CHEMICAL ENGINEERING TRANSACTIONS
VOL. 90, 2022

A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.cetjournal.it

Guest Editors: Aleš Bernatík, Bruno Fabiano

ISBN 978-88-95608-88-4; **ISSN** 2283-9216

DOI: 10.3303/CET2290023

Safety Analysis as Integral Part of Chemical Processes Intensification and Integration

Zuzana Labovská*, Branislav Šulgan, Juraj Labovský, Ľudovít Jelemenský

Institute of Chemical and Environmental Engineering, Slovak University of Technology in Bratislava, Radlinského 9, 812 37 Bratislava, Slovakia
zuzana.labovska@stuba.sk

In recent years, process intensification and integration have played a key role in the world's production of esters. This is successfully achieved by the reactive distillation process. In this work, intensification of the ethyl acetate production process is studied comparing three case studies: conventional process set-up (ethyl acetate is produced in a chemical reactor) is designed as a base case study; reactive distillation with a separation unit is derived from the conventional process set-up, and intensified of the latter pathway by the integration of a heat pump. Effect of the intensification was evaluated by multilevel assessment based on energy requirements, economic, environmental, and safety analyses. Safety evaluation was based on the Chemical Process Quantitative Risk Analysis performing individual risk estimation for all case studies.

1. Introduction

Intensification of processes is nowadays considered as one of the most promising development strategies in modern chemical engineering research. On the other hand, process intensification and optimization to achieve maximum efficiency with minimum energy and economic demands also has its drawbacks. Not all changes in the production process which lead to production increase and reduce energy intensity are also suitable in terms of process safety. Therefore, it is always necessary to assess the effect of the optimization of material, energy inputs, and process equipment on the safety of the whole process. A strong trend in process intensification is the integration of more unit operations into one piece of equipment to decrease the operation and investment costs; however, increasing the process complexity increases the system non-linearity which can result in unpredictable system behavior and complicated system regulation in case of a dangerous situation or industrial accident. Optimization of a real industrial unit is always a compromise between technological, economic, and safety or environmental requirements. Finding a compromise regarding many safety measures and investment costs is especially demanding. Also, significant discrepancies often occur between the energy optimization results and safety analysis requirements when energetic media saving or their recycling leads to inacceptable risk of serious industrial accidents. For this reason, simultaneous analysis of "commonly" optimized and safety parameters should prevent introducing undesired risks into the production process or at least provide early warning of potentially dangerous system behavior because of a production process modification.

2. Case studies

In this work, intensification of ethyl acetate production process is studied. Esterification reaction of acetic acid (AA) by ethanol (EtOH) is assumed to form ethyl acetate (EtAc) in a continuous stirred tank reactor (CSTR) or a reactive destination column (RD). The same initial input specifications were entered for all case studies: equimolar raw material input (10 kmol h^{-1} of both ethanol (EtOH) and acetic acid (AA)); process inlet and outlet streams temperature of 25°C; atmospheric pressure. The maximum reactant conversion was required. Process design specifications for all case studies were defined to produce approximately 10 kmol h^{-1} of ethyl acetate (EtAc) with the purity of min. 99.9 mol. %. All process parameters were optimized according to these criteria. Detailed process models, including the heat pump environment, have been compiled and optimized in the Aspen Plus software.

Paper Received: 14 December 2021; Revised: 12 March 2022; Accepted: 28 April 2022
Please cite this article as: Labovská Z., Šulgan B., Labovský J., Jelemenský Ľ., 2022, Safety analysis as integral part of chemical processes intensification and integration, Chemical Engineering Transactions, 90, 133-138 DOI:10.3303/CET2290023

2.1 Conventional process set-up

The conventional process (Figure 1) composed of a continuous stirred tank reactor and several separation columns is reported as the most widespread commercial ethyl acetate production method (Santaella et al., 2015). At least three distillation columns are needed to separate the reaction mixture from the CSTR. First, unreacted acetic acid has to be regenerated, which is a high energy-consuming separation and azeotropic distillation is recommended to reduce energy consumption in the first column (Smith, 2005). One of the process products (EtAc) is used as an azeotropic agent. A decanter has to be deployed to overcome the distillation boundary and thus allow separation of pure EtAc in a second distillation column. The third column is usually used for water regeneration. Despite several options for columns and recycles integration, this process is energy intensive (Toth, 2019). Moreover, large recycles are used due to the distillation boundary and the equipment has also to be relatively large.

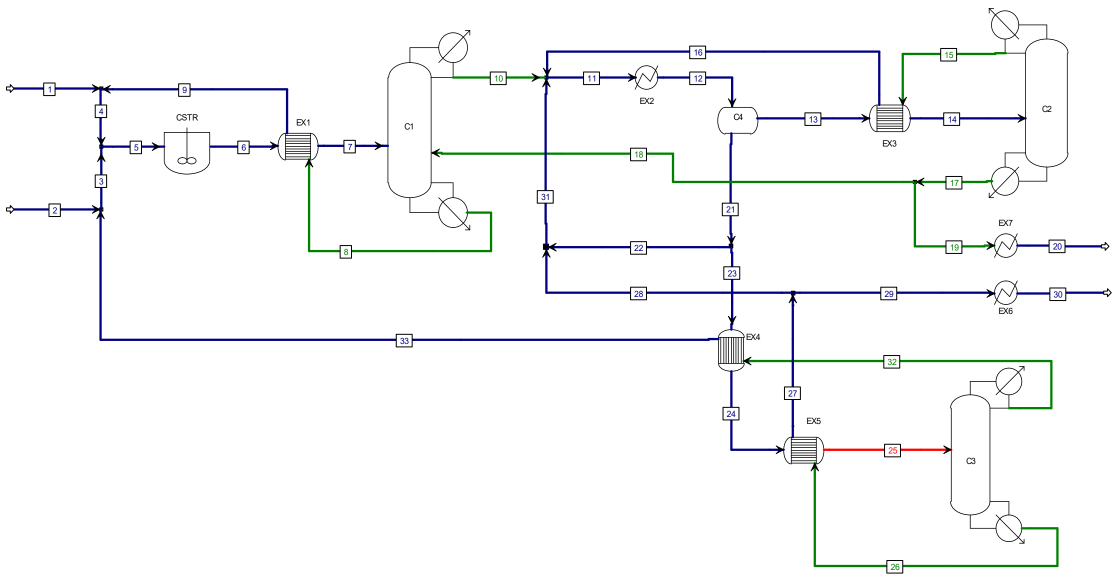

Figure 1: Ethyl acetate production via conventional process set-up adapted from (Šulgan, 2020)

2.2 Reactive distillation process with separation unit

Reactive distillation with a separation unit (RD) is used as the second method for ethyl acetate industrial production (Kiss and Jobson, 2018). As RD is a multifunctional reactor concept combining the mechanisms of reaction and separation in one single unit, benefits such as the reduction of equipment and plant size, improvement of process efficiency, and, consequently, better process economy are expected. RD column, decanter, and two distillation columns are employed (Figure 2). A water-ethanol-ethyl acetate azeotropic mixture is obtained in the RD column and it is then separated in a similar way as in the conventional method.

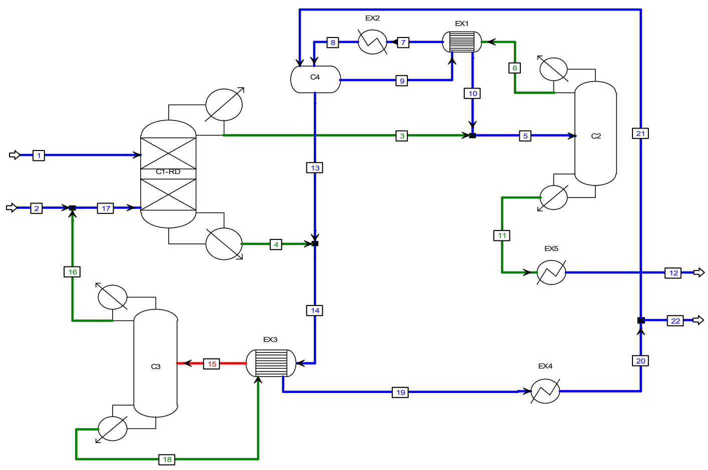

Figure 2: Ethyl acetate production via reactive distillation with a separation unit adapted from (Šulgan, 2020)

2.3 Reactive distillation process with separation unit and heat pump

Energy intensification of the reactive distillation process with separation unit was achieved using a heat pump (Figure 3). A column separating pure ethyl acetate was selected for the implementation of a mechanical vapor recompression heat pump (MVRHP) implementation. The column overhead vapor was compressed to higher pressure to increase its temperature and energy content and was used as a heating medium in the column reboiler (Feng et al., 2017); alternatively, the bottom liquid was flashed in a valve and used to condense the overhead vapor. Integration of a heat pump is expected to lead to process intensification, significant energy savings, and to utility cost reduction.

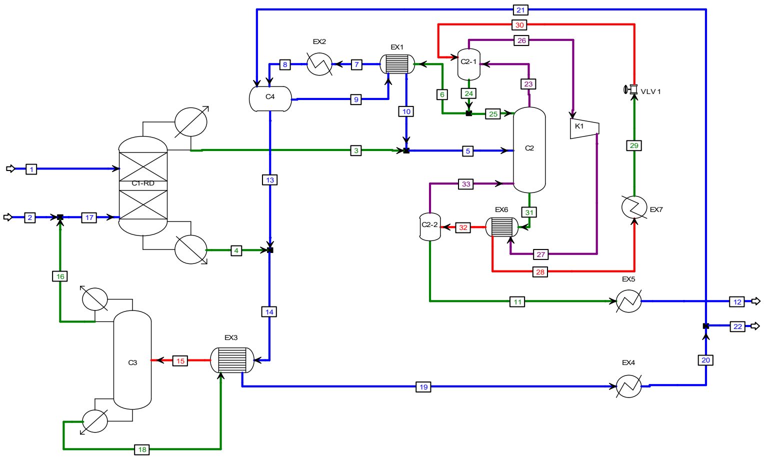

Figure 3: Ethyl acetate production via reactive distillation with separation unit and an MVRHP adapted from (Šulgan, 2021)

3. Results and discussion

As a result of processes optimization in the Aspen Plus software, parameters of the main product stream for all case studies (stream 20 in Figure 1, stream 12 in Figure 2, stream 12 in Figure 3) are the same (molar flow rate: 10.0 kmol h^{-1}, EtAc molar fraction: 0.999, H_2O molar fraction: 0.0002, and EtOH molar fraction: 0.0008). For the designed processes, four different points of view were applied to evaluate their pros and cons. To evaluate the process efficiency and compare it with other alternatives, several indicators, including energy, economy, environmental and safety aspects of all selected process alternatives, were used.

3.1 Process Energy Intensity

Energy consumption of individual equipment units for all processes (conventional process - Figure 1, RD column with a separation unit - Figure 2, and RD column with a separation unit and an MVRHP - Figure 3) were calculated based on the simulation results. Reboiler duty, condenser duty, compressor required network, and cooling duty of heat exchangers including heat integration were evaluated. The sum of overall required heating and cooling duties, except for heat integration and compressor network was calculated and normalized to the specific energy consumption (SEC) related to the production of one ton of pure EtAc. A summary of energy requirements is listed in Table 1.

Table 1: The number of equipment units and energy requirements for designed processes

	Conventional Process (Figure 1)	Column with a Separation Unit (Figure 2)	RD Column with a Sep. Unit and an MVRHP (Figure 3)
Number of main equipment units	5	4	4+K1(compressor)
Number of heat exchangers	7	5	7
Overall cooling duty [kW]	3014.72	2840.50	1244.67
Overall heating duty [kW]	2998.48	2825.74	1065.79
SEC (cooling duty) [kWh $t^{-1}{}_{EtAc}$]	3424.69	3226.77	1413.93
SEC (heating duty) [kWh $t^{-1}{}_{EtAc}$]	3406.24	3210.01	1210.73

From Table 1 it is clear that the RD column with a separation unit (Figure 2) is more energy-efficient than the conventional process. The specific energy consumption (SEC) is lower by 6% in case of both heat consumption and cooling demands. However, significant changes of heating and cooling demands occurred when using the MVRHP. Heating demands related to the production of one ton of pure EtAc (SEC) decreased by up to 62%. When using an MVRHP, a large column condenser is not needed and only a small air cooler is used to remove waste heat, thus, a large amount of cooling duty can be saved. When using an MVRHP for RD column with a separation unit, cooling specific energy consumption (SEC) savings of up to 56.2% can be achieved.

3.2 Economy Aspects

Economic evaluation of the presented case studies is based on optimized simulations of the process models. Electricity, cooling water, and steam are energy utilities and their costs were obtained from the Aspen Plus database (electricity: 0.0775 USD kWh^{-1}, cooling water: 0.0317 USD m^{-3}, steam (0.7 MPa): 0.0179 USD kg^{-1}). Utilities consumption was calculated based on energy requirements of individual case studies and are listed in Table 2. The conventional process (Figure 1) is the most energy-intensive, which is reflected in steam and cooling water consumption. An RD column with a separation unit (Figure 2) is slightly less energy-intensive compared to the conventional process (Figure 1) because of process integration and intensification via reactive distillation. Consequently, when an MVRHP is used in the RD column with a separation unit (Figure 3), the followings saving compared to the original RD column with a separation unit (Figure 2) are achieved: steam consumption decrease of 62.3%; cooling water consumption decrease of 61.6%, but electricity consumption increase by 5.9 times.

Table 2: Utility consumption of individual case *studies*

	Conventional Process (Figure 1)	RD Column with a Separation Unit (Figure 2)	RD Column with a Sep. Unit and an MVRHP (Figure 3)
Electricity [kW]	104.2	58.1	345.1
Cooling water [m^3 h^{-1}]	233.1	219.4	85.0
Steam (0.7 MPa) [kg h^{-1}]	5,220.0	4,920.7	1,856.0

Equipment cost, except for compressor, was calculated using the Aspen Process Economic Analyzer software (ASPEN Technology, 2000). Capital cost as well as installed cost are listed in Table 3. From Table 3 follows that employing the RD column concept (Figure 2) can decrease total capital cost by 11 % in comparison with conventional process (Figure 1), however when an MVRHP is used (Figure 3), the total equipment cost as well as installed cost increased compared to processes without MVRHP by 13.5%.

Table 3: Comparison of total capital, installed annual, and utilities costs of designed processes

	Conventional Process (Figure 1)	Column with a Separation Unit (Figure 2)	RD Column with a Sep. Unit and an MVRHP (Figure 3)
Total capital cost [mil. USD]	9.91	8.84	10.21
Total installed cost [mil. USD]	3.74	3.33	3.85
Total annual cost [mil. USD $year^{-1}$]	9.15	9.04	8.61
Total utilities cost [mil. USD $year^{-1}$]	0.89	0.81	0.51

3.3 Environment Aspects

As it can be seen from Table 2, the MVRHP configuration reduces the energy consumption significantly, which has a direct positive effect on the environment as well as on the amount of greenhouse gases produced. However, in case of CO_2 emissions, a compressor can produce much more CO_2 emissions than a reboiler with the same energy consumption (kW). Therefore, CO_2 emission estimation was included in the presented work. In the CO_2 emission estimation model, used electricity was assumed to be imported to the plant from an electricity producer and distributor (average CO_2 emission factor of electricity: 166.87 kg MWh^{-1}). Heat (0.7 MPa steam) is produced directly at the plant. To generate saturated steam, a steam boiler with the overall efficiency of 93.5% was used (CO_2 emission factor: 55.68 kg_{CO2} GJ^{-1}, calorific value: 34.89 MJ m^{-3}, oxidation factor: 1). CO_2 emissions of individual case studies are summarized in Table 4, from which follows that the presence of the MVRHP (Figure 3) significantly reduces CO_2 emissions (around 56% in comparison with RD column without MVRHP).

Table 4: CO_2 emissions of individual case studies

	Conventional Process (Figure 1)	RD Column with a Separation Unit (Figure 2)	RD Column with a Sep. Unit and an MVRHP (Figure 3)
CO_2 emission (electricity) [t year^{-1}]	141.9	79.1	469.9
CO_2 emission (heat) [t year^{-1}]	6832.4	6440.7	2429.3
overall CO_2 emissions [t year^{-1}]	6974.3	6519.8	2899.2

3.4 Safety Analysis

Overall safety analysis in this work is based on the Chemical Process Quantitative Risk Analysis (GCPQRA 1989). To evaluate and compare safety aspects of the presented alternatives, individual risk estimation was performed for each presented case study. For each type of units, a predefined set of representative incidents was prepared. The final choice of incidents is complex and requires judgment from an analyst; therefore, three main factors were taken into consideration: size of the release, state of released material (liquid, vapor), and character of the release (instantaneous or continuous). Probabilities were adjusted based on a recommendation from (Vílchez et al., 2011). Consequence modeling was performed using standard software system ALOHA (Areal Location of Hazardous Atmospheres) provided by the US Environmental Protection Agency. Results of individual risk estimation for the presented case studies are depicted in Figure 4. To compare all investigated case studies, individual risk is presented in form of risk profiles as a function of distance. Based on the risk profiles, it is possible to conclude that, from the safety point of view, the conventional process set-up (Figure 1) and reactive distillation column with a separation unit (Figure 2) are practically identical and implementing an MVRHP (Figure 3) increases the individual risk of the process. This conclusion was expected because, as the MVRHP is included, the compressor, flash separators, throttle valve, cooler and increased number of pipelines have to be taken into account when preparing the set of representative incidents.

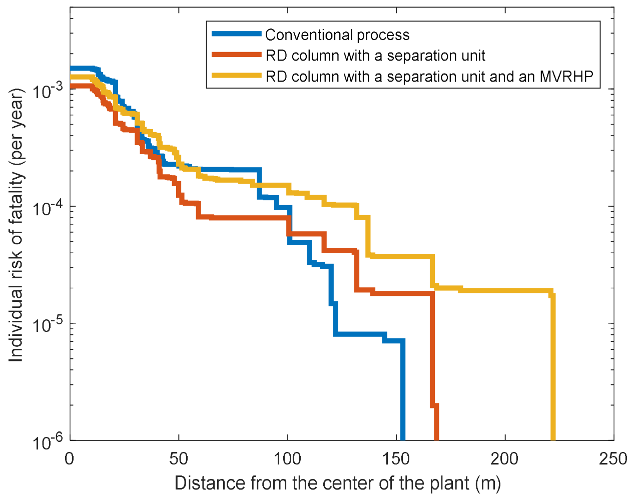

Figure 4: Individual risk of fatality estimation for presented case studies

4. Conclusions

To evaluate the process efficiency and compare the alternatives, several indicators, which consider energy, economy, environmental, and safety aspects of all selected process alternatives, are used. Energy requirements of processes were quantified by specific energy consumption (SEC) method. Proportional reduction in overall heating and cooling consumptions for all three designed processes is clearly visible in Figure 5a. Economy evaluation includes equipment costs as well as utilities cost. The reduction of process energy requirements leads to decrease of utilities cost; however, the integration and intensification of the equipment results in increased capital and installed costs. Proportional changes of utility costs and installed costs for all three case studies is clearly depicted in Figure 5b. Also, the reduction of process energy requirements has a direct positive effect on the CO_2 emissions which has great environmental benefits. MVRHP configuration reduces the emission arising from direct heat production; however, emissions from electricity production are slightly higher as it can be seen in Figure 5c. Integration and intensification of processes which lead to energy, economic, and environmental benefits are not advantageous in terms of process safety; on the contrary, they increase the distance up to which individual risk of fatality is lower than 10^{-5} resp. 10^{-4} $year^{-1}$ as shown in Figure 5d.

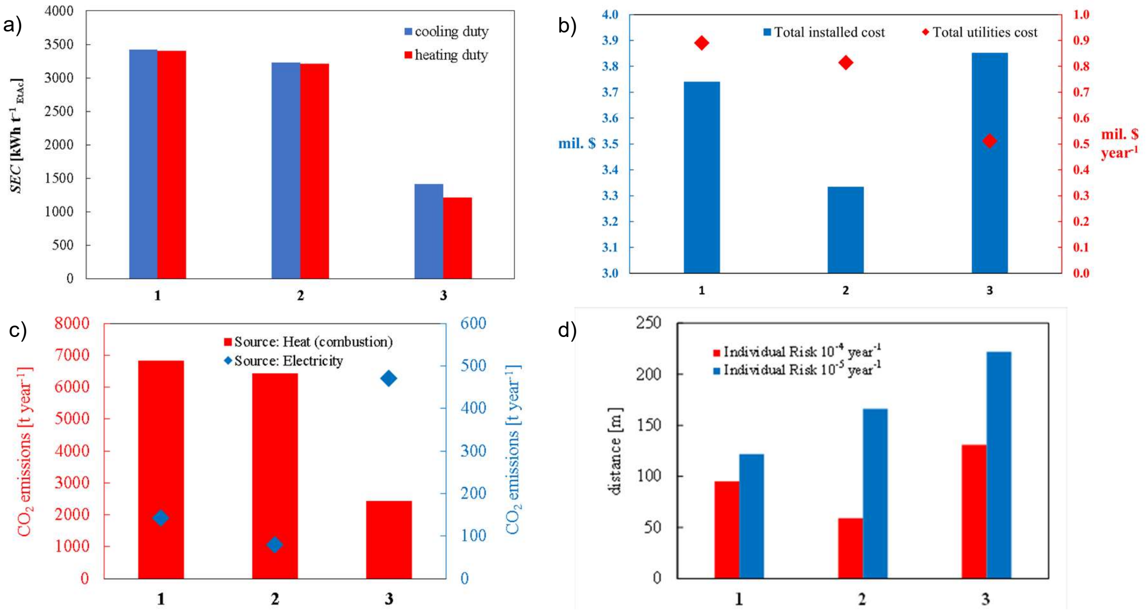

Figure 5: Comparison of: a) energy, b) economy, c) environmental and d) safety indicators of all case studies: 1- conventional process, 2 - RD column with a separation unit, 3 - RD column with a separation unit and an MVRHP

Acknowledgments

This work was supported by the Slovak Research and Development Agency under contract No. APVV-18-0134 and by the Slovak Scientific Agency, Grant no. VEGA 1/0511/21.

References

ASPEN Technology. 2000, *Aspen Plus®: Aspen Plus User Guide*; version 12.0; Aspen Technology Inc.: Cambridge, MA, USA.

Feng, S., Ye, Q., Xia, H., Li, R. and Suo, X., 2017, Integrating a vapor recompression heat pump into a lower partitioned reactive dividing-wall column for better energy-saving performance. Chem. Eng. Res. Des., 125, 204–213.

GCPQRA, 1989, *Guidelines for Chemical Process Quantitative Risk Analysis*. The Center for Chemical Process Safety. American Institute of Chemical Engineers: New York, NY, USA

Kiss, A. A. and Jobson, M., 2018, Taking Reactive Distillation to the Next Level of Process Intensification, *Chem. Eng. Trans.*, 69, pp. 553–558.

Santaella, M. A.; Orjuela, A. and Narváez, P. C., 2015, Comparison of different reactive distillation schemes for ethyl acetate production using sustainability indicators, Chem. Eng. Process. Process Intensif., 96, pp. 1–13.

Smith, R., Chemical Process Design and Integration, 2015, John Wiley & Sons Inc., ISBN13 (EAN): 9781119990130

Šulgan, B., Labovský, J., Labovská, Z., 2020, Multi-aspect comparison of ethyl acetate production pathways: Reactive distillation process integration and intensification via mechanical and chemical approach, In Processes. 8, iss. 12, art. no. 1618.

Šulgan, B., Labovský, J., Variny, M., Labovská, Z., 2021, Multi-Objective Assessment of Heat Pump-Assisted Ethyl Acetate Production. In Processes. 9, iss. 8, art. no. 1380.

Toth, A. J., 2019, Comprehensive evaluation and comparison of advanced separation methods on the separation of ethyl acetate-ethanol-water highly non-ideal mixture, Sep. Purif. Technol., 224, pp. 490–508.

Vílchez, J.A., Espejo, V., Casal, J., 2011, Generic event trees and probabilities for the release of different types of hazardous materials. J. Loss Prev. Process Ind., 24, 281–287.