Design and Optimization of Acetic Acid Dehydration Processes

Kung-Ling Li, I-Lung Chien, and Cheng-Liang Chen*
Department of Chemical Engineering
National Taiwan University, Taipei 10617 Taiwan

***Abstract*—Acetic acid is the most widely used aliphatic carbonic acid used as a reaction partner during the manufacture of acetic acid esters, or employed as a solvent in the production of cellulose acetate. Although acetic acid and water do not form any azeotrope, use of simple distillation to separate these two components is still not practical due to its high energy consumption rate. In this work, some separation designs that with high potential for energy saving for dehydration of acetic acid, such as multi-effect distillation, azeotropic distillation, and liquid-liquid extraction, etc., are investigated and analyzed in detail. It shows that the liquid-liquid extraction with methyl *tert*-butyl ether (MTBE) as extraction agent is the most promising separation method in this system due to its lower energy consumption and the total annual cost (TAC).**

I. INTRODUCTION

Acetic acid (HAC) dehydration is an important operation in the production of aromatic acid, such as terephthalic acid or in the manufacture of cellulose acetate. Although acetic acid and water do not form an azeotrope, straight distillation consumes too much energy. Due to the closeness in the volatility of acetic acid and water in dilute aqueous solution, the simple distillation needs a large number of column stages and high reflux ratio to obtain pure HAC. In this work, many approaches, including multi-effect distillation, heterogeneous azeotropic distillation, and hybrid extraction/distillation process, etc., would be investigated to design the most desirable HAC dehydration process with the lowest total annual cost (TAC).

In multi-effect heat integrated systems, the columns are operated under different pressures, which allows the heat removal from the condenser of the higher pressure column to be the heat supply to the reboiler of the lower pressure column. In this case, the feed will be separated into two parts and operated under different pressures, and the split fraction can be used to control the amount of exchanged heat.

For the use of azeotropic distillation in the separation of HAC and water, the process contains a dehydration column, a decanter, and a stripping column. The entrainer used before 1932 was ethylene dichloride, and later normal propyl acetate and normal butyl acetate were used to reduce the organic reflux and heat duty required in the dehydration column. Luyben et al. (1998)[1] offered a realistic vinyl acetate monomer example for academic studies. In the paper by Chien et al. (2004)[2], three entrainers had been used, and isobutyl acetate was a better entrainer to reduce the energy requirement. Therefore, in this work, vinyl acetate and isobutyl acetate have been selected to demonstrate heterogeneous azeotropic distillation via Aspen simulation.

Hybrid extraction/distillation process is a separation process that combines an extraction column and the azeotropic distillation process together. The process flowsheet is referenced from De Dietrich Process Systems[3]. This process design is considered to be comparatively effective because of the lower total energy requirement needed in the process. The choice of extraction solvent severely affects the efficiency of the extraction process. Kürüm et al. (1995)[4] evaluated 34 types of possible entrainers for acetic acid purification with extraction followed by azeotropic distillation in terms of selectivity, distribution coefficient, recoverability, density, chemical reactivity, viscosity, vapor pressure and freezing point, toxicity, cost, and so on, and concluded that ethyl acetate, diisopropyl ether, and methyl *tert*-butyl ether (MTBE) are the most promising entrainers. Therefore, ethyl acetate and MTBE have been selected as the extraction solvents to run the simulation and help to analyze the effect of different extraction solvent toward hybrid extraction/distillation process.

II. COMPONENTS AND THERMODYNAMIC MODEL

The systems of each separation methods are simulated using Aspen Plus$^{®}$ (Aspen Technology, Inc., 2001)[5] with nonrandom two-liquid (NRTL) activity coefficient model accompanied with Hayden-O'Connell (1975)[6] second virial coefficient model, which is used to account for the dimerization of HAC in vapor phase.

In heterogeneous azeotropic distillation and hybrid extraction/distillation process, there are three components existing in the system in which liquid-liquid separation region would form. The set of NRTL parameters obtained here can not only well describe the vapor-liquid binary system, but also the liquid-liquid ternary system. In heterogeneous azeotropic distillation section, vinyl acetate (VAC) and isobutyl acetate (IBA) are used as entrainers, respectively. And, ethyl acetate (EA) and methyl *tert*-butyl ether (MTBE) are used as extraction agents in the hybrid extraction/distillation section. The set of NRTL parameters for the ternary systems of acetic acid-water-vinyl acetate, and acetic acid-water-ethyl acetate are Aspen Plus built-in NRTL parameters. For acetic acid-water-isobutyl acetate system, the NRTL parameters are followed from Chien at al. (2004)[2], and NRTL parameters of acetic acid-water- methyl *tert*-butyl ether are from Miao at al. (2007)[7]. These NRTL parameters are listed in Tables I-IV.

---

*Corresponding author. Tel.: +886-2-33663039; fax: +886-2-23623040
Email address: CCL@ntu.edu.tw

TABLE I. PARAMETER VALUES FOR NRTL MODEL OF ACETIC ACID-WATER-VINYL ACETATE TERNARY SYSTEM.

Component i	HAC	Water	HAC
Component j	**Water**	**VAC**	**VAC**
a_{ij}	-1.9763	0	0
a_{ji}	3.3293	0	0
b_{ij} (K)	609.8886	1364.6	38.385
b_{ji} (K)	-723.8881	415.7	189.2358
α_{ij}	0.3	0.2	0.3

TABLE II. PARAMETER VALUES FOR NRTL MODEL OF ACETIC ACID-WATER-ISOBUTYL ACETATE TERNARY SYSTEM.

Component i	HAC	Water	HAC
Component j	**Water**	**IBA**	**IBA**
a_{ij}	0	0	0
a_{ji}	0	0	0
b_{ij} (K)	-211.310	1809.079	90.268
b_{ji} (K)	652.995	489.609	194.416
α_{ij}	0.3	0.2505	0.3

TABLE III. PARAMETER VALUES FOR NRTL MODEL OF ACETIC ACID-WATER-ETHYL ACETATE TERNARY SYSTEM.

Component i	HAC	Water	HAC
Component j	**Water**	**EA**	**EA**
a_{ij}	-1.9763	9.4632	0
a_{ji}	3.3293	-3.7198	0
b_{ij} (K)	609.8886	-1705.68	-235.279
b_{ji} (K)	-723.8881	1286.138	515.8212
α_{ij}	0.3	0.2	0.3

TABLE IV. PARAMETER VALUES FOR NRTL MODEL OF ACETIC ACID-WATER-METHYL *TERT*-BUTYL ETHER TERNARY SYSTEM

Component i	HAC	Water	HAC
Component j	**Water**	**MTBE**	**MTBE**
a_{ij}	0	0	0
a_{ji}	0	0	0
b_{ij} (K)	-307.16	1307.33	-47.36
b_{ji} (K)	597.97	707.56	-113.15
α_{ij}	0.3	0.3	0.3

III. PROCESS DESIGN

In this study, three different kinds of methods were used to separate HAC and water compared with simple distillation. In the following section, each separation process will be described in detail, and discussion and conclusion will focus on comparing total energy requirement of each separation process.

Rigorous process simulation is performed to find the optimum design and operating conditions of these dehydration methods. The feed composition of 29 wt% of HAC and 71 wt% of water is considered for Aspen Plus®. The feed rate is assumed to be 107,800 kg/h and it is saturated liquid phase. The main product is kept at 99 wt% of HAC and the by-product must not have HAC loss more than 500 ppm. However, the temperature over 127°C in distillation column is undesirable and needs to be avoided.

Design variable of total number of trays of distillation columns is a compromise between total equipment cost. In the following sections, the optimum total number of trays and feed tray location are determined by minimizing total annual cost (TAC). The calculation procedure for TAC of Douglas (1988)[8] is followed with the payback period assumed to be 3. The cost of vacuum system and rotating-disk contactors (RDC) for extraction as well as utility cost is calculated by the way in Seider et al. (2009)[9]. The TAC is defined as below:

$$\mathrm{TAC} = \text{operating cost} + \frac{\text{capital cost}}{\text{payback period}} \qquad (1)$$

The operating cost includes the steam for the reboilers and the cooling water for the condensers. The capital cost includes the column shell and trays for distillation columns, extraction column, reboilers, condensers, and decanter.

A. Multi-Effect Distillation

Multi-effect distillation means that the column pressures are adjusted such that the cooling in one column can be used as heating in another column. For multi-effect distillation with partial heat integration, high-pressure condenser heat removal is not equal to the low-pressure reboiler heat input. By adjusting the split fraction of the feed, the HP condenser heat removal and LP reboiler heat input can be equal, and this is called complete heat integration.

Fig. 1 shows the simulation result of multi-effect distillation with partial heat integration. The HP column is operated under atmospheric pressure, and 0.8 atm for the LP column. The bottom temperature of the LP column has a 10 °C temperature difference with the top temperature of the HP column. This operating pressure can also allow the use of cooling water in condenser, thus save the utility cost in cooling. In this case, HP condenser provides not enough energy to the LP reboiler, thus the LP column still needs an additional reboiler energy input. If the split fraction to the LP column is adjusted to 0.5413, the two-column system forms a complete heat integration system, which is shown in Fig. 2.

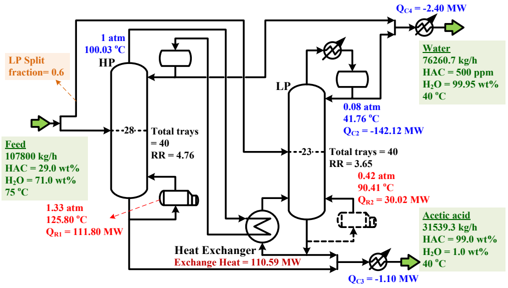

Figure 1. Simulation results of multi-effect distillation with partial heat integration.

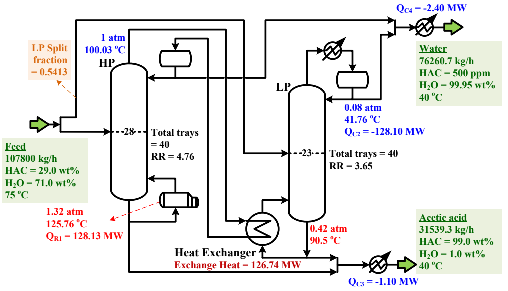

Figure 2. Simulation results of multi-effect distillation with complete heat integration.

B. *Heterogeneous Azeotropic Distillation*

Heterogeneous azeotropic distillation, which is a specific technique of adding another component to generate a new, lower-boiling azeotrope that is heterogeneous, is commonly used in industry. In this work, the two candidate entrainers, vinyl acetate and isobutyl acetate, both form a minimum-boiling azeotrope with water separately. The dehydration column is a heterogeneous distillation column which can be designed to obtain high-purity acetic acid at the bottom while releasing minimum-boiling entrainer-water azeotrope as distillate at the top of the column. With this column design, the tangent pinch of pure water end can be avoided in the top of the column. Since the entrainer-water azeotrope is heterogeneous, it can be sent to a decanter to form two liquid phases. The organic phase will be refluxed back to the azeotropic column to provide enough entrainer inside the column. The aqueous phase containing mostly water will be sent into a stripping column to further reduce the entrainer residue in water, thus forming the by-product in the bottom. The distillate of the stripping column is also at the entrainer-water azeotrope which can be recycled back into the decanter.

Figures 3 and 5 show the ternary maps of the vinyl acetate and the isobutyl acetate systems with some stream composition locations indicated in Figures 4 and 6, which are the summarized simulation results of the two systems, respectively. Assuming at ideal condition, the top vapor composition of the dehydration column should be at the entrainer-water azeotrope and the column bottom composition should be very close to the pure acetic acid corner both in Figures 3 and 5. Because of the feed composition and the other inlet stream, the organic reflux, is known, from mass balance of the dehydration column, the interception of the two inlets and outlets mass balance lines can be used to estimate the organic reflux flowrate.

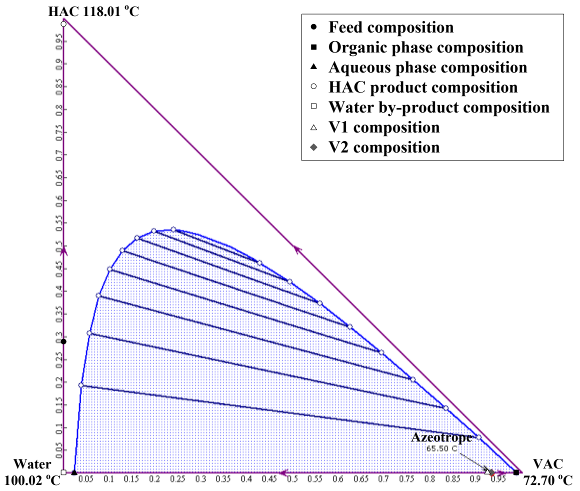

Figure 3. Mass basis ternary diagram for the acetic acid-water-vinyl acetate system.

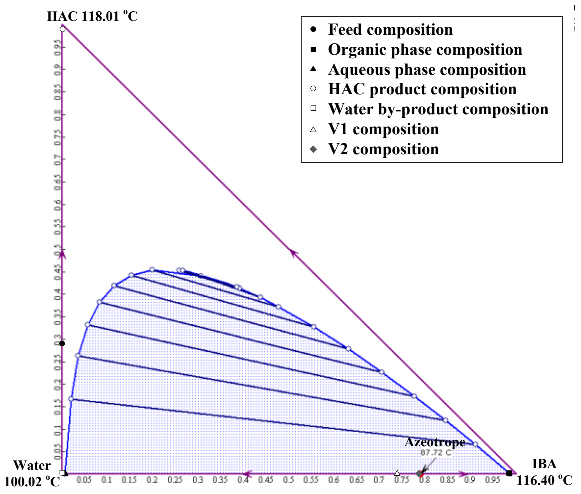

Figure 5. Mass basis ternary diagram for the acetic acid-water-isobutyl acetate system.

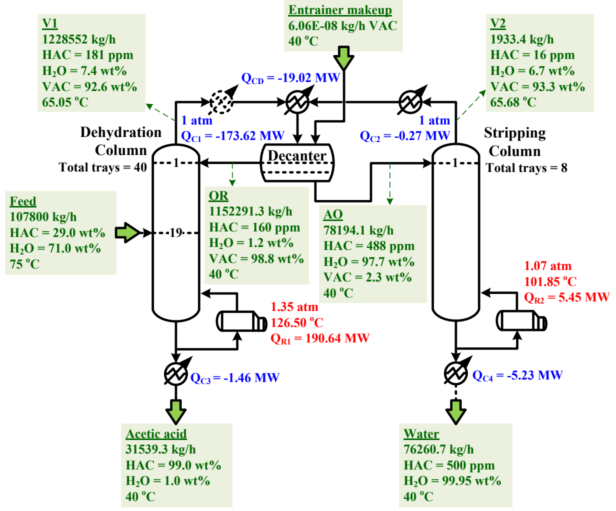

Figure 4. Simulation results of heterogeneous azeotropic distillation with vinyl acetate as entrainer.

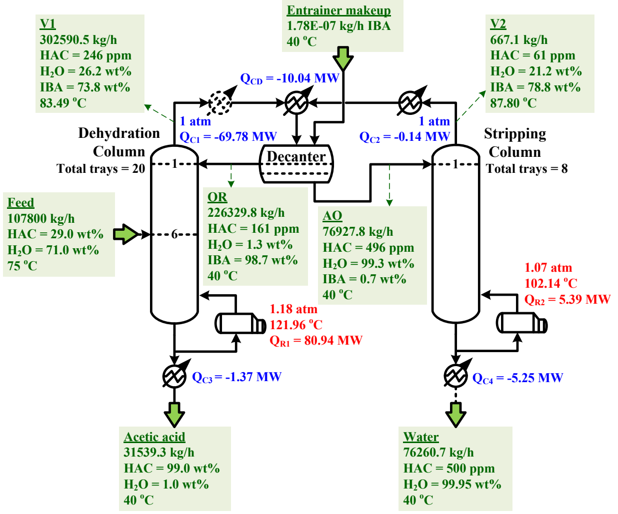

Figure 6. Simulation results of heterogeneous azeotropic distillation with isobutyl acetate as entrainer.

Since the interception point is closer to the organic reflux, the flowrate of reflux stream is quite high. In Chien et al. (2004), only one column is used in the system. Since the designed feed composition and specified product purities are all different from this work, a second water stripping column is needed to further purify the water by-product. With the aid of stripping column, the entrainer makeup in each case can be neglected.

The total energy consumption of the IBA system is much lower than the VAC case. Therefore, using isobutyl acetate as the entrainer is more favorable than applying the vinyl acetate in industry. Comparing vinyl acetate and isobutyl acetate systems, it is better to choose the entrainer that forms an azeotrope whose composition contains more water in the mixture. This means that the entrainer is more capable of carrying water to the top of the column, thus isobutyl acetate is considered to be the better entrainer than vinyl acetate in this system.

C. Hybrid Extraction/Distillation Process

Hybrid extraction/distillation process simply means that the liquid-liquid extraction is followed by an azeotropic distillation process. And liquid-liquid extraction, which is also known as solvent extraction, is a method to separate compounds based on their relative solubilities in two different immiscible liquids, usually water and an organic solvent. Two extraction agents, ethyl acetate and methyl *tert*-butyl ether, form a minimum-boiling azeotrope with water, shown in Figures 7 and 9, thus can be processed with the design of azeotropic distillation column series after extraction. With the aid of extraction column, residual concentrations of 0.1 wt% to 0.5 wt% can be achieved. The extract contains most HAC and solvent, which is processed to an azeotropic dehydration column to obtain high-purity HAC as bottom product. The raffinate contains very little HAC and mostly water, which will form the by-product through a stripping column. The two distillates of azeotropic column and water column are both heterogeneous thus can form two phases in a decanter. The organic phase contains mostly the solvent, and is treated as recycled solvent used repeatedly in the extraction column. The composition of aqueous phase is almost the same as the raffinate, and thus combined with raffinate stream together as the feed to the stripping column.

In addition to total number of trays and feed tray locations, in this case, the ratio of extraction solvent flowrate and feed flowrate fed into the extraction column is the most important design variable, and it should be put as the outer cycle of the optimization procedure. If the ratio is low, HAC loss in the raffinate might be higher, and heating utility used in the dehydration column might be higher if the ratio is high, due to the higher solvent amount going into the column. Moreover, total number of extraction column stages is also an additional design variable that should be optimized.

Normally, low boiling extraction agents are used. Characteristics like solubility in water, distribution coefficient, price, and composition of the azeotrope must be taken into account for the purpose of this selection. Table V shows the characteristic of ethyl acetate and methyl *tert*-butyl ether. The average distribution coefficients do not differ amazingly between these two. However, the economic viability of overall process greatly depends on the energy requirement of the solvent recovery in the dehydration column. Thus the energy consumption in the case of using MTBE as extraction agent ought to be lower than using EA due to the lower vaporisation enthalpy and water proportion in the azeotrope in MTBE. The optimized Aspen Alus$^{®}$ simulation results are summarized in Fig. 8 and 10 for EA and MTBE systems with compositions of main streams marked on the ternary diagram in Fig.s 7 and 9.

D. Comparison of the Three Separation Methods

Table VI sums up total energy consumption and TAC of the three methods for dehydration of acetic acid. As mentioned before, direct distillation is a traditional way used in separation which consumes most energy in operation and has the highest TAC, thus is the most undesirable dehydration manner. Depending on operating distillation columns in a pressure-staged way, multi-effect distillation with heat integration successfully saves the energy requirement as well as TAC. The process with complete heat integration can further save energy than the one with partial heat integration, but in industry, the arrangement of partial heat integration is more commonly used.

Heterogeneous azeotropic distillation is a mature method utilized in dehydration process for several years. This design avoids the separation from the tangent pinch in pure water end, which is a more economic way. In addition, using IBA as entrainer would generate a less organic reflux flowrate than using VAC, thus effectively save more energy requirement. Among all these separation methods, hybrid extraction/ distillation process can be considered as the most effective way for the dehydration of acetic acid. EA and MTBE are both used in industry already, but MTBE rose up as the most promising entrainer in recent years due to its higher selectivity, lower density, lower vaporisation enthalpy and cheaper price. From the simulation results, MTBE amazingly reduce the operating heating energy from traditional direct distillation. The reason for this result is that this design can not only avoid the tangent pinch in pure water end as the way azeotropic distillation do, but also get rid of most water in feed mixture without any energy consumption. Consequently, it lately becomes to be the most desirable dehydration methods.

IV. CONTROL STRATEGY DESIGN

Hybrid extraction/distillation process with MTBE as extraction agent will be studied in detail in this section. The overall control strategy of this system would be developed in order to hold the specifications of both the bottom products of columns in spite of feed flowrate and composition deviation. In control strategy development, no online composition measurement is available. It will be inferred by some tray temperature control strategy.

TABLE V. CHARACTERISTICS OF EA AND MTBE AS EXTRACTION AGENTS IN HYBRID EXTRACTION/DISTILLATION PROCESS.

Names			**EA**	**MTBE**
Average distribution coefficient		**kg/kg**	0.84	0.75
Density		**kg/m^3**	900	740
Enthalpy of vaporisation		**kJ/kg**	395	322
Boiling point		**°C**	76.7	55.0
Azeotrope	**Water**	**wt%**	8.47	4.00
	Temperature	**°C**	70.4	52.6

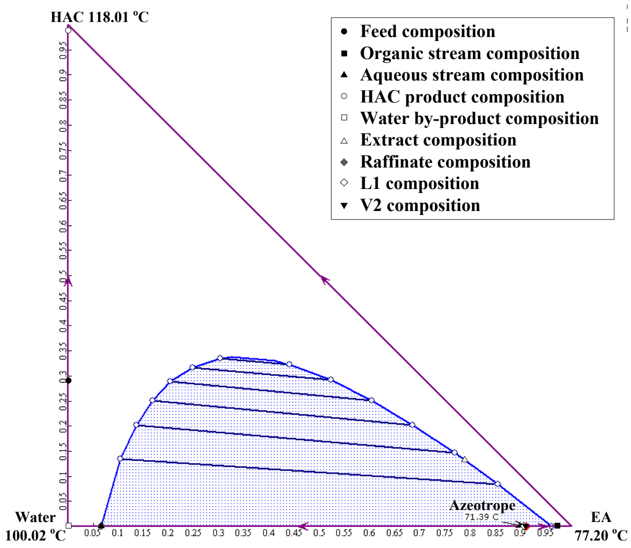

Figure 7. Mass basis ternary diagram for the acetic acid-water-ethyl acetate system.

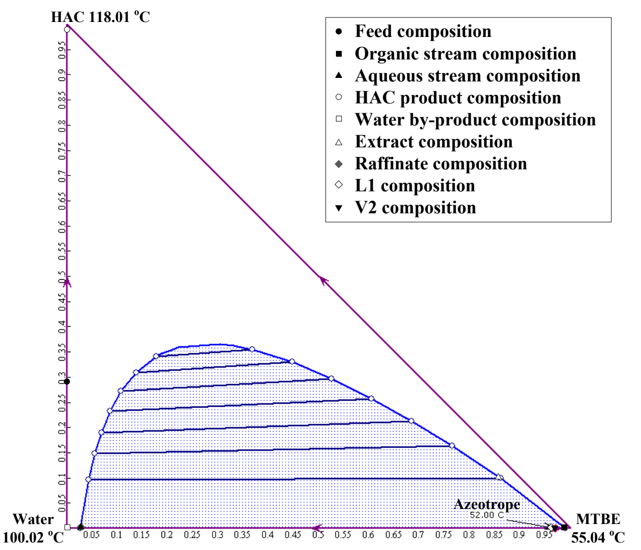

Figure 9. Mass basis ternary diagram for the acetic acid-water-methyl *tert*-butyl ether system.

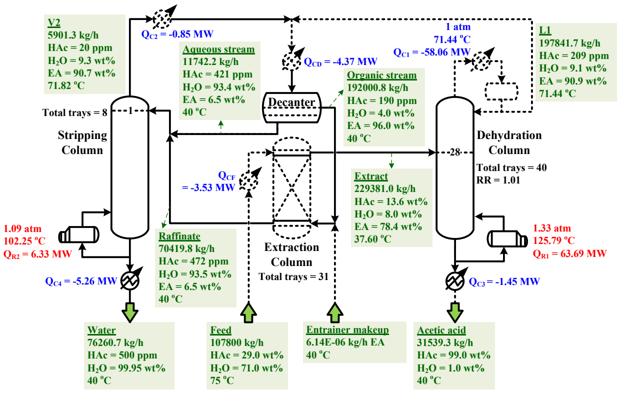

Figure 8. Simulation results of liquid-liquid extraction with ethyl acetate as entrainer.

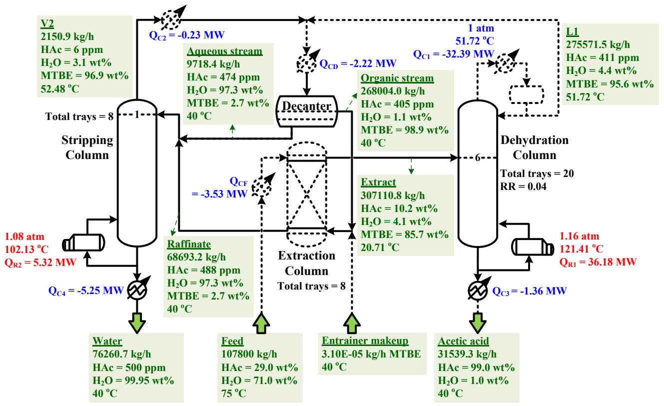

Figure 10. Simulation results of liquid-liquid extraction with methyl *tert*-butyl ether as entrainer.

TABLE VI. THE COMPARISON OF TOTAL ENERGY CONSUMPTION AND TOTAL ANNUAL COST OF THE FOUR ACETIC ACID DEHYDRATION METHODS.

	Column trays	Extraction column trays	Main product		Total cooling duty (MW)	Total heating duty (MW)	Energy saving (%)	TAC
			Flowrate (kg/h)	HAc purity (wt%)				($$10^6$/yr)
Direct distillation	40	None	31539.0	99.0	-283.1	279.64	--	31.37
Multi-effect distillation								
Partial heat integration	40/40	None	31539.3	99.0	-145.62	141.82	35.02	19.30
Complete heat integration	40/40	None	31539.3	99.0	-131.60	128.13	44.05	17.90
Heterogeneous azeotropic distillation								
VAC	40/8	None	31539.3	99.0	-199.60	196.09	14.36	25.34
IBA	20/8	None	31539.3	99.0	-86.58	86.33	62.24	11.11
Hybrid extraction/distillation process								
EA	40/8	31	31539.3	99.0	-73.52	70.02	69.32	9.64
MTBE	20/8	8	31539.3	99.0	-44.98	41.50	81.74	6.12

Since the simulation of extraction column is not available for pressure-driven simulation in Aspen Dynamics^{TM}, flow-driven will be used. Tray sizing option is utilized to calculate the column diameter, and tray spacing is set to be 0.6096 m. Other equipment sizing recommended by Luyben (2002)[10] is used here. The volume of the reboiler and condenser are sized to give 10 min holdup with 50% liquid level, and decanter which needs longer settling time is sized to have 20 min holdup with 50% liquid level.

The overall control strategy is simple, requiring only temperature control loops in each distillation column to hold the bottom product specifications by manipulating the reboiler duties in each column. The inventory control loops are shown in Fig. 11. However, there exists another degree of freedom in the dehydration column, but the top product composition doesn't have to be maintained at a specific value, thus it can only use the reflux ratio as a cascade control set point to the top product level controller. Since the reflux ratio in the dehydration column is quite low, it is better to choose RR rather than R/F as the set point when disturbance comes in.

V. CONCLUSIONS

Traditional acetic acid dehydration process needs high-energy consumption since acetic acid and water form a tangent pinch near pure water end. In order to save the energy requirement, the ways which can avoid the tangent pinch become more promising. Heterogeneous azeotropic distillation and hybrid extraction/distillation process both can avoid the tangent point with the help of entrainer, thus reduce the energy requirement in the process. It is found that the hybrid extraction/distillation process with MTBE saving more energy in the recovery of the solvent becomes the best acetic acid dehydration method.

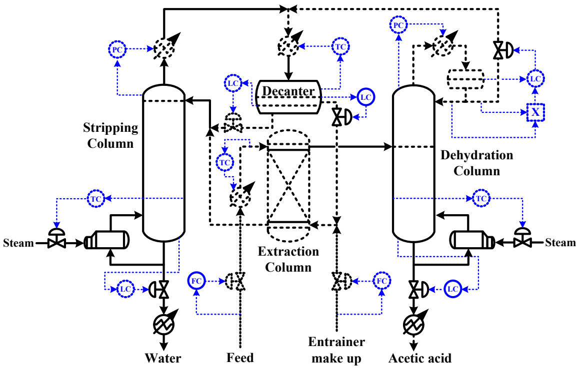

Figure 11. Inventory control loops of hybrid extraction/distillation process.

REFERENCES

[1] M. L. Luyben, and B. D. Tyréus, "An industrial design/control study for the vinyl acetate monomer process", Computers Chem. Engng, vol. 22, 1998, pp.867-877.

[2] I. L. Chien, K. L. Zeng, H. Y. Chao, and J. H. Liu, "Design and control of acetic acid dehydration system via heterogeneous azeotropic distillation", Chemical Engineering Science 59, 2004, pp. 4547-4567.

[3] Member of De Dietrich Process Systems, "Recovery of acetic acid by means of liquid-liquid extraction", De Dietrich Process Systems.

[4] S. Kürüm, Z. Fonyo, and Ö. M. Kut, "Design strategy for acetic acid recovery", Chem. Eng. Comm., vol. 136, 1995, pp. 161-176.

[5] J. G. Hayden, J. P. O'Connell, "A generalized method for predicting second virial coefficients", Industrial and Engineering Chemistry Process Design and Development 14, 209, 1975.

[6] Aspen Technology, Inc., 2001, "Aspen Plus User's Manual 11.1", Aspen Technology, Inc., Cambridge.

[7] X. Miao, H. Zhang, T. Wang, and M. He, "Liquid-liquid equilibria of the ternary system water+acetic acid+methyl *tert*-butyl ether", J. Chem. Eng. Data, vol 52, 2007, pp. 789-793

[8] J. M. Douglas, "Conceptual design of chemical process", McGraw-Hill, New York, 1988.

[9] W. D. Seider, J. D. Seader, D. R. Lewin, and S. Widagdo, "Product and process design principles: synthesis, analysis and evaluation", 3rd edition, Donald Fowley, United States of America, 2009

[10] M. L. Luyben, "Plantwide Dynamic Simulators in Chemical Processing and Control.", Marcel Dekker, New York, 2002