ABSTRACT

We describe a model and calculation technique that supports the design of reactive distillation columns using ChemCAD simulation software. The approach is illustrated for the production of ethyl acetate because it is inevitably needed as an active solvent used in a wide range of applications across many industries.

Ethyl acetate is normally produced by esterification of ethanol and acetic acid. A reactive distillation column, combining the reaction and separation into a single stage, is proposed. The ethyl acetate is always distilled and withdrawn out of the reaction zone, the equilibrium is shifted to the right and the reactants conversion is improved. These are the advantages of this combination. Sensitive analyses are carried out to investigate the influence of the different parameters such as pressure, reflux ratio, feed stage location. The effect of reactants excess on the reactants conversion and the ethyl acetate production is also studied. The optimum operation conditions and all design parameters of the reactive distillation column are determined on the ground of the analyses carried out.

Keywords: reactive distillation, modelling, ethyl acetate, sensitive analyses, homogenous catalyst.

INTRODUCTION

Reactive distillation (DR) represents an integration of a chemical reaction and distillation in a single multifunctional process unit. Chemical equilibrium limitations can be overcome, higher selectivity can be achieved, and the heat of reaction can be used in situ for distillation. These are the basic advantages of the integration considered.

The most important industrial applications of DR are in the field of esterification processes such as the synthesis of methyl acetate [1, 2]. Another usage of DR refers to the preparation of the ethers MTBE, TAME, and ETBE, which are produced in large amounts as fuel components because of their excellent antiknock properties [3]. Due to the interaction between the reaction and the distillation in one single apparatus, the steady-state and dynamic operational behavior of DR can be very complex. Therefore, suitable process control strategies have to be developed and applied. This is another very important area of current and future research and development.

Models and calculation techniques that have been developed to support the design of reactive distillation columns using ChemCAD 6.3.1 simulation software are described in this paper. Ethyl acetate synthesis is used as a model system to demonstrate the approach.

Ethyl acetate is one of the most widely used fatty acid ester and is a quick-drying solvent with excellent solubility. As an excellent industrial solvent it finds an application as an important component of extractants used for antibiotics concentration and purification [4, 5] and an intermediate in the manufacture of various drugs [6]. This solvent is applied in the manufacture of adhesives, cleaning fluids [7], nail-polish removers and silk
Other applications of ethyl acetate are associated with the manufacture of synthetic fruit essences, flavors and perfumes. It can be used as the standard material and solvent for analytical reagents and chromatography analysis.

Ethyl acetate is produced through esterification of ethyl alcohol and acetic acid. This process is described as an acid catalyzed equilibrium synthesis developed by Emil Fischer. The mechanism proposed for esterification involving an alcohol and carboxylic acid is an acid promoted acyl substitution, which results in the substitution of an alkoxy group for the hydroxyl portion of the carboxyl group.

The water formed in the course of the reaction (and also from the 90% alcohol used as a raw material) is continuously removed. The conditions chosen provide the maximum conversion of acetic acid, which is costlier than ethyl alcohol.

The model of continuous reactive distillation column is used to produce ethyl acetate in this study. It is well recognized that the equilibrium limitations overcome, the higher selectivity achievements, the process cost reduction, and the plant size reduction are among the advantages of this integration. The DR column represents an entire chemical plant, where the costs and the energy consumed are several times less those of the conventional process.

The reactive distillation setup allows overcoming the reaction equilibrium for increased conversion of ethanol and acetic acid. In turn, the combination of the separation by distillation and the reaction zones leads to complex interactions in the course of vapor-liquid equilibrium establishment affecting the mass transfer rates and the chemical kinetics. These interactions result in important nonlinearities and multiplicities in the process dynamics. This in turn poses a great challenge in these systems design.

The objective of this work is to define a reliable DR model of a steady state regime of ethyl acetate production.

The research provides a comprehensive understanding of the effect of reactant amount excess, feeds stage location, pressure and reflux ratio on the conversion in the reactive distillation, and a demonstration of solution multiplicity in a reactive distillation system for esterification.

**THERMODYNAMIC REQUIREMENTS**

The mathematical description of DR should include both mass transfer (associated with the distillation) and chemical processes (associated with chemical reactions) as it is a combination of distillation and a chemical reaction.

**A Fluid phase equilibrium**

The mass transfer processes associated with the distillation represent bidirectional diffusion through the vapor/liquid interphase surface. In other words, the correct description of the fluid phase equilibrium is necessary. The thermodynamic data required for the phase equilibrium description were obtained in this study on the ground of the K-value methods. The liquid-phase activity coefficients were well represented by the NRTL equation. The NRTL binary interaction parameters (BIPs) for all compounds were obtained from ChemCAD data bank. The Hayden–O’Conell model with association parameters was used to account for the acid dimerization in the vapor phase.

**Reaction kinetics**

The production of ethyl acetate by esterification of acetic acid with ethanol can be described by the following equation:

\[
CH_3COOH + C_2H_5OH \rightleftharpoons C_4H_8O_2 + H_2O
\]

The reaction proceeds slowly at room temperature involving about 65% of the reactants. The reaction rate can be accelerated by the addition of acidic catalysts. Furthermore, the equilibrium is shifted strongly to the right through the resulting water removal from the system. To model the reaction kinetics the equilibrium reaction considered is represented by two kinetically controlled reactions. They proceed simultaneously. The reactions parameters are specified on the ground of the experimental data of Nada S. Ahmed Zeki et al. The authors study the kinetics of acetic acid esterification with ethanol in presence of sulfuric acid as a homogeneous catalyst obtained in the course of isothermal batch experiments. The values of the activation energy and the pre-exponential factor are obtained at a constant catalyst loading. Thus, the catalyst effect on the reaction kinetic is not taken into account. In this study the cata-
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The catalyst feed stream is not included in the work flowsheet for two reasons:

As was mentioned above, the chemical reaction parameters have been obtained at a constant catalyst loading [16]. Thus, the catalyst amount did not change the rate of the chemical reaction.

Zeki at al. have used only a drop of sulfuric acid (about 0.05 ml) in a reaction volume of 300 ml [16]. In our case 25 kmol/h acetic acid and 25 kmol/h ethanol were used. These amounts would have required a catalyst of 0.0076 kmol/h. Such a tiny quantity would not have changed the molar balance in the column.

The values of the activation energy and the pre-exponential factor of 34576 J/mol and 52313 J/mol, correspondingly, are taken from Zeki et al. [16]. These parameter values indirectly take into account the presence of sulfuric acid as a catalyst.

SIMULATION METHODS

In order to simulate the reactive distillation process the SCDS module in ChemCAD 6.3.1 software is used. SCDS is a rigorous multi-stage vapor-liquid equilibrium module which simulates any single column calculation. By this module columns of unlimited stages, five feed streams, and four side products can be simulated. SCDS can simulate rigorous distillation of two-phase or three-phase non-ideal K-value chemical systems. It uses the Newton-Raphson convergence method with simultaneous correction [17] and calculates the derivatives of each equation rigorously, including the \( \frac{\partial K}{\partial x} \) (derivative of K-value with respect to the composition) term which is significant in chemical system simulation.

 Reactive distillation is simulated using SCDS as a platform or template for the addition of chemical reaction specifications. The reactions may be defined as kinetic and/or equilibrium and may occur in the liquid and/or vapor phase, simultaneously. Expressions of equilibrium and rates of reaction can be implanted from external files.

Our flow-sheet for ethyl acetate production is shown in Fig. 1.

In the Fig. 1 flows 1 and 2 are feed streams of acetic acid and ethanol, respectively. According to the esterification reaction stoichiometry, 1 mol of acetic acid reacts with 1 mol of ethanol. Therefore, the amounts of 25 kmol/h pure acetic acid (stream 1) and 25 kmol/h ethanol (stream 2) were selected for the initial feed streams 1 and 2. The ethanol feed stream corresponds to a mixture of 90 % ethanol and 10 % water, thus the final amount of stream 2 is 27.75 kmol/h.

Initially, the feed streams have the ambient temperature of 20°C. On the rectification column entry these streams can be preheated. This process is performed in a multichannel heat exchanger (apparatus number 2 in Fig. 1). The LNGH module of ChemCAD environment is used to model the heat exchanger. The LNGH heat exchanger is used to simulate the exchange of heat bet-
tween multiple hot and cold streams. The total number of hot and cold input streams is limited to seven. If there are \(x\) inputs to a unit, one must make \(x-1\) specifications to define completely the unit. The condition of the unspecified stream is computed to satisfy the heat balance requirements.

Column operating pressure of 1 atm as an initial approximation is accepted. Aiming this, the input streams pressure must be slightly higher than the atmospheric pressure. Therefore, the feed flows of acetic acid and ethanol are compressed by pumps 3 and 4 up to 1.2 atm.

The conversion is increased by flashing off the ethyl acetate from the reaction mixture. The reactive column has balanced feeds and is designed so that the lighter reactant ethanol is fed at the bottom, while the heavier acetic acid is fed from the top. The column consists of three sections. The reaction takes place predominantly in the middle (reactive) section. The bottom section serves to strip off the ethanol from water and return it to the reaction zone. The vapors leaving the reactive section consist of ethyl acetate-ethanol azeotrope, which is ‘broken’ in the rectifying section by addition of acetic acid acting as an entrainer.

99.99% of pure water heated to the boiling point at a working pressure (1 atm - 100°C) is removed from the bottom of the column. It is appropriate to recover the heat of this water stream (stream 4). That is why it is used as a hot agent in the heat exchanger 2 for heating the feed streams. As the amount of this flow is small its heat is not enough to preheat the feed streams of acetic acid and ethanol. Therefore, an additional stream 10 of heating water is added. The stream 10 has the flow and the temperature of stream 4 to provide the additional heat required to preheat the feed streams.

**SENSITIVE ANALYSES**

Sensitive analyses were carried out to obtain the optimum operation conditions. They were performed using the parameters exerting the most significant influence on the yield of ethyl acetate. These parameters refer to the excess of the reactants, the feed stage location for both feed streams, the influence of the reflux ratio and the operating pressure.

**Reactants excess**

This analysis shows the influence of some reactants excess on the yield of the desired product - ethyl acetate. The initial flow rates of the two reactants, 25 kmol/h CH₃COOH and 25 mol/h C₂H₅OH, respectively, are set in view of the stoichiometry of the chemical reaction (1 mol CH₃COOH reacts with 1 mol C₂H₅OH).

The feed stream of ethanol is maintained constant (25mol/h), while the feed flow of acetic acid is varied aiming to study the acetic acid effect on the flow of ethyl acetate. This is illustrated in Fig. 2.

![Fig. 2. Influence of HAc flow on the ethyl acetate production.](image)
It is seen that the increase of the acetic acid amount increases the flow of ethyl acetate - the maximum value of 24.4 kmol/h is reached at about 200 kmol/h CH$_3$COOH.

Similar analysis regarding the influence of ethanol excess is carried out (see Fig. 3).

As in the previous case, the increase of ethanol amount increases the flow of ethyl acetate - the maximum value of 24.4 kmol/h product is obtained at 51 kmol/h C$_2$H$_5$OH.

It follows from Figs. 2 and 3 that the maximum yield of ethyl acetate reached in both cases is 24.4 kmol/h. Ethanol is less expensive than acetic acid. To get the maximum amount of ethyl acetate it is necessary to introduce CH$_3$COOH in an excess of 200 kmol/h, or C$_2$H$_5$OH in an excess of 51kmol/h. Thus, it is more appropriate to work with an excess of ethanol rather than an excess of acetic acid. Based on the results of these sensitive analyses we accept to deal with 24.4 kmol/h of CH$_3$COOH and 51 kmol/h of C$_2$H$_5$OH.

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**Fig. 3. Influence of EtOH flow on the ethyl acetate production.**

**Fig. 4. Influence of HAc feed stage location.**
Feed stages number

Sensitive analyses of the complex effect of the feed trays number referring to the upper feed stream of acetic acid and the lower feed stream of ethanol are carried out. The location of both feed streams has an impact on the amount of the resulting ethyl acetate.

Initially we fix the trays number at 15 for the lower feed stream and vary the number of the feed trays of the upper feed stream from 1 to 13. Thus, the influence of the location of the upper feed of acetic acid is investigated. The result is shown in Fig. 4.

Fig. 4 shows that the amount of ethyl acetate remains practically constant at about 24.5 kmol/h in case the location of the upper feed is changed from the third to the eleventh stage.

A similar analysis referring to the location of the lower feed stage is carried out. In this case, the number of the feed trays of the upper acetic acid feed is fixed, while the location of the lower ethanol feed is varied. Thus, the number of the feed trays of the upper feed is fixed respectively to 8, 10, 12 and 13. The results obtained are shown in Fig. 5. The figure shows that the ethyl acetate yield increases when the upper feed stage is fixed at 10 but the lower feed stage location number is varied (Fig. 5). Therefore, we select the upper feed stage location at tray 10. This is visualized in Fig. 6.

Fig. 5. Influence of EtOH feed stage location for the any values of HAc feed stage location.

Fig. 6. Influence of the below ethanol feed location at the tenth feed tray for the upper feed.
It is seen from Fig. 6 that the increase of the number of the lower feed tray location decreases the ethyl acetate yield. But as this decrease is quite small, the flow of ethyl acetate is kept constant at a value practically equal to that at the bottom of the column - stage 19.

The location of the lower ethanol feed stream can be optimized if the effect of the feed tray number of this stream on the other parameters related to the column performance is known. The production of pure water (99%) as a bottom product (in addition to ethyl acetate) is one of the objectives of this study. A parametric analysis to see how the lower feed tray location influences the bottom water purity is made.

Fig. 7 shows that the amount of water as a bottom product coming from stages ranging from 12 to 18 remains almost constant. Its purity is greater than 99%. Thus, the lower ethanol feed stream has been located on a tray with a number greater than 12.

Another sensitive analysis referring to the ethanol feed stream location is carried out. Fig. 8 illustrates the influence of ethanol feed stream location on the reboiler heat duty.
Fig. 8 shows that the increase of the number of the feed stage results in increase of the reboiler heat duty. From this viewpoint the ethanol feed stage should be 10. Thus, in terms of purity of the bottom water the number of the ethanol feed stage should be greater than 12, but from the viewpoint of the reboiler heat duty it should be 10. If the upper acetic acid feed is placed at 10-stage, then the ethanol feed should be located at least several trays below to provide a reactive section of the column for a normal proceeding of the chemical reaction.

Taking into account the analysis presented above, stage 10 for upper acetic acid feed stream and sage 13 for ethanol feed stream are chosen.

**Reflex ratio**

Fig. 9 illustrates is the sensitive analysis regarding the influence of the reflux ratio on the yield of ethyl acetate. The reflux ratio is varied from 0.5 to 9. The figure shows that initially the reflux ratio increase brings about a fast increase of the ethyl acetate yield. The latter stays almost constant after the reflux ratio reaches a value of 2.5. Small fluctuations are observed at reflux ratios between 3 and 4. Therefore, an optimal reflux ratio of 4 is chosen.

**Pressure effect**

Fig. 10 illustrates the pressure effect on the ethyl acetate yield. In this case the pressure is changed from 0.5 Bar to 10 Bar. It is seen that the ethyl acetate yield practically does not change at pressure of 0.5 Bar and 1 atm (first two points in Fig. 10), but it starts to decrease with further pressure increase. Thus, functioning under vacuum (at pressure of 0.5 Bar) can be chosen. Since the ethyl acetate yield is practically the same at vacuum and pressure of 1 atm (see Fig. 10), we choose pressure of 1 atm as the optimal one. Otherwise, the vacuum distillation performance would be more expensive.

The results of the sensitive analyses carried out provide the determination of the optimal conditions of the distillation column operation: 20 stages, 10 upper acetic acid feed stages, 13 lower ethanol feed stages, a reflux ratio of 4 and an operating pressure of 1 atm.

**A MODEL SOLUTION AT THE OPTIMAL OPERATING CONDITIONS**

The definition of the optimal operating conditions of the distillation column provides the solution of the mathematical model at these conditions. Fig. 11 shows the temperature profile of the liquid phase on the stages of the reactive distillation column with plates numbered from the top to the bottom of the column.

Fig. 11 shows that the temperature increases non-linearly from the top to the bottom of the column. This is typical of any conventional rectification process. In our case, tangible temperature increase is observed between the 17th and the 20th stage, where the volatile compounds ethanol and ethyl acetate (see Fig. 11) are almost run out.

Fig. 12 presents the component flows in the liquid phase on the various stages.

Ethyl acetate and water are the products of the chemical reaction examined. The first one is highly volatile (a slight component) and is concentrated at the top of the column. The second one is non volatile (a heavy compound) and is removed from the bottom of
In the reaction zone, between stages 10 and 13, the water flow is maintained almost constant. Then this product yield is increased to its final maximum value. From stage 10 to stage 1 (the top of the column) the water flow rate in the liquid phase decreases to its minimum value.

The opposite trend is observed in case of the ethyl acetate flow rate. The ethyl acetate flow rate is very small in the lower non-reactive zone of the column (stages 14 - 20). Then it dramatically increases in the reactive zone (trays 10 - 13) because of the chemical reaction proceeding. A slight increase of the rate of ethyl acetate is observed above the reactive zone (from 9-th to 6-th stage).

Then from stages 6 to 1 the ethyl acetate flow increases more rapidly reaching its maximum final value. The amount of the reactants (acetic acid and ethanol) is the highest on the feed tray where they are fed (stage 10 for the acetic acid and stage 13 for ethanol).

As the variation of acetic acid flow rate is not clearly seen in Fig. 12, it is presented additionally in Fig. 13. Fig. 13 shows that the largest amount of acetic acid
is observed at the feed stage for this reactant - stage 10. The acetic acid belongs to the heavy components in this system and which is why it is expected to concentrate at the bottom of the column. Due to the chemical reaction, in the reaction zone (trays 10 - 13), the acetic acid flow decreases greatly and consequently tends to reach a minimal final value at the last 20-th stage. In the upper separation zone of the column (between stages 9 and 1), the flow of this reactant decreases dramatically (at stages 10 and 9), then it increases slightly (from stage 8 to stage 3), and finally decreases again (from stage 3 to stage 1). In other words, there is a maximum in the function expressing the acetic acid flow rate. It is located at tray 3. The type of the dependence obtained can be explained as follows:

In the reaction zone, due to the heat generated by the chemical reaction, some of the acetic acid quantity is evaporated, which results in this compound increase in the vapor phase.

In the separation zone, above that of the reaction proceeding (from stage 9 to stage 1), the temperature decreases quickly. Since the acetic acid is a hardly volatile component, it condenses and enters the liquid phase. Therefore, its flow there begins to increase (see Fig. 13 - stages from 8 to 3). Due to the presence of ethanol in the liquid phase and the increase of the acetic acid flow rate the chemical reaction takes place. Whereby the yield (flow rate) of acetic acid decreases (see Fig. 13 - stages from 3 to 1).

In our case ethanol belongs to volatile components, therefore it will be concentrated at the top of the column. Thus the flow rate (concentration) of this compound from the ethanol feed stage 13 to the bottom of the column will decrease. Most noticeably this decrease occurs between stages 15 and 20. In the reactive part of the column (between stages 10 and 13) this reactant flow is smaller due to the chemical reaction. An extremum is observed in the function expressing the ethanol flow in the reaction zone towards tray No. 1 (the top of the column). It is located at the 5-th tray. The extremum can be explained in analogy with that referring to the acetic acid flow rate.

**CONCLUSIONS**

The DR column for ethyl acetate production by esterification of acetic acid with ethanol is simulated. The design of the technological scheme is energy saving and allows heat recuperation from the hot water flow at the bottom of the column.

The sensitive analyses are incorporated to solve the optimization problem formulated with an objective function: to maximize the amount of the produced ethyl acetate, to minimize the reboiler heat duty, and maximize water flow purity. The effect of the reactants excess, the feeds stage location, the reflux ratio and the operating pressure over the objective function are investigated. The present investigation shows that the optimal param-
eters of DR column refer to 10 upper acetic acid feed stages, 13 lower ethanol feed stages, reflux ratio of 4, and operating pressure of atm. It is more appropriate to use an excess of ethanol rather than an excess of acetic acid. This is due to the smaller excess necessary and the lower cost of ethanol. A maximum final conversion of 2.04 ethanol/acetic acid molar ratio is obtained.

A model solution is provided at the optimal operating conditions pointed above. Full temperature and concentration profiles of the DR column are obtained. The developed stimulation model enables better understanding of ethyl acetate production on the ground of acetic acid esterification with ethanol. The results of optimization procedures can be used for economic assessment and as a starting point in creating a pilot plant for ethyl acetate production.

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REFERENCES

