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Unfavorable energy integration of reactive dividing wall column for simultaneous esterification reactions

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Abstract−Thermal integration in a reactive dividing wall column (RDWC) can dramatically reduce energy consumption. This study, however, addresses unfavorable energy integration of the concurrent esterification of butyl, amyl, and hexyl alcohols in the RDWC. The reaction kinetics and vapor-liquid-liquid equilibrium of reactive mixtures are utilized to assess the feasibility of energy integration in a multi-partitioned RDWC. The thermal integration effect of an RDWC is elucidated by comparing its energy efficiency with that of the direct sequential configuration of a reactive distillation column followed by a non-reactive distillation column. The unfavorable thermal integration in the RDWC originates from the large internal flow to satisfy the product purities. Therefore, a single RDWC sequence showed higher energy consumption and total annual cost than the direct RD sequence for the simultaneous triple esterification.

Keywords: Unfavorable Energy Integration, Reactive Distillation, Reactive Dividing Wall Column, Simultaneous Esterification Reactions

INTRODUCTION

Sustainability has recently become an important issue in process design. The concept of process intensification or process simplification has been introduced to achieve sustainable systems in terms of improved energy efficiency [1,2]. This has led to reduced CO_2 emission in line with CO_2 capture and utilization [3]. The implementation of process intensification can be found in reactive distillation (RD) [4-7], bubble columns or circulating catalyst reactor [8,9], and heat integrated distillation columns [10,11].

An RD integrates reaction and distillation and makes them work at the same time in a single unit. The reaction occurring with distillation gives significant benefits compared to the conventional sequence of a reactor followed by separation units. The continuous product removal by distillation enables the reaction to proceed to the forward direction and overcomes the reaction equilibrium. The application and geometrical analysis of methyl tertiary-butyl ether and methyl acetate RD systems has been reported [12]. RD has been applied in several recent manufacturing processes, such as the production of phenol, carbonates, and chiral chemicals [13].

After introducing RD to various processes, further improvements are realized by combining RD and thermal integration of dividing wall column (DWC). This integrated process is called a reactive dividing wall column (RDWC). Because the DWC reduces investment and operating costs by integrating several separation units into one column and reduces the number of reboiler or condenser units [14-16], the RDWC shows the advantage of both RD and DWC. By proceeding the reaction in an RD section and multi-component separation in a non-reactive section of the single shell, the overall process can be simplified and reduce energy consumption [17-20]. Introduction of RDWC to the dimethyl ether production achieved energy savings of 11.6% compared to the conventional RD process [21]. The RDWC for the production of diethyl carbonate reduced the total annual cost of the conventional RD process by 13.9% [22]. Simultaneous production of n-amyl acetate (AmAC) and n-hexyl acetate (HexAC) using an upper reactive dividing wall column (URDWC) showed a savings in the total reboiler duty by 8.7% compared to the direct sequence [23].

However, the thermal integration form of RDWC is not widely implemented yet because of the complex design variables to consider, such as the number of reaction stages and vapor/liquid exchange stages and the position of the reactive dividing wall. A conventional direct sequence of the triple esterification RD system (n-butyl acetate (BuAC), AmAC, and HexAC) has been proposed [24]. The direct sequence is composed of an RD column followed by a non-reactive DWC. Further process intensification of the triple esterification system using an RDWC has not been reported due to the complicated design requirements. Whether energy integration of the triple esterification in the RDWC can lead to lower energy consumption, however, has not been studied.

This study introduces the design of RDWC for co-producing the three esters (BuAC, AmAC, and HexAC) and reports unfavorable energy integration of the RDWC for the triple esterification system. Design alternatives using multiple vapor-liquid exchanging streams in the RDWC are suggested, and the thermal integration effect of each alternative is elucidated in comparison with the direct sequence. While the RDWC system for the co-production of the three esters is assumed to be more effective than the non-heat integrated RD system, the detailed analysis in energy and cost demonstrates that the conventional direct sequence is more efficient than

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the RDWC.

REACTIVE DISTILLATION DESIGN ALTERNATIVES

In the esterification of n-butanol (BuOH), n-amyl alcohol (AmOH), and n-hexanol (HexOH), the alcohol reacts with acetic acid (AC) and produces ester and water using an acid catalyst. The kinetics for each reaction has been studied in recent works [24,26-28], which is summarized in the Supporting Information (S1). The binary parameters for the determination of activity coefficients are employed from previous studies [24,27,28]. The vapor-liquid-liquid (V-L-L) phase equilibrium is calculated with the NRTL-NTH property method in Aspen Plus^{TM}. The dynamic property of singular points for the given triple esterification system and the parameters for the NRTL model are provided in Supporting Information (S2 and S3). The Wegstein method is used for the tear stream convergence method, and the error tolerance of the simulation convergence option is set to 1.0×10^{-4}. For block convergence, the rigorous distillation model RADFRAC is used for the simulation of the reactive section and the PETROFRAC model is used for the non-reactive section. The calculation option in the column is set to "strongly non-ideal liquid" for the azeotropic mixture.

1. Direct Sequence for Simultaneous Three Esterifications

The direct sequence with a single RD column and two consecutive distillation columns for the concurrent production of BuAC, AmAC, and HexAC is suggested as in Fig. 1. After the complete conversion of alcohols into esters in the RD column, the liquid product stream (149.19 kmol/hr) with a molar composition of 33.27 mol% AmAC, 33.44 mol% BuAC, and 33.05 mol% HexAC flows from the bottom of the RD column to the distillation section for the separation of the pure esters. BuAC is separated in the first column (99.01 mol% BuAC) and AmAC (99.07 mol% AmAC) and HexAC (99.20 mol% HexAC) are recovered in the second column by their difference in the relative volatility. The total reboiler duty is 9,679.15 kW and the total condenser duty is −8,744.82 kW.

2. Design Requirements for RDWC in a Multiple Esterification Process

To achieve the complete conversion of alcohols and separation of high purity esters in the RDWC, AC and alcohols should be completely consumed in the RD section and the non-reactive section should mainly consist of ester products. Moreover, each reactive and non-reactive section should satisfy the material balance for every component.

2-1. RDWC with One Dividing Wall for Binary Esterification Reactions

To design the RDWC for the double esterification reactions, specifications such as the mole flow rate of vapor-liquid exchanging streams and the location of connected stages should be considered. As an example, the RDWC for the binary esterification of AmOH and HexOH is represented in Fig. 2 [22]. The RDWC consists of the RD section for the concurrent double esterification followed by the non-reactive section for the separation of AmAC and HexAC. If we take the non-reactive section as the material balance envelope in Fig. 3(a), the entering and leaving streams that

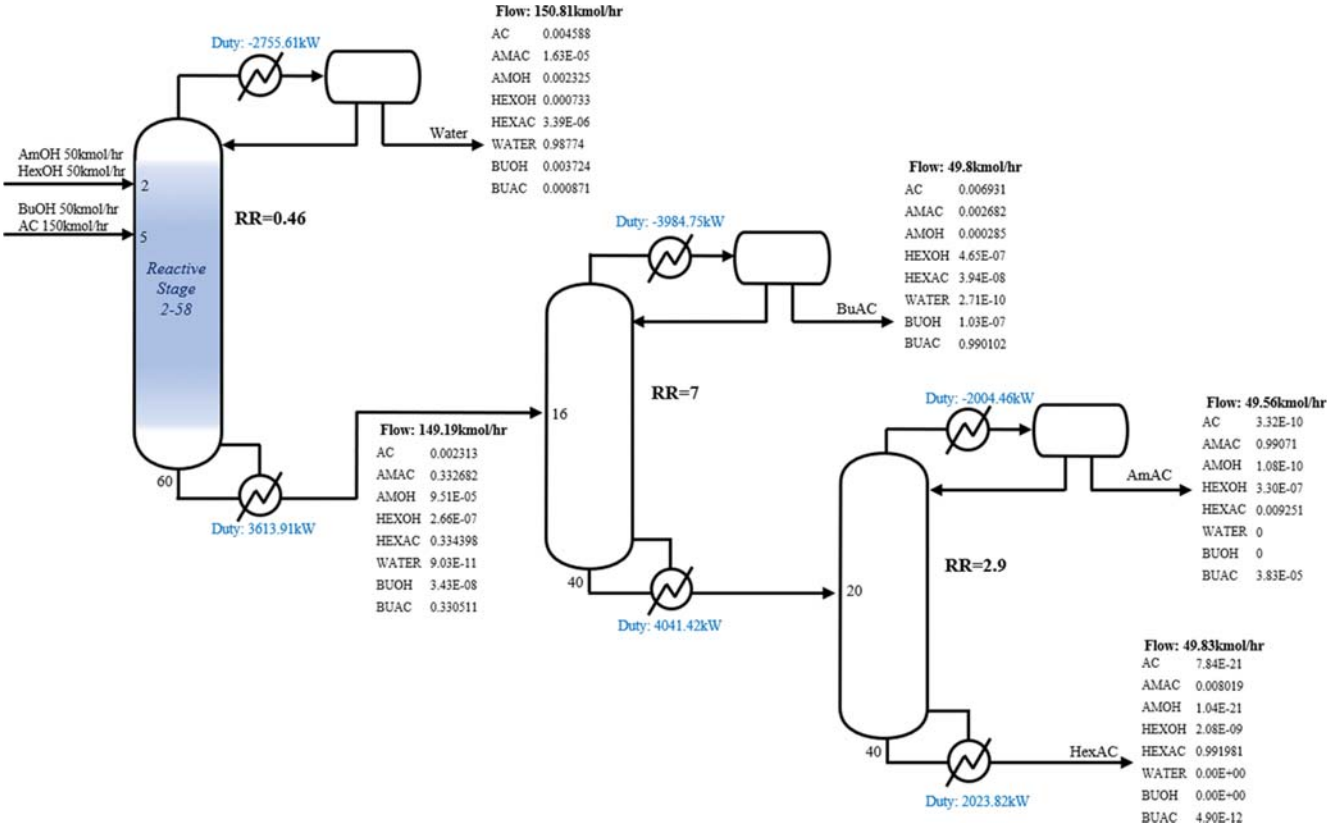


Fig. 1. Direct sequence for the simultaneous production of BuAC, AmAC, and HexAC.

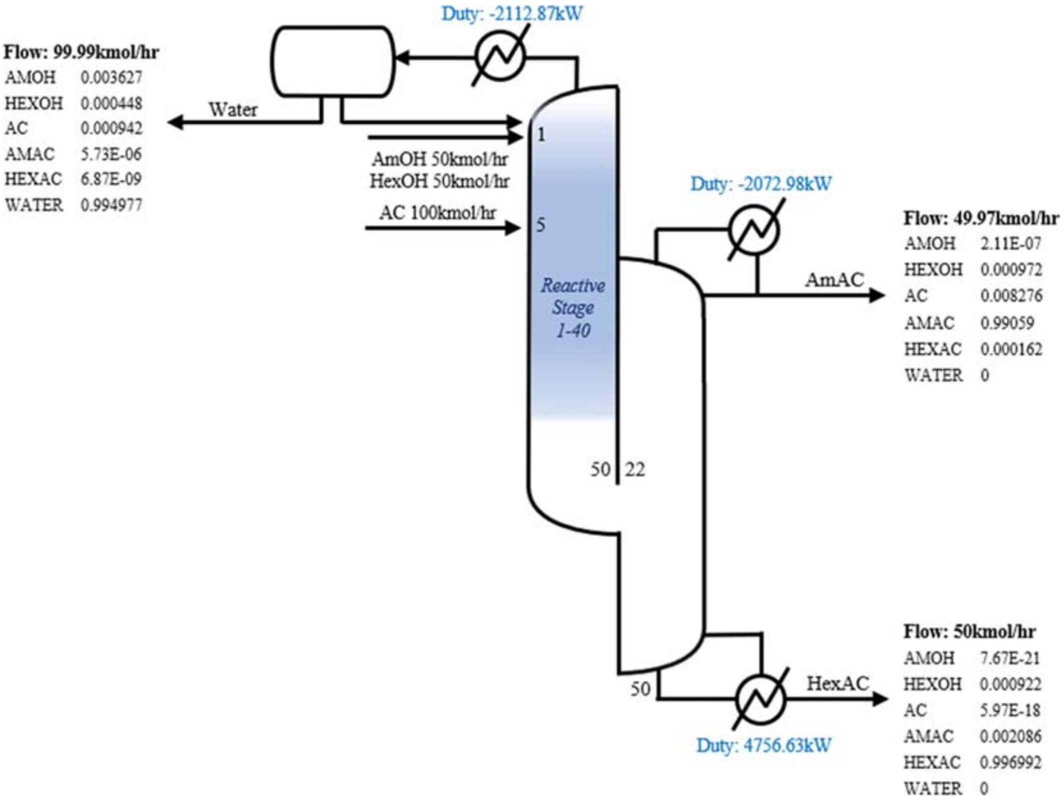


Fig. 2. RDWC for the double esterification process of AmAC and HexAC.

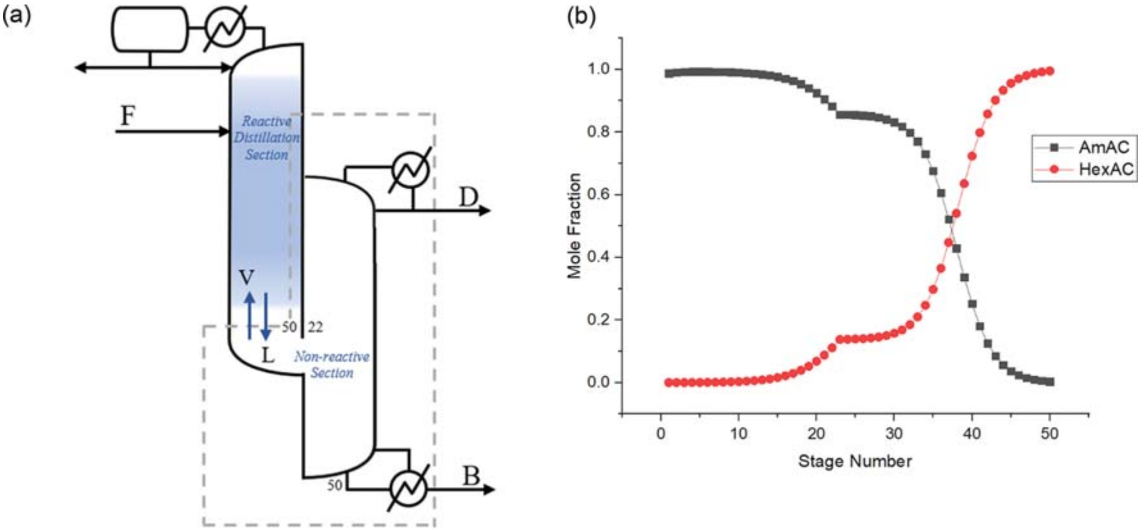


Fig. 3. (a) Mass balance envelope of the non-reactive section in an RDWC with a single partition for AmAC and HexAC coproduction and (b) vapor composition profile of the non-reactive section in an RDWC sequence.

cross the boundary are the exchanging liquid and vapor streams, distillate, and bottom with the corresponding molar flow rates of L, V, D, and B. The overall mass balance and component mass balance in the non-reactive section envelope can be developed as below:

$$L-V=D+B \quad (1)$$

$$Lx_i-Vy_i=D_i+B_i \quad (2)$$

D_i and B_i refer to the molar flow rate of component i in the distillate and bottom product, respectively;. x_i and y_i are the mole fraction of component i in the exchanging vapor and liquid stream. According to Eq. (1), the net input from the RD section to the non-reactive section by the counter-flowing liquid and vapor stream (L–V) must equal the sum of the AmAC and HexAC product flow rate as the distillate and bottom products (D+B). The composition (x_i and y_i) should be determined considering Eqs. (1) and (2) for a given liquid flow rate (L).

When the liquid stream flows from the RD section to the non-reactive section at a flow rate (L) of 350 kmol/hr, the exchanging vapor flow rate (V) should be 250 kmol/hr by the overall mass balance in Eq. (1) (for each 50 kmol/hr of AmAC and HexAC production). Assuming the mole fraction of AmAC in the distillate is close to 1 (D_{AmAC}=50 kmol/hr and B_{AmAC}=0 kmol/hr), the available liquid and vapor composition (x_{AmAC} and y_{AmAC}) sets satisfying the balance requirements can be considered. With the complete conversion of AmOH and HexOH in the RD section, we assume the vapor and liquid in the non-reactive section mainly consists of AmAC and HexAC (49.63 mol% AmAC and 49.86 mol% HexAC in 100 kmol/hr of net flow from the RD section to the non-reactive section). Because the top and the bottom products predominantly consist of the binary mixture, the vapor and liquid com-

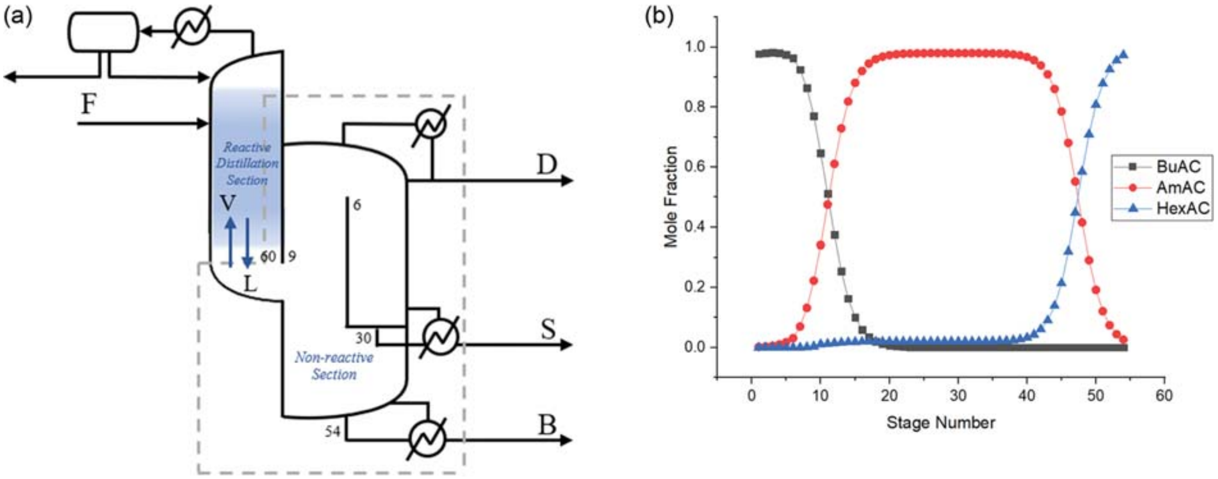
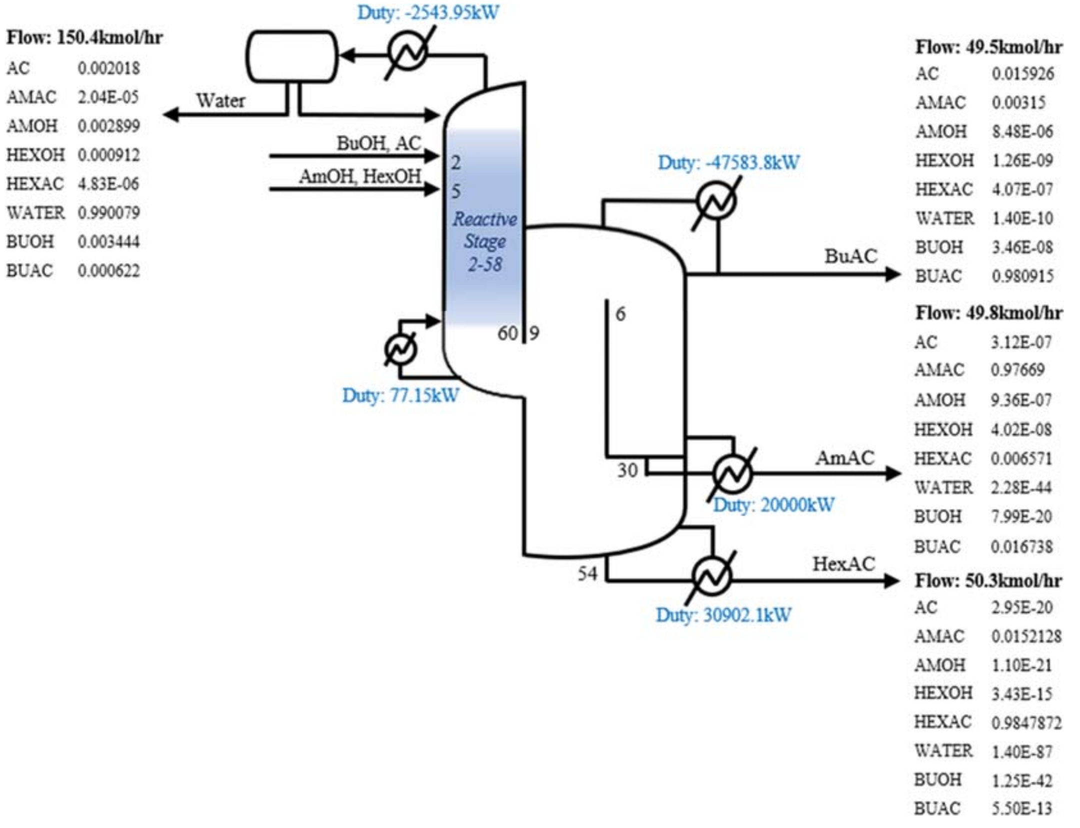


Fig. 4. (a) Mass balance envelope of the non-reactive section in an RDWC with two partitions for BuAC, AmAC, and HexAC coproduction and (b) vapor composition profile of the first non-reactive section in the RDWC sequence using a single exchange stream set.



Flow: 150.4kmol/hr	
AC	0.002018
AMAC	2.04E-05
AMOH	0.002899
HEXOH	0.000912
HEXAC	4.83E-06
WATER	0.990079
BUOH	0.003444
BUAC	0.000622

Flow: 49.5kmol/hr	
AC	0.015926
AMAC	0.00315
AMOH	8.48E-06
HEXOH	1.26E-09
HEXAC	4.07E-07
WATER	1.40E-10
BUOH	3.46E-08
BUAC	0.980915

Flow: 49.8kmol/hr	
AC	3.12E-07
AMAC	0.97669
AMOH	9.36E-07
HEXOH	4.02E-08
HEXAC	0.006571
WATER	2.28E-44
BUOH	7.99E-20
BUAC	0.016738

Flow: 50.3kmol/hr	
AC	2.95E-20
AMAC	0.0152128
AMOH	1.10E-21
HEXOH	3.43E-15
HEXAC	0.9847872
WATER	1.40E-87
BUOH	1.25E-42
BUAC	5.50E-13

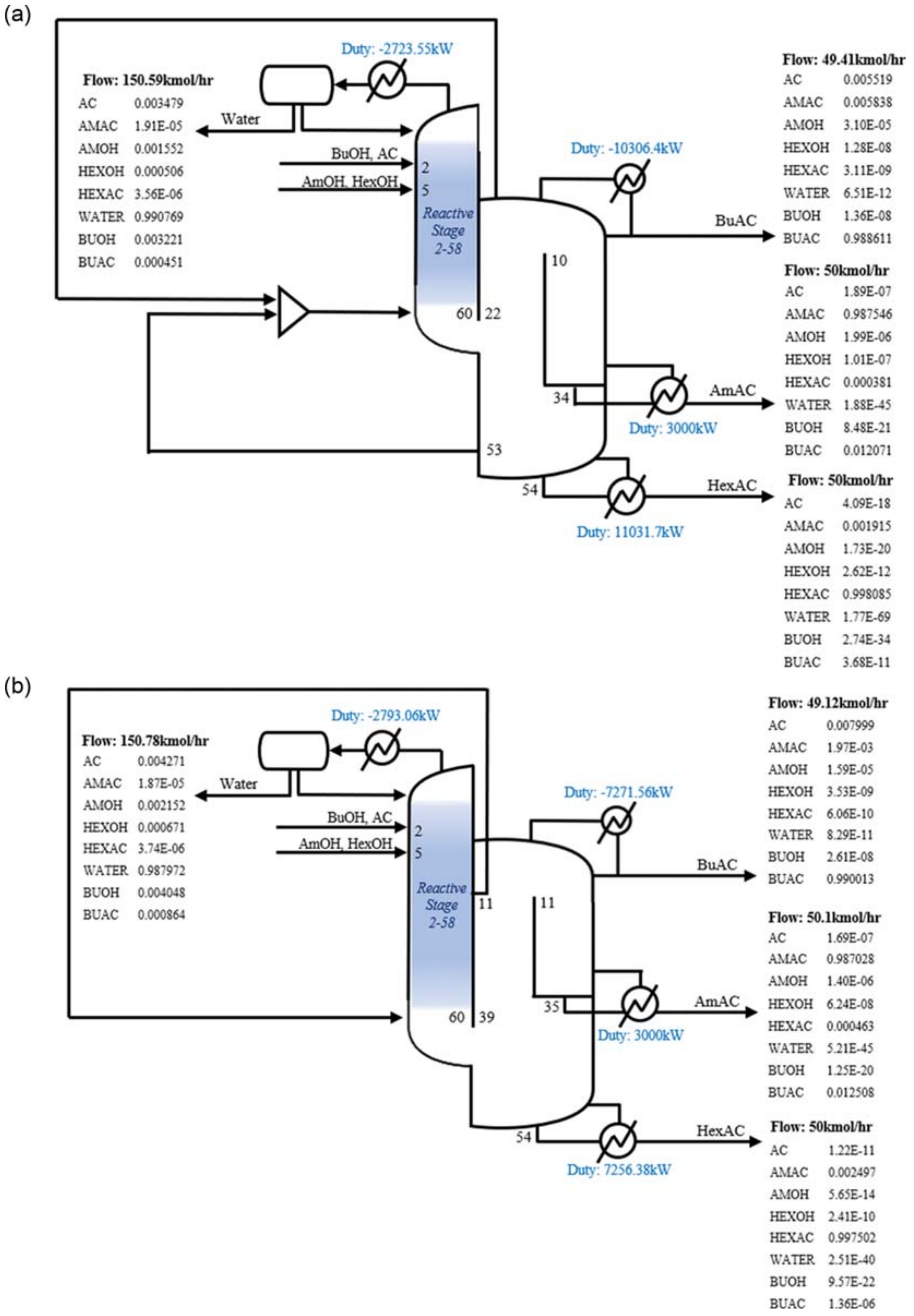
Fig. 5. Normal RDWC using a single exchange stream set for the simultaneous production of BuAC, AmAC, and HexAC.

positions in the non-reactive section of Fig. 3(b) satisfy the following relationship:

$$y_{AmAC}+y_{HexAC}\approx 1 \quad (3)$$

$$x_{AmAC}+x_{HexAC}\approx 1 \quad (4)$$

Due to the volatility difference, the vapor molar fraction of AmAC is the highest on the top of the non-reactive section and



(a)

Flow: 150.59kmol/hr	
AC	0.003479
AMAC	1.91E-05
AMOH	0.001552
HEXOH	0.000506
HEXAC	3.56E-06
WATER	0.990769
BUOH	0.003221
BUAC	0.000451

Flow: 49.41kmol/hr	
AC	0.005519
AMAC	0.005838
AMOH	3.10E-05
HEXOH	1.28E-08
HEXAC	3.11E-09
WATER	6.51E-12
BUOH	1.36E-08
BUAC	0.988611

Flow: 50kmol/hr	
AC	1.89E-07
AMAC	0.987546
AMOH	1.99E-06
HEXOH	1.01E-07
HEXAC	0.000381
WATER	1.88E-45
BUOH	8.48E-21
BUAC	0.012071

Flow: 50kmol/hr	
AC	4.09E-18
AMAC	0.001915
AMOH	1.73E-20
HEXOH	2.62E-12
HEXAC	0.998085
WATER	1.77E-69
BUOH	2.74E-34
BUAC	3.68E-11

(b)

Flow: 150.78kmol/hr	
AC	0.004271
AMAC	1.87E-05
AMOH	0.002152
HEXOH	0.000671
HEXAC	3.74E-06
WATER	0.987972
BUOH	0.004048
BUAC	0.000864

Flow: 49.12kmol/hr	
AC	0.007999
AMAC	1.97E-03
AMOH	1.59E-05
HEXOH	3.53E-09
HEXAC	6.06E-10
WATER	8.29E-11
BUOH	2.61E-08
BUAC	0.990013

Flow: 50.1kmol/hr	
AC	1.69E-07
AMAC	0.987028
AMOH	1.40E-06
HEXOH	6.24E-08
HEXAC	0.000463
WATER	5.21E-45
BUOH	1.25E-20
BUAC	0.012508

Flow: 50kmol/hr	
AC	1.22E-11
AMAC	0.002497
AMOH	5.65E-14
HEXOH	2.41E-10
HEXAC	0.997502
WATER	2.51E-40
BUOH	9.57E-22
BUAC	1.36E-06

Fig. 6. RDWC using (a) three vapor exchanging streams and (b) two vapor exchanging streams for the simultaneous production of BuAC, AmAC, and HexAC.

gradually decreases as moving down the column in Fig. 3(b), whereas HexAC is enriched at the bottom of the column. The gradual change of the composition along the non-reactive section of the column makes it possible to find the point satisfying Eqs. (1) and (2). The finalized exchanging streams between the RD section and the non-reactive section is 350 kmol/hr (L) of the liquid stream (0.26 mol% HexOH, 0.31 mol% AC, 24.13 mol% HexAC, and 75.30 mol% AmAC) from the RD section and 250 kmol/hr (V) of the vapor stream (0.33 mol% HexOH, 0.27 mol% AC, 13.84 mol% HexAC, and 85.56 mol% AmAC) from the non-reactive section, both at 158.94 °C. The RDWC sequence produces 50 kmol/hr of AmAC and HexAC, each with purity of 99.06 mol% and 99.70 mol%, respectively.

2-2. RDWC with Two Dividing Walls for Three Esterification Reactions

Different from designing an RDWC for the double esterification, the degree of freedom increases as the number of components increases [29] in the three esterification system. Similar to the non-reactive section in the double esterification RDWC sequence, the mass balance in the non-reactive section of RDWC with the two dividing walls can be represented as given below (Fig. 4(a)):

$$L-V=D+S+B \tag{5}$$

$$Lx_i-Vy_i=D_i+S_i+B_i \tag{6}$$

where S represents the side product flow rate, which refers to the second volatile ester product stream (AmAC).

Unlike the binary system, the incoming flow to the non-reactive section consists of three ester products and the column profile of each component shows different behavior. The column profile of the first non-reactive section in the RDWC sequence using a single exchange stream set is represented in Fig. 4(b). The mole fraction of BuAC is highest at the top of the column but it drops sharply moving down the column. The least volatile product (HexAC) has the highest molar fraction at the bottom and lowest at the top. Considering Eqs. (5) and (6), we determined the exchanging streams. However, the single vapor-liquid exchanging stream set cannot meet the proper mass balance to achieve the desired product purity (above 99 mol%) due to the drastic composition change in the column profile (Fig. 5). Thus, we propose design alternatives with additional vapor exchanging streams to satisfy the product purity and recovery (Fig. 6) for the simultaneous production of the three esters in a multi-partitioned RDWC.

3. Multi-partitioned RDWC for Simultaneous Three Esterifications

3-1. RDWC with One Exchange Stream Set

The normal multi-partitioned RDWC in Fig. 5 consists of the RD section for the concurrent triple esterification, two non-reactive sections, and the two separation walls for the separation of three esters. The liquid stream with a flow rate of 460.42 kmol/hr (33.74 mol% of AmAC, 11.57 mol% of HexAC, and 54.38 mol% of BuAC) from the bottom of the RD section enters stage 10 of the non-reactive section while 310.82 kmol/hr (34.04 mol% of AmAC, 1.10 mol% of HexAC, and 64.66 mol% of BuAC) of the vapor stream from stage 10 of the non-reactive section enters the bottom of the RD section. The vapor split ratio in the finalized RDWC sequence is 0.104 (to the RD section) at the bottom of the first partition wall between the RD section and the first non-reactive section, and 0.436 (to the second non-reactive section) at the second partition wall between two non-reactive sections. In the multi-partitioned RDWC, the purity of all ester products is lower than 99 mol% (97.67 mol% of AmAC, 98.09 mol% of BuAC, and 98.48 mol% of HexAC).

Although the reaction extent is high in the RD section (148.91 mol, 99.27 mol% of AC consumed), a single set of vapor and liquid exchanging streams could not be found to satisfy the high purity of ester products (99 mol%) even with the high reflux ratio in the non-reactive section, as in Table 1. The total reboiler duty is 50,979.25 kW (inter-reboiler in the RD section of 77.15 kW, the first non-reactive section of 30,902.10 kW, and the second non-reactive section of 20,000 kW) and the total condenser duty is −50,127.75 kW (the RD section of −2,543.95 kW and the non-RD section of −47,583.80 kW).

3-2. RDWC with Two Additional Vapor Streams

Both low product purity and high reboiler duty demonstrated the inefficiency of the conventional RDWC using a single vapor-liquid exchanging stream set (Table 1). To improve upon this, we introduced additional vapor exchanging streams to secure all ester components in the material balance. The RDWC using three vapor exchanging streams is proposed in Fig. 6(a). The liquid stream coming out from the bottom of the RD section is connected to stage 23 of the non-reactive section. Considering the net flow

Table 1. Result of the non-reactive section in each RDWC design alternative

		RDWC with one vapor exchange stream	RDWC with three vapor exchanging streams	RDWC with two vapor exchanging streams
Internal flow rate*	1st non-reactive section	Liquid: 3,111 kmol/hr Vapor: 3,079 kmol/hr	Liquid: 936 kmol/hr Vapor: 934 kmol/hr	Liquid: 448 kmol/hr Vapor: 561 kmol/hr
	2nd non-reactive section	Liquid: 2,012 kmol/hr Vapor: 1,963 kmol/hr	Liquid: 339 kmol/hr Vapor: 290 kmol/hr	Liquid: 413 kmol/hr Vapor: 363 kmol/hr
Molar reflux ratio	1st non-reactive section	95	9.53	13.8
	2nd non-reactive section	1.03	1.17	1.14
Total reboiler duty of non-reactive section		50,902 kW	14,032 kW	10,256 kW

*Internal flow rate of each non-reactive section is calculated by averaging the flowrate of each stage except the top and the bottom stage.

entering the non-reactive section of each ester product (BuAC, AmAC, and HexAC), we provide three vapor exchanging streams coming out from stages 1, 23, and 53 of the non-reactive section to stage 60 of the RD section. Multiple vapor streams are used to achieve high product purity by matching each ester product net flow $(Lx_i - Vy_i)$ to the non-reactive section close to 50 kmol/hr, while maintaining other impurity net flow close to zero.

In fact, the compositions of the liquid and vapor stream coming out from the RD section and the non-reactive section in the connected stage (stage 23 of the non-reactive section and stage 60 of the RD section) showed a significant departure from satisfying the net flow (mass balance) requirements. The liquid stream with a flow rate of 485 kmol/hr from the bottom of the RD section consists of 41.22 mol% AmAC, 34.25 mol% BuAC, and 24.32 mol% HexAC. Compared to the liquid stream entering the non-reactive section, the vapor stream leaving stage 23 of the non-reactive section mainly consists of AmAC (65.08 mol% AmAC, 27.69 mol% BuAC, and 7.09 mol% HexAC). Additional vapor streams near the top (stage 1) and the bottom (stage 53) of the non-reactive section are used to supplement the BuAC and HexAC flow to the RD section to match the net flow from the RD section to the non-reactive section close to 50 kmol/hr for each ester product. After recycling the additional two vapor streams from stages 1 and 53 in the non-reactive section, the total 336 kmol/hr of vapor stream (44.75 mol% AmAC, 34.76 mol% BuAC, and 20.27 mol% HexAC) is fed to the bottom (stage 60) of the RD section.

Ester products with purity close to 99 mol% (mole fractions of 0.988-0.998) are produced. The total reboiler duty is 14,071.54 kW (the first non-reactive section of 11,071.54 kW and the second non-reactive section of 3,000 kW) and the total condenser duty is −13,067.72 kW (the RD section of −2,723.54 kW and the non-reactive section of −10,344.18 kW). Using additional vapor exchanging streams enabled reduction of the internal vapor/liquid flow rates (Table 1) and the energy savings of 73.16% in the TUC (27,062 kW) compared to the RDWC with a single exchanging stream set (101,107 kW), as given in Table 2.

3-3. RDWC with One Additional Vapor Stream

To reduce the heat consumption and the number of interconnected vapor-liquid streams of RDWC, an RDWC using two vapor exchanging streams is proposed, as shown in Fig. 6(b). The liquid stream from the bottom (stage 60) of the RD section enters stage 40 of the non-reactive section, and the two vapor streams come out from stages 11 and 40 of the non-reactive section. The liquid stream with a flow rate of 492.82 kmol/hr from the bottom of the RD section consists of 31.48 mol% AmAC, 52.31 mol% BuAC, and 15.98 mol% HexAC, whereas the vapor stream from the non-reactive section consists of 225.60 kmol/hr from stage 40 (37.70 mol% AmAC, 49.31 mol% BuAC, and 12.79 mol% of HexAC) and 119 kmol/hr from stage 11 (17.32 mol% AmAC, 82.46 mol% BuAC, and 0.0025 mol% HexAC).

Ester products with purity higher than 98.70 mol% are produced. The total reboiler duty is 10,256.38 kW, which is reduced 27% compared to the RDWC with three vapor exchanging streams (Table 2). The reboiler duty of the non-reactive section is 7,256.38 kW, and the stripper reboiler duty is 3,000 kW. The total condenser duty is −10,064.62 kW (the RD section of −2,793.06 kW and the non-reactive section of −7,271.56 kW).

UNFAVORABLE ENERGY INTEGRATION OF REACTIVE DIVIDING WALL COLUMN

The energy integration effect in the multi-partitioned RDWC for producing the three esters is analyzed by a comparative analysis with the direct sequence. The energy and economic efficiency of the design alternatives are analyzed by calculating the TUC and TAC, which are shown in Tables 2 and 3. The calculation procedure is provided in Supporting Information (S4 and S5) [30].

In the case of RDWC with a single exchange stream set, the material balance in the non-reactive section to produce high purity products cannot be perfectly satisfied due to the restricted vapor composition profile in the first non-reactive section, as shown in Fig. 4(b). BuAC, the lightest component in the ester product mixture, mainly exists at the upper part of the first non-reactive section because BuAC and AmAC flow to the second non-reactive section for the separation. The mole fraction of BuAC in the vapor flow drops sharply starting from stage 6 where the second partition wall starts (Fig. 4(b)). Similarly, the HexAC mole fraction sharply increases at the bottom (starting from stage 43) of the non-reactive section. Thus, the vapor composition mainly consists of AmAC and HexAC at the bottom part of the non-reactive section and BuAC and AmAC at the top part of the non-reactive section. The composition profile results in the depletion of HexAC at the vapor exchanging stream from stage 10 of the non-reactive section (34.04 mol% AmAC, 64.66 mol% BuAC, and 1.10 mol%

Table 2. TUC of each design alternative for the simultaneous production of BuAC, AmAC, and HexAC

Case No.	Sequence	Reactant feed (kmol/hr)				Product (kmol/hr)			Total reboiler duty [kW]	Total condenser duty [kW]	TUC [kW]
		HexOH	AmOH	BuOH	AC	HexAC	AmAC	BuAC			
1	Direct sequence	50	50	50	150	49.43	49.10	49.35	9,679	−8,745	18,424
2	RDWC with one vapor exchanging stream	50	50	50	150	49.53	48.64	48.56	50,979	−50,128	101,107
3	RDWC with three vapor exchanging streams	50	50	50	150	49.90	49.38	48.85	14,032	−13,030	27,062
4	RDWC with two vapor exchanging streams	50	50	50	150	49.88	49.45	48.63	10,256	−10,065	20,321

Table 3. Economic evaluation on each design alternative for the simultaneous production of BuAC, AmAC, and HexAC

Case	Direct sequence	RDWC with one vapor exchanging stream	RDWC with three vapor exchanging streams	RDWC with two vapor exchanging streams
TUC (kW)	18,424	101,107	27,062	20,321
Total operating cost ($1,000/yr)	4,035	21,053	5,825	4,429
Steam	2,754	14,506	3,993	2,918
Cooling water	1,116	6,395	1,662	1,284
Catalyst	165	152	170	226
Total investment cost ($1,000)	2,940	11,285	4,251	3,429
Column	1,560	3,546	2,059	1,761
Reboiler	894	5,079	1,465	1,055
Condenser	486	2,660	728	612
Compressor	0	0	0	0
TAC ($1,000/yr)	5,015	24,815	7,242	5,572

HexAC). The HexAC-depleted composition of the vapor exchanging stream results in an imbalanced net flow (L-V) of the ester products (49.56 kmol/hr of AmAC, 49.39 kmol/hr of BuAC, and 49.86 kmol/hr of HexAC in 149.60 kmol/hr of net flow). The imbalanced net flow entering the non-reactive section makes it difficult to achieve high purity of product with a high reflux ratio. The high reflux ratio results in large internal flow in the non-reactive section (Table 1). Also, a greater amount of unconverted reactant AC (0.79 kmol/hr) in the RD section of RDWC flows out into the non-reactive section compared to the flow from RD to non-RD distillation column in the direct sequence (0.35 kmol/hr). Thus, the product streams in the RDWC showed low purity and recovery even with the high reflux and reboiler duty in the non-reactive section (Tables 1 and 2).

In the multi-partitioned RDWC for the given RD system, multiple vapor exchanging streams are introduced to achieve high purity of the product. Considering the mass balance of each ester product in the RDWC, a design alternative using three vapor exchanging streams is suggested (Fig. 6(a)): the first stream from the top of the non-reactive section (stage 1), mainly consisting of BuAC; the second stream from the stage in the middle of the non-reactive section (stage 23), mainly consisting of AmAC; the third stream from the stage near the bottom of the non-reactive section (stage 53), mainly consisting of HexAC. Using the three vapor exchanging streams results in high internal flow in the non-reactive section (Table 1). To achieve high purity and high recovery of the ester products, the column requires a high reflux ratio (molar reflux ratio of 9.53 in Table 1). Also, the internal flow sharply increases as the reflux ratio rises. In the non-reactive section, the average liquid flow rate is 935.84 kmol/hr and the vapor flow rate is 934.39 kmol/hr for the first non-reactive section and 339.45 kmol/hr and 289.53 kmol/hr for the second non-reactive section (Table 1). This is much higher than the direct sequence (the average liquid and vapor flow rate of 426.96 kmol/hr and 383.67 kmol/hr in the first distillation column and 186.66 kmol/hr and 183.98 kmol/hr for the second distillation column, respectively). The high reflux ratio and high internal flow rate lead to higher reboiler duty of the multi-partitioned RDWC (14,032 kW) compared to that of the direct sequence (9,679 kW).

When reducing the number of vapor exchanging streams, two vapor streams are provided from stages 11 and 40 of the non-reactive section. By eliminating one vapor stream from stage 1 in the three vapor streams RDWC sequence, the internal flow rate and reboiler duty of the non-reactive section has been decreased compared to the three vapor exchanging streams RDWC sequence, as given in Table 1. The TUC of the sequence is 20,321 kW, which is lower than the RDWC using three vapor exchanging streams (27,062 kW). However, it is still high compared to the direct sequence (18,424 kW) because the RDWC recycles the product from the non-reactive to the RD section through the vapor exchanging stream, whereas there is no recycling flow in the direct sequence (Table 2).

The economic analysis also elucidates the negative energy integration effect of RDWC on the given multiple esterification system. All RDWC alternatives show higher TAC compared to the direct sequence (Table 3). The increment in the TAC originates from two sources: (1) Increase in utility and capital costs due to the high reboiler duty and (2) Increase in capital cost due to the large column size of the RDWC unit. The diameter size of the two distillation columns in the direct sequence is 2.02 m and 1.41 m, respectively, whereas the diameter of the non-reactive section in the RDWC sequence with two exchanging streams is 3.4 m (equivalent diameter, considering two non-reactive sections) due to the large vapor and liquid flow inside the column (Table 1). Although the RDWC can decrease the capital cost by integrating the RD section and the non-reactive distillation section into a single column, the results show high investment cost for all of the RDWC sequences due to the large column diameter ($1,560,000 for direct sequence and $1,761,000 for RDWC with two vapor exchanging streams). From the marked deterioration in energy and economic efficiency in actual simulations, we found the unfavorable energy integration effect of RDWC in the given multiple esterification process.

CONCLUSION

This work has introduced a multi-partitioned RDWC sequence for three concurrent esterifications and demonstrated the unfavorable energy integration effect in the RDWC for the given multiple esterification system. The three concurrent esterifications of BuOH, AmOH, and HexOH using a normal RDWC with a single vapor-liquid exchanging stream set showed a higher TUC (101,107 kW) and TAC (24,815,000 $/yr) compared to the direct sequence (TUC of 18,424 kW and TAC of 5,015,000 $/yr). Unlike the RDWC with a single dividing wall for the double esterification system, balancing the flow of each ester product in the RDWC with two dividing walls for the triple esterification system by using a single exchanging stream requires both a high reflux ratio and high reboiler duty. Using multiple vapor-liquid exchanging streams reduces the reflux ratio by satisfying the mass balance of ester products. However, multiple exchanging streams lead to high internal liquid and vapor flow rates, resulting in higher reboiler duty and larger column size. Although the RDWC reduces the number of units by combining the RD section and the non-reactive section into a single unit, the high number and flow rates of vapor-liquid exchanging streams at the dividing wall lead to unfavorable energy integration. The analysis of the energy integration in the RDWC can be applied to the esterification of higher carbon number alcohols. Although the trend of energy consumption depends on the phase equilibrium and kinetic rate of each esterification process, the present study on the energy integration effect enables us to design an optimum RD sequence of multiple reactions in intensified unit operation.

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NOMENCLATURE

RD : reactive distillation [-]
DWC : dividing wall column [-]
RDWC : reactive dividing wall column [-]
URDWC : upper reactive dividing wall column [-]
AC : acetic acid [-]
BuAC : n-butyl acetate [-]
BuOH : n-butyl alcohol [-]
AmAC : n-amyl acetate [-]
AmOH : n-amyl alcohol [-]
HexAC : n-hexyl acetate [-]
HexOH : n-hexyl alcohol [-]
TAC : total annual cost [10^3 $/yr]
TUC : total utility consumption [kW]

SUPPORTING INFORMATION

Additional information as noted in the text. This information is available via the Internet at http://www.springer.com/chemistry/journal/11814.

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