A Heat-Integrated Reactive Distillation Process for Methyl Lactate Hydrolysis

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ABSTRACT

Lactic acid is predominantly produced through microbial fermentation of renewable feedstocks. However, direct separation and purification of lactic acid from the fermentation broth is difficult. A two-step process involving (1) esterification of raw lactic acid with methanol to produce methyl lactate, and (2) hydrolysis of the methyl lactate to produce high-purity lactic acid, is commonly used. The hydrolysis step is typically carried out in a reactive distillation (RD) column to overcome equilibrium limitations by continuous removal of the product(s). However, the conventional RD process is highly energy intensive and has relatively low thermodynamic efficiency. We show that the energy requirement of the RD column can be significantly reduced by implementing external heat integration via a heat pump. Specifically, we show that a vapor-recompression-based reactive distillation (VRC-RD) column offers up to 63.4% energy savings relative to the conventional RD column. The energy savings are further increased to 64.9% in a pre-compressor split (PCS-VRC-RD) configuration. This reduction in the total utilities requirement results in an increase in thermodynamic efficiency from 21.4% for the conventional RD column to 38.7% for the VRC-RD column and to 40.3% for the PCS-VRC-RD column. For a payback period of 5 years, these energy savings respectively correspond to 32.0% and 33.8% reduction in the total annual cost (TAC) relative to the conventional RD column.

1. Introduction

Lactic acid (LA) has numerous applications in food, bioplastics, cosmetics, pharmaceutical, fertilizers, and chemical industries. The viability of making an inexpensive biodegradable polymer — poly-lactic acid — from LA has led to extensive interest in the production of high-purity LA [1]. Lactic acid can be produced by both chemical and microbial routes. The chemical route generally results in a racemic mixture of LA with equal amounts of right- and left-handed enantiomers. On the other hand, microbial fermentation of renewable carbohydrates can be used to produce a specific stereoisomer. Because of the accessibility of cheap raw materials and high selectivity, the microbial fermentation route accounts for over 90% of the LA production [2,3]. However, the downstream separation and purification of LA from the fermentation broth is difficult because of LA's strong affinity to water and its tendency to self-polymerize [2]. It has been estimated that these separation and purification steps account for up to 50% of the total production cost [4].

The most attractive method for upgrading raw LA in the fermentation broth to high-purity LA is a two-step reaction process [5]. In the first step, raw LA is esterified using an alcohol. Su et al. [6] have shown that methanol is the most suitable alcohol for this process. Impurities including unfermented sugars and high-boiling organic acids (e.g., succinic acid) stay in the esterification reactor, typically a CSTR. In the second step, the purified LA-ester is hydrolyzed in a reactive distillation (RD) column over a catalyst. The continuous removal of products helps overcome the reaction equilibrium limitation and allows recovery of high-purity LA from the bottoms of the column. Nevertheless, because of the low thermodynamic efficiency of distillation, the RD column is the most energy intensive operation in the LA upgradation process and directly affects the overall process economics [6]. It is therefore a prime target for optimization and process intensification.

The esterification–hydrolysis route for the purification of raw LA has been considered by several researchers. Most of these works have focused the design and operation of the RD column. For example, Kumar et al. [5] proposed a continuous process for the recovery of lactic acid using a continuous stirred tank reactor (CSTR) for esterification and an RD column for hydrolysis. Experimental data were fitted to a pseudo-homogeneous kinetic model which was then used to simulate

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and optimize the overall process design. Mo et al. [7] designed a continuous RD column for methyl lactate hydrolysis by minimizing the total annual cost (TAC) with respect to number of stages in both rectifying and reactive sections and the corresponding feed locations. In addition, the controllability of the proposed design was established. Su et al. [6] compared the performance of C1–C4 alcohols for the esterification of lactic acid and identified methanol and n-butanol as the most economical choices. Processes based on ethanol and iso-propanol were found to be expensive because of the requirement of an entrainer to break the alcohol–water azeotrope.

Some recent works have attempted to develop intensified processes for LA purification. In this context, the dual reactive dividing-wall column (dual RDWC) is perhaps the most elegant solution proposed to date. Pazmiño-Mayorga et al. [8] have proposed to execute both the forward (i.e., esterification in CSTR) and the reverse (i.e., hydrolysis in RD column) reactions in a single piece of equipment. On one side of the wall, pre-concentrated LA solution from the evaporator is esterified using methanol. Methyl lactate and water are rectified in the vapor phase, whereas impurities and corresponding esters are removed from the bottoms. A common rectifying section at the top of the column purifies methanol toward the top of the column whereas water and methyl lactate are effectively returned as reflux to both sides of the wall. On the other side of the wall, hydrolysis of methyl lactate with water produces lactic acid, which is then enriched toward the bottoms. The overall design is promising and can substantially reduce the total production cost of LA. However, the technology has not been demonstrated at an industrial scale. Furthermore, to the best of our knowledge, no previous study on methyl lactate hydrolysis addresses heat integration of the RD column for reducing overall energy requirement of the process.

Process intensification (PI) aims to achieve remarkable improvements in process efficiency by replacing existing unit operations with ones that are both more compact and more efficient. These improvements lead to reduction in the number of equipment, process complexity, operational cost, and inherent risks associated with the chemical processing. In this context, process improvements in the reaction and separation processes have the highest potential to generate cleaner, smaller, energy efficient, environment friendly, and cost-effective technologies. Reactive distillation (RD) is a prominent example of such process intensification. Combining reaction and separation — both critical unit operations in any chemical process — in a single equipment offers several advantages. From a reaction engineering perspective, this leads to improvement in both the selectivity and the conversion and ultimately reduces the catalyst requirement. From a separations' perspective, it can help avoid the formation of azeotropes and reduce utilities requirement. From an economics' perspective, both the capital investment and the operating expenses can be considerably reduced. From an environmental perspective, the carbon footprint of the overall process can be reduced [9]. Separation of mixtures that is difficult to achieve through conventional distillation can be efficiently achieved through reactive distillation, e.g., azeotropic systems or components with close boiling points [10]. RD processes are particularly beneficial for equilibrium-limited reactions, e.g., (trans-)esterification, hydrolysis, etherification, and alkylation, because the continuous removal of product(s) can shift the reaction equilibrium in the direction of product formation [11]. Steady-state designs, feasibility studies and RD process implementation for a variety of reactions have been widely reported in literature [12–18].

In a conventional distillation column, heat is added to the column at a high temperature (T_R) in the reboiler and is removed from the column at a low temperature (T_C) in the condenser. Because energy is degraded over the temperature range of $T_R - T_C$, thermodynamic efficiency of such columns is typically low (5–20%) [19]. Because distillation processes are often the most energy-intensive operations in a chemical industry, design of energy-efficient distillation processes can have a substantially positive effect on the overall energy efficiency of the process. Significant efforts have been made to improve the energy efficiency

of distillation processes by using heat-integrated technologies. The most common techniques developed in this respect include dividing-wall column (DWC), vapor recompression (VRC), internally heat-integrated distillation (HIDiC), and multi-effect distillation (MED) [20]. Numerous examples of substantial energy savings and higher energy efficiency of heat-integrated nonreactive distillation processes as compared to their conventional alternatives have been reported in literature [21–25].

Although RD columns offer significant advantages over the conventional reactor–column combination, the issue of low thermodynamic efficiency persists: their reboilers still require high-grade energy and their condensers can only provide low-grade energy. However, like nonreactive distillation processes, energy efficiency of RD processes can also be improved by heat integration. The heat integration schemes for RD processes can be roughly classified into two categories, namely internal heat integration (e.g., HIDiC) and external heat integration (e.g., heat-pump systems) [26]. Internal heat integration splits the RD column into two parts and employs a compressor to transfer heat from the rectifying section (at high pressure) to the stripping section (at low pressure). HIDiC schemes use tray-to-tray heat exchangers and can often eliminate condenser or reboiler. Kiss [27] reported that internal heat integration of an RD process for fatty esters production offered ca. 45% energy savings. Gao et al. [28] demonstrated that an internally heat-integrated RD process for TAME synthesis required ca. 34.2% lower operating cost and ca. 6.6% lower total annual cost (TAC) than the conventional RD process. Using a series of quaternary systems operating under stoichiometric as well as excess ratios, Jiao et al. [29] demonstrated that the location of the reactive zone in the RD column significantly affects the TAC of the process. Huang and co-workers developed principles of internal heat integration in RD processes in a series of papers, including the design principle of internal heat integration between reaction and separation [30], and effects of internal heat integration on process dynamics [31]. They further demonstrated the application of internal heat integration in RD processes for MTBE synthesis [32] and for high-purity ethylene glycol production [33].

A significant limitation of RD technology is that the optimal conditions for reaction (e.g., pressure and temperature) must match the conditions suitable for distillation [9]. Because implementation of internal heat integration in an RD column can considerably change column profiles and operating conditions, it can rarely be established in practice [34]. On the other hand, external heat integration, also known as the heat pump system, has little interfere with the column profiles and operating conditions and is therefore a more suitable design for RD columns, especially when a delicate balance must be maintained between the reaction and separation operations. Practical studies have demonstrated the potential of such designs to considerably reduce the net energy consumption for many continuous as well as batch RD columns [34].

Heat pump systems reduce the energy consumption of a distillation column by coupling the reboiler with the condenser. Heat pumps can be classified into two categories, namely mechanical- and absorption-based heat pumps. In vapor recompression (VRC) type mechanical heat pumps, the top product is compressed to an elevated pressure, hence raising its temperature above the bottoms stream, and is then used to heat the bottoms product. In bottom flashing (BF) type mechanical heat pumps, the bottoms product is flashed in a throttling valve to reduce its pressure, hence reducing its temperature, and this throttled stream is then used to condense the top vapor. Absorption heat pumps (AHP) enhance the energy efficiency in a closed-loop fluid system based on absorption equilibrium [35].

Chen et al. [20] developed alternative designs for the methyl acetate hydrolysis process using VRC, DWC, and double-effect distillation and showed that the heat-integrated processes offer 15–65% TAC savings relative to the conventional RD process. Wang et al. [36] reported that reactive VRC distillation for hexamethylene-1,6-dicarbamate synthesis reduced the operating cost and TAC by 42.6% and 34.6%, respectively.

Shi et al. [19] demonstrated that up to 50% TAC savings can be realized by coupling VRC-type heat pump with a reactive DWC. Shrikhande et al. [37] compared VRC- and BF-type heat pump configurations for the ethyl levulinate production and obtained up to 61.2% reduction in utilities requirement and up to 35.5% reduction in TAC. Sharma et al. [38] reported ca. 18.3% reduction in utilities costs and ca. 8.4% reduction in TAC with a payback period of 4 years for VRC-integrated reactive DWC for formic acid production. Chen et al. [39] reported ca. 26.3% savings in energy consumption, 87% reduction in CO_2 emissions, and ca. 20.7% reduction in TAC for a similar VRC-integrated reactive DWC for isobutyl acetate synthesis. Feng et al. [40] reported ca. 13.8% reduction in TAC when the conventional RD column for the transesterification of methyl acetate with isopropyl alcohol was heat-integrated in a VRC-type design. Jana and Mane [41] showed that for wide-boiling mixtures where conventional heat pump scheme does not offer significant energy savings, a double-reboiler configuration including a heat-integrated intermediate reboiler resulted in ca. 46% energy savings. Kumar et al. [26] demonstrated that the thermal efficiency of an RD column with wide-boiling mixture can be significantly enhanced by using a multi-stage VRC design with intermediate reboilers.

Although numerous RD processes have been reported in literature for a wide range of chemical systems, few of them have been designed with heat integration to reduce the overall energy consumption. In this work, a steady-state RD process for methyl lactate hydrolysis, similar to the one reported by Mo et al. [7] is developed. Next, two heat-integration schemes based on mechanical vapor recompression are designed and evaluated based on total utilities requirement, total annual cost, and carbon emissions.

2. Methodology

2.1. Process Description

Production of high-purity LA from raw LA involves a combination of esterification and hydrolysis steps. The effluent from the fermentation tanks is a raw solution of lactic acid in water and contains many impurities including unfermented sugars and high-boiling organic acids. First, this fermentation broth is evaporated to remove bulk water [5]. The concentrated solution of LA thus obtained is fed to a CSTR where it is esterified using methanol. Nonreactive impurities (e.g., unfermented sugars) are unaffected by this process, but lactic acid as well as reactive impurities present in the solution are esterified. However, under the conditions of the esterification reactor, only methyl lactate (i.e., the ester of lactic acid and methanol) is obtained in vapor phase. All other impurities as well as their esters remain in solution and are purged from the bottom of the CSTR. The vapor stream from the CSTR contains esterification products, i.e., methyl lactate and water, as well as any unreacted methanol. This stream is fed to the RD column where the hydrolysis reaction takes place in the presence of a catalyst. Methanol and water are recovered in the distillate stream, which is further distilled for the separation and recycling of methanol. The bottoms stream from the RD column is a concentrated solution of LA in water with some unreacted methyl lactate.

2.2. Simulation of the Conventional RD Column

Methyl lactate hydrolysis can be represented by the following reversible reaction:

$$MethylLactate + Water \Leftrightarrow LacticAcid + Methanol \qquad (1)$$
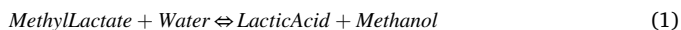
Among these components, methanol (product) is the lowest boiling and lactic acid (product) is the highest boiling. The two reactants, i.e., methyl lactate and water, are intermediate boilers. UNIFAC-HOC model was used to model the nonideal vapor–liquid equilibrium. The built-in association parameters of Aspen Plus® were used to compute fugacity coefficients. The UNIFAC-HOC model predicts that methyl lactate and

water form a homogeneous minimum-boiling binary azeotrope ($P = 1\ atm$; $T = 99.87\ °C$; $x_{water} = 0.97$) [7]. However, the continuous hydrolysis reaction effectively bypasses the azeotropic composition. No other binary or ternary azeotrope was detected in the system.

Assuming a pseudo-homogeneous model, Mo et al. [7] have reported the following kinetics for the hydrolysis of methyl lactate over an acidic cation-exchange resin catalyst:

$$\ln(K_e) = \frac{-1291.4}{T} + 2.5543 \qquad (2)$$

$$r = (k_0 + k_w \cdot w) \cdot \exp\left(\frac{-E}{RT}\right) \cdot \left(C_{ML}C_W - \frac{C_{LA}C_{MeOH}}{K_e}\right) \qquad (3)$$

where K_e is the equilibrium constant, T is the absolute temperature in Kelvin, w is the catalyst loading in g/L, E is the activation energy in kJ/mol, and R is the gas constant. C_{ML}, C_W, C_{LA}, and C_{MeOH} are molar concentrations (in mol/L) of methyl lactate, water, lactic acid, and methanol, respectively. The following values for the activation energy and rate constants have also been reported:

$$E = 45.84 kJ/mol$$

$$k_0 = 600.52 \frac{L}{mol \cdot \min}$$

$$k_w = 44.34 \frac{L^2}{g \cdot mol \cdot \min}$$

For the present work, the column design and the steady-state operating conditions for the conventional RD column have been taken from the work of Mo et al. [7]. We note here that this reference configuration was obtained after detailed optimization of the total annual cost (TAC) of the RD column with respect to the number of trays in different sections as well as the feed location. Moreover, the controllability of the proposed design has already been established. The column is operated at atmospheric pressure and consists of 44 trays. Trays 1–4 are included in the rectifying section while trays 5–44 are included in the reactive section. Saturated liquid feed containing 10 mol% methyl lactate and 90 mol% water is introduced on tray 8 from the top at a flow rate of 10 kg/s. The reaction is assumed to occur only in the liquid phase with the pseudo-homogeneous kinetics described above. The column diameter is 2.44 m (8 ft), with a 90% active tray area and a 10 cm liquid holdup on each tray. Assuming 50% (W/V) loading, the catalyst loading on each reactive tray is ca. 210 kg. Pressure drop is assumed to be negligible. The column is simulated using the RADFRAC module of Aspen Plus® V10. Distillate flow rate (1.2 kg/s) and product purity (95 wt.% methanol) are treated as design specifications while reflux ratio and reboiler duty are manipulated to meet these specifications.

A schematic of the conventional RD column is shown in Figure 1. We note here that the RD column is simulated without integrated condenser and reboiler available with the RADFRAC module. Instead, two external HEATER blocks are used to model the condenser and the reboiler. The liquid produced by the total condenser is split between column reflux and top product to achieve the desired reflux ratio. Because only partial vaporization is achieved in the reboiler, an additional FLASH2 block is installed to separate the bottoms liquid product and vapor boil-up streams. The reflux and the boil-up are converged as tear streams. As described in more detail later, this flowsheet arrangement allows a direct comparison with the heat-integrated configurations developed in this work. The column configuration and results from the converged steady state simulation are summarized in Table 1 and Table 2.

3. Heat Integration

Because the design and operation of an RD column require a careful balance between the reaction and separation operations, it is highly desirable that any heat integration scheme does not interfere with the
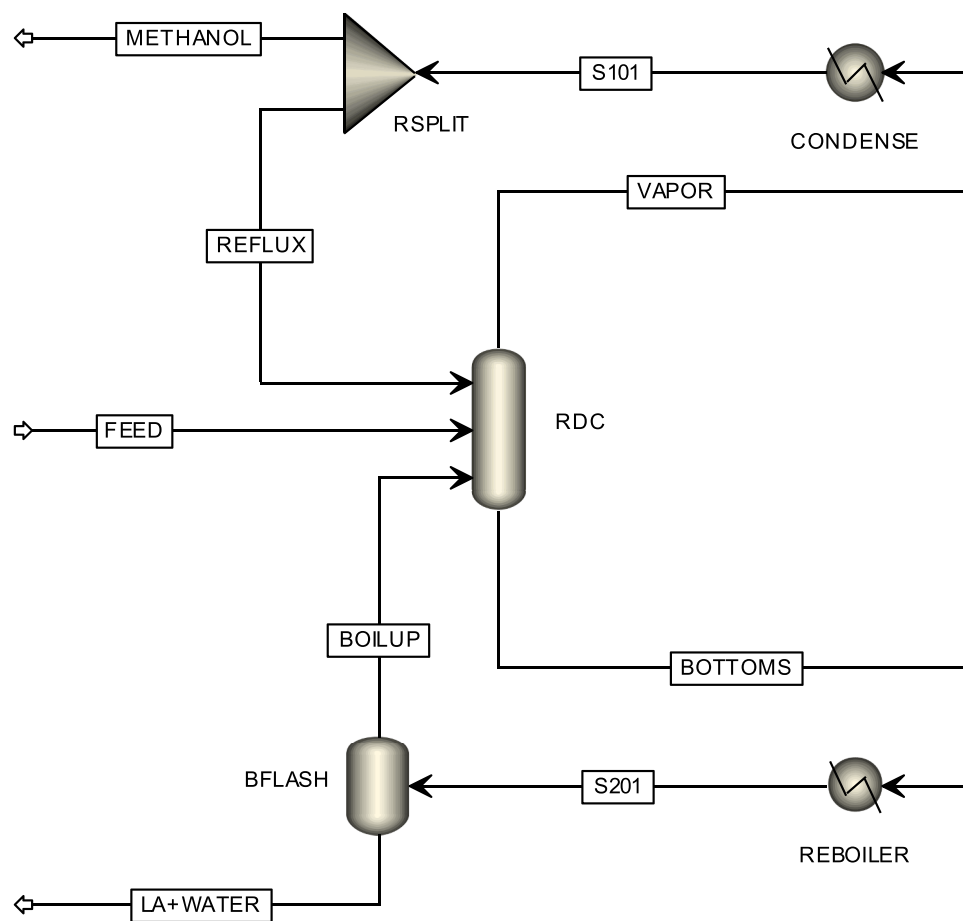
Figure 1. Schematic representation of the conventional reactive distillation column for methyl lactate hydrolysis

Table 1
Data for the conventional reactive distillation column

Number of trays	44
Trays in the rectifying section	1–4
Trays in the reactive section	5–44
Feed tray from top	8
Column diameter (m)	2.44
Catalyst per tray (kg)	210.14
Feed flow rate (kg/s)	10.0
Distillate flow rate (kg/s)	1.2
Bottoms flow rate (kg/s)	8.8
Reflux ratio	5.437
Condenser temperature (K)	341.1
Reboiler temperature (K)	374.4
Condenser duty (kW)	9,015
Reboiler duty (kW)	9,282

Table 2
Product mass fractions for the conventional reactive distillation column

	Top Product (METHANOL)	Bottom Product (LA+WATER)
Methanol	0.9500	0.0007
Water	0.0500	0.6120
Methyl lactate	—	0.0211
Lactic acid	—	0.3662

column operation. In other words, the liquid and vapor flows and the temperature and composition profiles of the column must remain unchanged after heat integration. A mechanical heat pump is the most suitable external heat integration scheme to satisfy this constraint.

Pleşu et al. [42] have developed a quantitative criterion for evaluating the suitability of heat pump use in distillation systems during early stages of design. The parameter of interest is the inverse Carnot efficiency defined by

$$\frac{Q_R}{W} = \frac{1}{\eta_{Carnot}} = \frac{T_C}{T_R - T_C} \tag{4}$$

where Q_R is the reboiler duty, W is the mechanical work involved, and T_C and T_R are the absolute temperatures of the condenser and the reboiler, respectively. They found that heat pump integration is feasible when the inverse Carnot efficiency exceeds 10, and unfeasible when it is below 5. Further evaluation is recommended when the inverse Carnot efficiency is between 5–10.

For the conventional RD column for methyl lactate hydrolysis, the condenser and reboiler temperatures obtained from steady state simulation are 341.1 K and 374.4 K, respectively. The corresponding inverse Carnot efficiency is ca. 10.2 indicating the potential suitability of a mechanical heat pump for external heat integration. We note here that bottom flashing (BF) type mechanical heat pump scheme cannot be developed in this case because the RD column is already operating at atmospheric pressure. Therefore, the scope of this work is limited to the development of vapor recompression (VRC) type mechanical heat pumps.

In a VRC type mechanical heat pump, the hot utility used in the reboiler is partially or completely replaced by integrating the reboiler with the condenser. However, because the condenser is at a lower temperature than the reboiler, the natural direction of heat transfer in the integrated configuration would be from the reboiler to the condenser. In addition, economic considerations regarding heat transfer

area require that at least 5–10 K temperature difference is maintained at all points in the heat exchanger. To create a positive temperature difference driving force for heat transfer in the reverse direction, i.e., from the condenser to the reboiler, the top vapor from the column is first mechanically compressed to increase both its pressure and temperature as well as its saturation temperature. The higher the temperature of the compressed overhead vapor, the greater the energy supplied to the reboiler. However, the temperature at the exit of the compressor is also directly proportional to the compression ratio. The higher the compression ratio, the greater the power required by the compressor. In summary, the compression ratio must be selected such that the dew point temperature of the compressed overhead vapor is about 5–10 K higher than the bubble point of the column's bottom liquid.

In this work, we have selected a minimum temperature approach of 10 K as the design basis. Because the reboiler temperature in the conventional RD column is ca. 375 K, the dew point of the compressed overhead vapor must be increased to 385 K. The corresponding

saturation pressure is 476.2 kPa, and the required compression ratio is 4.7.

A schematic of the vapor-recompression-based reactive distillation column (VRC-RD) is shown in Figure 2. The key difference between this configuration and the conventional RD column (Figure 1) is the addition of an integrated heat exchanger (INTHEX) for heat transfer between the compressed overhead vapor and the bottoms liquid. A compressor is installed upstream of INTHEX to increase the pressure of the overhead vapor and an expansion valve is installed downstream of INTHEX to reduce the pressure back to the column pressure. Because the thermal energy of the compressed vapor is not fully utilized in INTHEX, an additional preheater (PREHEAT) is installed to recover some of the heat that is ultimately needed for the reboiler. This self-heat recuperation (SHR) increases the suction temperature of the compressor and reduces the heat differential across the heat pump [43].

Table 1 shows that for the conventional RD column, the reboiler duty is slightly higher than the condenser duty. In the VRC-RD scheme, the
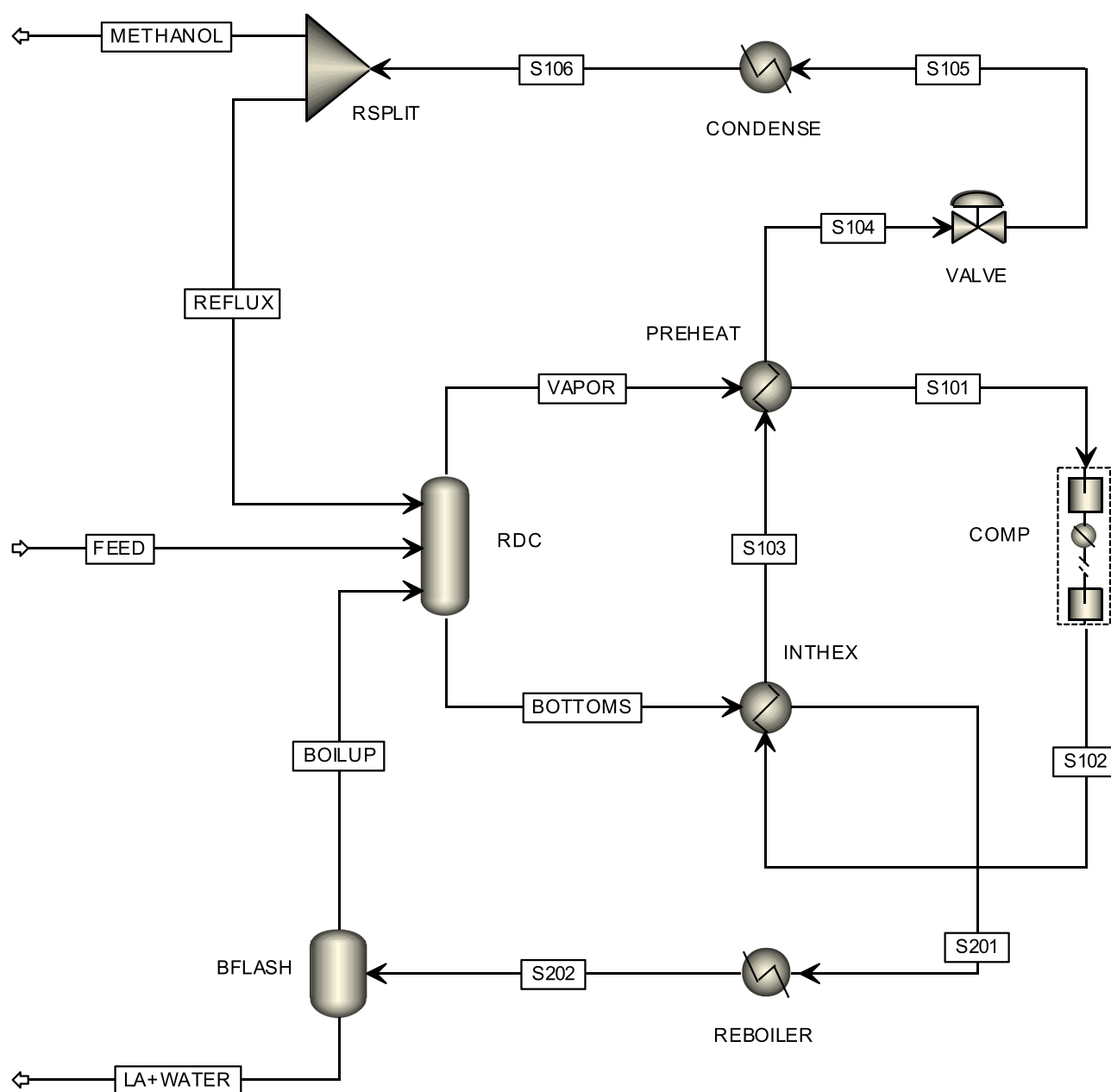

Figure 2. Schematic representation of the vapor-recompression-based reactive distillation column (VRC-RD)

mechanical work of compression adds further heat to the system which must ultimately be removed in the condenser. Because the total condenser duty is now higher than the reboiler duty, the maximum heat that can be exchanged in the integrated heat exchanger (INTHEX) is equal to the reboiler duty. The energy of the compressed vapor is not fully utilized even after maximum heat exchange with the bottoms liquid. This allows a further modification of the process where the column overhead vapor is split and only a fraction of it is compressed and heat-integrated, while the other fraction is directly sent to the condenser. The objective of this modification is to reduce both the

capital and the operating costs of the compressor by reducing the vapor flow through it [44]. A schematic of the modified configuration with pre-compressor split (PCS-VRC-RD) is shown in Figure 3.

4. Performance Indicators

The performance of the heat-integrated configurations relative to the conventional RD column was assessed in terms of energy, economic, and environmental aspects.
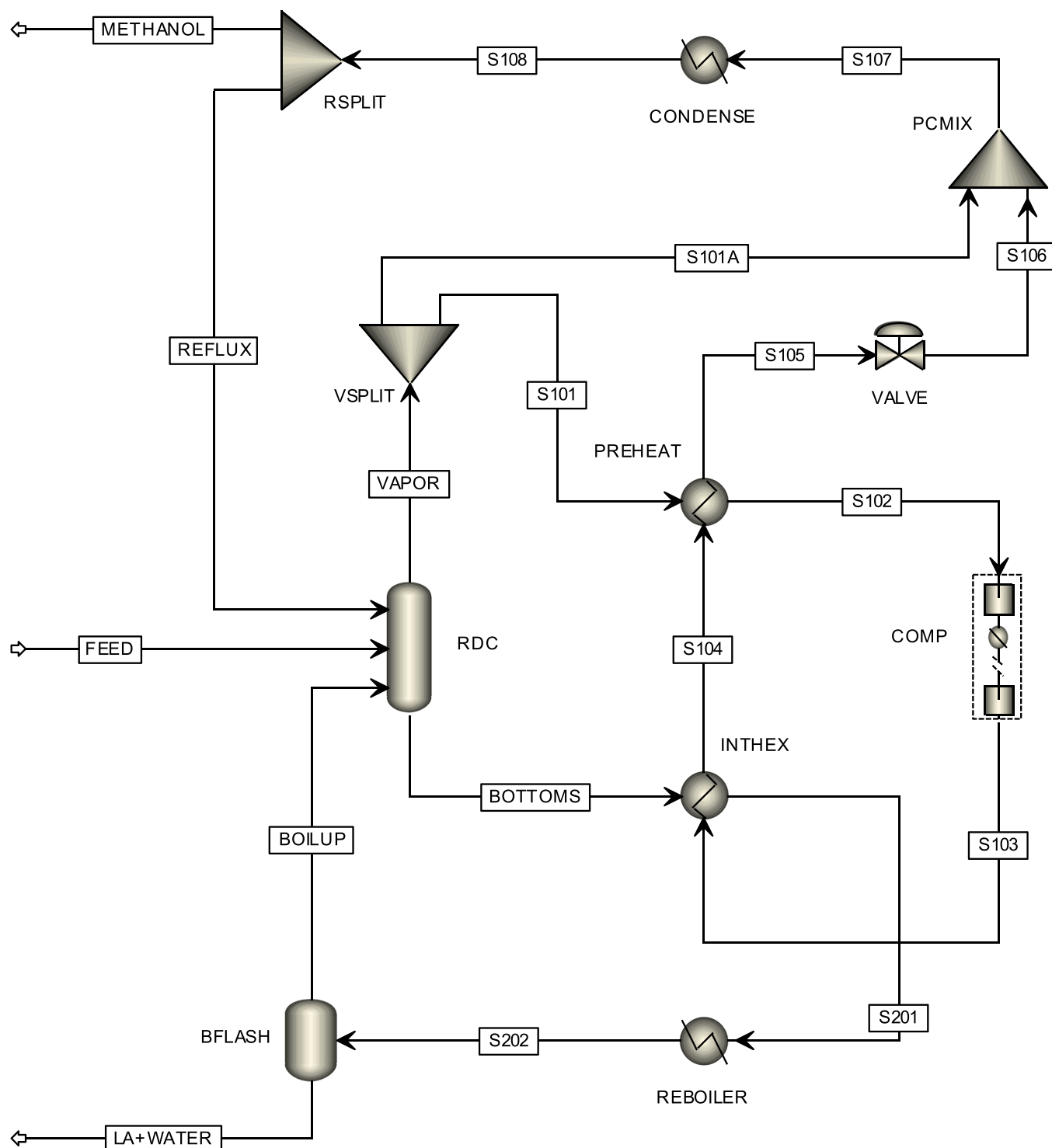

Figure 3. Schematic representation of the vapor-recompression-based reactive distillation column with pre-compressor split (PCS-VRC-RD)

4.1. Thermodynamic Efficiency

Thermodynamic performance of a system and the extent of utilization of available energy can be evaluated in terms of second-law efficiency [45]:

$$\eta = \frac{W_{\min}}{W_{\min} + LW} \tag{5}$$

where $W_{\min}$ is the theoretical minimum work requirement of the process and LW is the lost work. These quantities can be calculated as follows:

$$W_{\min} = \sum_{out} nb - \sum_{in} nb \tag{6}$$

$$LW = \sum_{in} \left[nb + Q\left(1 - \frac{T_0}{T_s}\right) + W_s \right] - \sum_{out} \left[nb + Q\left(1 - \frac{T_0}{T_s}\right) + W_s \right] \tag{7}$$

where $b = h - T_0 s$ represents the amount of available energy per mole of a stream (in kJ/mol), n is the molar flow rate of the stream in kmol/s, and h and s are the molar enthalpy and the molar entropy of the stream in kJ/mol and kJ/mol/K, respectively. T_0 and T_s represent the reference temperature and the stream temperature in Kelvins, respectively. Finally, Q and W_s represent the heat flow and the shaft work crossing the boundary of the system, respectively.

Thermodynamic efficiency calculations in this work are based on a reference temperature of 298.15 K. Stream information including molar flow rate, molar enthalpy, and molar entropy is extracted from steadstate simulation results. For the conventional distillation column, duties of condenser and reboiler are used but there is no shaft work. For the heat-integrated configurations, there is no reboiler duty, but the shaft work is equal to the compressor duty.

4.2. Energy Savings

The conventional RD column requires cooling water (cold utility) in the condenser and medium-pressure steam (hot utility) in the reboiler. The VRC configurations additionally require electricity for driving the compressor. A multiplication factor of 3 is used for converting the electricity requirement to equivalent thermal energy requirement [41]. The total utilities requirement for a process are calculated as

$$Q_T = Q_C + Q_R + 3W \tag{8}$$

where Q_T is the total utilities requirement for the process, and Q_C, Q_R, and W are the condenser, reboiler, and compressor duties, respectively. Utilities savings relative to the conventional RD column are calculated as

$$Utility\ savings\ (\%) = \frac{Q_T - Q_{T,RD}}{Q_{T,RD}} \times 100 \tag{9}$$

4.3. Economic Comparison

The VRC configurations require installation of a compressor and additional heat exchangers. This represents significant capital investment and must be offset by the resulting energy savings. Economic comparison of heat-integrated configurations with the conventional RD column is based on total annual cost (TAC):

$$TAC = \frac{Capital\ investment}{Payback\ period} + Annual\ operating\ cost \tag{10}$$

The capital investment includes the installed costs of the distillation column (including trays), condenser, reboiler, flash vessel, compressor, preheater, and integrated heat exchanger. The costs of pumps, valves, and piping, etc. are not considered as they are relatively small and vary little between different configurations. The column diameter is initially estimated for the conventional RD column using tray sizing mode in

Aspen Plus®. It is then kept unchanged for all configurations, considering that VRC is an external heat integration approach and does not affect the liquid and vapor flows in the column. The installed costs of the equipment are estimated using Aspen Process Economic Analyzer®.

The operating costs include the costs of cold and hot utilities and the cost of electricity for the compressor. Electricity consumption of feed and reflux pumps is not considered as it is very small compared to that of the compressor. The following cost factors are used:

> Cost of electricity = 0.1 \$/kWh
> Cost of medium-pressure steam = 18 \$/ton
> Cost of cooling water = 0.05 \$/ton

The operating costs are converted to annual basis assuming 8,000 hours of operation per year. The capital investment is converted to annual basis assuming a payback period of 5 years.

4.4. Carbon Dioxide Emissions

Carbon dioxide is the most significant greenhouse gas in the context of process industry. Total CO_2 emissions from a process are a direct indicator of the carbon footprint of the process. In the conventional RD column, the use of medium-pressure steam in the reboiler is the most significant cause of CO_2 emissions. The heat-integrated configurations developed in this work effectively substitute this steam with electricity for the compressor. However, electricity production is itself a major source of CO_2 emissions in a process. Total CO_2 emissions for the heat-integrated configurations are calculated using Aspen Plus® and compared with the CO_2 emissions for the conventional RD column to assess the environmental impact of heat integration.

5. Results and Discussion

5.1. Conventional RD Column

Results from the converged steady state simulation of the conventional RD column are summarized in Table 1 and Table 2. The corresponding temperature and composition profiles are shown in Figure 4 and Figure 5, respectively. The distillate from the column contains 95 wt.% methanol and 5 wt.% water. The concentrations of methyl lactate and lactic acid are negligible. The bottoms product contains 36.6 wt.% lactic acid and 2.1 wt.% unconverted methyl lactate. This corresponds to a methyl lactate conversion of 95.2% in the column. The condenser and reboiler temperatures are 341.1 K and 374.4 K, respectively. The difference between these temperatures is only 33.3 K. Even after
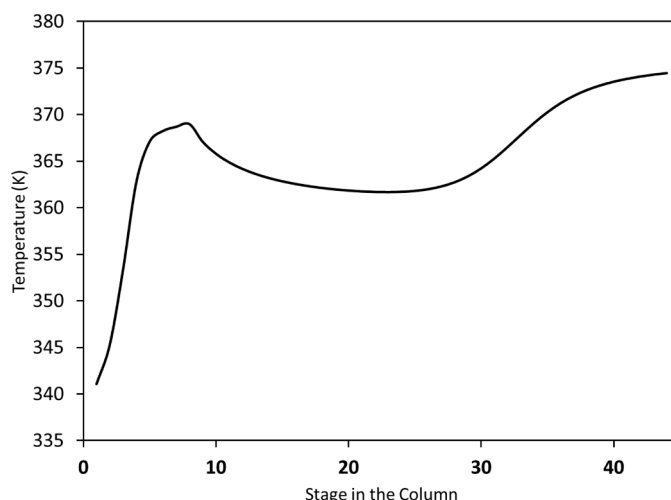

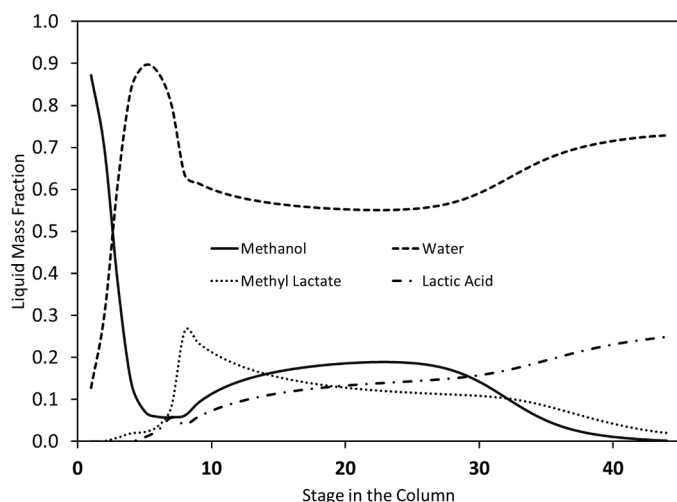**Figure 4.** Temperature profile of the reactive distillation column

Figure 5. Composition profile of the reactive distillation column

accounting for the required minimum ΔT of 10 K for heat transfer, the required rise in the temperature of the top vapor is only ca. 44 K. This can be achieved using a low compression ratio, indicating that the process is a suitable candidate for VRC-type heat integration.

Results of the economic analysis of the conventional RD column are presented in Table 3. Although the reboiler duty (9,282 kW) is only slightly higher than the condenser duty (9,015 kW), the cost of the hot utility (325.84 $/h) is considerably higher than the cost of the cold utility (85.68 $/h). The cost for electricity is not reported in this case because a compressor is not required. The annual operating cost of the process is 3.29 million $. The total installed equipment cost of the process is 1.48 million $, with the installed cost of the RD column (1.06 million $) being the most significant element. This corresponds to an annualized value of 0.3 million $ for the capital investment for a period

Table 3

Comparison of conventional and heat-integrated reactive distillation columns

	RD	VRC-RD	PCS-VRC-RD
Configuration			
COMP Pout (kPa)	101.3	476.2	476.2
PREHEAT duty (kW)	—	77	74
INTHEX duty (kW)	0	9,282	9,282
VSPLIT bypass	—	—	0.0389
Operating Costs			
Total cooling duty (kW)	9,015	1,474	1,407
Total heating duty (kW)	9,282	0	0
Total electric power (kW)	—	1,741	1,674
Total cooling cost ($/h)	85.68	14.01	13.37
Total heating cost ($/h)	325.84	0	0
Total electricity cost ($/h)	—	174.12	167.35
Installed Equipment Costs			
RDC tower ($)	1,059,900	1,059,900	1,059,900
CONDENSE exchanger ($)	159,300	75,500	75,300
REBOILER exchanger ($)	122,700	—	—
BFLASH vessel ($)	135,200	135,200	135,200
COMP compressor ($)	—	3,042,200	3,018,600
PREHEAT exchanger ($)	—	61,600	61,600
INTHEX exchanger ($)	—	295,700	299,200
Summary			
Total utilities (kW)	18,297	6,698	6,427
Total operating cost ($/year)	3,292,198	1,505,072	1,445,785
Total capital investment ($)	1,477,100	4,670,100	4,649,800
Total annual cost ($/year)	3,587,618	2,439,092	2,375,745
CO_2 emissions (ton/year)	17,577	4,832	4,644
Utilities savings (%)	—	63.4%	64.9%
TAC savings (%)	—	32.0%	33.8%
CO_2 emissions reduction (%)	—	72.5%	73.6%
Minimum theoretical work (kW)	678	678	678
Lost work (kW)	2,498	1,075	1,007
Thermodynamic efficiency (%)	21.4%	38.7%	40.3%

of 5 years. The annual operating cost is therefore 11 times higher than the annualized value of the capital investment, making a strong case for reducing operating cost even if at the expense of increased capital investment. Because the cost of hot utility accounts for ca. 80% of the total operating cost, substitution of hot utility can be expected to result in considerable economic benefit.

5.2. Vapor-Recompression-based Reactive Distillation (VRC-RD) Column

The VRC-RD configuration shown in Figure 2 is a combination of vapor recompression and self-heat recuperation (SHR). The top vapor leaving the column is at its saturation point (341.1 K). It is first sent to a preheater (PREHEAT) where its temperature is raised by 5 K by exchanging heat with the hot stream (S103) leaving the integrated heat exchanger (INTHEX). SHR has both technical and economic advantages in this case. From a technical perspective, compression of saturated vapor can cause partial condensation and the resulting liquid can rapidly damage the equipment by erosion [46]. Superheating the vapor before feeding the compressor avoids this problem. Secondly, increasing the suction temperature of the compressor reduces the heat differential across the heat pump, resulting in more efficient utilization of energy within the process [43]. From an economic perspective, SHR allows to recover some of the energy that is ultimately needed in the reboiler. On the cold side, in the absence of SHR, this energy would be provided through compression. Because electrical energy required for compression is considerably more expensive, energy recovery through thermal integration is economically preferable. On the hot side, in the absence of SHR, the unrecovered energy would ultimately increase the cooling duty of the trim-condenser.

The superheated vapor is compressed to a pressure of 476.2 kPa, increasing its temperature to 478.2 K. The corresponding bubble point temperature is 384.6 K, ca. 10 K higher than the temperature of the bottoms liquid leaving the column. Both these streams are now sent to the integrated heat exchanger (INTHEX) where the bottoms liquid is heated using the compressed superheated vapor (S102). As already pointed out, the maximum heat that can be exchanged in INTHEX is equal to the reboiler duty (9,282 kW). As a result of this heat exchange, the bottoms liquid is partially vaporized (molar vapor fraction of 40.3%) while its temperature increases by 1 K. The compressed vapor stream enters INTHEX with a considerable degree of superheating. In the first zone of the heat exchanger, 1,479 kW of sensible heat transfer takes place, and the temperature of the vapor stream drops from 478.2 K to 386.1 K (dew point temperature). In the second zone of the heat exchanger, 7,803 kW of latent heat transfer takes place, while the ΔT between the hot and cold streams remains approximately constant (10.1–10.8 K). The hot stream leaves in a partially condensed state with a molar vapor fraction of 4.6%, indicating that its energy is not fully utilized in INTHEX. It is then sent to the preheater where more energy is recovered, and the molar vapor fraction is reduced to 3.6%. The stream is then passed through an expansion valve where its pressure is reduced to match the column pressure. This results in significant vaporization and the molar vapor fraction increases to 16.5%. The resulting cooling effect reduces the temperature from 384.6 K to 339.2 K. The remaining condensation takes place in the condenser using cooling water as before.

Results of the economic analysis of the VRC-RD column are presented in Table 3. The total installed cost of the process has now increased to 4.67 million $, with an annualized value of 0.93 million $ for 5 years. This represents an increase of 316% over the conventional RD column and is largely because of the addition of a compressor (3.04 million $). In addition, two new heat exchangers are installed (0.36 million $) while the reboiler is eliminated (0.12 million $). The hot utility is completely eliminated (100% reduction) while the cold utility is reduced to 1,474 kW (83.6% reduction). The electricity consumption in the compressor is 1,741 kW (174.12 $/h). Using a multiplying factor of 3 for converting electrical energy to equivalent thermal energy, the total utilities requirement for the process has reduced to 6,698 kW

(63.4% reduction). The annual operating cost has now reduced to 1.51 million $ (54.3% reduction). This large reduction in utilities consumption and annual operating cost is partly offset by the increase in capital investment. However, the net effect on the total annual cost is still favorable, as it is reduced to 2.44 million $ (32.0% reduction).

5.3. Vapor-Recompression-based Reactive Distillation Column with Pre-Compressor Split (PCS-VRC-RD)

In the VRC-RD configuration, the energy of the compressed vapor is not fully utilized even after maximum heat exchange with the bottoms liquid. This is evident from the molar vapor fraction of the hot stream leaving PREHEAT (S104) being greater than zero (3.6%). The primary source of adding this energy to the hot stream is through compression. Because electrical energy used for compression is considerably more expensive than the thermal energy, any unutilized energy at the exit of PREHEAT represents an economic loss. Overall process economics can be improved if this energy is not added to the hot stream in the first place. This can be achieved by splitting the column overhead vapor and using only a fraction of it for the heat pump system. By reducing vapor flow through the compressor, both its capital and operating costs can be reduced. The split fraction is adjusted such that the molar vapor fraction of the hot stream leaving INTHEX is reduced to zero while ensuring a minimum temperature approach of 10 K in the exchanger. Simulation results show that these objectives can be achieved by passing 96.1% of the column overhead vapor through the heat pump loop, while the remaining 3.9% of the vapor can be directly sent to the condenser. Further sensible heat is recovered from the hot liquid in PREHEAT before it is flashed and sent to the trim-condenser.

Results of the economic analysis of the PCS-VRC-RD column are presented in Table 3. Both the electricity consumption in the compressor and the cooling utility requirement in the trim-condenser are reduced by ca. 68 kW. Using a multiplying factor of 3 for converting electrical energy to equivalent thermal energy, this pre-compressor split of column overhead vapor results in a further reduction of 271 kW in the total utilities requirement for the process, representing 4% reduction relative to the standard VRC-RD configuration and a cumulative 64.9% reduction relative to the base case. The annual operating cost is reduced to 1.45 million $ (56.1% reduction relative to the base case). Similarly, the total annual cost is reduced to 2.38 million $ (33.8% reduction relative to the base case).

5.4. Thermodynamic Efficiency

The minimum theoretical work requirement for the process is estimated at 678 kW (Table 3). Because the feed as well as the product compositions are same in all cases, this number remains unchanged. Considerable degradation of energy occurs in the conventional RD column, as shown by the relatively large value of the lost work (2,498 kW) for this configuration. This results in a thermodynamic efficiency of 21.4%. We note here that this calculated thermodynamic efficiency is higher than typical distillation columns because of the involvement of reactive driving force. Nevertheless, the number is still low and can be further improved.

The conventional RD column relies exclusively on the hot utility for the addition of heat to the system and on the cold utility for the removal of heat from the system. Because the temperature of the cooling water is relatively close to the reference temperature, the corresponding exergy flow, $Q\left(1 - \frac{T_0}{T_s}\right)$, is relatively small for the condenser. On the other hand, the temperature of the medium-pressure steam required for operating the reboiler is significantly higher than the reference temperature and results in significant exergy contribution. In other words, the main source of lost work and low thermodynamic efficiency in the conventional RD column is the reboiler. Because the integrated heat exchanger in the VRC-RD and PCS-VRC-RD configurations results in a

more efficient utilization of energy, the lost work is considerably reduced in the heat-integrated processes. In fact, the reboiler is eliminated in both configurations and the corresponding exergy flow is instead replaced with the compressor duty. Even after including the multiplying factor of 3 for the electrical energy as described above, there is a net reduction in the total utilities requirement for both heat-integrated processes. As a result, the lost work is considerably reduced and the thermodynamic efficiency increases to 38.7% and 40.3% for the VRC-RD and PCS-VRC-RD configurations, respectively.

5.5. Carbon Dioxide Emissions

Total CO_2 emissions from the conventional RD process are estimated at 17,577 ton/year. The most significant cause of CO_2 emissions in this process is the use of medium-pressure steam. The heat-integrated configurations developed in this work effectively substitute this steam with electricity for the compressor, which is itself a major source of CO_2 emissions. However, Table 3 shows that the heat pump system results in a net reduction in the total utilities requirement. The corresponding total CO_2 emissions for the VRC-RD and PCS-VRC-RD configurations are 4,832 ton/year (72.5% reduction) and 4,644 ton/year (73.6% reduction), respectively.

6. Conclusions

A heat-integrated reactive distillation process based on mechanical vapor recompression and self-heat recuperation was developed for the methyl lactate hydrolysis. The process was simulated using Aspen Plus® and compared with the conventional reactive distillation column in terms of energy, economic, and environmental aspects. First, a standard VRC configuration with self-heat recuperation (VRC-RD) was developed and optimized for maximum heat integration. This configuration achieved 63.4%, 72.5%, and 32.0% reduction in total utilities requirement, total CO_2 emissions, and total annual cost, respectively. Next, a modified VRC configuration with pre-compressor split (PCS-VRC-RD) was developed to eliminate underutilized heat circulation from the heat pump loop. This configuration achieved 64.9%, 73.6%, and 33.8% reduction in total utilities requirement, total CO_2 emissions, and total annual cost, respectively. These savings are substantial and confirm the economic as well as environmental advantages of the proposed heat-integrated process.

CRediT authorship contribution statement

Adila Anbreen: Data curation, Formal analysis, Investigation, Methodology, Software, Validation, Visualization, Writing – original draft. **Naveed Ramzan:** Conceptualization, Funding acquisition, Project administration, Supervision, Writing – review & editing. **Muhammad Faheem:** Conceptualization, Data curation, Funding acquisition, Investigation, Methodology, Project administration, Software, Supervision, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no competing financial or personal interest.

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