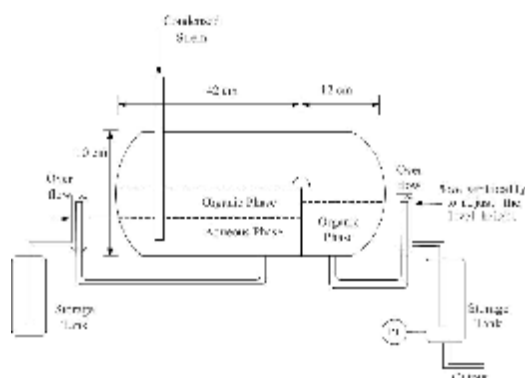

Fig. 6. Schematic of decanter and storage tank.

The U-tube can be moved vertically to adjust aqueous and organic levels. The organic-phase product overflowing over the weir in the decanter is sent to a storage tank whose level is controlled by manipulating the outlet flow from the decanter to the stripper. The reflux ratio (organic phase recycle flow/organic phase flow to stripper) is kept constant. The aqueous phase product (H_2O) is withdrawn from the system after liquid-liquid separation using U-tube based level control. The reboilers in the RD and the stripper is heated with hot oil in a closed circulation system (Fig. 2). The temperature of the heater is set to $180^\circ C$. The distribution of the flows are flow controlled. The base level of stripper is maintained by a U-tube level control and the RD base level is controlled by the heat input (Hung et al., 2006; Lai et al., 2006). For composition analysis, the liquid or condensed samples were taken from the column and/or decanter, and they are subsequently analyzed using gas chromatograph (GC).

4. START-UP PROCEDURE AND EXPERIMENTAL RESULTS

In this section, the effects of different start-up procedures on the production will be explored. Necessary conditions for a successful operation of the type II RD include:
1. The overhead vapor composition from the RD must lie in the two-liquid (LLE) zone and the liquid phases consist of a aqueous phase, rich of water, and the organic phase, rich in acetate.
2. The overhead vapor composition of the stripper must lie in the two-liquid (LLE) zone.
3. The organic phase composition should fall in the pure acetate part of the composition space, separated by a distillation boundary (Fig. 1).

In the following, the start-up procedures and the start-up conditions will be addressed in details.

4.1 Start-up procedure

The start-up of this type of RD is not as trivial as we originally thought. One of the reasons is already mentioned: we have to ensure phase separation in the decanter. Several trial runs with different conditions are conducted on this pilot plant. A systematic start-up procedure emerges with reproducible results for the production of high-purity product. It is found that the initial holdup conditions are essential in this start-up procedures and some of the temperatures in different parts of the columns are also important. The following steps summarize a reliable start-up procedure.

1. Initial charges:
   a. Fill the decanter (up to the weir height) well as the storage tank (up to 50% level; Fig. 6) with EtAc product.
   b. Fill the bottom of the stripper up to 50~75% level with EtAc product.
   c. Fill the RD column base up to 75% level with acid feed.

2. Utility systems:
   a. Turn on the hot oil system heater and the temperature is set to $180^\circ C$.
   b. Turn on the chilled water supply for the decanter and the temperature of chilled water is set to $10^\circ C$.

3. Heating up and fresh feeding:
   a. Heat up the RD column base by adjusting the hot oil flow rate manually (see Figure 7A, zone S1). Once the bottoms temperature reaches $100~110^\circ C$, start to feed the acid and alcohol to the RD column base (see Figure 7A, zone S2). By this procedure, the RD column base level is maintained and the reaction proceeds.
   b. The bottom of stripper is pre-heated gradually along with Step 3-a (see Figure 7B, zone S5).
   c. When the temperature of bottom rectifying section (TI-207) reaches $70~75^\circ C$, change the hot oil flow rate such that the stripper bottoms temperature is kept around 80oC (see Figure 7B, zone S6).

4. Reflux and adjustment:
   a. After the RD column top temperature (TI-201) reaches $72^\circ C$, open the reflux flow valve and send the organic phase flow to the stripper.
   b. Note that, at this moment, the RD column temperatures may exhibit certain degree of oscillation (see Figure 7A, zone S3).

c. Adjust the reboiler duty of the RD column such that the level in the column base is maintained.

d. Manipulate the heat input to the stripper such that the stripper bottoms temperature is above 81℃. The reason is that the in-flow of organic phase from the decanter will decrease the stripper temperature (see Figure 7B, zone S7a).

5. Product withdrawal:
a. Open the aqueous product valve to discharge the water-rich product when the aqueous-phase in the decanter accumulated to a certain amount.

b. Put the level control of the organic storage thak level on automatic. During the transient, the temperatures in the stripper is subject to disturbance (see Figure 7B, zone S7b).

c. Withdraw EtAc product from the stripper when the stripper bottoms temperature becomes greater than 81℃ or significant base level built-up is observed.

6. Fine tune:
a. Adjust the RD reflux flow rate such that the RD top temperature (TI-201) is to maintained in the range of 72~75℃.

b. Manipulate the heat input to the stripper reboiler to maintain the bottoms temperature around 81~84℃.

c. Two to three hours into the start-up, the system is reaching a steady state (see Figure 7A, zone S4 and Figure 7B, zone S8). At this stage, the control of the base level in the RD is switched to automatic. Also, the organic reflux flow back to the RD is controlled at a constant ratio to the flow rate to the striper.

7. Composition analysis:
a. Keep this steady-state for 2~3 hours. During this period, samples from the RD column and stripper and from the organic/aqueous phase are collected for subsequent analysis.

4.2 Experimental Results

For this heterogeneous reactive distillation system with two liquid phase, it is important to obtain phase separation in the decanter and initial charges play a critical role for this criterion. The effects of initial charges to the start-up are investigated. Five experiments with different initial charges and different operating condition were performed and Table 1 summarizes the feed condition, initial holdup compositions, and operating conditions of each run. It is clear that, except for the first run (Run#1), high-purity acetate can be produced from the pilot-scale type-II process. The evolution of tray temperatures in the RD and the stripper is shown in Fig. 8 for a typical start-up time of ~4 hours. According to the

start-up procedure, the duration is divided into four distinct zones (e.g. Figure 7A, zone S1~S4 for the RD column, Figure 7B, zone S5~S8 for the stripper). Fig. 7 shows the temperature responses in the RD column and the stripper of one typical run (Run 5).
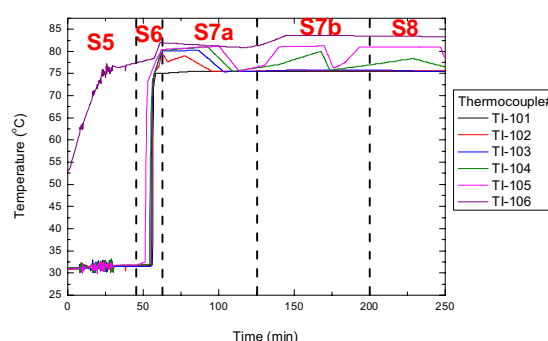
(A)
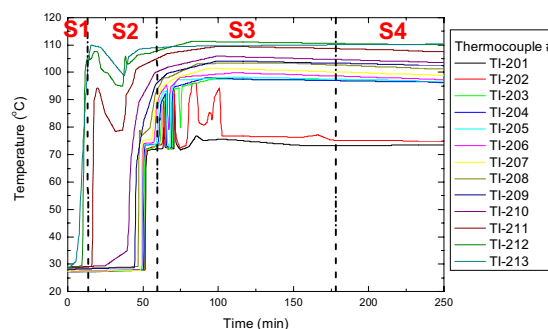
(B)

Fig. 7. The start-up temperature profile in (A) RD column, and (B) Stripper.

It shows that in the first hour, the temperatures front propagated toward the top of the RD column and the development of the temperature front lags behind that of the RD column, because it was heated up a little later. At the introduction of reflux flow to the RD column, tray temperature oscillation was observed, especially for those close to the column top. Similarly, the feeding of the organic product into the stripper also casued stripper temperature to oscillate, at a lower frequency. However, RD tray temperatures stabilized almost 2 hours into the start-up. Figure 8 shows the steady-state composition (aqueous, organic, RD column base, stripper base) profiles in the quaternary composition space for all 5 runs. From this figure, Run 2~Run 5 have high purity of acetate, but, the purity of the acetate from Run 1 is much lower than expected. As one can see, in Runs 2~4, the top compositions in the RD column all fall inside the distillation region which containing pure acetate (see Zone A of Figure 9). The RD top composition of Run 5, after mixing with the overhead vapor from the stripper, also crossed the boundary as can be seen in the aqueous composition. That means the organic feed and the product of the stripper in Runs 2~5 are in the same distillation region. On the other hand, Run 1 has an aqueous composition in Zone D, which is different from those of Runs 2~5 and far off the boundary line connecting the EtOH-H$_2$O and EtOH-

EtAc-H$_2$O azetropes. A likely scenario is that, despite having achieving certain degree of LLE, the overall organic phase composition has not reached equilibrium, as a result of initial charge to the decanter. However, this organic product was fed to the stripper for further purification and consequently, a high purity acetate has never been obtained.

Table 1 The Feed Condition, Initial Holdup Composition, Operating Condition of Each Run.

Run #	1	2	3	4	5
Date yy-mm-dd	2006 04-17	2006 05-12	2006 05-22	2006 05-29	2006 06-12
Feed Condition					
X$_{acid}$ (wf)	0.99	0.99	0.99	0.99	0.99
X$_{EtOH}$ (wf)	0.9447	0.9447	0.9447	0.9447	0.9447
F$_{acid}$ (cc/min)	10	10	10	15.7	15.7
F$_{EtOH}$ (cc/min)	10.6	10.64	10.6	16.64	16.64
Molar ratio	0.985	0.985	0.985	0.985	0.985
WHSV	0.644	0.644	0.644	1.01	1.01
Initial Holdup Composition					
RD Base (V$_{Acid}$/V$_{EtOH}$)	4/1	4/1	**Pure acid**	15/1	**Pure acid**
Decanter (V$_{EtAc}$/V$_{water}$)	1/1	4/1	**Pure EtAc**	**Pure EtAc**	**Pure EtAc**
Stripper bottoms	none	Pure EtAc	Pure EtAc	Pure EtAc	Pure EtAc
Operation condition					
Feed to RD(cc/min)	62.3	100.6	125	84	80
Feed to Stripper (cc/min)	62.3	60	90	60	140
Reflux Ratio	1	1.68	1.39	1.4	0.57
Hot oil flow rate (L/min)					
RD	2.2	2.1	3	2	2
Stripper	0.5	1.5	0.3	0.2	2
Acetic Acid Conversion (%)	~100	~100	~100	~100	~100
X$_{B,EtAc}$ (wf)	0.7764	0.9942	0.9831	0.9809	0.9992

Fig. 8. Composition (aqueous, organic, RD base, stripper bottoms) profiles in quaternary composition space for run#1~5.
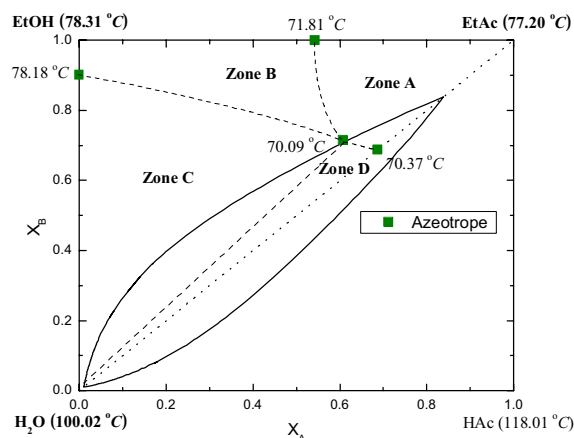

Fig. 9. The distillation zones.

4.3 The effect of operating condition

In Table 1 and Figure 8, the data show that, as the reflux flow is getting larger, the tie line in the two-phase region tends to be parallel to the base line of EtAc-H$_2$O line. Thus, the increase of reflux flow will lead to an increase in EtAc composition into the stripper, and, enhance the separation of EtAc toward a higher purity. A larger reflux flow or reflux ratio will enhance the top composition of the RD column to fall onto the right-hand side of the boundary line between the three-component and EtAc-H$_2$O azeotropes (see Figure 8 upper). On the other hand, according to experimental results, the bottoms product composition in the stripper is directly proportional to the reboiler heat duty in use (see Table 1 and Figure 8). This phenomenon complies very well with the characteristics obtained from simulations.

### 4.4 Effect of initial holdup composition and startup procedure

In view of Figures 8~10 indicate that important factors for a successful start-up can be concluded. Figure 10(A) shows the compositions of initial column holdup for Run 1. As shown in Figure 10 and Figure 10(B), Run 1 differs from Run 5 in the initial composition in the decanter and in the base of the stripper.
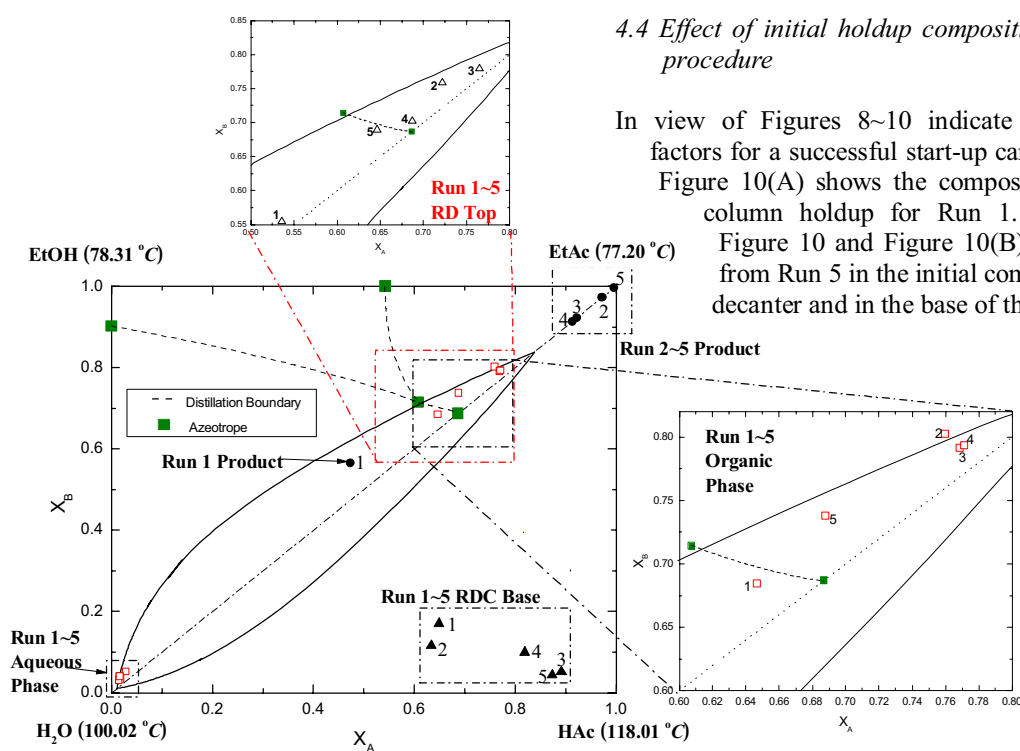
In Run 1, the decanter is charged with equal volume of acetate and water. This initial composition locates in the two-liquid-phase region on the water-rich side while not having any holdup in the bottoms of the stripper. The stripper do not start to separate acetate from the acetate-alcohol-water mixture before the organic phase from the decanter reaches its bottoms. This is somewhat different from the start-up procedure mentioned in the previous section. In the start-up period of Run 1, the top product from the RD column does not have a true LLE. More importantly, it falls into Zone C in Figure 9. Once in Zone C, it never traverses the distillation boundary between the two azeotropes mentioned. That means the stripper will never be operated in Zone A and high-purity acetate cannot be obtained.
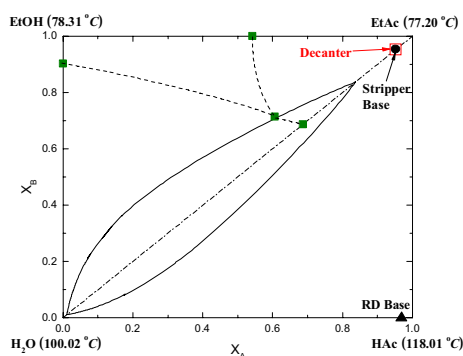
(A)
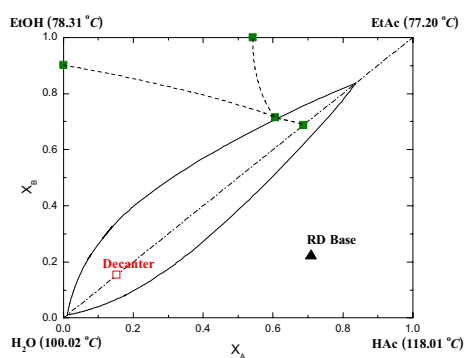
(B)

Fig. 10. The transformed liquid composition in the quaternary system for (A) Run 1 Initial charge composition, (B) Run 5 Initial charge composition, (X_A = X_{HAc} + $X_{Acetate}$, X_B = $X_{Alcohol}$ + $X_{Acetate}$).

4.5 Resulting remarks

(1) Based on the above observations, to have a lumped composition in the decanter to lie in Zone A is critical. For this reason, the decanter is initially charged with acetate of 99 wt% as shown in Figure 10B.

(2) To ensure the organic feed to the stripper lying on the right distillation region (i.e. Zone A), the stripper bottom is initially charged with acetate (product from previous runs).

(3) During the start-up, it is important to operate the temperature of RD top at 72~75℃. This will make the composition from the RD top close to the ternary azeotrope.

(4) It is also important to operate the bottoms temperature in the stripper above 81℃. Remember, this is only necessary but not sufficient. If the composition of organic phase feed from the decanter does not lie in Zone A, the temperature does not guarantee high-purity product.

(5) The start-up procedures given in section 4.1 comply well with the conceptual design.

5. CONCLUSION

This paper presents an experimental validation to the conceptual designs of the type-II RD process for the production of ethyl acetate. This type-II RD process was initial proposed by Tang et al (2005) and further studied by Lai et al (2006). In this work, a pilot plant is setup for the production of high purity EtAc from azeotropic alcohol and industrial acetic as feeds. Several experiments were performed to look for the feasibility of this type-II RD for the production of high-purity acetate and to search for an efficient start-up procedure. The results clearly indicate that high-purity acetate (up to 99.5 wt%), indeed, can be obtained and an efficient start-up procedure is learned from experimental runs. Unlike conventional distillation, initial charges to the column, decanter, and stripper play important role for an efficient start-up.

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