



## Enhanced Conversion of EtOH in Reactive Divided Wall Column for the production of EtAc

Nalam Chandra Sekhar<sup>a\*</sup>, Ajmeera Ramesh<sup>b</sup>, Ratna Srinath Rao B<sup>c</sup>, Krishna Bhaskar K<sup>d</sup>

<sup>a,b,c</sup>Department of Petroleum and PetroChemical Engineering, University College of Engineering,

JNTU Kakinada, Andhra Pradesh, India

<sup>d</sup>Department of Mechanical Engineering, University College of Engineering,

JNTU Kakinada, Andhra Pradesh, India

<sup>a\*</sup> Corresponding author: nalamchandrasedkhar09@gmail.com ,

### Abstract

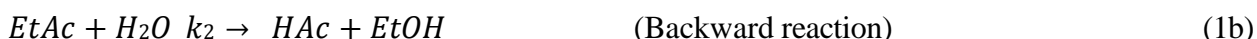
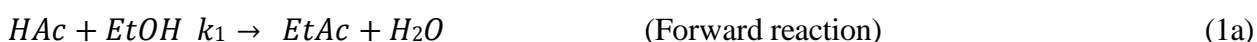
Conventionally Ethyl Acetate (EtAc) is produced by esterification of ethanol (EtOH) in reactors (mostly CSTR) followed by a finishing distillation column to separate all the components. In many revamped processes, finishing column is converted to RD column to enhance EtOH conversion. However, due to presence of water on the trays where maximum conversion takes place, backward reaction significantly reduces the overall conversion. The present work demonstrates that putting a dividing wall in the stripping section of the column enhances the EtOH conversion by about 3-4 % as compared to simple reactive distillation column.

**Keywords:** Reactive divided wall column, Esterification, Non-Equilibrium model, NRTL

**DOI:**10.53555/ecb/2021.10.1.02

### INTRODUCTION

Distillation has been extensively used in chemical industries over the years for separation. Reactive distillation (RD) has emerged as an energy-efficient process by integrating distillation and reaction for some selected reactive system in which optimum reaction temperature lies within the operating temperature range of distillation column. Esterification of acetic acid reaction for the production of ethyl acetate (*EtAc*) is one such system. On the other hand, as a result of process intensification, divided wall distillation columns (DWC) have emerged as viable alternative for using single column in place of conventional cascade of distillation columns [1]. Although RD [2] and DWC are quite old processes, the first patent for the reactive divided wall column (RDWC) was filed in the year 1984 by [3], however, only recently a systematic study was carried out at Akzo Nobel Chemicals revealing about 35% capital and 15% on energy saving in an RDWC [4]. Due to this, acceptability of RD columns in the industrial scale esterification of acetic acid (HAc) and ethanol (EtOH) for the production of high-purity ethyl acetate (EtAc) based on the following reversible reaction is increasing.



In most of the old industrial units, it was produced in large reactors followed by a finishing distillation column to separate EtAc from the mixture of EtAc, HAc, EtOH, and water. Due to reversible nature of reaction, it is not possible to attain more than 65% conversion of EtOH when HAc and EtOH are in stoichiometric ratio. In many industrial units, to attain maximum conversion of EtOH [15], excess amount of HAc is fed to the reactor and a mixture of water and HAc along with unconverted EtOH are separated in a finishing column. Some of these old units have been revamped by converting finishing column to a finishing

RD column [4] by providing PTSA (para toluene sulfonic acid) catalyst in the stripping section of the finishing column.

Singh *et al.* (2014)[4] have presented a detailed experimental analysis of an large scale finishing RD column in this a pre-reactor was used to produce ethyl acetate (EtAc) using ethanol in presence of excess of acetic acid (in 1:170 mol ratio). Even with such a high EtOH:HAc ratio, only 90-94% conversion of ethanol is attained in the pre-reactor. It has been reported by the authors that only about 25% conversion of the residual EtOH could be attained as the presence of water near the feed plate caused significant increase in the backward reaction leading to considerable reduction in the conversion efficiency.

Keeping this in view, in the present work we have introduced a new configuration of an RD process for the esterification by introducing a dividing wall in the stripping section of the RD column (Fig. 1) so that water present in the feed can be separated from some of the reacting species (on the other side of the dividing wall) and backward reaction (equation 1b) is reduced. Thus the conventional RD column is converted to an RDWC (Reactive Divided Wall Distillation Column). One auxiliary heater/cooler was also provided at the top of the divided segment of the column. This RDWC was simulated using a non-equilibrium model, "RadFrac" of AspenPlus™.

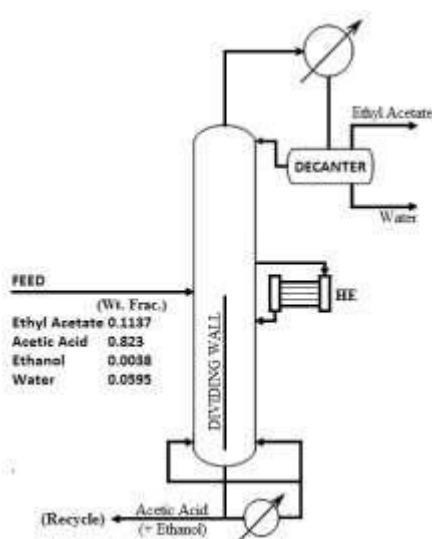


Fig. 1(a):The schematic diagram of RDWC

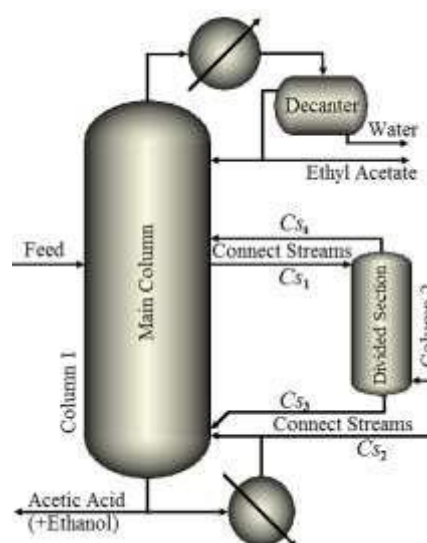


Fig. 1(b):Analog of the Proposed RDWC

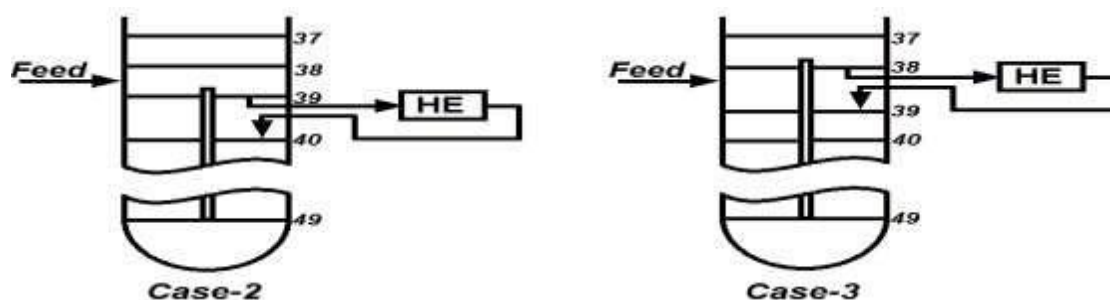


Fig. 1(c): Two cases of dividing wall in the stripping section of RDWC

Existence of different azeotropes: EtOH-H<sub>2</sub>O, EtOH-EtAc, EtAc-H<sub>2</sub>O and EtOH-EtAc-H<sub>2</sub>O, in the system; due to this selection of thermodynamic model parameters becomes pivotal [6]. Based on the reported values of binary vapour-liquid equilibrium data of [7-8], a new set of binary parameters for the EtOH-EtAc-HAc-H<sub>2</sub>O system was obtained by regression. The same binary parameters were used in all the three cases studies (one for RD column, and two for RDWC, referred as case 1, 2 and 3, respectively) of the present work. Simulation results of the present work revealed that there exists an optimum value of heating/cooling rate in the auxiliary heater (depending on the reflux flow rate, liquid split ratio at the top and the vapor split ratio at the bottom of the dividing wall) that leads to significant improvement in the conversion of residual ethanol and purity of EtAc in final product.

**PROCESS DESCRIPTION AND MODEL SELECTION:**

The schematic representation of the proposed design of RDWC and its analogues Petlyuk column [9] are shown in Fig. 1(a) and (1b), respectively. For the modeling and simulation point of view, a divided wall column is analogous to a Petlyuk column in all respect [10-11]. The proposed RDWC consists of a distillation column having 50 stages including a total condenser and a kettle type re-boiler. An auxiliary heat exchanger (HE, shown in Fig. 1a) is also provided to adjust temperature of the connect stream  $C_{s1}$  (Fig. 1b). There are 48 bubble-cap trays in the main column and the pre-reacted feed from the reactor enters the column (at a pressure of 340kpa) on the 39<sup>th</sup> stage (i.e., 38<sup>th</sup> tray) counted from top of the column. Condensate from the total condenser is sent to a decanter to separate organic (EtAc rich) and water phases. One fraction of organic phase coming from the decanter is sent back to the main section (13000-16000kg/hr) as a reflux and remaining part is withdrawn as ethyl acetate product.

Two different cases of dividing the entire stripping section (including and excluding feed tray) are considered in the present work (Fig. 1c). Liquid from the tray just above the divided segment is split into two parts. One part of it (with a predefined mass flow rate and temperature) is sent to the right hand side of the dividing wall (Fig. 1a) through a heat exchanger. This is equivalent to setting a predefined value of mass flow rate and temperature of the connect stream  $C_{s1}$  of the analogue Petlyuk column (Fig. 1b). Remaining part of liquid split goes to the left hand side of the dividing wall (Fig 1a) or the mail column of the Pelyuk analogue (Fig. 1b).

Thus, present simulation was conducted for three cases. In the first case an RD column without any dividing wall was considered for validation purpose. In case 2, trays below the feed plate (stage number 40) to the bottom most tray (stage number 49) were divided into two parts, and in third case, feed tray was also included in the divided section (i.e., stage number 39 to 49 were divided).

Liquid streams coming out from both sides of the bottom stage (stage number 49) are mixed in the column bottom and one part of it is sent to the reactor back as acetic acid rich recycle stream and remaining stream for total vaporization sent to thermos-siphon re-boiler. This vapor stream from re-boiler is also separated into two streams and one of them (with a predefined mass flow rate) is sent to the right hand side of the dividing wall as a connect stream ( $C_{s2}$ ) and rest goes to left hand side of the dividing wall (or mail column of analog configuration). Other process conditions and the column specifications are given in Table 1 and Table 2. To obtain maximum amount of purity and conversion, optimum values of connecting stream flow rates and their temperatures were obtained.

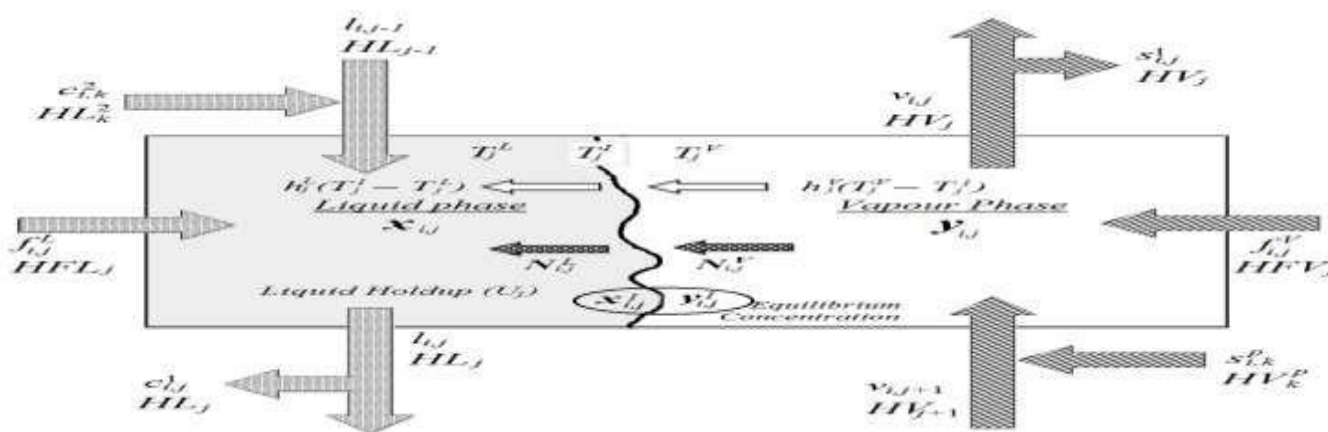
**Table 1: Design parameter used for simulation in the present work**

<b>Tray numbers 2-38 (Case-1) 2-37 (Case-2)</b>		
	Column 1 (Main column)	
Internal diameter	1800mm	
Tray spacing	337.5mm	
Active area	2.168m <sup>2</sup>	
Weir type	"V" notch	
Down comer length	452mm	
Hold up on each tray	112 lit	
No to bubble cap on each tray	77	
<b>Tray numbers 39-49 (Case-1) 38-49 (Case-2)</b>		
	Column 1 (Main column)	Column 2 (Divided section)
Internal diameter	900mm	900mm
Tray spacing	400mm	400mm
Active area	1.084m <sup>2</sup>	1.084m <sup>2</sup>
Down comer length	452mm	452mm
Hold up on the tray	56lit	56 lit
No to bubble cap on each tray	30	30

**Table 2: Operating parameters used in Main column and Divided Section**

Parameter	Column 1	Column2
Feed	24200kg/hr	
Ethanol(mass fraction)	0.0038	
Acetic acid	0.822	
Ethyl acetate	0.1138	
Water	0.0595	
Liquid Reflux to top tray	13000-16000 kg/hr	20000-25000kg/hr(Cs1)
Bottom flow	20825 kg/hr	calculated(connect stream 3)
Feed temperature	101 °C	80-120 °C (connect stream 1) 80-120 (connect stream 2)
Feed pressure	303 kpa	303 kpa
Split ratio (Cs1/Cs2)		1.9-3.2

There are many different shortcut and rigorous ways of formulating and solving distillation problems [12]. Many of them are available in the well-known commercial software –AspenPlus™.RadFrac and MultiFrac are two rigorous models being widely used for solving research problems. Whereas MultiFrac is specially designed for simulating multiple columns (such as Petlyuk column) using non-equilibrium (NEQ) model, but incorporating chemical reaction is not possible in MultiFrac. On the other hand, RadFrac can solve both equilibrium (EQ) and non-equilibrium (NEQ) models, and chemical reaction can also be specified for any number of trays or stage segment. Therefore, to simulate complex configuration of two columns (Fig. 1b) as single unit with chemical reaction, RadFrac with NEQ option was used. Contrary to the equilibrium stage models MESH equations where used to solve the overall material and energy balance on each stage, in the NEQ modeling these balance equations are applied separately for each phase on a stage (Fig. 2) along with transport equations applied to inter-phase heat and mass transfer [5]. For divided wall columns, these model equations (normally used in the residual form) are slightly modified by introducing an additional connect streams  $c_{ik}^p$  and  $s_{ik}^p$ . A brief description of these model equations are discussed in the following residual form where, superscript  $L, V$  or  $I$  represent liquid phase, vapour phase or vapour-liquid interface, and  $U$  and  $N$  are the liquid holdup and the inter-phase mass transfer rate (mol/s) across the vapour liquid interface, respectively. The residual value of component  $i^{th}$  on any stage  $j^{th}$  in liquid phase is given by:



**Fig .2:** Schematic representation of

material and energy streams considered in rate-based model

$$M_{ij}^L \equiv (l_{ij-1} + c_{ik}^p) - l_{ij} + f_{ij}^L + N_{ij}^L + r_{ij}U_j = 0 \tag{2}$$

where  $c_{ik}^p$  is the molar flow rate of  $i^{th}$  component in the liquid fraction of connect stream originating from stage number  $k$  of  $p^{th}$  column. Inter-phase mass transfer rate of  $i$  component is calculated in terms of the effective mass transfer coefficient,  $k_{ij}^L$  and the overall molar flux  $N_j^L$  as

$$N_{ij}^L = \frac{k_{ij}^L}{i_j} a_j (x_{ij}^L - x_{kj}^L) + x_{ij}^L \frac{N_j^L}{j} \tag{3}$$

Material balance for vapour phase on  $j^{\text{th}}$  stage is represented as

$$M_{ij}^V \equiv (v_{ij+1} + s_{kj}^p) - v_{ij} + f_{ij}^V - N_{ij}^V = 0 \quad (4)$$

and

$$N_{ij}^V = \frac{k_{ij}^V}{a_{ij}} (y_{ij} - y_{ij}^l) + y_{ij}^l \frac{N_{ij}^V}{j} \quad (5)$$

where  $s_{kj}^p$  is the molar flow rate of  $i^{\text{th}}$  component coming through the vapour phase of the connect stream originating from  $k$  stage of  $p$  column. To ensure equality of mass flux in the vapour and liquid phases, following additional constraint is introduced.

$$M_{ij}^L \equiv N_{ij}^L - N_{ij}^V = 0. \quad (6)$$

Vapour and liquid phases energy balance equations are

$$E_j^V \equiv V_{j+1} HV_{j+1} + S_k^p HV_k^p + \left( \sum_{i=1}^c f_{ij}^V \right) HFV_j - V_j HV_j - \Delta_j^V a_j (T_j^V - T_j^L) - \frac{N_j^V}{j} HV_j = 0 \quad (7)$$

and

$$E_j^L \equiv L_{j-1} HL_{j-1} + \sum_{i,k} c_{ik}^p HL_k^p + \left( \sum_{i=1}^c f_{ij}^L \right) HFL_j - L_j HL_j + \Delta_j^L a_j (T_j^L - T_j^V) + \frac{N_j^L}{j} HL_j = 0, \quad (8)$$

respectively, where  $HV$  and  $HL$  are vapour and liquid phase enthalpies. To ensure equality of energy transport between the phases in steady state, following equation can be used.

$$E_j^L \equiv \Delta_j^L (T_j^V - T_j^L) - \Delta_j^V (T_j^L - T_j^V) + \frac{N_j^V}{j} HV_j - \frac{N_j^L}{j} HL_j = 0. \quad (9)$$

Based on the two-film theory of mass transfer, the equilibrium composition on the two sides of the interface is given by

$$Q_{ij}^L \equiv K_{ij} x_{ij}^L - y_{ij}^L = 0 \quad (10)$$

where  $K_{ij}$  is the vapour-liquid equilibrium ratio. Applying rigorous thermodynamic analysis for low to moderate pressure, it gives

$$K_{ij} = \frac{\gamma_{ij}^L p_{ij}^L}{p} \quad (11)$$

Many correlations are available to estimate liquid phase activity coefficient  $\gamma_{ij}^L$  which are selected on the basis of suitability of the model for a particular system. NRTL model is recommended by many researchers [6,13-14] for non-ideal systems. Considering high non-ideality of the liquid mixture of  $HAc$ ,  $EtOH$ ,  $EtAc$ , and  $H_2O$ , NRTL model was selected for predicting VLE and LLE applications. However, the binary parameters available in Aspen Plus library were not able to predict experimental binary VLE data reported by many researchers [4-6,12]. Considering this, a new set of binary parameters was obtained by regressing VLE data using inbuilt regression tool of Aspen Plus. The same binary parameters were used in all simulation runs of the present work. For the estimation reaction rate ( $r_{ij}$ ) appearing in equation (2) for a component  $j$  ( $=HAc, EtOH, EtAc$  and  $H_2O$ ) on any  $i^{\text{th}}$  stage is given by [16].

$$-r_{H_2O} = -r_{EtAc} = r_{EtOH} = r_{HAc} = k_1 \frac{C_{HAc}}{1 + C_{HAc} + C_{EtOH}} - \frac{k_2}{K_C} \frac{C_{H_2O} C_{EtAc}}{C_{H_2O} + C_{EtAc}} \quad (12)$$

where

$$k_1 = (4.195 C_k + 0.08815) \exp\left(-\frac{6500.1}{T}\right) \quad (13)$$

and

$$K_C = (7.558) - 0.012T. \quad (14)$$

The parameter  $C_k$  appearing in equation (13) is the catalyst concentration (volume percent).

## **RESULTS AND DISCUSSION**

The present work consists of three case studies, namely RD column without divided wall (Case-1), RDWC with dividing wall from below the feed tray to the bottom of the column (Case-2), and RDWC with dividing

wall from feed tray (inclusive) to the bottom of the column so that feed remains on one side of the wall (Case-3). For all three cases, NRTL thermodynamics with regressed binary parameters (Table 3) was used. Predictions of Case-1 (RD column) were used mainly for validation purpose. The predicted concentration profiles of EtAc and water in RD column are compared with the plant data of [16] and simulation results of Singh et al. (2015)[5]. It is evident from Fig. 3(a,b), that the present results have further improved as compared to those of Singh et al. (2015)[5] in a way that predicted concentration profiles of EtAc (Fig. 3a) and water (Fig.3b) are closure to the actual plant data.

After validating the simulation results for RD column, the dividing wall was introduced by adding a second column (having 11 trays in case-2 and 12 trays in case-3) and 4 connect streams between the main column and the second column as shown in Fig 1.b. The connect stream configuration is given in Table 4

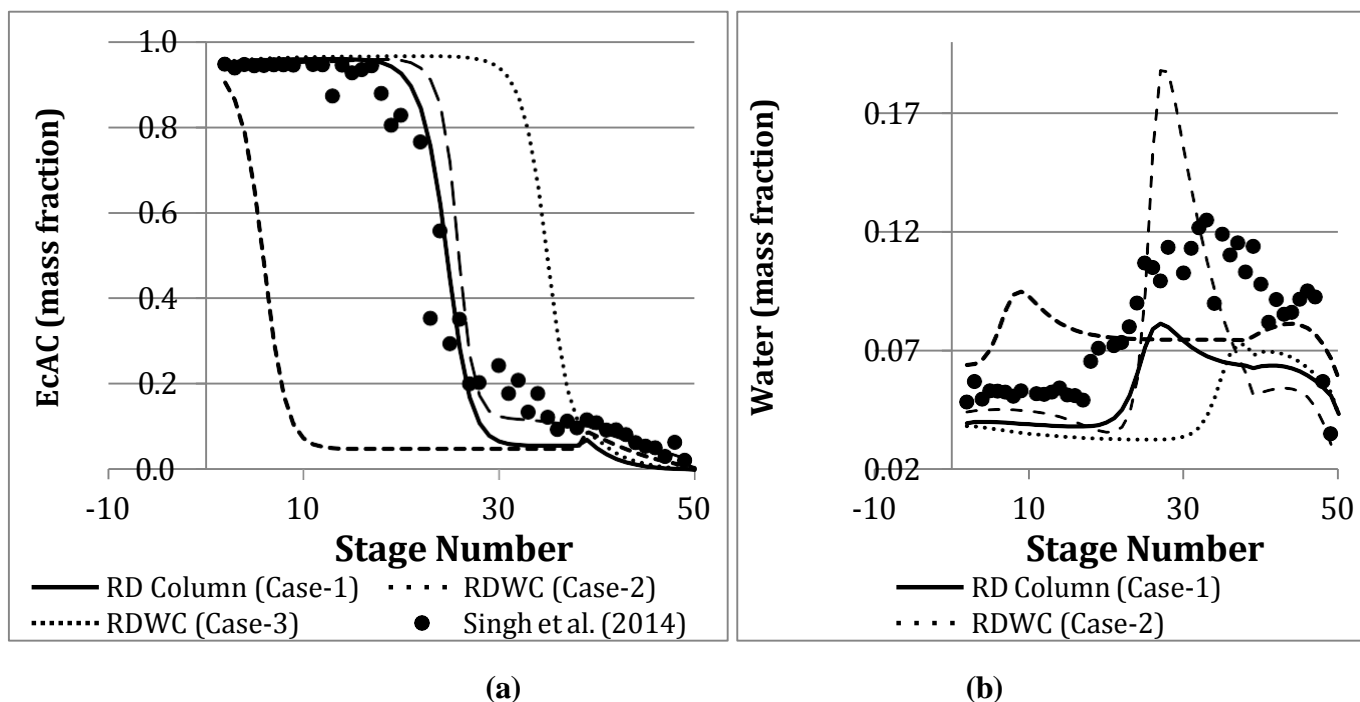


Fig.3: Comparison of predicted concentration profile of (a) EtAc, and (b) Water with the plant scale RD column in various cases

In all cases, feed enters the main column on 39<sup>th</sup> stage. Thus in case-2 feed gets divided on both sides of the wall whereas in case-3 it remains only on one side of the wall. Remarkable difference in the concentration profile (as well as purity) of EtAc in these two cases (case-2 and case-3) was observed (Fig. 3). Further, it was observed that if connect streams flow rates are reduced, in both the cases of RDWC (case-2 and case-3), the concentration profile shifts towards that of the RD column and in case-2, almost coincide with the RD profile when liquid flow rate on both sides of the column are almost equal (22600kg/hr) and the total liquid flow rate on both the sides of dividing wall are equal to the liquid flow rate in the RD column (Fig. 4).

Table 4: Connect stream (Cs) specifications (in all cases, feed enters on 39<sup>th</sup> stage)

Cs. No.	Source		Destination		Phase	Flow rate (kg/h)	Temperature (°C)
	Column	Stage	Column	Stage			
1	1	39 (Case-2) 38 (Case-3)	2	1	Liquid	25000	80-120
2	1	50	2	11 (Case-2) 12 (Case-3)	Vapor	13000	-
3	2	11 (Case-2) 12 (Case-3)	1	50	Liquid	-	-

4	2	1	1	39 (Case-2) 38 (Case-3)	Vapor	-	-
---	---	---	---	----------------------------	-------	---	---

Because the reflux flow rate and feed flow rates are kept constant in the all cases, this will ultimately lead to the same L/V ratio in the stripping section (undivided section of the column). However, with change in connect stream flow rates, L/V ratio in the divided segment changes considerably. It was also observed that while changing these L/V ratio by changing connect-streams flow rates and temperature, there was a significant change in conversion of EtOH and purity of EtAc (Fig. 5a,b). Since the large number of combination of L/V ratio (ratio of the flow rates of connect-stream 1 to the connect-stream 2) in the divided segment is possible, optimum values of connect streams, as well as temperature, were obtained by using the sensitivity analysis tool in Aspen plus<sup>TM</sup>(v8.4). The optimized values are shown in Table 5

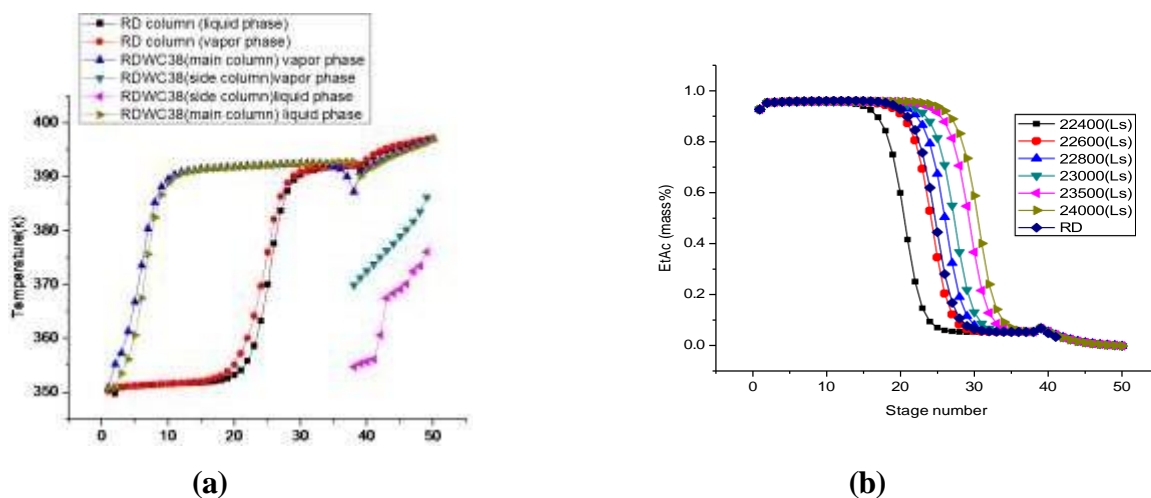


Fig.4: (a)Temperature profile of liquid and vapor phase in case (1&3) (b)EtAc concentration profile of RDWC is shifting towards the RD column profile by changing connect stream flow rate in Case-2.

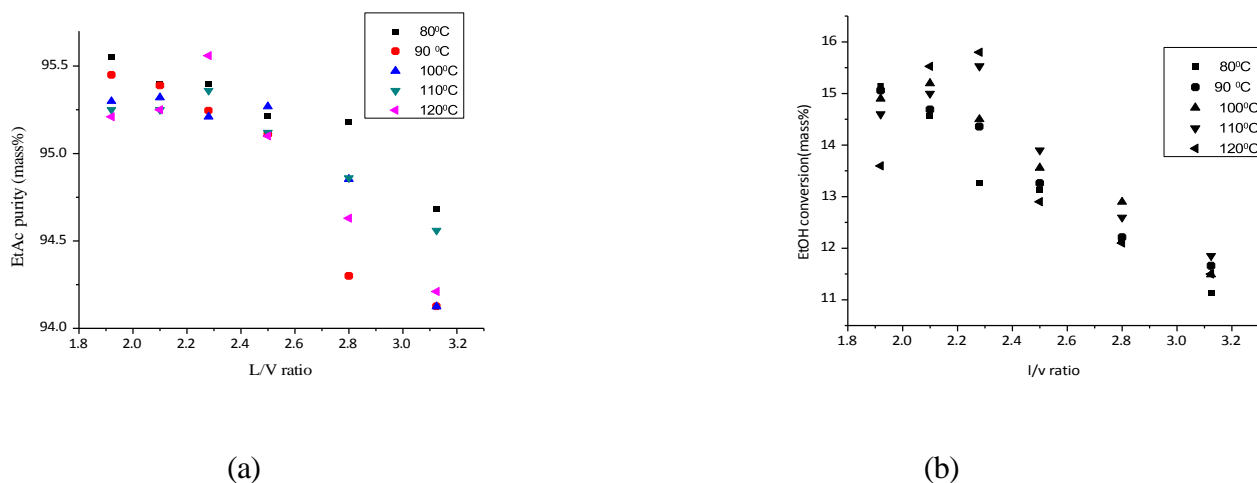


Fig. 5(a) Effect change in temperature of connect stream on EtAc purity 5(b) Effect change in temperature of connect stream on EtOH conversion

Table 5: Optimum values of the connect streams

S.NO	Vary variable	Optimum values(case1)	Optimum values(case2)	Optimum values(case3)
1	Reflux rate	16000(kg/hr)	16000(kg/hr)	14500/hr
2	Vapor split rate	-	13000(kg/hr)	10038 (kg/hr)
3	Liquid split rate	-	25000(kg/hr)	13000 (kg/hr)
4	Liquid split temperature	-	358.74 °C	385.71 °C
5	Liquid split temperature		384.16 °C	392.94 °C

Obviously, Case-3 gives a better conversion of EtOH and better purity of EtAc, this is because of the fact that the water concentration in the liquid phase is lowest in the stripping section where most of the reaction taken place as shown in Fig. 3(b). Shifting of the water peak from near the feed plate in RD (i.e., Case-1, without divided wall) to 8<sup>th</sup> or 9<sup>th</sup> tray in Case 3, is perhaps due to changes in the temperature profile inside the column as shown in Fig. 4a. It is interesting to note that although connect stream temperature is quite low the temperature profile in the main column is significantly higher than that of the RD column, which ultimately leads to remove water from stripping section to the top of the column. Contrary to this, in Case 2, temperature profile in the main column is even lower than the RD column (not shown in figure), due to this with lowering of temperature, most of the water is shifted towards the bottom of the column.

## **CONCLUSIONS**

As pointed out earlier that the presence of water below the feed plate leads to backward reaction causing a decrease in the conversion of EtOH. In all 3 cases studied in present work it is observed that peak concentration of water is almost same, however, its location is different in three cases. Maximum conversion of EtOH is observed in Case 3, where feed is retained on one side of the dividing wall. This may be due to the fact that peak of water concentration in Case-3 is located at a place where there is no catalyst present on the stage. On the other hand the extent of backward reaction in Case2 is lower than that of RD column, due to lower temperature of connect streams flow rate. In addition to these, in Case3, concentrations of acetic acid (HAc) and ethanol (EtOH) are higher in the top section of the column leading to considerable forward reaction, this may be the reason why we have maximum conversion in Case3.

## **REFERENCES**

1. Delgado-Delgado, Raúl, et al. "From simulation studies to experimental tests in a reactive dividing wall distillation column." *Chemical Engineering Research and Design* 90.7 (2012): 855-862.
2. Keyes, D. B. "Esterification processes and equipment." *Industrial & Engineering Chemistry* 24.10 (1932): 1096-1103.
3. Kaibel, G. "Method of carrying out chemical reactions and for the simultaneous fractionation of a mixture into several fractions by a distillation column." *European Patent EP126 288* (1984): A2.
4. Kiss, Anton A., Hans Pragt, and Cornald van Strien. "Overcoming equilibrium limitations in reactive dividing-wall columns." *Computer Aided Chemical Engineering*. Vol. 24. Elsevier, 2007. 467-472.
5. Singh, Damandeep, Raj Kumar Gupta, and Vineet Kumar. "Experimental studies of industrial-scale reactive distillation finishing column producing ethyl acetate." *Industrial & Engineering Chemistry Research* 53.25 (2014): 10448-10456
6. Singh, Damandeep, Raj Kumar Gupta, and Vineet Kumar. "Simulation of a plant scale reactive distillation column for esterification of acetic acid." *Computers & Chemical Engineering* 73 (2015): 70-81.



7. Ellis, S. R. M., and R. D. Garbett. "A new equilibrium still for the study of partially miscible systems." *Industrial & Engineering Chemistry* 52.5 (1960): 385-388.
8. Calvar, N., A. Dominguez, and J. Tojo. "Vapor-liquid equilibria for the quaternary reactive system ethyl acetate+ ethanol+ water+ acetic acid and some of the constituent binary systems at 101.3 kPa." *Fluid phase equilibria* 235.2 (2005): 215-222.
9. Petlyuk, F. B. "Thermodynamically optimal method for separating multicomponent mixtures." *Int. Chem. Eng.* 5 (1965): 555-561.
10. Wolff, Erik A., and Sigurd Skogestad. "Operation of integrated three-product (Petlyuk) distillation columns." *Industrial & Engineering Chemistry Research* 34.6 (1995): 2094-2103
11. Sangal, V. K., V. Kumar, and I. M. Mishra. "Divided wall distillation column: rationalization of degree of freedom analysis." *Theoretical Foundations of Chemical Engineering* 46.4 (2012): 319-328.
12. Simandl, J., and W. Y. Svrcek. "Extension of the simultaneous-solution and inside-outside algorithms to distillation with chemical reactions." *Computers & chemical engineering* 15.5 (1991): 337-348.
13. Tabari, Amir, and Arshad Ahmad. "A semicontinuous approach for heterogeneous azeotropic distillation processes." *Computers & Chemical Engineering* 73 (2015): 183-190.
14. Lai, I-Kuan, et al. "Design and control of reactive distillation for ethyl and isopropyl acetates production with azeotropic feeds." *Chemical Engineering Science* 62.3 (2007): 878-898.
15. Lai, I-Kuan, et al. "Production of high-purity ethyl acetate using reactive distillation: experimental and start-up procedure." *Chemical Engineering and Processing: Process Intensification* 47.9-10 (2008): 1831-1843.
16. Alejski, Krzysztof, and Francoise Duprat. "Dynamic simulation of the multicomponent reactive distillation." *Chemical Engineering Science* 51.18 (1996): 4237-4252.