Fine Chemical Engineering
http://ojs.wiserpub.com/index.php/FCE/

UNIVERSAL WISER PUBLISHER

Short Communication

High Pressure-Driven Batch Distillation Optimal Control for Methylacetate-Methanol Separation

Marija Stojkovic*

Independent Researcher, 10 Copenhagen Street, 53100 Mayenne, Loire County, France
Email: maria.stojkowitz3@gmail.com

Received: 13 September 2023; **Revised:** 19 September 2023; **Accepted:** 19 September 2023

Abstract: The pressure-swing distillation process with high-pressurized batch columns (HHP), with and or without a recycling stream, for separating methyl acetate-methanol is studied from the aspect of optimal control. The results show that even though not heat integrated, the HHP process benefits productivity. Based on the maximum recovery, the dynamic controllability without any kind of heat integration is researched. The optimal cyclic reflux ratio operating policy is extended to the separation of a third non-ideal minimum boiling azeotrope and close boiling mixture of industrial importance, and it shows significant reductions in energy expenditure since the derived discontinuous energy function tends to show cyclic "behavior" again. The proposed process, however, has the economic potential of both capital and energy by internal heat integration, ie. connecting the reboiler of the lower high-pressurized column to the condenser of the higher high-pressurized column. In the future, even more azeotropes, both minimum and/or maximum boilers, should be investigated in order to establish a "heuristic guidance" for HHP design and industrial usage.

Keywords: pressure-swing, batch distillation, methylacetate, methanol, optimal control, direct method

1. Introduction

Wastewater from the pharmaceutical and textile production units contains the greatest quantities of methyl acetate and methanol and is considered as pollution or green unfriendly. The separation of the previously mentioned minimum boiler is done in downstream processes, by unconventional distillation methods, such as extractive (ED), pressure-swing distillation (PSD), pressure-swing extractive (PSE), ionic extractive (IE), etc., whereas the usage of the most of the entrainers re-require the continuation of the downstream processing so as to eliminate by further synthesis/dilution/etc. From the list above, the batch pressure-swing method, theoretically seems as the best option, however, still unresearched from the aspect of controllability.

Hilal et al.[1] defined the term "autoextractive distillation", whereas the experiments were performed for compositions of methanol (10-90%), splitting the entrainer into two branches after the optimal location found, to conclude for its concentration inverse proportionality and the fact to increase the relative volatility, which implies that the specific consumption of the entrainer must be reduced as well, and finally the economical benefits proved along with the purity achieved (90%). However, Huang et al.[2] compared three scenarios for different content of the more volatile component, with and/or without heat integration, to conclude that the first scenario defined with 95% of the more volatile component brought the most in terms of both total annual cost and energy reduction in both cases. However,

DOI: https://doi.org/10.37256/fce.5120243656

after the full integration, it is the scenario with the lowest content in more volatile components that was the "most sensitive" to the full heat integration, as the total annual cost almost doubled despite the fact that reboiler heat duty increased by 37.75%.

Gao et al.[3] investigated the separation of a particular binary mixture dwelling between the standard and vacuum pressure of 20 kPa, by considering steady-state conditions via taking total annual cost and/or total reboiler heat duty, as the objective function, so as to present a fully heat-integrated process but with a low level of controllability. Zhang et al.[4] studied two cases for a similar azeotrope, by going from vacuum to a higher pressurized column, and inverse, whereas in the previously mentioned case reflux ratio for low-pressure (LP), the column was even 4 times greater compared to the second case. Moreover, partial/full heat integration respectively brought 22.4%/33.3% in total heat input savings, and 17.14%/26.64% in total annual cost, respectively. Cao et al.[5] experimented with eight different feed temperatures to examine their influence on total annual cost: the larger the shift in pressure is the lower the recycle flow rate, and the energy expenditure in two reboilers is 8-12 atm. Graczová et al.[6] varied heat flux in heat exchangers, to prove that there exists a trade-off between the usage of the larger equipment (columns, condensers, exchangers), to obtain the lowest difference between condenser and exchanger(s) duties with the usage of the unique exchanger of regenerated entrainer, and on the other side, the option of the usage of at least two heat exchangers at the expense of the greater total energy requirement.

Yang et al.[7] worked on the extractive pressure-swing continuous process, so as to compare four designs, whereas the lowest total annual cost and/or energy expenditure was shown for the largest shift in pressure (between vacuum 0.6 atm and higher 10 atm). Compared against the base case of standard pressure extractive, 62.6%/92.52% in total annual cost/entrainer savings of (quantity/flow rate), respectively. Zhang et al.[8] reported a thermodynamic study for different ionic liquids as potential entrainers, reported the minimum mole fractions of electrolyte to break the azeotrope at standard temperature is 0.123 for 1-butyl-3-methylimidazolium chloride ([C4MIM][Cl]), similarly, as Zhu et al.[9] who fitted parameters obtained experimentally after the optimization with COSMO-SAC employed for entrainers ([BMIM][Cl],[HMIM][Cl]). Chen et al.[10] chose a part of the industrial scheme of polyvinyl alcohol (PVA), to present the pressure swing with side withdrawal, applying temperature control to cope with large feed disturbances consisting of 4 loops: 1. First loop: all flow rates controlled (reflux, distillate, feed, reflux), pressure controlled by manipulating heat duty in the condenser of LP column, even temperature of the entrainer flow rate controlled by manipulating reboiler duty and reflux ratio for high-pressure (HP) column. 2. Second loop, assumed reflux ratio for HP column fixed. 3. Third loop: provides compensation control, by calculating the relationship between boiling temperature and pressure of the liquid entering the entrainer feed stage through the specific equation. 4. Fourth loop: keeps temperature difference between reboiler and sensitive pate constants calculated previously.

Wang et al.[11] investigated extractive pressure-swing for a ternary mixture of methyl acetate-methanol-water, to compare with vapor side stream, applying double-loop classical control: 1. In the first layer: double temperature control keeps internal reflux constant by proportional control of reflux rate and entrainer feed stage temperature controlled by reverse action of reboiler duty. 2. In the second layer: the temperature from the first loop acts as a feedforward of the ratio of reboiler duty to feed. Luyben[12] researched a continuous pressure-swing process, arising pressure from the vacuum of 0.25 bar to higher (7 bar), treating the maximum boiler of methanol-trimetoxysilane, for the reason of composition shift by about 10%, by adjusting pressure, on the other side reported the effects of pressure in HP column, by increasing pressure from 4 to 8, consequent by an increase in reboiler heat duty of LP/HP respectively, by 21.69%/27.88%, respectively. Munoz et al.[13] investigated a similar mixture of alcohols/acetates, (minimum boiler), to define the optimal ratio entrainer to feed in the extractive distillation case, which is 1.33 as it brought the lowest total annual cost, but not the optimal reboiler heat duty. Cui et al.[14] did the electrification of the process and the greatest total annual cost reduction of 47.82% was perceived by self-heat recuperation technology, while emissions are 14/3 times respectively, reduced compared to conventional/heat pump assisted process, respectively.

In this work, high-pressure driven pressure-swing batch distillation of methyl acetate-methanol azeotrope was theoretically investigated from the aspect of optimal control. The insights given show significant potential for the energy savings predictions, by both external and/or internal heat integration, since if only higher pressure increased by a unit, there would exist an affordable difference in the exit temperature (ie. approx. 40 °C). Futural works should give also the perspective predictions in total annual cost reduction, and green friendliness estimation, as given by Aqar et al.[15-17] and Aqar and Mujtaba.[18]

2. Materials and methods

2.1 *Optimal control problem*

In this short communication, the author aims to expand the optimal control strategies to the separation of the other mixtures with minimum boiling azeotrope, by pressure-swing batch distillation. In particular, a case of methyl acetate-methanol is taken into examination, because it is a part of the industrial manufacturing process of polyivinyl acrylate (PVA). The optimal control problem can be described as follows: For a given pressure-swing batch distillation configuration (-total number of trays, -working pressure), batch composition, the distillation task, and overall time horizon, determine the optimal reflux ratio so as to maximize the distillate, subject to any constraints (model equations, bounds on the optimization variables).

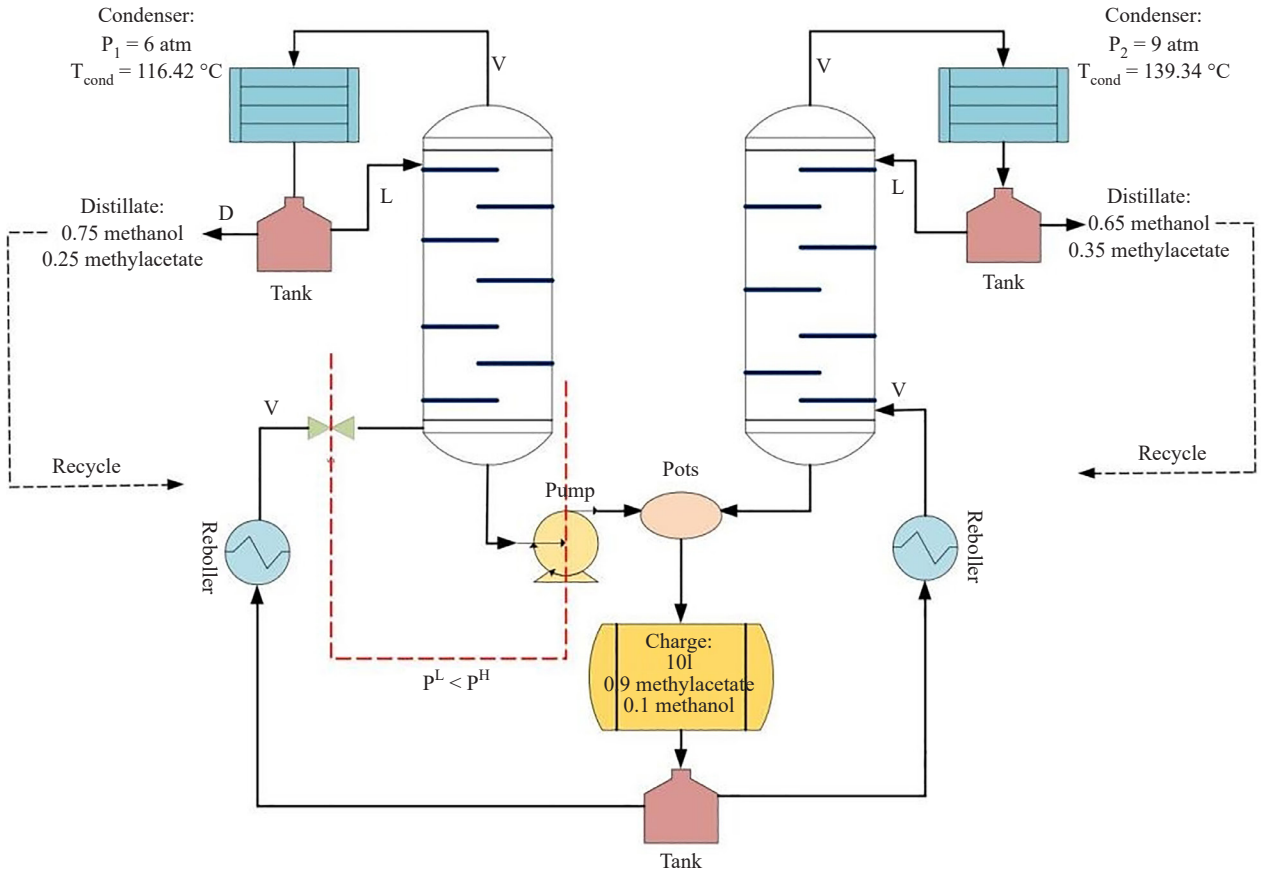

Figure 1. Double-rectifier columns with recycle streams and internal heat integration for pressure-swing batch distillation

The pressure-swing process scheme presented in Figure 1, assumes "one-pass" through the column at the time, in other words it is assumed that columns work consecutively ("two-step" process), in a double batch rectifier configuration. But the maximum achievable distillate concentration at lower pressure is 75% of methanol, but it decreases to 65%. A small gap in total pressures brings not many benefits in terms of purification (since the gap of only 10%), but it makes sense for internal heat integration since the temperature(s) gap has been already existed between the bottom of the the first high-pressurized column (HP_1) and top of the second high-pressurized column (HP_2) rectifier, counting more than 30 °C if the pressure increased to 10 atm. Moreover, in Table 1, the parameters corresponding to the thermodynamics model NRTL with extended coefficients (for temperature dependence), and originating from Gmehling

et al.[19] are tabulated, and verified with the work of the authors Wang et al.[17] Table 2 and Table 3 contain the extended Antoine coefficients and physical properties, respectively, obtained from Aspen HYSYS.[20] In Figure 2, the vapor-liquid equilibria are presented for a mixture of methyl acetate-methanol at different pressures (6 and 9 atm), whereas the NRTL model applied is verified by ChemCad[21] professional simulator.

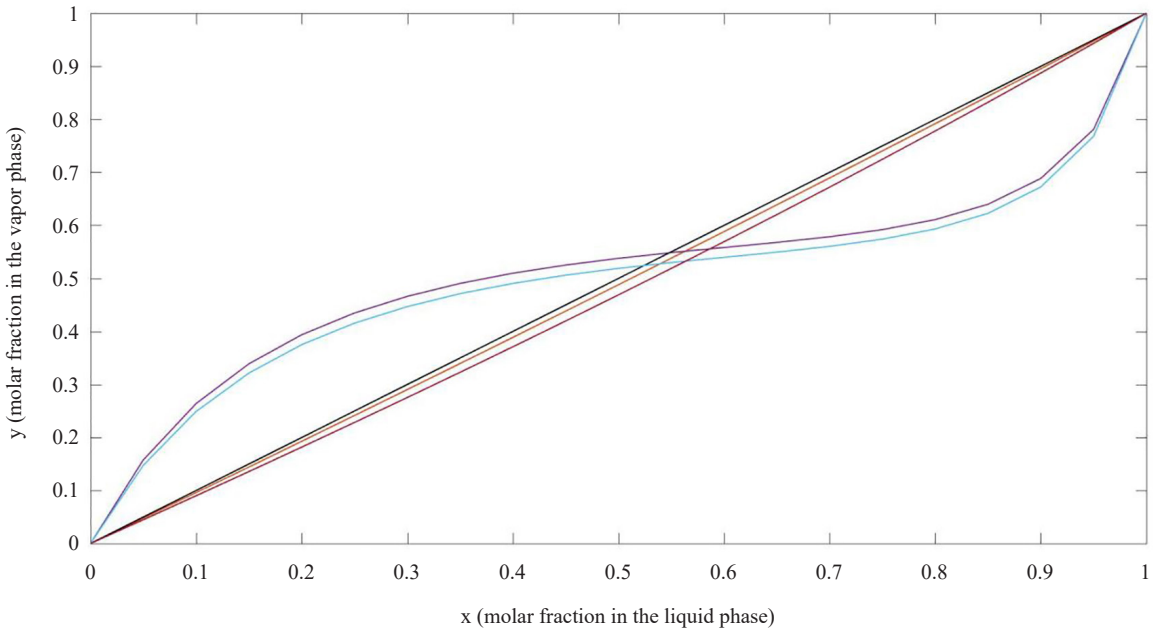

Figure 2. Vapor-liquid equilibrium curves for methylacetate-methanol mixure at different pressures
Note: Blue line stands for the high pressure of 9 atm, and red stands for the high pressure of 6 atm.

Table 1. Binary interaction parameters for NRTL model (extended parameters)

Component i	Component j	A_{ij}	A_{ji}	B_{ij}	B_{ji}
		[cal/mol]	[cal/mol]	[cal/mol]	[cal/mol]
Methylacetate	Methanol	6.9761	-3.1925	-2118.54	1223.30

Table 2. Extended Antoine parameters for methylacetate/methanol from Aspen

Component	C_1	C_2	C_3	C_4	C_5	C_6	C_7	T_{min}/T_{max}
Methylacetate	54.3592	75.8102	0	0	-5.6473	$2.108 \times 10^{-11.8}$	6.0	175.15/505.65
Methanol	-5618.60	-6904.50	0	0	-8.8622	7.4664×10^{-6}	2.0	175.47/512.50

Table 3. Physical properties of the components (Aspen Plus)

Component	Methylacetate	Methanol
M/g mol^{-1}	79.0794	32.0421
T_c/K	506.55	512.50
P_c/KPa	4,750.00	8084.00
ω	0.3312	0.5658
Z_c	0.2570	0.2220
v_c [cm^3/mol]	0.2280	0.1170

3. Results and discussion

The working conditions and predefined parameters are tabulated in Table 4, whereas concentrations are expressed from methyl acetate, and HP_1/HP_2 refers to low/high-pressure column, respectively. In Table 5, the optimal results obtained by control solver BOCOP, are tabulated, for the total number of stages, the total number of trays (*N)*, for HP_1/HP_2, rectifier column, respectively. The optimal control problem formulation has been already detailed by Stojkovic et al.[22]

In the first step, ie. the first high-pressurized column (N_1 = 32) where total pressure is set at 6 atm, as expected the initial and final arc match with maximum distillate rate (infinite reflux condition, rectifier). It is to note that the very first and second zero periods are disregarded due to their extremely short duration, surrounding the complex structure of singular arcs. The optimal control trajectory is composed of 46 bang arcs of maximal distillate rate, measured duration of "equivalent bang cycles" is 0.0712 h. But only 4 singular arcs exist, appearing as consecutive two as second, and two as penultimate, with a tendency to have a duration of approximately 10.47% of the total time. In summary, the optimal control structure for the HP_1 column presented in Figure 3 contains 46 bang arcs, 45 zero arcs, and 4 singular arcs. Finally, there are 91 switchings between different types of optimal control. Last but not least, remember that both the total number and position of singular arcs are the same for all the HP_1 cases tabulated.

In the second step, ie. the second high-pressurized part of the process, where total pressure is set at 9 atm, as supposed the initial and final arc match with the maximum distillate rate (infinite reflux condition-rectifier). First to observe is that the total number of bang arcs is considerably decreased compared to the HP_1 step, by even 28.57%. Further, it is observed that the optimal control trajectory is composed of almost all bang-bang arcs, with two consecutive singular arcs closely following after the starting bang arc, and a complex singular arc structure preceding the bang period. There are 65 commutations between different types of control, an interesting fact is that only one singular arc exists, and again is 'positioned' again in the penultimate period, whereas here it lasts approximately 7.15% of the total operation time (t_f), and noted measured duration of the "equivalent bang cycles" is 0.0712 h.

Table 4. Working conditions

Parameter	P	U_N^0	U_i^0	V	t_f	x_N^0	y^*
	[atm]	[atm]	[l]	[mol/h]	[h]		
Predefined/ initial value	HP_1: 6 HP_2: 9	20	0.1	11	1.6	0.1	HP_1: 0.74 HP_2: 0.64

Table 5. The optimal results by BOCOP solver

Product recovered	N	$U_a(t_f)$	Recovery rate without recycle, [%]	Recovery rate with recycle, [%]	Discr. scheme, nb. of points
Methanol	17	7.4420	48.25	87.07	Gauss, 2,200
		7.1322	47.24	85.87	
Methylacetate	22	5.6384	48.86	95.24	Gauss, 2,200
		5.3068	47.42	92.38	
		5.1547	46.19	85.69	
		5.0099	46.38	80.42	
		4.7488	42.34	74.16	

Table 5 presents the achieved quantities and recovery rates for cases with/without recovery stream, respectively, where the HP_1/HP_2 step, respectively, is processed under the lower/higher pressure of (6-7)/(6-10), respectively. If the operation included and/or not, respectively, included the recycle stream: The recovery rates for the HP_1/HP_2 step, respectively, are observed to increase by even less than 2.0% for an increase in pressure by unit. On the other side for the same total pressure, the recycle stream provides an improvement in recovery rate of somewhat more than 38% for the HP_1 step. However, for the HP_2 step, with the decrease in the higher total pressure set, it gradually (stepwise) increases in intervals of 31.82%/46.38%, respectively.

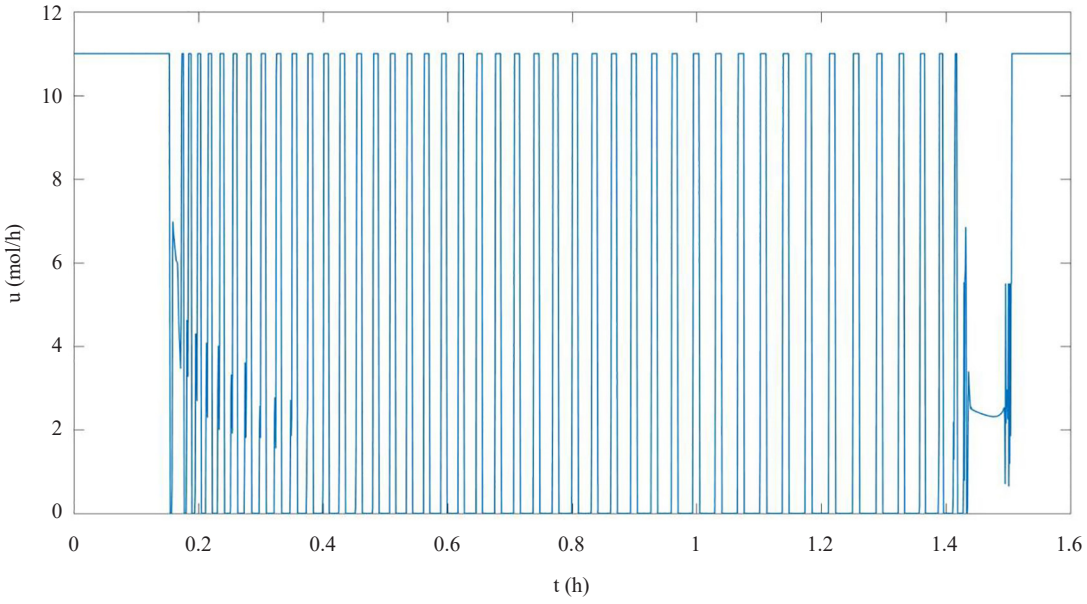

Figure 3. The optimal distillate rate for $u(t)$ for the HP_1 step

Table 6. The optimal results by BOCOP solver

Step	Pressure	Total number of cycles	Number of bang periods	Number of zero periods
HP_1	6	91	46	44
	7	92	46	45
	7*	86	43	41
HP_2	6	73	37	36
	7	67	33	32
	8	65	33	32
	9	61	30	29
	10	60	29	28

*single period tf = 0.8 h

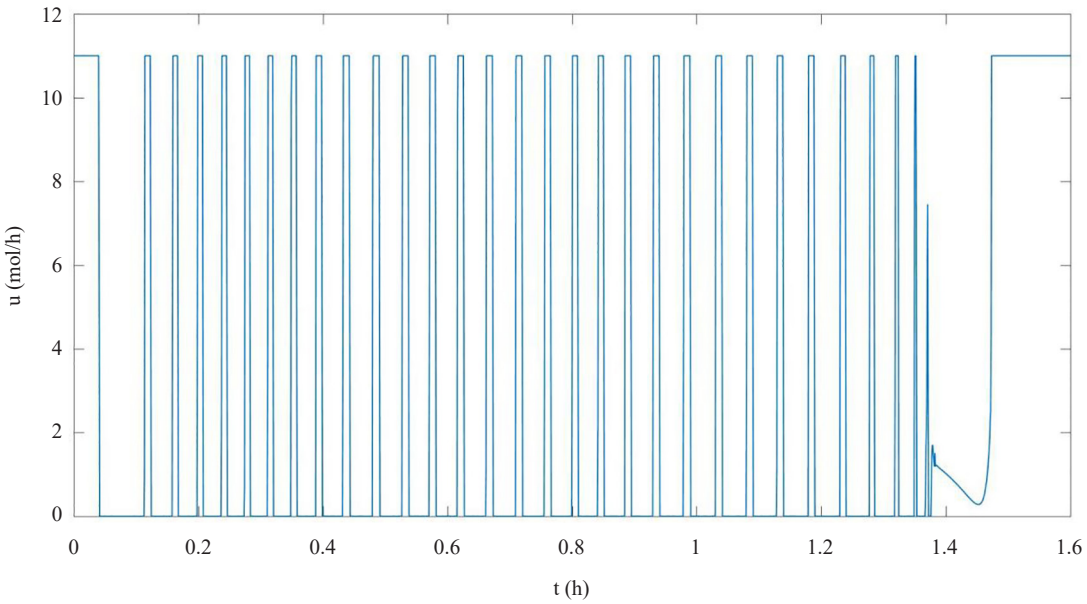

Figure 4. The optimal distillate rate for the HP_2 step

In Table 6, the units of sequences of the optimal control structure such as bang and zero are tabulated, but the singular arcs are excluded: 1) For the HP_1 step one can observe a very similar structure for an increase of one unit of total pressure. But for the overall time horizon reduction from double to single period: the optimal control pattern changes gradually, as the difference in the total number of cycles between the patterns for minimal and maximal total pressure set is 6. 2) For HP_2 step one can observe a clear difference in the optimal control pattern, for an increase of pressure by one unit, the total number of cycles decreases consecutively by 2/4, respectively. Furthermore, a parametric

sensitivity study brought the knowledge: for a gap of 4 atm (between the minimal and maximal total pressure imposed), the total number of cycles decreases by even 12, and the pattern is shortened by a regular sequence of bang-zero repeated for even 7 times (Figure 4). The total number of singular arcs is not tabulated, for reason that the only two consecutive singular arcs in the same position (penultimate) are observed in all cases. Accordingly, it is recommended to have at least one recycle stream, in order to bust the recovery rate, and for further improvements "trade" between the overall process duration, which implicates heat input requirement, and recovery rate should be done.

Moreover, in Figure 5, the output for the temperature evolutions along with the optimal solution is presented. Above, the temperatures on all the stages of the column for the first high-pressurized rectifier (HP_1 step) are depicted. From here, the interval of temperature increases along with the rectifier, going from the bottom to the top (batch to accumulator), following the optimal trend from the minimal temperature of 111.53 °C to the maximal one at 122.04 °C, at the specified working pressure of P_1 = 6 atm. As previously stated, verify that the methanol is recovered in the product tank. Below, the optimal temperature evolutions are presented for the second high-pressurized rectifier, HP_2 step of the process, at the specified working pressure of P_2 = 9 atm, temperature rise from the bottom to the top, following the trend within the temperature interval from the minimal temperature of 126.34 °C to the maximal temperature of 139.34 °C. Hereby, previously written goes in favor of the fact that methyl acetate is recovered in the second high-pressurized column product tank. As a consequence, it is verified that the ultimate goal of the designed two-step process, ie. consecutive production of methanol and methyl acetate is achieved. Consequently, there is space for future works, if the pressure gap is broadened, as it busts the difference between top and bottom temperatures, and implies possible internal/external heat integration. Lastly, the overall horizons of temperatures covered for different pressures applied, is confirmed with the azeotropic data given by Wang et al.[23]

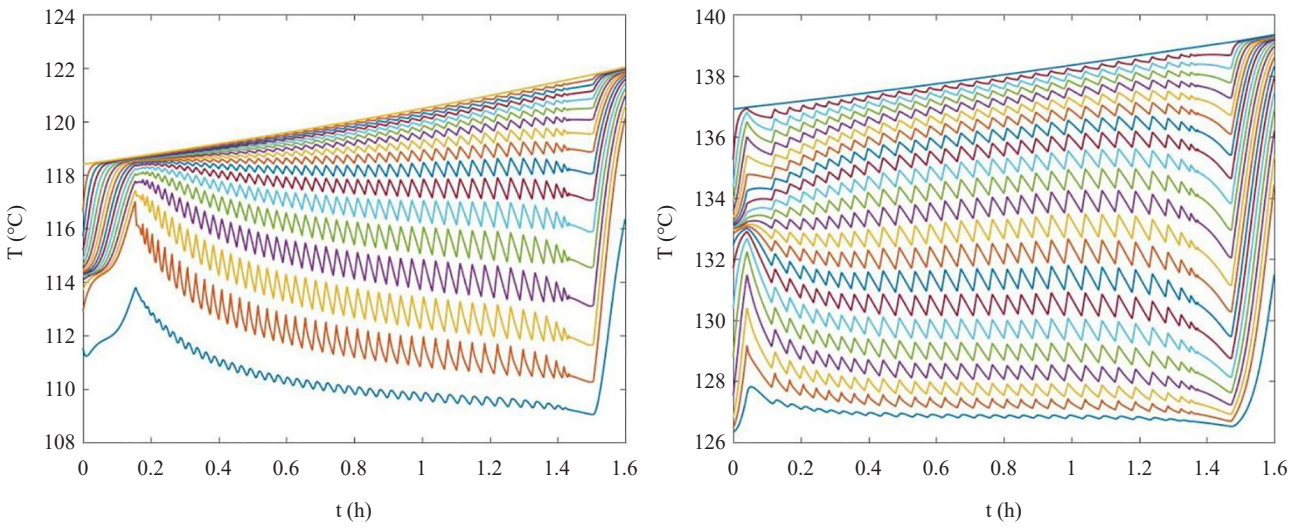

Figure 5. The optimal temperature evolutions for: 1) left: HP_1 step, 2) right: HP_2 step

3.1 *The influence of time interval*

The influence of the total time period imposed, ie. single period or double period, on the structure of the optimal control pattern is observed, as well. In Figure 6, the optimal control patterns for low pressure set at 7 atm, are plotted over different time horizons. First to observe is the very first bang arc, that approximately 4 times longer in duration in favor the later (single), interestingly, the ending bang arcs can be considered equal (less than 1.5% of difference). One can also observe that, with the elongation of the time parameter, the structure becomes more complex: Firstly, the total number of cycles is increased by around 6.5% (or even 6 more in favor of a double period). It is that one can perceive an additional sequence of "zero-bang-zero-singular-bang-zero", as additionally included to the previously obtained

structure for a single period duration. Moreover, the ending sequence singular arc(s) tends to last almost equally and of similar complexity of curvature. Finally, for the particular case examined at the total pressure set at 7 atm, the recovery rate considerably increased, only after recycling as it is to reach more than 98% compared against the later (double period). Based on the maximum recovery rate, the "optimal high pressure found for the first/second, respectively, the high-pressurized column is 7 atm/6 atm, respectively, whereas the 'optimal time, found is to be 1.6 h/0.8 h, respectively. Importantly, the overall time horizon imposed influenced, the optimal control pattern to change, as the difference in the total number of cycles between the minimal and maximal total pressure varied by 6. In summary, for the single period duration, the "equivalent bang sequences" are "squizzed" or positioned more closely to each compared with the double period case, and at the expense of the zero arcs, which are shortened. A very important conclusion can be derived from previous observations: closely related operational cyclic strategies are valid over different time horizons, and this enables us to plan in advance the production without fear of the possible appearance of complex sequences afterward. As previously stated, also encouraged to examine a particular process on a shorter total time duration, so as to have a "solid base" for future studies.

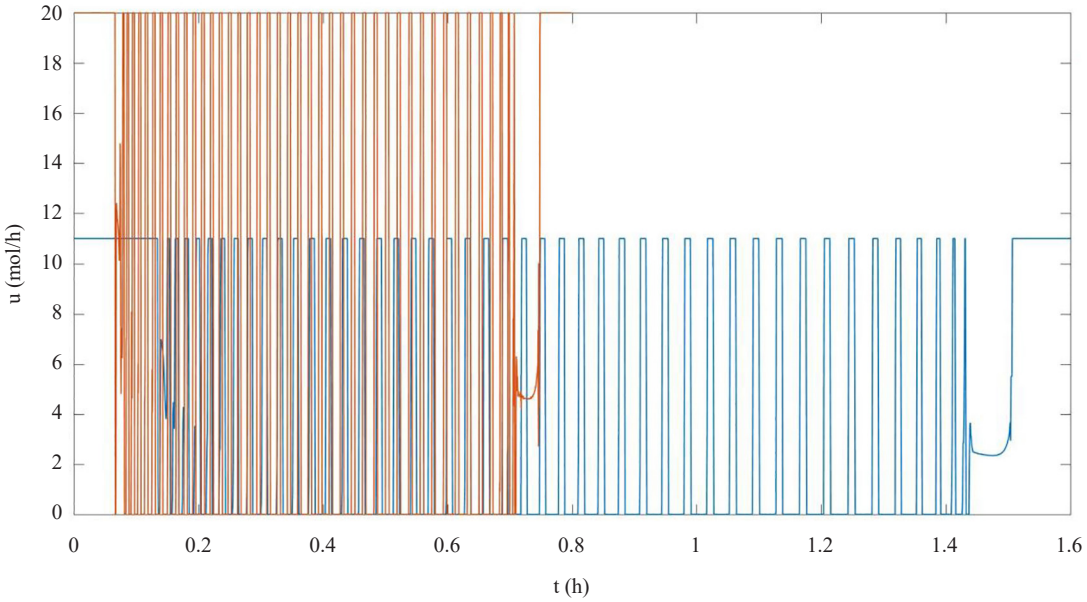

Figure 6. The influence of a number of periods on the control structure: 1) red: time period set at 0.8 h, 2) blue: time period set at 1.6 h

When it comes to verification, it should be remembered that the accuracy of the results comes from the displayed temperature change per stage for the observed component, and for each respective part of the high-pressurized process. Performing the economic analysis, on the other hand, would be very difficult for several reasons: 1) very short duration of the previously named "equivalent bang arcs", appearing even in the form close to the "impulses", which make up the absolute majority among the bang periods; 2) a very short "distance time duration" between the "equivalent bang arcs", marked as "zero arcs" as well, making up the absolute majority among zero arcs, generally (Table 6). On the other hand, the estimation for the energy expenditure in the reboiler, could be done by the professional software tool ChemCad, tracking the change of energy with time, but only after scaling up the process (for the increased values of the batch pot, and consequently total time).

In Figure 7, finally, the elevated pressure part of the process, (ie. P_2 = 10 atm), could only be approximately simulated by the professional simulator, ChemCad, due to the existence of the complex singular arc in the pre-ultimate period as seen on the Figure 4, from this reason, it is considered as "attached" to the very last 'bang arc". The presented below gives a clear idea of the "discontinuous energy function" (almost ie. quasi-bang-zero-bang Stojkovic[24]), since it

is estimated to lower the heat at the minimal value close to zero for almost 78.32% of the total duration of the process, moreover, the defined period can be separated in two intervals: 1) period of almost constant energy, which duration is somewhat more than 10%; 2) the second very long period of linear increase, which average value does not exceed 15% of the maximum achieved in the final period of "quasi-bang" , where estimated instantaneously to rise the heating to its maximum and keep it till the end of the process or for almost 14% of the total processing time. The HP_1 step, however, being even more complex in its optimal control structure, ie. having an even increased total number of bang/zero arcs, respectively, or by 30% more compared to the HP_2 step, is characterized by even more narrow placement of "equivalent bang arcs" connected by sometimes even instantaneous zero arcs, therefore not addressed in the verification step. The cyclic reflux ratio optimal control strategy is confirmed in coping with the feed disturbances by keeping "stable" the product composition (not more than 5%).

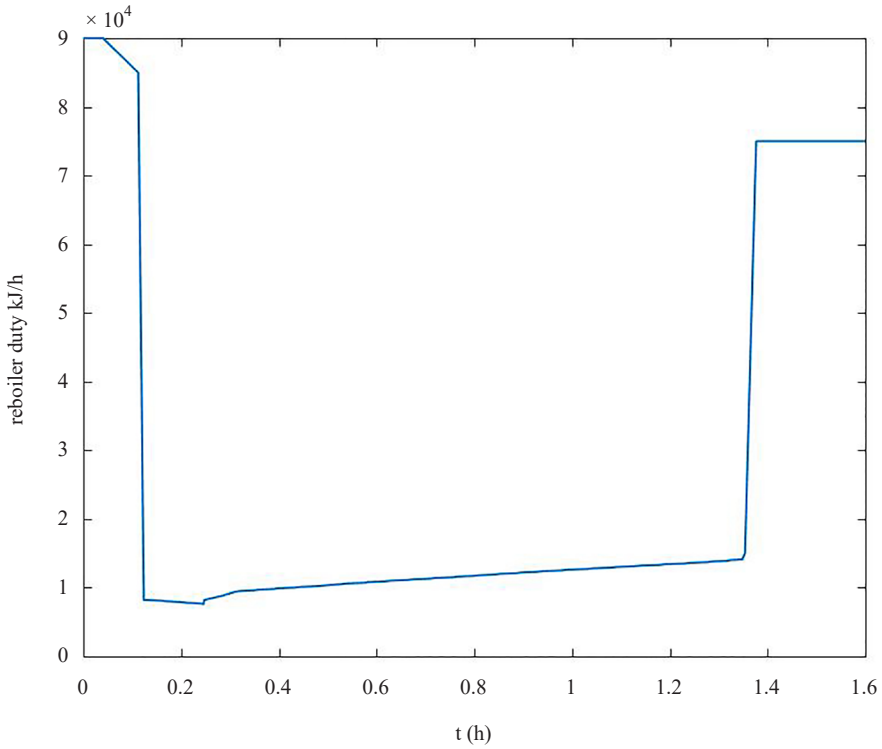

Figure 7. Discontinuous reboiler energy function

4. Conclusions

A high-pressure-swing batch distillation process (HHP) for separating the minimum boiler of methyl acetate-methanol is researched. The optimal cyclic reflux ratio policy is proposed for both schemes, with and without a recycling stream, considering varying predefined total times, and finally adjusting the total pressures to achieve optimality. The outcome of the study was to find the optimal total pressures over the optimal overall time horizon in the sense of the maximum recovery rate. Furthermore, the study indicates the strong potential of the proposed strategy for both internal and/or external heat integration, which further implies reducing the total annual cost of the process being a part of the already existing industrial methods commercially used in PVA production.

Conflict of interest

The author declares no competing financial interest.

References

[1] Hilal, N.; Yousef, G.; Langston, P. The reduction of extractive agent in extractive distillation and auto-extractive distillation. *Chem. Eng. Process: Process Intensif.* **2002,** *41*, 673-679.

[2] Huang, K.; Shan, L.; Zhu, Q.; Qian, J. Adding rectifying/stripping section type heat integration to a pressure-swing distillation (PSD) process. *Appl. Therm. Eng.* **2008,** *28*, 923-932.

[3] Gao, X.; Zhu, B.; Ma, J.; Yang, D. A combination of pressure-swing and extractive distillation for separating complex binary azeotropic system. *Chem. Eng. Process: Process Intensif.* **2017,** *122*, 269-276.

[4] Zhang, Q.; Liu, M.; Li, C.; Zeng, A. Heat-integrated pressure-swing distillation process for separating the minimum-boiling azeotrope ethyl-acetate and ethanol. *Sep. Purif. Technol.* **2017,** *189*, 310-334.

[5] Cao, Y.; Li, M.; Wang, Y.; Zhao, T.; Li, X.; Zhu, Z.; Wang, Y. Effect of feed temperature on economics and controllability of pressure-swing distillation for separating binary azeotrope. *Chem. Eng. Process: Process Intensif.* **2016,** *110*, 160-171.

[6] Graczová, E.; Šulgan, B.; Barabas, S.; Steltenpohl, P. Methyl acetate-methanol mixture separation by extractive distillation: Economic aspects. *Front. Chem. Sci. Eng.* **2018,** *12*, 670-682.

[7] Yang, A.; Sun, S.; Shi, T.; Xu, D.; Ren, J.; Shen, W. Energy-efficient extractive pressure-swing distillation for separating binary minimum azeotropic mixture dimethyl carbonate and ethanol. *Sep. Purif. Technol.* **2019,** *229*, 115817.

[8] Zhang, Z.; Hu, A.; Zhang, T.; Zhang, Q.; Sun, M.; Sun, D.; Li, W. Separation of methyl acetate + methanol azeotropic mixture using ionic liquids as entrainers. *Fluid Ph. Equilibria.* **2015,** *401*, 1-8.

[9] Zhu, Z.; Geng, X.; He, W.; Chen, C.; Wang, Y.; Gao, J. Computer-aided screening of ionic liquids as entrainers for separating methyl acetate and methanol via extractive distillation. *Ind. Eng. Chem. Res.* **2018,** *57*, 9656-9664.

[10] Chen, Y.; Liu, C.; Geng, Z. Design and control of fully heat-integrated pressure swing distillation with a side withdrawal for separating the methanol/methyl acetate/acetaldehyde ternary mixture. *Chem. Eng. Process: Process Intensif.* **2018,** *123*, 233-248.

[11] Wang, H.; Ji, P.; Cao, H.; su, W.; Li, C. Design and control of extractive disitllation for the separation of methyl acetate-methanol-water. *Korean J. Chem. Eng.* **2018,** *35*, 2336-2347.

[12] Luyben, W. L. Methanol/trimetoxysilane azeotrope separation using pressure-swing distillation. *Ind. Eng. Chem. Res.* **2014,** *53*, 5590-5597.

[13] Munoz, R.; Monton, J. B.; Burguet, M. C.; de la Torre, J. Separation of isobutyl alcohol and isobutyl acetate by extractive distillation and pressure-swing distillation: Simulation and optimization. *Sep. Purif. Technol.* **2006,** *50*, 175-183.

[14] Cui, C.; Long, N. V. D.; Sun, J.; Lee, M. Electrical-driven self-heat recuperative pressure-swing azeotropic distillation to minimize process cost and CO_2 emission: Process electrification and simultaneous optimization. *Energy.* **2020,** *195*, 116998.

[15] Aqar, D. Y.; Rahmanian, N.; Mujtaba, I. M. Methyl lactate synthesis using batch reactive distillation: Operational challenges and strategy for enhanced performance. *Sep. Purif. Technol.* **2016,** *158*, 193-203.

[16] Aqar, D. Y.; Rahmanian, N.; Mujtaba, I. M. Investigation about profitability improvement for synthesis of benzyl acetate in different types of batch distillation columns. *Chem. Eng. Trans.* **2018,** *70*, 541-546.

[17] Aqar, D. Y.; Al Alak, H. H.; Rahmanian, N.; Mujtaba, I. M. The investigation of purity imrpovement for the production of methyl propionate in different types of batch distillation. *J. Oil Gas Petrochem. Technol.* **2018,** *5*, 63-75.

[18] Aqar, D. Y.; Mujtaba, I. M. Economic feasibility of an integrated semi-batch reactive distillation operation for the production of methyl decanoate. *Sep. Purif. Technol.* **2021,** *257*, 117871.

[19] Gmehling, J. M.; Krafczyk, J.; Fischer, K. *Azeotropic Data*; Wiley-VCH, 2004.

[20] Aspentech. *Aspen Property System: Physical Porperty Methods and Models 11.1*; Aspen Technology, Inc: Burlington, M.A., 2001.

[21] Chemstations Inc. *ChemCAD Dynamic Column Calculation User's Guide*; Chemstations: Houston, TX, 2007.

[22] Stojkovic, M.; Gerbaud, V.; Shcherbakova, N. Cyclic operation as optimal control reflux policy of binary mixture

batch distillation. *Comp. Aid. Chem. Engng.* **2018,** *108*, 98-111.
[23] Wang, Y.; Qi, P.; Yang, X.; Zhu, Z.; Gao, J.; Zhang, F. Exploration of a heat-integrated pressure-swing distillation process with a varied-diameter column for binary azeotrope separation. *Chem. Eng. Commun.* **2019,** *206*, 1689-1705.
[24] Stojkovic, M. *Pressure-Driven Batch Distillation Optimal Control for Acetone-Methanol Separation*; ChemrXiv, 2022.