

High-Purity Methyl Acetate via Reactive Distillation

Computer simulations were used to test methods of minimizing the size of reactors and recycle streams, maximizing yields and conversions, and refining the methyl acetate in as few steps as possible.

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The manufacture of high-purity methyl acetate via the reaction of methanol and acetic acid is difficult because of reaction equilibrium limitations and the formation of methyl acetate-methanol and methyl acetate-water minimum-boiling azeotropes. Conventional processes use schemes with multiple reactors in which a large excess of one of the reactants is used to achieve the high conversion of the other reactant. Some use a series of vacuum and atmospheric distillation columns to change the composition of the methyl acetate-water azeotrope (1). The refined methyl acetate is separated from the unconverted reactants, and the methyl acetate-methanol azeotrope is then recycled to the reactors. Other schemes use several atmospheric

distillation columns and a column with an extractive agent, such as ethylene glycol monomethyl ether (2), to act as an entrainer to separate the methyl acetate from methanol.

Early attempts to produce refined methyl acetate via reactive distillation failed because the formation of azeotropes was not recognized (3). More recent work (4) found that enrichment beyond the methyl acetate-methanol azeotrope can occur in a reactive distillation column, but concluded that refined methyl acetate cannot be obtained in the primary reactive distillation column and that a second column is required to fractionate methyl acetate from the methyl acetate-methanol azeotrope. Additional problems are posed in commercial processes by the presence of impurities in the methanol and acetic acid feedstocks. Such impurities may be (or may form) intermediate boiling compounds that will contaminate the product, accumulate in the process recycle streams, and require additional distillation columns for their removal.

This article describes the development of Eastman Kodak's commercial process for the production of high-purity methyl acetate via countercurrent reactive distillation (5). The development and scale-up steps described include concept inception, laboratory testing, bench-scale testing, pilot plant development, modeling and design, full-scale construction and operation, and final troubleshooting and optimization.

Background

As part of the development of the plants in the Eastman Chemicals from Coal Project (6,7), a conventional process

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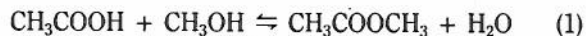
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had been tentatively chosen in 1980 for the manufacture of high-purity methyl acetate. This process had as its primary components two reactors and eight distillation columns. Developmental work on this process, which included pilot plant testing, had been completed. Because of the complexity of such a process, however, it was deemed desirable to continue the optimization work and to pursue the search for a more economical process. A key consideration was time because detailed engineering and the procurement of materials for the plants (chemicals from coal complex) was about to begin. Delays in plant construction could be quite expensive and negate any savings due to optimization work.

After additional literature and patent reviews, many ideas were considered. Computer simulations were used extensively to test such ideas, most of which dealt with ways to minimize the size of the reactors and recycle streams, maximize yields and conversions, and refine the methyl acetate in a minimum number of steps given reaction equilibrium constraints, the constant boiling mixtures or azeotropes that methyl acetate forms with methanol and water, and the presence of several impurities in the raw materials to be used. It was at this time that a proposal was made to carry out the reaction and distillation steps in one vessel so that refined methyl acetate could be made without additional purification steps and with no unconverted reactant streams to be recovered. At the heart of this process was the countercurrent methyl acetate reactor column.

Concept. In the reaction step of conventional methyl acetate processes, liquid methanol is reacted with liquid acetic acid in the presence of an acidic catalyst to form methyl acetate and water. The rate of the reaction is a function of the temperature, the catalyst concentration, and the concentrations of the products and reactants. The reactor size is then determined by the temperature, the catalyst concentration, the ratio of acetic acid to methanol in the feed, and the desired conversion. The reaction is



$$K_e = \frac{(X_{\text{MeOAc}})(X_{\text{H}_2\text{O}})}{(X_{\text{HOAc}})(X_{\text{MeOH}})} \quad (2)$$

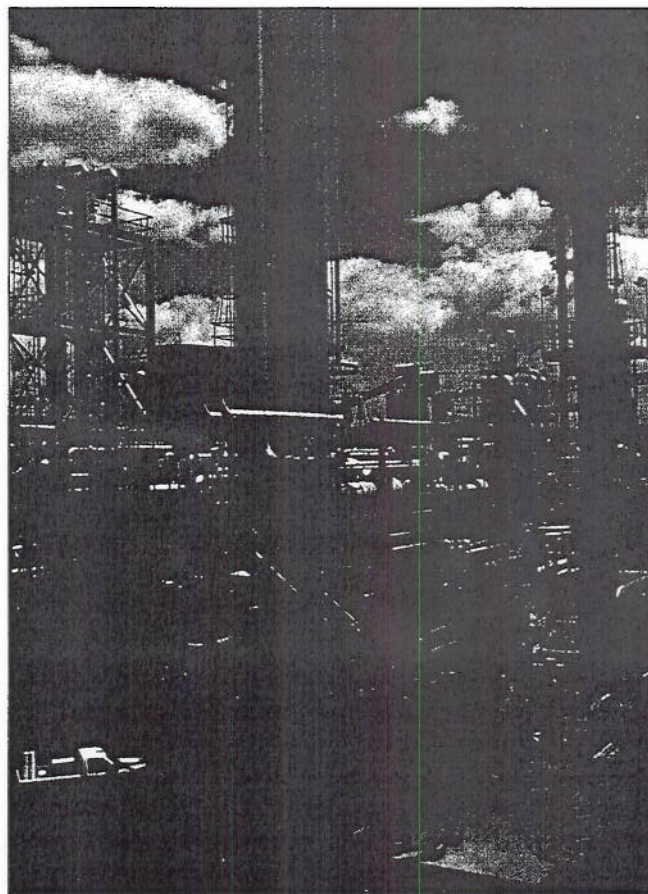
Because the reaction is reversible and the equilibrium constant is 5.2 (reasonably independently of temperature), the reactor product stream will have all four reaction components. As long as the reactor is a standard plug flow or back-mixed reactor, the maximum achievable extent of reaction is given by the liquid phase equilibrium constraint. Therefore, high conversion of one reactant can be achieved only with a large excess of the other reactant. If the reacting mixture is allowed to flash, however, there is a vapor

composition that is related to the liquid composition by the activity coefficients and vapor pressures of the components in the mixture (assuming no reaction in the vapor phase).

$$\frac{y_{\text{MeOAc}} y_{\text{H}_2\text{O}}}{y_{\text{HOAc}} y_{\text{MeOH}}} = \left(\frac{\gamma_{\text{MeOAc}} P_{\text{MeOAc}}^\circ \gamma_{\text{H}_2\text{O}} P_{\text{H}_2\text{O}}^\circ}{\gamma_{\text{HOAc}} P_{\text{HOAc}}^\circ \gamma_{\text{MeOH}} P_{\text{MeOH}}^\circ} \right) K_e \quad (3)$$

At vapor-liquid and reaction equilibria, the ratio of products to reactants in the vapor phase is higher than in the liquid phase because of the higher volatility of methyl acetate relative to the other components. Thus, the overall extent of the reaction achieved between the vapor and liquid phases is greater than can be achieved in the liquid phase alone.

Because the reaction is reversible, the rate of reaction in the liquid phase is increased by removing one of the products (methyl acetate) preferentially to the other components in the reacting mixture. Furthermore, if the reactants (methanol and acetic acid) can flow countercurrent in a se-



Commercial methyl acetate plant with countercurrent reactive distillation column.

quence of flashing reactors, the high concentrations of reactants at opposite ends will ensure the high conversion of both reactants at the opposite ends of the series of flashing reactors. Thus, the concept of a series of countercurrent flashing reactors can be used to great advantage for this particular reaction.

Conventional processes for the manufacture of methyl acetate also have to deal with the problem of refining the methyl acetate. Unreacted acetic acid can be separated easily from methyl acetate and methanol by a distillation step in which acetic acid and water are underflowed. Refining the acetic acid for recycle is a well-known (8), energy-intensive procedure that involves azeotropic distillation and decanting equipment. A tougher problem is the purification of methyl acetate in the presence of the minimum boiling mixtures (azeotropes) of methyl acetate with water (5 wt% water, boiling point = 56.1°C) and methyl acetate with methanol (18 wt% methanol, boiling point = 53.9°C) given that the methyl acetate boiling point (57°C) is very close to that of the azeotropes.

As discussed earlier, conventional refining schemes use vacuum columns to change the boiling points and compositions of the azeotropes or use extractive agents to remove water and methanol by extractive distillation. This, of course, requires additional distillation columns and recycle streams. Distillation modeling and laboratory experiments, however, show that one such extractive agent is acetic acid. Therefore, the countercurrent flow of acetic acid and methyl acetate with its azeotropes can be used to purify methyl acetate. This occurs as a natural consequence of the countercurrent flow in the sequence of flashing reactors discussed previously.

The conceptual basis of the countercurrent reactive distillation column is summarized in Figure 1. The reaction occurs in the middle or reaction section in a series of countercurrent flashing stages. Above this section, water (and, to a lesser extent, methanol) is extracted with acetic acid in the extractive distillation section below the acetic acid feed. Acetic acid and methyl acetate are separated above the acetic acid feed, in the rectification section. In the lowest column section, methanol is stripped from by-product water. Thus, refined methyl acetate is the overhead product of the reactor column, and water is the bottom product.

To make the concept practical, a suitable catalyst is needed and impurities with intermediate boiling points (which, if not removed, would accumulate in the column) must be removed through a sidedraw at an appropriate point in the reactor column. Unless no impurities are present in the process feed streams, a system for the removal of intermediate boiling impurities is required regardless of the processing scheme.

The initial proposal for the countercurrent reactive distil-

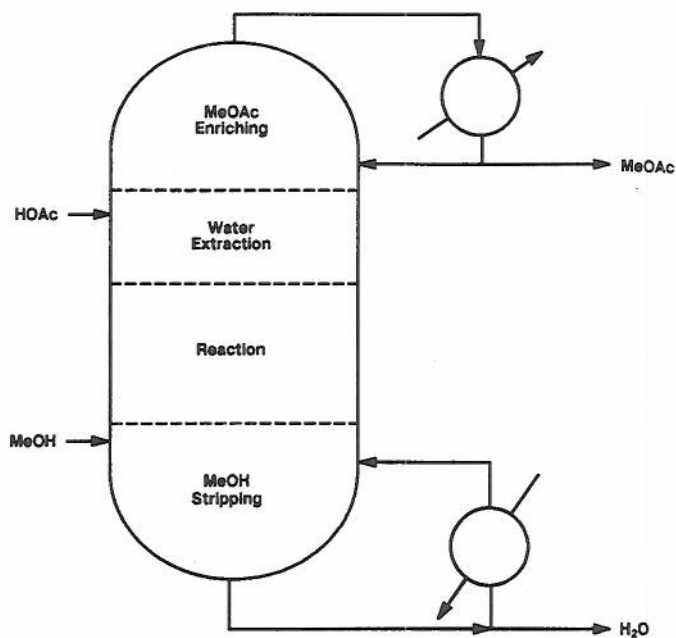


Figure 1. Conceptual diagram of the MeOAc countercurrent reactive distillation column.

lation process was based on these concepts. Because preliminary economic analysis revealed that the idea was attractive, laboratory testing was recommended.

Process development

Laboratory development. Physical property and kinetic data for various catalysts were gathered using batch laboratory equipment. The rate equation developed for the design of the commercial reactor column (with sulfuric acid as the catalyst) was

$$r = k_0 \exp(-E/RT) [C_{\text{MeOAc}} C_{\text{H}_2\text{O}} - C_{\text{HOAc}} C_{\text{MeOH}}/K_e] \quad (4)$$

where $k_0 = k_1(X_{\text{H}_2\text{SO}_4})^2 + k_2(X_{\text{H}_2\text{SO}_4})$ for $X_{\text{H}_2\text{SO}_4} \leq 0.004$ and $k_0 = k_3 - k_4 \exp[k_5/(X_{\text{H}_2\text{SO}_4} - 0.004)]$ for $X_{\text{H}_2\text{SO}_4} > 0.004$.

Unlike other equations available in the literature (9-12), this rate equation covers the full range of compositions encountered in the reactor column. Other catalysts tested were found to be less satisfactory. For example, much higher concentrations of phosphoric acid are required compared to the sulfuric acid rates required. An acidic resin such as Amberlite 200 requires complex reaction- and flashing-stage mechanical designs. Other catalysts are simply too expensive unless a catalyst recovery system is provided.

Feasibility tests were carried out in the laboratory using packed and sieve tray columns. Typical methyl acetate production rates in the laboratory reactor columns were 0.05-0.10 lb/h (22.7-45.4 g/h). This work demonstrated the feasibility of the reactor column concept and showed that sulfuric acid would be the most suitable catalyst. The results of computer simulations showing the extractive efficiency of acetic acid were confirmed, and it was determined that, for reasonable catalyst concentrations, hold-up requirements would be a critical design factor for the reactor column. Because a new economic analysis showed favorable results, larger scale testing was recommended.



High conversion of one reactant can be achieved only with a large excess of the other.



Bench-scale development. A 5 lb/h (2.27 kg/h) methyl acetate production capacity, 4 in. (10.16 cm) in diameter by 30 ft (9.14 m) high, glass reactor column with high hold-up trays in the reaction section and packed sections for methanol stripping, methyl acetate-acetic acid rectification, and extractive distillation was built for further development of the process. This reactor column provided more realistic testing; feed materials expected to be used during full-scale operation were used, corrosion testing was started, column composition profiles at different operating conditions were determined, and impurities were removed through a side-draw.

Operating this column revealed that reflux ratio was a very important factor in the process. Work described in recent literature on this subject (4) fails to achieve satisfactory results primarily because of operation at excessively high reflux ratios and insufficient reaction holdup. The bench-scale unit also showed that process control, such that high-purity methyl acetate is the overhead product and water the bottom by-product, would be quite difficult unless a robust control system could be developed to control both ends of the reactor column and keep the feeds in stoichiometric balance. Based on the results of the corrosion testing, Carpenter 20 Cb-3 was tentatively chosen as the most suitable material of construction for the commercial reactor column.

The data obtained were used to prepare a preliminary full-scale design and a new economic analysis. The results reinforced the expectation that this could be a viable commercial process if the identified problems could be overcome. A pilot-plant-scale reactor column was then designed based on the preliminary full-scale design, and pilot plant testing began.

Pilot plant development. A 100 lb/h (45.4 kg/h) methyl acetate production capacity, 8 in. (20.3 cm) in diameter in the stripping and reaction sections and 6 in. (15.2 cm) in diameter in the extraction and rectification sections by 100 ft (30.5 m) high, Carpenter 20 Cb-3 reactor column was built. This reactor column had high hold-up reverse flow bubble-cap trays in the reaction and stripping sections and Pall ring packing in the extraction and rectification sections. Special precautions were taken to ensure adiabatic operation, for accurate reflux ratio measurements. The purpose of this plant was to confirm the feasibility and controllability of the process and to provide the design data needed for full-scale implementation. It also allowed the testing of the reactor column design and a system for the removal of intermediate boiling impurities. Figure 2 shows the process flow diagram.

The intermediate boiling impurity removal system consisted of a stripping column and a concentration column. This system allowed the recycle of methyl acetate and unreacted acetic acid from the sidestream back to the reactor column. Detailed corrosion studies were made of the

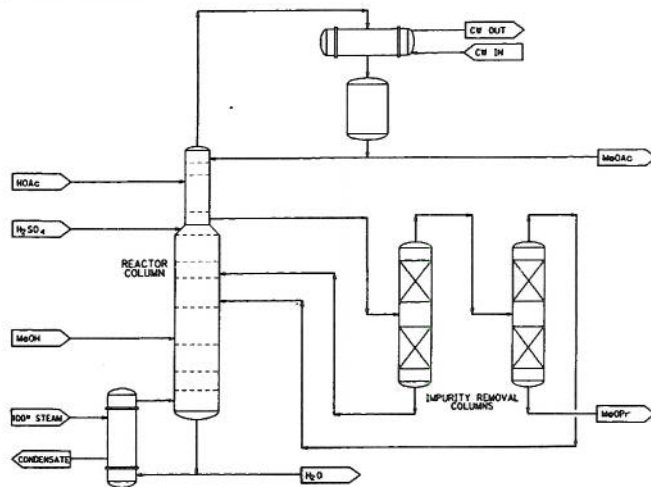


Figure 2. Process flow diagram of the methyl acetate plant.

best candidates for materials of construction for all the equipment that would be needed in the commercial plant. A control strategy suitable for the control of a column in which reactive distillation and three different types of fractionation occur simultaneously was developed. In addition, both the top and bottom product compositions were to be controlled. The reactor column control strategy is presented in Figure 3. Scaleup and design data, such as column tray compositions and the optimum reflux ratio were gathered for use in the full-scale design. Figures 4 and 5 show typical reactor column composition and temperature profiles, respectively. Instrumentation, on-line analyzers, and other equipment to be used in the commercial plant were tested, and operating procedures were developed.

Perhaps the most important result of the pilot plant work was the demonstration of the reactor column's ability to

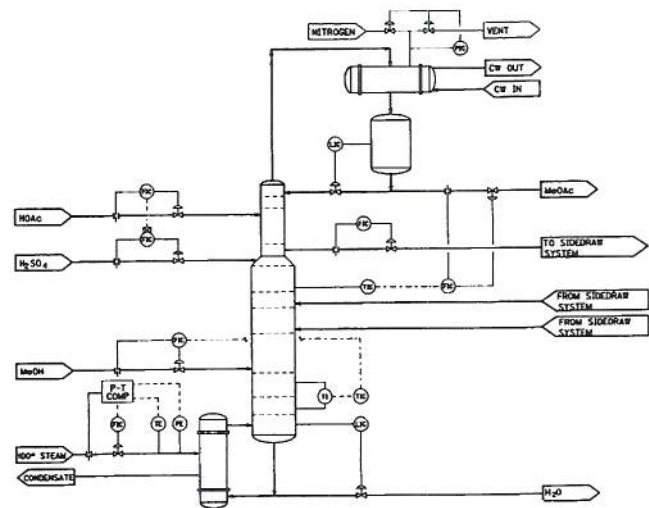


Figure 3. Control strategy for the methyl acetate reactor column.

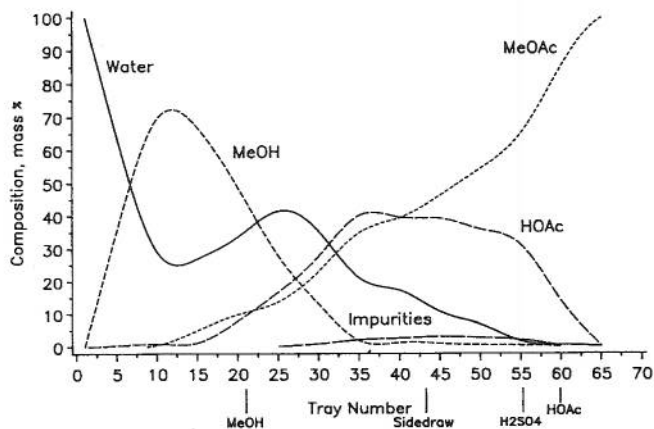


Figure 4. Composition profiles.

produce refined methyl acetate with excellent quality, over a significant period of time, at high yields, and in such a manner that process control and recovery from upsets could be performed easily and without the use of complex control equipment. For example, production of methyl acetate with a typical composition of 99.5 wt% methyl acetate and 0.33 wt% water, 0.15 wt% methanol, 0.02 wt% methyl propionate/isopropyl acetate, and less than 0.01 wt% acetic acid (while simultaneously underflowing by-product water containing only traces—less than 0.1 wt%—of unreacted acetic acid and methanol) was demonstrated on several two-week runs. The operation of this unit also showed that controlling the position and composition of the reaction profile within the reaction section of the column was critical both to controlling the process and to recovery from upsets. This finding had significant implications for the mechanical design of the reaction trays and the control strategy.

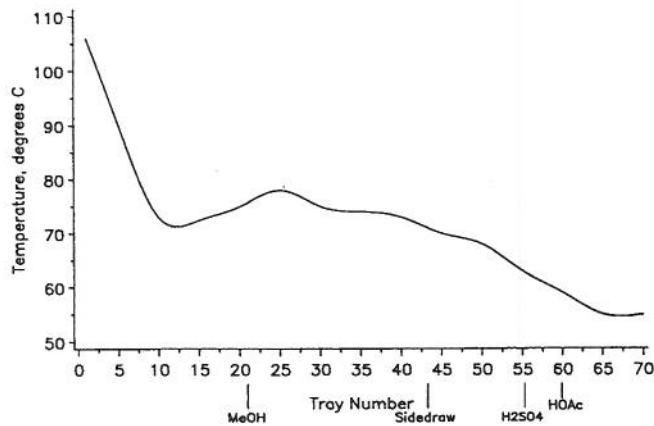


Figure 5. Temperature profile.

These results and a new economic analysis confirmed the feasibility and economic advantages of the process. They showed that the single reactive distillation column was an elegant and economical solution to a challenging chemical manufacturing problem. The countercurrent reactive distillation process was then chosen for full-scale implementation. The entire development process from concept inception to the start of detailed engineering for the commercial plant was completed in less than a year.

Modeling and design

At the time the conceptual proposal was made, Tennessee Eastman had not yet developed a reactive distillation computer simulator. Therefore, given the urgency of the project and the need to develop the concept quickly, stage-to-stage hand calculations were done utilizing a flash with reaction program to calculate vapor and liquid compositions in the reaction section. The distillation sections were simulated using an existing distillation staging computer program.

Concurrently with the pilot plant work, two reactive distillation computer programs were developed. One was a dynamic simulation based on the DYFLO (13) subroutines; the other was a modification of an existing in-house, steady-state staging program. The steady-state simulator used Thomas's algorithm (to solve the tridiagonal matrices) as well as a Newton-Raphson convergence algorithm. Both programs were rather difficult to use and converge, but they provided the information necessary for the design of the reactor column. Both programs predicted the experimentally observed temperature and composition profiles with remarkable accuracy. The staging program also possessed limited hydraulic calculation capabilities.

Of course, the state of the art of reactive distillation has progressed substantially in the past several years. Much work has been presented in the literature on how to perform the required calculations in an efficient and robust manner. Holland (14) documents the techniques and makes recommendations on when to apply the different convergence styles.

Tennessee Eastman now has a proprietary reactive distillation computer simulation capable of handling up to 200 stages, many components, and simultaneous reactions for a range of variables such as feed and sidedraw locations, feed compositions and temperatures, reflux ratios, catalyst feed rates, etc. This program also performs hydraulic and tray-rating calculations. It is currently used, among other applications, for the optimization and improvement of the commercial countercurrent reactive distillation methyl acetate process.

Full-scale design construction and operation. As pilot plant development neared completion, detailed engineering for the commercial plant was started. Design heat and material balances were prepared, column and tray designs for the different sections of the reactor column were finalized, and process and instrumentation diagrams were prepared. When the plot plan and construction drawings were completed, construction of the plant began. Although the pilot plant work demonstrated that the process requires only one



The most important result of the pilot plant work was the demonstration of the reactor column's ability to produce high yields of refined methyl acetate over a significant period of time with easy process control and recovery from upsets.



reactor column and two impurity removal columns, the final process flowsheet has, as its main components, one reactor column and three distillation columns. A methanol recovery column has been added in order to process the underflow of the reactor column for two reasons: 1) to lower the reactor column's base temperature by allowing some methanol underflow, thus reducing the corrosion rate at that point, and 2) to provide a method for minimizing chemical losses during upsets of the reactor column operation. The full-scale reactor column is operated frequently without the methanol recovery column, and it has even been operated without the sidedraw columns when high-purity acetic acid and methanol feedstocks were available.

During the construction phase, which proceeded on schedule and within budget, operating procedures were written. They included procedures for start-up, normal operation, normal shutdown, emergency shutdown, troubleshooting, rate changes, and so on. Upon completion of the construction phase, plant inspection and water checkout took place. Many problems were identified and corrected at this stage. Typical problems included improper installation of equipment, construction debris blocking flow-through lines, and incorrect sizing or calibration of equipment and instrumentation.

After plant checkout, the commercial methyl acetate process was started up in May of 1983. This was the first plant to start up in Eastman's new chemicals-from-coal complex. The most challenging debugging and troubleshooting took place as the production rate was raised toward the design rate of 50,000 lb/h (22,700 kg/h), and limitations were eliminated as they were identified. In some instances, the limitations were due to improper matching or control of utility supplies to the different plants in the complex (resulting, for example, in insufficient flow of cooling tower water to the methyl acetate plant). Other limitations were due to improperly sized equipment, such as condensers and pumps, but the most difficult problems to correct were related to the scale-up and design of the reactor column itself.

The pilot plant development work showed that the reactor column could be satisfactorily operated at reflux ratios ranging from 1.5 to 2.0 with an optimum ratio of approximately 1.7. For economic reasons, the commercial unit was designed for a reflux ratio of 1.5, which reduced operational flexibility if a higher reflux ratio was required in the full-scale reactor column. Furthermore, each reactor column section was designed for the expected steady-state vapor and liquid loading with a minimum safety factor. Finally, due to the high hold-up requirements of the reaction zone trays, the design calculations had to be performed by

extrapolating correlations used for the design of standard bubble-cap trays, acknowledging the risk that such extrapolations may not be accurate. Bubble caps with 5 in. (12.7 cm) risers were used in reverse flow trays with 5 in. (12.7 cm) outlet weirs and a tray spacing of 24 in. (61 cm).

To provide sufficient hold-up for the reaction, sumps were provided in the flow-reversing areas and at the bottom of the downcomers (5). The design of the downcomer sumps was such that the bottom of the sump protruded 10 in. (25.4 cm) below the bottom of the tray, directly above the next outlet weir. This design created a vertical entrance opening to the downcomer that was only 9 in. (22.9 cm) high.

The liquid on the tray is highly aerated, more so than in normal distillation, because of the generation of low-boiling methyl acetate. Thus, highly aerated liquid entered the high hold-up downcomer sump where additional methyl acetate was generated and flashed in a manner that can best be described as effervescence (as seen through an observation port in the pilot plant reactor column). The vapor disengaged from the downcomer liquid had to flow back through the 9-in. (22.9-cm) opening into a wall of froth generated by the outlet row of bubble caps. Excessive pressure drop developed across the trays with the highest vapor loads, the downcomers backed up, and column flooding ensued. Confirmation of the high froth level on the trays was provided by the high liquid entrainment seen in the vapor sidedraw. The problems encountered were diagnosed by using pressure drop measurements and by analyzing reactor column composition and temperature profiles. Gamma radiation scanning allowed the determination of both clear liquid and froth heights.

Actual operation has shown that reflux ratios of 1.65 to 1.85 (depending on production rate, desired product composition, catalyst rate, etc.) are needed. Furthermore, start-up, rate changes, or improper process operation cause the composition profile (and, therefore, the vapor/liquid loading profile) to shift up or down in the reactor column, which causes problems if the profile shift increases the vapor/liquid loading in a column section beyond what that particular section can handle effectively.

All problems have now been corrected by debottlenecking the different reactor column sections. Froth-related problems were corrected in the vapor sidedraw system as well. To ensure no acetic anhydride production losses (methyl acetate is one of the key raw materials to the acetic anhydride plant in the complex), temporary fixes were provided by unloading liquid and vapor flows from the top section of the reactive distillation section of the column via external bypass lines, relocation of the sidedraw system's lines,

The plant is very easy to operate as long as it is kept within its hydraulic capability limits.

and the spreading and shifting of the reaction zone by splitting the sulfuric acid catalyst feed. The ultimate solution, which was implemented during normal scheduled complex shutdowns, was the modification of the reaction trays. The outlet row of bubble caps was removed from the trays in the upper section of the reaction zone of the column in order to provide a deaeration zone for the froth, and the outlet weir height was lowered on the most heavily loaded trays. In addition, the column's operating pressure was increased from 3 to 10 psig (122 to 170 kPa). It is particularly noteworthy that, in spite of the challenges encountered, absolutely no production losses were incurred in the complex due to the scale-up problems encountered in this plant.

In conclusion

The countercurrent reactive distillation process is routinely operated at rates above 100% of design or at other rates as production requirements dictate. Depending on the operating rate, product quality meets or exceeds specifications. Process improvement and optimization have allowed process operation at up to 125% of design.

This plant has been proven to be extremely easy to operate as long as it is kept within its hydraulic capability limits. At the design rate, the plant has operated for several months at a time with essentially no operator intervention and all automatic control loops closed and operational. Process optimization has reduced catalyst usage to approximately 50% of original design, and product yields have been found to be greater than expected. Stoichiometric operation in the full-scale plant has been demonstrated during month-long trials, eliminating the need for a methanol recovery column in future plants provided that adequate corrosion protection is built in for the reactor column's base.

The plant is highly heat integrated. Reboiler condensates are flashed to generate atmospheric steam to preheat the acetic acid feed, and the hot by-product wastewater is used to preheat the methanol feed. The vapor sidedraw provides most of the heat to run the impurity-stripping column. Most importantly, the reactor column is inherently heat integrated. It can be thought of as four distillation columns, one on top of the other, with the top and bottom of each "column" acting as the reboiler and condenser for the "columns" above and below, respectively.

This process is a simple and elegant solution to the challenge of producing low-cost, high-purity methyl acetate for Eastman's chemicals-from-coal complex. It is the culmination of the work of many scientists and engineers who had to solve significant problems in equipment design, specification of construction materials, development of a suitable control system, piloting, modeling and simulation, commercial start-up and troubleshooting of the final process, and process improvement and optimization. ■

Nomenclature

C	= Concentration (lb · mol/ft ³);
E	= activation energy (= 9198 cal/mol);
K_c	= liquid equilibrium constant;
k_p	= preexponential rate constant (ft ³ /lb · mol/h);
k_i	= constants for rate constant expression ($i = 1-5$);
p^o	= pure component vapor pressure;
R	= gas constant (= 1.987 cal/mol/K);
r	= reaction rate (lb · mol/h)
T	= Temperature (K);
x	= liquid mole fraction;
y	= vapor mole fraction;
γ	= liquid phase activity coefficient.
MeOAc	= methyl acetate
MeOH	= methanol
HOAc	= acetic acid

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