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Plant-wide design and control of acetic acid dehydration system via heterogeneous azeotropic distillation and divided wall distillation

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Abstract

Energy-saving plant-wide design and plant-wide control of an acetic acid dehydration system with the feed containing methyl acetate and *p*-xylene are investigated in the study. A heterogeneous azeotropic distillation using isobutyl acetate as an entrainer is designed to obtain high-purity acetic acid at the column bottom and to keep a small acetic acid loss through the top aqueous draw. The accumulation of *p*-xylene in the column is avoided by adding a side product stream. The mixture in the aqueous phase of decanter, containing mostly water, methyl acetate, and isobutyl acetate is separated using a divided wall distillation column. The whole acetic acid dehydration system includes a heterogeneous azeotropic distillation column and a divided wall distillation column.

The control strategies using temperature loops are proposed for this acetic acid dehydration system. For the heterogeneous azeotropic distillation column, the requirements for acetic acid compositions in both the aqueous phase of the decanter and the column bottom can be satisfied by designing entrainer inventory temperature control and cascade temperature control simultaneously. The stages of controlled temperatures are chosen by singular value decomposition and closed-loop analysis methods based on the criteria of minimum entrainer makeup. For the divided wall distillation column, steady-state analysis methods are used for the selection of proper controlled and manipulated variables and the determination of their pairings. Dynamic simulation results demonstrate that the proposed plant-wide control strategy can maintain product purities and reject external disturbances in feed flow and composition changes as well as internal disturbances such as changes in liquid and vapor splits.
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1. Introduction

Heterogeneous azeotropic distillation column (HADC) is commonly used in industry to separate azeotropes or mixtures with relative volatility close to one. The divided wall distillation column (DWDC) is a promising energy-saving alternative for separating multi-component mixtures. However, many studies show the controllability of both columns is nontrivial. In this work, the integration of both columns is studied, and the energy required for the separation of a five-component mixture is hence significantly saved. Feasible control structure for rejections of external and internal disturbances is also proposed for this novel integrated system.

Previous research works in azeotropic distillation were comprehensively reviewed by Widagdo and Seider [1]. The system showed complex characteristics such as parametric sensitivity, multiple steady states, long transient, and nonlinear dynamics. Bozenhardt [2] used average temperature control, on-line break point control, and five feedforward control loops for the ethanol dehydration system using ether as an entrainer. Rovaglio et al. [3] proposed

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average temperature control and two additional feedforward control loops for the same system but using benzene as an entrainer. They also reported the importance of keeping a proper column entrainer inventory for obtaining a good controller performance. Chien et al. [4] proposed an inverse double temperature loop control strategy for the isopropanol + water system using cyclohexane as an entrainer. Kurooka et al. [5] applied nonlinear control strategy to a HADC that separated a three-component mixture of water, *n*-butyl acetate, and acetic acid. Ulrich and Morari [6] examined the influence of the fourth component impurities on the operation and control of a HADC for dewatering a heavy-boiling component using methyl *tert*-butyl ether as a light entrainer. Chien et al. [7] investigated the design and control strategy of acetic acid dehydration system by heterogeneous azeotropic distillation. Different inventory control strategies using organic reflux and entrainer makeup flows were analyzed. Recently, Chien et al. [8] investigated the design and operation of an industrial acetic acid dehydration column with feed impurity.

Successful commercial applications of DWDC technology have been reported [9,10]. Several studies have indicated that it can save up to 30% on energy consumption compared with conventional direct or indirect distillation sequences [11–15]. However, such columns have not widely used in industrial practice largely due to controllability concerns [16]. Hernandez and Jimenez [17] discussed the controllability of different distillation arrangements including the divided wall distillation. They found that DWDC was the most difficult to control. Using the same controllability indexes as those of Hernandez and Jimenez [17], Serra et al. [18] compared the controllability of different multi-component distillation arrangements and showed that some specific operation conditions favored the operation of a divided wall distillation. Halvorsen and Skogestad [19] studied the energy consumption of a DWDC using shortcut analysis. They found that the two additional degrees of freedom: liquid and vapor split ratios are important to the energy efficiency of the column. Optimal values can be found at only suitable combinations of liquid and vapor split ratios. The liquid split ratio depends on the flow distributor at the top of the divided wall section and the hydraulics of the column internals. Sometimes liquid may be collected outside the column, redistributed, and hence controlled if required. The vapor split ratio is usually determined by the physical location of the wall and the pressure drop of the divided sections. The split of vapor flow is therefore not controlled. Abdul Mutalib and coworkers [20,21] investigated the effect of liquid and vapor splits on the design and control of divided wall distillation. They found that design for liquid and vapor splits should be based on the highest product specifications. They also found that two proposed composition control schemes are satisfactory in operation.

Acetic acid (HAc) is a very important organic product in the chemical industry. Most of the HAc produced is mainly used for the production of vinyl plastics, hot-melt adhesives, textile finishes, latex paints, and acetic anhydride. Nevertheless, end-product production is almost always accompanied by recycling streams containing HAc/water mixtures. Furthermore, the synthesis of HAc itself results in the production of water as a by-product. Separation of HAc/water mixtures is therefore an important operation in the chemical industry. Straight distillation consumes too much energy. Due to the closeness in the volatility of HAc and water in dilute aqueous solution, a large number of trays and a high reflux ratio are necessary to obtain pure HAc. Thus heterogeneous azeotropic distillation using an entrainer is more efficient for the separation of HAc and water.

In this study, the investigation of energy-saving plant-wide design of a HAc dehydration system using isobutyl acetate (IBA) as an entrainer via heterogeneous azeotropic distillation and divided wall distillation is first time conducted. The feed components besides HAc and water also contain small amounts of methyl acetate (MA) and *p*-xylene (PX) to match some real industrial application scenarios. Note that the impurity existence increases the design and operation difficulties. A HADC is designed to obtain high-purity HAc product at bottom and to keep a top HAc loss below some specified value through the aqueous outlet stream. Three components (water, MA, and IBA) in the aqueous phase are separated using a DWDC. Plant-wide control strategies will be proposed for the HAc dehydration system to maintain product purities and to reject external disturbances in feed flow and composition changes as well as internal disturbances such as changes in liquid and vapor splits. In the control study, strategy using only stage temperature will be considered so that it can be easily applied to industry. Under the consideration of the overall product purities, a novel control strategy of implementing the inventory control of an entrainer in a HADC is developed to guarantee the operability of its associated DWDC.

2. Plant-wide design

In this section, two different plant-wide design methods, conventional and energy-saving schemes for the HAc dehydration system are discussed. The conventional scheme includes a HADC and two columns in indirect sequence. It compares with the energy-saving one using a DWDC in addition to a HADC.

2.1. Thermodynamic model

There are five components in the HAc dehydration system. The system is simulated using ChemCad. Nonrandom two-liquid (NRTL) activity coefficient model was used for the vapor–liquid–liquid equilibrium of this system. The modification provided by the software to account for the dimerization of HAc in the vapor phase is incorporated in the simulation. Table 1 lists the NRTL parameters for

Table 1
Parameter values for NRTL model

Component i	Component j	A_{ij}	A_{ji}	B_{ij}	B_{ji}	Alpha
HAc	H_2O	0	0	−211.31	652.995	0.3
HAc	IBA	0	0	90.286	194.416	0.3
HAc	MA	0	0	−239.2462	415.2702	0.3
HAc	PX	0	0	466.217	215.826	0.3
H_2O	IBA	0	0	1809.079	489.609	0.2505
H_2O	MA	0	0	860.256	442.401	0.383
H_2O	PX	5.91818	−6.03013	784.86	2909.308	0.162808
IBA	MA	0	0	−137.569	187.6801	0.3
IBA	PX	0	0	1025.975	−724.011	0.1017
MA	PX	0	0	1353.844	−439.0727	0.3

Table 2
Comparison of azeotropic compositions and temperatures between experimental data and the data predicted by NRTL model

Components	Experimental data		NRTL model		Azeotrope type
	Azeotropic composition (mol%)	Azeotropic temperature (°C)	Azeotropic composition (mol%)	Azeotropic temperature (°C)	
HAc-PX	(82.0, 18.0)	115.3	(80.7, 19.3)	115.0	Homogeneous
H_2O-IBA	(61.0, 39.0)	87.5	(63.1, 36.9)	87.6	Heterogeneous
H_2O-MA	(12.5, 87.5)	56.3	(11.2, 88.8)	56.2	Homogeneous
H_2O-PX	(74.5, 25.5)	92.0	(75.5, 24.5)	92.3	Heterogeneous

the system. The set of NRTL parameters for HAc, water, and IBA is obtained from Chien et al. [7]. The NRTL parameters for water and MA are obtained from ChemCad data bank. The other NRTL parameters are obtained from Wang [22] and Gau [23]. Table 2 shows the comparison of azeotropic compositions and temperatures for the system between experimental data [24] and the data predicted by the NRTL model. Four azeotropes, including two homogeneous azeotropes and two heterogeneous ones, may be found in the system. There are only small differences between these two sets of data.

2.2. Conventional plant-wide design

Fig. 1 shows the flowsheet of conventional plant-wide design. A HADC (namely, C1) is first studied by performing rigorous simulation. It should be noted that the following feeding and column specifications are similar to an

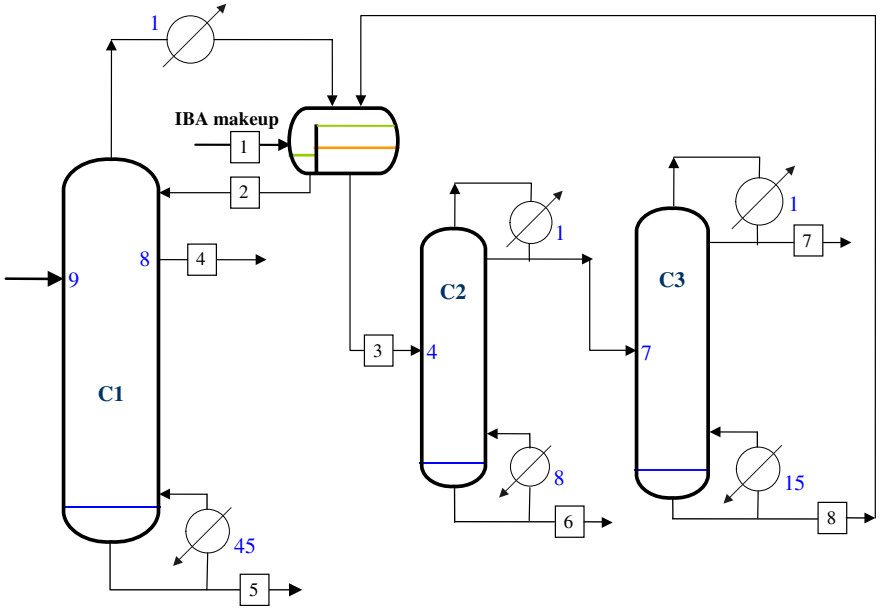

Fig. 1. Flowsheet for conventional plant-wide design.

Table 3
Simulation results for the conventional plant-wide design

Stream no.	1	2	3	4	5	6	7	8
Temperature (°C)	90	35	35	94.5	125.8	100	56.2	87.6
Mole flow (kmollh)								
HAc	0	0.307	0.192	0.333	999.474	0.192	0.000	0.000
H_2O	0	59.815	997.249	0.140	5.022	990.730	4.108	2.410
IBA	0.446	157.855	0.426	0.443	0.000	0.003	0.000	0.423
MA	0	541.318	29.993	0.007	0.000	0.003	29.989	0.000
PX	0	104.495	0.014	0.277	0.000	0.000	0.013	0.001
Mole percent								
HAc	0	0.036	0.019	27.779	99.500	0.020	0.000	0.000
H_2O	0	6.925	97.021	11.642	0.500	99.980	12.044	85.040
IBA	100	18.275	0.041	36.907	0.000	0.000	0.000	14.927
MA	0	62.667	2.918	0.585	0.000	0.000	87.918	0.000
PX	0	12.097	0.000	23.086	0.000	0.000	0.000	0.033

industrial case. The 45-stage column, including a total condenser and a partial reboiler, is operated at 1 atm. Its pressure drop is assumed to be 0.273 atm. A four-component mixture including HAc, water, and small amounts of MA and PX at 70 °C and 1 atm is fed to the stage 9, numbering from the column top. The same feed flow rate of 1000 kmol/h is used for HAc and water. The feed flow rates of MA and PX are 30 kmol/h and 0.29 kmol/h, respectively. In the simulation, the product at the column bottom is 99.5 mol% HAc. Vapor from the column top condenses and splits into two liquid phases in a decanter. The organic phase liquid, mainly consisting of the entrainer, is totally refluxed back to the column. The liquid of aqueous phase is totally drawn off as the distillate. The HAc loss through the aqueous phase product is set below 0.025 mol%. Component PX during nominal operation does not leave the column through either aqueous outlet stream or column bottom stream. A side stream is then withdrawn to prevent PX from accumulating inside the column. The PX impurity accumulation problem can also be found in the work of Chien et al. [8]. The stage location for the side stream is determined by choosing the stage with the highest PX composition. A small amount of entrainer makeup is added to the decanter to compensate for the entrainer loss through the aqueous outlet stream, column bottom stream, and side stream. The aqueous phase liquid is fed into a 8-stage column (namely, C2). Large amount of water is obtained at the bottom of column C2. The product containing mostly MA, IBA, and small amount of water at the top of column C2 is distillated and fed to a 15-stage column C3. The product containing MA and water is obtained from the distillate of column C3. It can be recycled to the oxidation reaction of PX to inhibit MA formation by the undesired decomposition reaction of HAc in the terephthalic acid production. The product containing IBA and water is withdrawn from the column bottom and recycled to the decanter to compensate for the entrainer loss. In designing the conventional two-column system, the desired purposes are to (1) withdraw water from column C2 bottom, (2) have no loss of MA and IBA at the column C2 bottom, and (3) completely separate MA and IBA at column C3 top and bottom, respectively. However, the existence of MA/water and IBA/water azeotropes limits the product purity of MA and IBA at column C3 top and bottom, respectively. Table 3 shows the simulation results of the optimal condition with the minimum reboiler duties of indirect sequence configuration in the conventional plant-wide design. From the table, it indicates that the aqueous phase and bottom HAc product specifications of C1 are satisfied. Large amount of PX in the feed is withdrawn from the side stream located at stage 8. The products of 99.98 mol% water, 87.92 mol% MA, and 14.93 mol% IBA are obtained from C2 bottom stream, top and bottom streams of C3, respectively.

2.3. Energy-saving plant-wide design

Fig. 2 shows the flowsheet of energy-saving plant-wide design. The same HAc product specifications for a HADC (C1) as those in the conventional plant-wide design are used. The liquid of aqueous phase totally drawn off as the distillate is fed to a DWDC, modelled by a prefractionator and a main column. The stage numbers in the prefractionator and the main column are the same as those for columns C2 and C3, respectively in the conventional plant-wide design. The aqueous phase liquid is fed to stage 4, the same feed position as that of column C2 in conventional plant-wide design, in the prefractionator. The side draw in the main column is also located at stage 8. The stage location for the side stream of the DWDC is determined by choosing the stage with the highest IBA composition.

In the DWDC, there are five design degrees of freedom: reflux flow, boilup flow, side draw flow, liquid split and vapor split ratios with only three product specifications. In this study, liquid split and vapor split ratios are used as the remaining degrees of freedom to minimize the reboiler duty while the other three are used to satisfy the purity specifications. Split ratio is specified as the ratio of the flow directed to the prefractionator to the flow directed to the main column. The optimal condition with the minimum

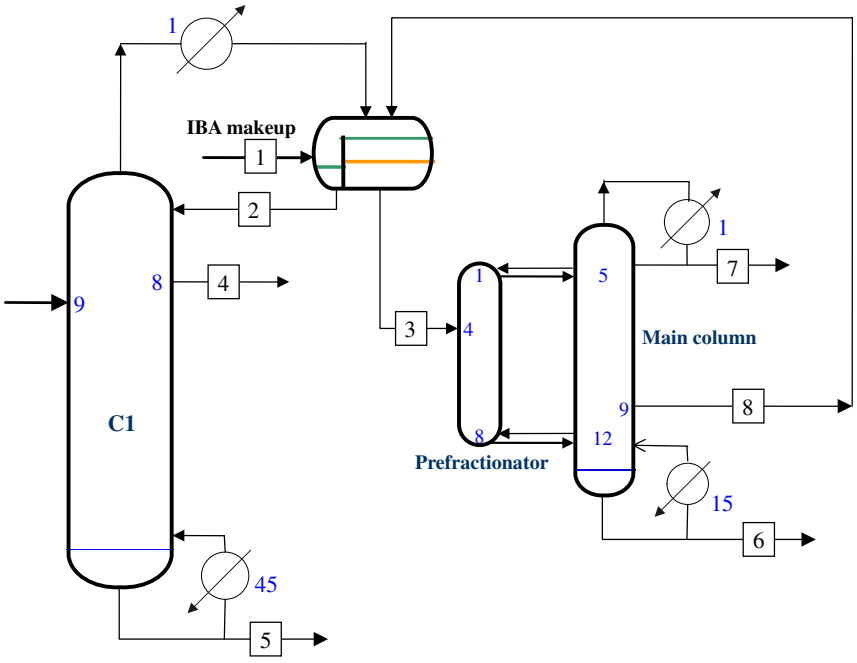

Fig. 2. Flowsheet for energy-saving plant-wide design.

energy consumption for the DWDC is obtained with liquid and vapor split ratios equal to 1.0 and 3.4, respectively when three product specifications of MA, IBA, and water in the DWDC are set at the same values as those shown in Table 3. It saves about 24.9% energy consumption compared with that of indirect sequence used in the optimal operating condition of conventional plant-wide design. However, it was found from further simulation results that water can be more easily separated from IBA for the DWDC with the same MA product purity at the DWDC top as that at the column C3 top. Much higher IBA product purity can be obtained at the side draw of the DWDC. Table 4 shows the simulation results of the nominal operating condition with the much higher IBA product purity for the energy-saving plant-wide design when liquid split and vapor split ratios are equal to 0.7 and 2.0, respectively. The distillate, side draw, and bottom products of the main column are 87.92 mol% MA, 34.08 mol% IBA, and 99.981 mol% water, respectively. The side draw product containing IBA and water is recycled to the decanter to compensate for the entrainer loss.

Fig. 3 shows the relationship between reboiler duty and two split ratios when three product specifications in the DWDC are set at the same values as those shown in Table 4. The optimal condition with the minimum energy consumption is obtained with liquid and vapor split ratios equal to 1.0 and 3.4, respectively. It saves about 28.3% energy consumption compared with that of indirect sequence used in the optimal condition of conventional plant-wide design. A near-flat region with low energy consumption is observed for high vapor split ratio, while a sharp region with high energy consumption is found for

Table 4
Simulation results for the energy-saving plant-wide design

Stream no.	1	2	3	4	5	6	7	8
Temperature (°C)	90	35	35	94.4	125.8	100	56.2	87.2
Mole flow (kmolh)								
HAc	0	0.297	0.186	0.332	999.482	0.186	0.000	0.000
H_2O	0	59.998	995.650	0.140	5.022	990.729	4.108	0.812
IBA	0.446	157.258	0.424	0.444	0.000	0.000	0.001	0.422
MA	0	542.259	29.997	0.007	0.000	0.000	29.995	0.004
PX	0	104.099	0.014	0.277	0.000	0.000	0.013	0.001
Mole percent								
HAc	0	0.034	0.018	27.686	99.500	0.019	0.000	0.000
H_2O	0	6.945	97.016	11.656	0.500	99.981	12.041	65.565
IBA	100	18.203	0.041	36.982	0.000	0.000	0.000	34.081
MA	0	62.768	2.923	0.589	0.000	0.000	87.918	0.291
PX	0	12.050	0.000	23.087	0.000	0.000	0.038	0.062

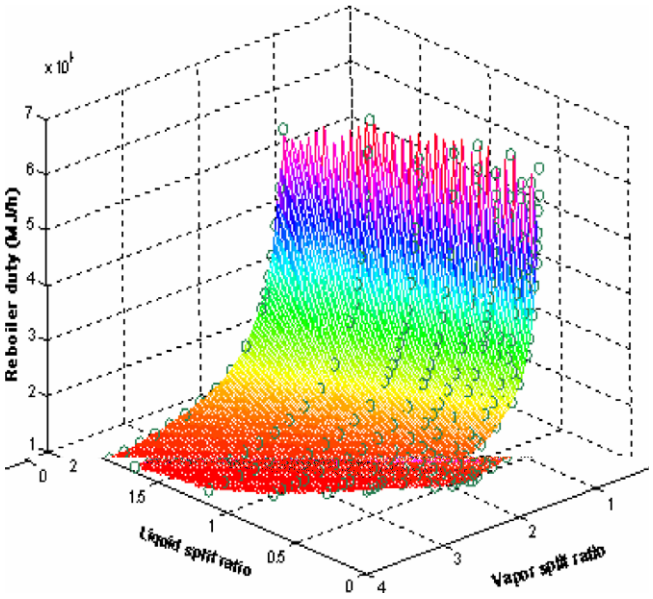

Fig. 3. The relationship between reboiler duty and two split ratios with product purities set at desired values.

low vapor split ratio. At a given vapor split ratio, the operation becomes infeasible when the liquid split ratio becomes too low. Similarly, a maximum vapor split ratio can be found for a given liquid split ratio. From the above steady-state analysis, the DWDC configuration can not only save capital cost, obtain higher IBA product purity but also consume less energy than the indirect sequence configuration for the studied system.

3. Plant-wide control

The HAc dehydrating system using the technologies of heterogeneous azeotropic distillation and divided wall distillation saves not only capital cost but also energy consumption. This section will investigate the control strategies of the energy-saving plant-wide system. In industrial applications, temperature control is usually used instead of composition control. The reason is that most product analyzers, such as gas chromatographs, suffer from large measurement delays and high investment and maintenance cost. Therefore, temperature control strategies will be developed and the following three plant-wide control strategies will be discussed.

3.1. Control strategy 1

The purpose of the control strategy of the HADC is to keep high-purity bottom HAc composition and a small HAc loss through top aqueous draw. In the study, reboiler duty is manipulated to maintain high-purity HAc composition at column bottom by controlling some stage temperature. The controlled stage temperature can be selected from a sensitivity analysis. Fig. 4 shows the profiles of stage difference temperature for ±0.1% changes in reboiler duty.

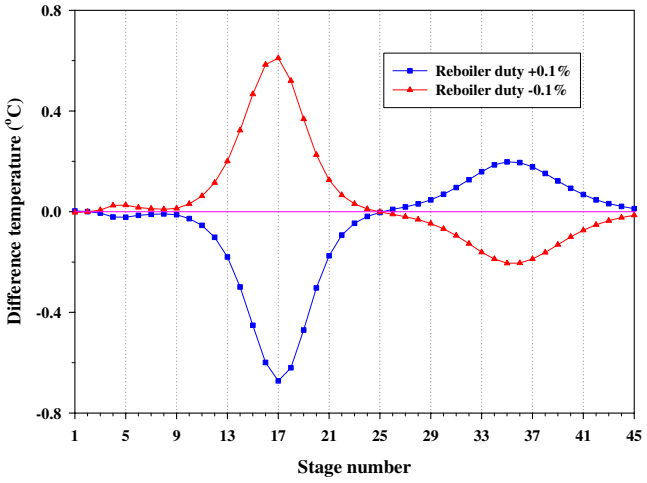

Fig. 4. Profiles of stage difference temperature for ±0.1% changes in reboiler duty.

The open loop tests show that temperature of stage 17 is a qualified candidate as the controlled variable of the temperature loop due to its highest sensitivity to reboiler duty change.

The temperature control strategy of the DWDC is designed to keep MA, IBA, and water compositions at column distillate, side draw, and bottom, respectively at their corresponding designed values. Proper manipulated variables and controlled stage temperatures need to be firstly selected. Two sets of manipulated variables are considered in this study. The manipulated variables for the first set, named LSV, include reflux flow, side draw flow, and reboiler duty. The second set, named DSV, has the same manipulated variables as the first set except reflux flow is replaced by distillate flow. To select the most appropriate stage temperature location used for control purpose, singular value decomposition method [25] was used. The controlled temperatures for the LSV set are selected at stages 4 ($T_{4(p)}$) and 5 ($T_{5(p)}$) in the prefractionator and stage 10 ($T_{10(m)}$) in the main column. The controlled temperatures for the DSV set are selected at stage 6 ($T_{6(p)}$) in the prefractionator and stages 6 ($T_{6(m)}$) and 10 ($T_{10(m)}$) in the main column. Selected stage temperatures for two different designs are all located at steep fronts.

Table 5 shows the RGA analysis of controlled stage temperatures and manipulated variables for two different

Table 5
RGA analysis of controlled stage temperatures and manipulated variables for two different designs

	L	S	V
$T_{4(p)}$	8.102	−0.001	−7.101
$T_{5(p)}$	−7.102	−0.001	8.103
$T_{10(m)}$	0	1.002	−0.002
	D	**S**	**V**
$T_{6(p)}$	−0.499	0	1.499
$T_{6(m)}$	1.500	−0.001	−0.499
$T_{10(m)}$	−0.001	1.001	0