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CYCLOHEXANOL PRODUCTION FROM CYCLOHEXENE IN A REACTIVE DIVIDED WALL COLUMN: A FEASIBILITY STUDY

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Abstract
In this paper, applicability of reactive divided wall column for two step reactions is investigated. Reactive divided wall column is designed conceptually and simulation studies show that cyclohexanol production from cyclohexene using formic acid as a reactive entrainer in reactive divided wall column is feasible.

Keywords: reactive divided wall column, reactive distillation, reactive entrainer, cyclohexanol

1. Introduction

Cyclohexanol is produced by many process routes such as gas phase oxidation of cyclohexane; hydration of benzene; direct hydration of phenol; direct hydration of cyclohexene. An alternative and novel process is esterification of cyclohexene with formic acid followed by hydration for which the reaction scheme is as shown in the Fig.1. Our previous analysis on this two step process for cyclohexanol includes experimental investigation of kinetic[1] and thermodynamics[2] of process, feasibility of coupled reactive distillation column schemes[3]. Our analysis on a reactive distillation[3] under vacuum through simulations shows that the esterification of cyclohexene with formic acid in first reactive distillation column followed by hydration of ester in the second reactive distillation column (i.e. coupled *RD* process) gives a better performance in terms of conversion and selectivity than other processes. Coupled *RD* process is shown in the Fig. 2. The performance of the process can be further improved by integrating two reactive distillation columns in a single unit. It is possible to combine both *RD* columns in a single unit either by placing them one above other or by placing them side by side with interconnecting the liquid streams (i.e. a reactive divided wall column configuration) with the possible mechanical modifications. By placing two RD columns one above other will give a similar performance like coupled *RD* process. However, the performance of *RDWDC* is purely dependent upon the thermal and hydrodynamic coupling between the two columns[4]. The present study addresses the feasibility of *RDWC* through simulations for cyclohexanol production by the same two step reaction scheme.

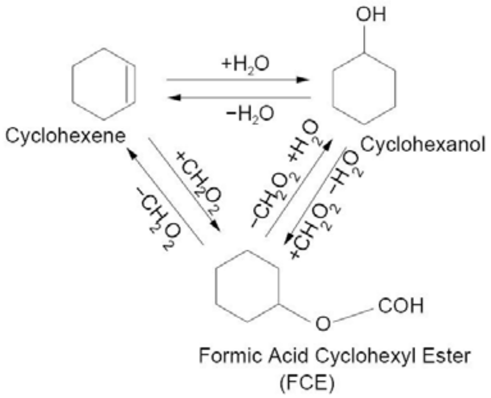


Figure 1. Reaction scheme

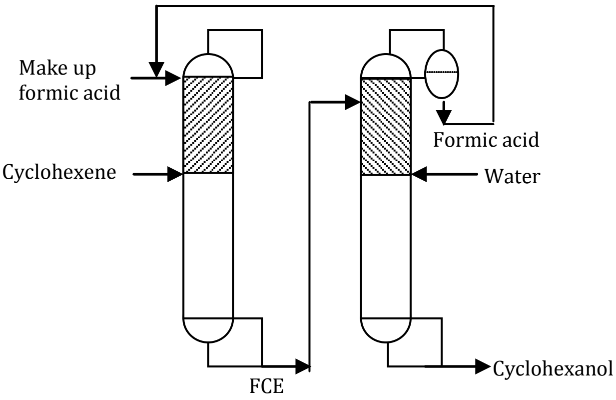


Figure 2. Coupled RD process

2. Kinetics and thermodynamic data

Reactions involved in the two step process for cyclohexanol using formic acid as reactive entrainer is given by eqs.(1)-(3). Experimentally developed activity based reaction kinetic model (eq.(4)) [1] has been used to perform the simulations. Kinetic parameters are summarized in Table 1.

$$\text{cyclohexene + formic acid} \leftrightarrow \text{cyclohexyl formate} \quad (1)$$

$$\text{cyclohexyl formate + water} \leftrightarrow \text{cylcohexanol + formic acid} \quad (2)$$

$$\text{cyclohexene + water} \leftrightarrow \text{cylcohexanol} \quad (3)$$

$$R = [m_{cat} k_f^{het} \frac{K_{ads,reactant1} K_{ads,reactant2}}{[1+\sum_i K_{ads,i} a_i]^2} + n_{FA} k_f^{\text{hom}}] \times (\prod a_{reactants} - \frac{\prod a_{products}}{K_{eq}}) \quad (4)$$

Where m_{cat} is the catalyst amount (kg) used, k_f^{hom} and k_f^{het} are the forward rate constants of homogeneous and heterogeneous reactions respectively. $K_{ads,i}$ are the adsorption equilibrium constant for *i* component. K_{eq} is the chemical equilibrium constant. N_{FA} is the molar amount of formic acid. a_i is the liquid phase activity of *i* component. Activity of the components is calculated using NRTL model for which binary interaction parameters are taken from our previous studies[2].

Table 1. Kinetic Parameters for two step process of cyclohexanol[1]

reaction	$k_{f,0}^{\text{hom}}$[1/s]	$E_{f,0}^{\text{hom}}$[J/mol]	$k_{f,0}^{het}$[mol/(kg$_{cat}$.s)]	$E_{f,0}^{het}$[J/mol]
esterification	1.7089x10^{11}	95467	4.5701x10^{25}	114395
ester hydrolysis	7.2738x10^{5}	53387	1.2148x10^{16}	100240
cyclohexene hydration			7.7083x10^{12}	93687

substance	$\Delta_f H^0_{liquid}$[J/mol]	S^0[J/(mol.K)]	C_P[J/(mol.K)]	K_{ads}
cyclohexene	-37820	216.33	148.83	0.056839
cyclohexanol	-351831	203.87	213.59	0.77324
water	-285830	69.95	75.38	19.989
FCE	-487129	275.50	219.50	3.6770
formic acid	-425379	129	99.84	7.7290 x 10^{-7}

3. Reactive divided wall column Studies

3.1. Process Description and conceptual analysis

RDWDC configuration shown in Fig. 3 consists of two different reactive sections (i.e. one section is for esterification and other is for hydration) for production of cyclohexanol. The two different sections are connected with the liquid outlet stream of esterification section. Formic acid (the liquid feed) and cyclohexane (the vapour feed) are fed to esterification section below the condenser and bottom stage of esterification section respectively. Formic acid cyclohexyl ester (FCE) with other components will be the feed to hydrolysis section from esterification section. Water is fed below reactive zone of hydrolysis section. Cyclohexanol is produced as a bottom product from *RDWDC*. Esterification side of *RDWDC* is operated under total reflux condition and hydrolysis section is operated with the finite reflux of aqueous phase and total reflux of organic phase from decanter. Input composition to decanter depends on the operating mole ratio of reactants (i.e. cyclohexene/formic acid). There are

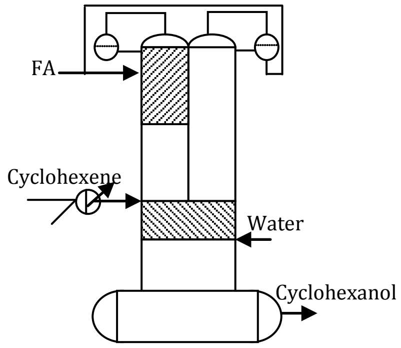
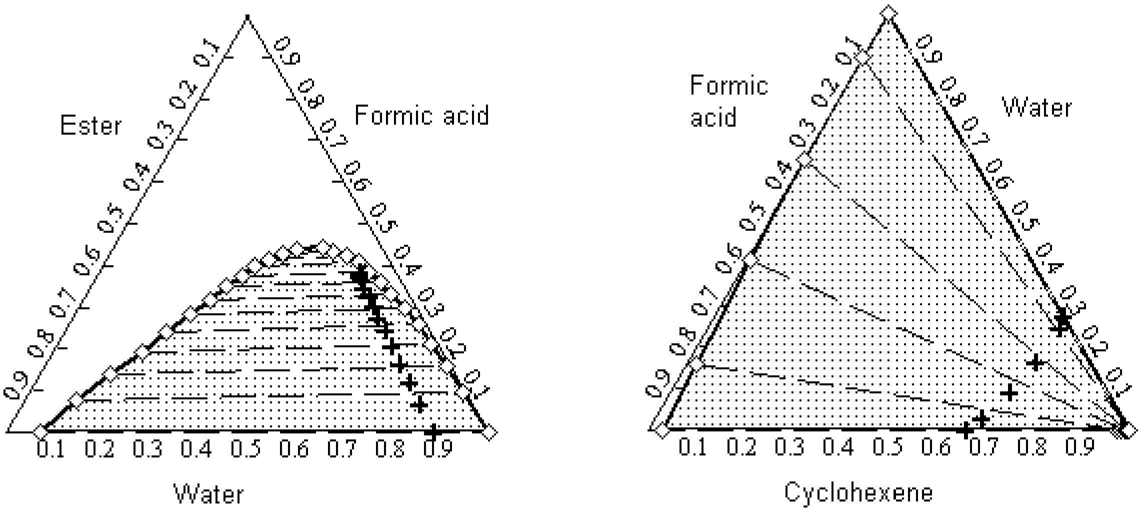


Figure 3.RDWDC configuration

two possible composition streams as input to decanter from hydrolysis section (i.e. formic acid and water when *RDWDC* operated in stoichiometric mole ratio or cyclohexene, formic acid and water when operated in excess of cyclohexne). From ternary plot with azeotrope shown in Fig. 4, in both the cases formic acid is recovered from the hydration section is recycled to the esterification section or a make up stream of formic acid should be provided depending upon the operating conditions.



(a) **(b)**

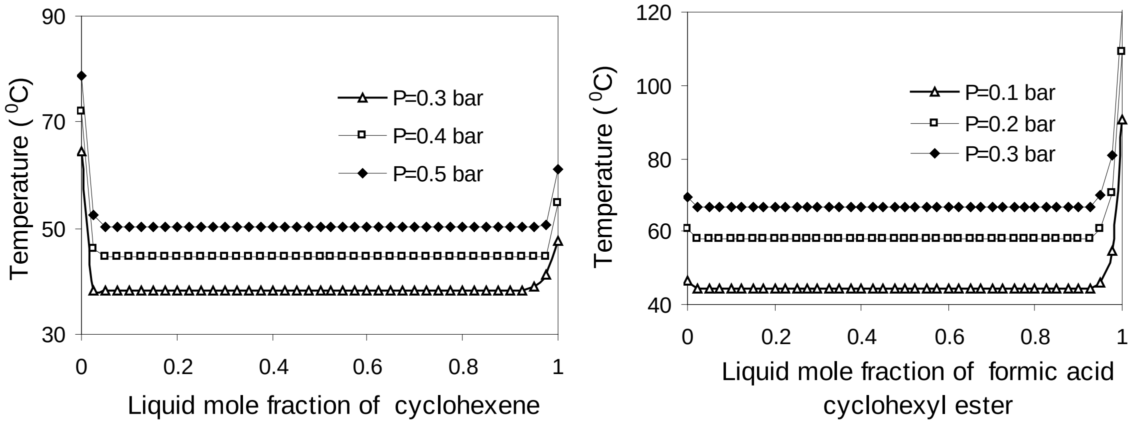
Figure 4. Ternary diagram of (a) cyclohexyl ester-water-formic acid (b) cyclohexene-water-formic acid

3.2 Parametric study

Two separate RADFRAC columns are used for the rigorous simulations using the above kinetic and thermodynamic data to design the *RDWDC* for equi molar flow of cyclohexane/formic acid and formic acid/water. Equilibrium based simulations with phase splitting are performed by considering the reaction in one of the liquid phase i.e. polar phase. Various parameters which affects the performance of *RDWDC* are pressure, mole ratio, the number of reactive and non-reactive stages and reboiler duty have been analysed. From the parametric studies, *RDWDC* column is designed and the feasibility of *RDWDC* for cyclohexanol production has been investigated.

3.2.1 Effect of pressure

From the kinetic studies[1], it was found that, above 60^{0}C formic acid decomposes to form carbon monoxide and water. Therefore the operating pressure of *RDWDC* chosen such that the temperature of the reactive section should not exceed 60^{0}C.The temperature-composition diagram for formic acid and cyclohexene mixture (Fig. 5a), explains that for various combinations of cyclohexene and formic acid compositions, if the operating pressure is kept below 0.5 bar the temperature will not exceed 60^{0}C.



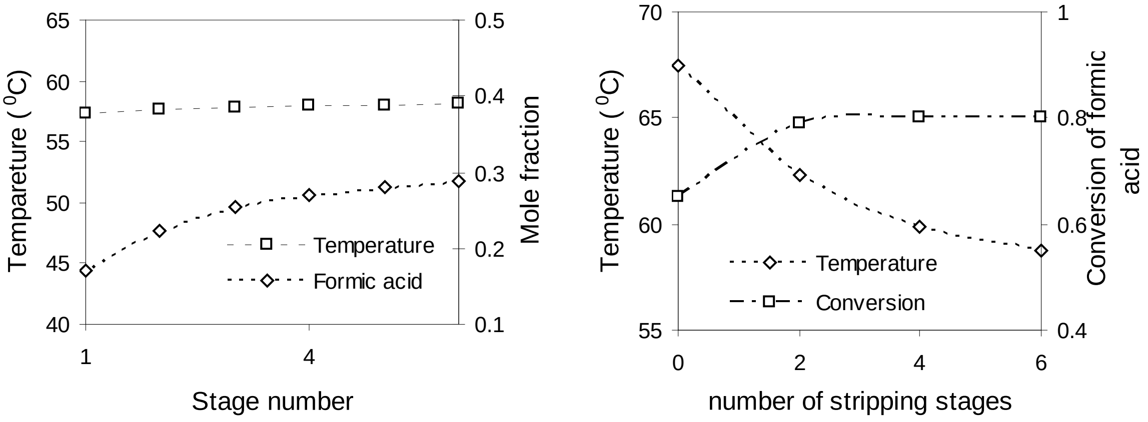
(**a**) (**b**)

Figure 5. T-x diagram of (a) cyclohexene-formic acid (b) water-FCE

Similarly, from Fig. 5b, the temperature is below 60^{0}C for the operating pressure in hydrolysis section is close to 0.2 bar. The simulations of base case configuration of *RDWDC* consists of 6 reactive stages with 0.3kg of total catalyst loading in each esterification (Heat duty for cyclohexene vaporization ~ 0.15 kW) and hydrolysis section (reboiler duty~0.1 kW) have been performed for various pressure to analyse the reactive zone temperature profiles. When RDWDC is operated at 0.2 bar pressure, the reactive zone temperature is below 60^{0}C in both esterification and hydrolysis section. Hence, the operating pressure is restricted to 0.2 bar pressure.

3.2.2 Effect of non-reactive stages

Formic acid and cyclohexene forms a minimum boiling azeotrope and presence of rectifying stages leads to enrich the azeotrope in rectifying section. Hence, presence of rectifying stages in the esterification section is not recommended. Fig. 6a shows the formic acid composition and temperature profile along the length of hydrolysis section. From Fig. 6a, when conversion of formic acid and cyclohexene is limited, aqueous phase refluxed to hydrolysis section have substantial amount of formic acid and is present on the reactive stages at temperature ~60^{0}C. Therefore, rectifying zone in hydrolysis section is necessary to avoid the decomposition of formic acid by enriching formic acid in rectifying section. Fig. 6b shows the effect of stripping stages on conversion and temperature of the bottom reactive stage of the esterification section. Presence of stripping stages in esterification section reduces the temperature in the reactive zone by separating FCE and also increases the conversion of formic acid. Presence of stripping stages in hydrolysis section also shows a similar effect.

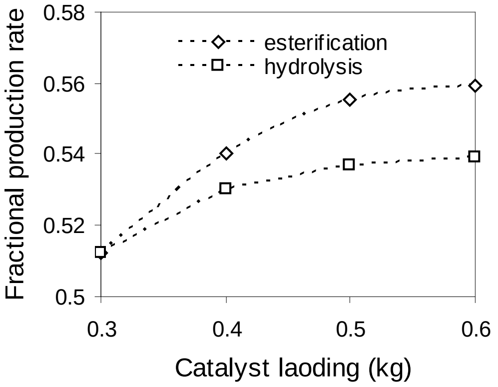


(**a**) (**b**)

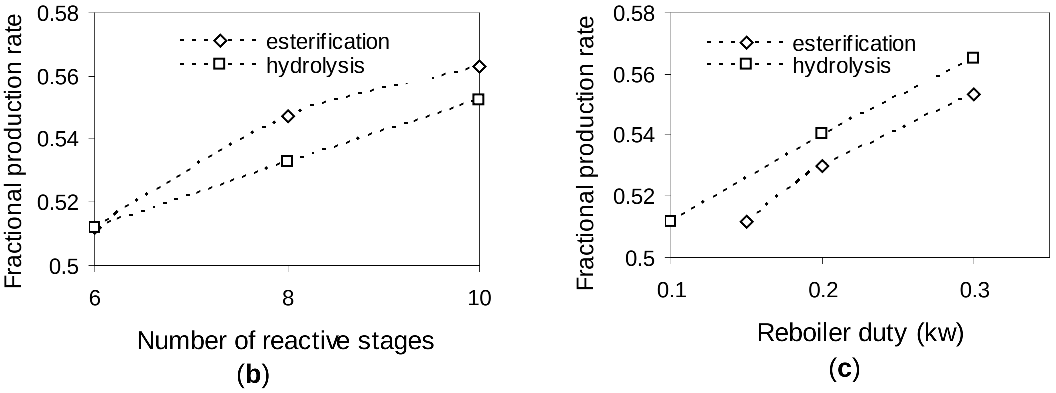
Figure 6. Effect of non reactive section on performance of base case RDWDC (**a**) rectifying zone in hydrolysis section (**b**) stripping zone in esterification section

3.2.3 Effect of Catalyst loading, reactive stages and reboiler duty

Fig. 7a shows the effect of catalyst loading in each sections on the performance of *RDWDC*. As the catalyst loading is increased in esterification and hydrolysis section, the conversion of formic acid and also the production of cyclohexanol increases. After total 0.6 kg of catalyst loading, there is no further increase in the cyclohexanol production for base case *RDWDC*. Fig. 7b shows the effect of reactive stages on base case *RDWDC* performance. Increase in number of reactive stages in both esterification and hydrolysis favours the formation of cyclohexanol. From Fig. 7c, increase in reboiler duty either in esterification or in hydrolysis increases the production rate of cyclohexanol.



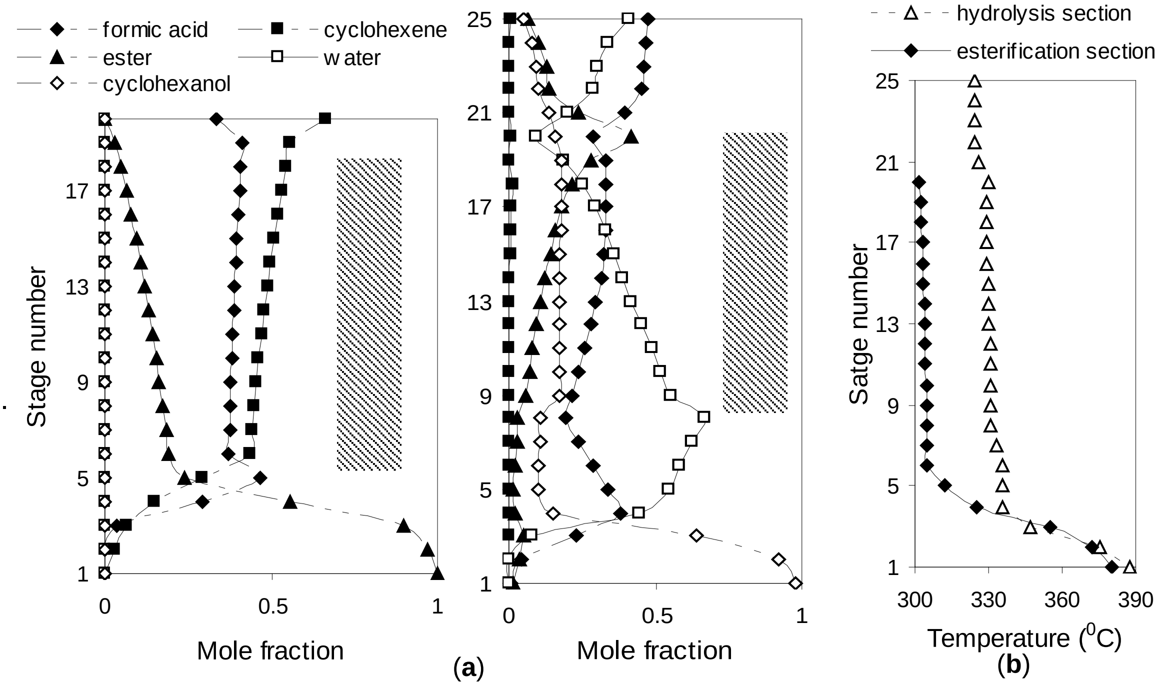
(**a**)



(**b**) (**c**)

Figure 7. Effect of (**a**) catalyst loading (**b**) reactive stages (**c**) reboiler duty on *RDWDC* performance

Hence from parametric study, one can achieve ~100% pure production of cyclohexanol by increasing catalyst loading, reactive stages, reboiler duty and providing non-reactive stages in *RDWDC* base configuration. Fig. 8 shows the composition and temperature profile of conceptually designed *RDWDC* for stiochiometric mole ratio of reactants (shaded region shows reactive zone).



(**a**) (**b**)

Figure 8. RDWDC omposition and temperature profile for Table 2 (except $Q_{hydrolysis}$ = 0.45 kW)

3.3 Feasibility of RDWDC

Feasibility of *RDWC* for cyclohexanol mainly depends on the temperature and pressure profile in the two sections of the column^4. Both the columns are operated at the same pressure i.e. 0.2 bar. From T/T_{max} *vs* number of stages (i.e. from Fig. 9), the temperature profile on either side of divided section is not similar. Hence, one can match the temperature profile of the different section of *RDWDC* by careful manipulation of operating parameters. The parameters which more prone to modify temperature profile of *RDWDC* are the ratio (formic acid/cyclohexene) and the reboiler duty. Fig. 9 shows the effect of mole ratio on temperature profile of *RDWDC*. As mole ratio increases, excess formic acid along with FCE will come from bottom of esterification section, which effect the temperature profile of stripping zone of esterification section. For higher mole ratio of formic acid to cyclohexene as shown in Fig. 9, a similar temperature profile in both section of *RDWDC* is obtained. Hence, production of cyclohexanol by two step process in *RDWDC* from cyclohexene is feasible. The other alternative of operating *RDWDC* is to use excess cyclohexene. From Fig. 3, less pure formic acid is recovered compared to excess formic acid approach due phase split between cyclohexene-water-formic acid. Fig.10 shows the final *RDWDC* composition and temperature profile.

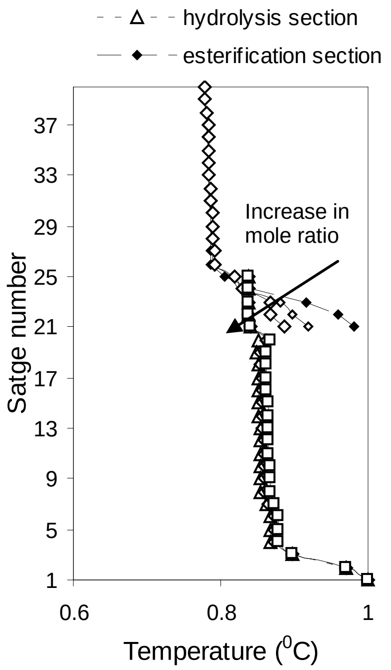
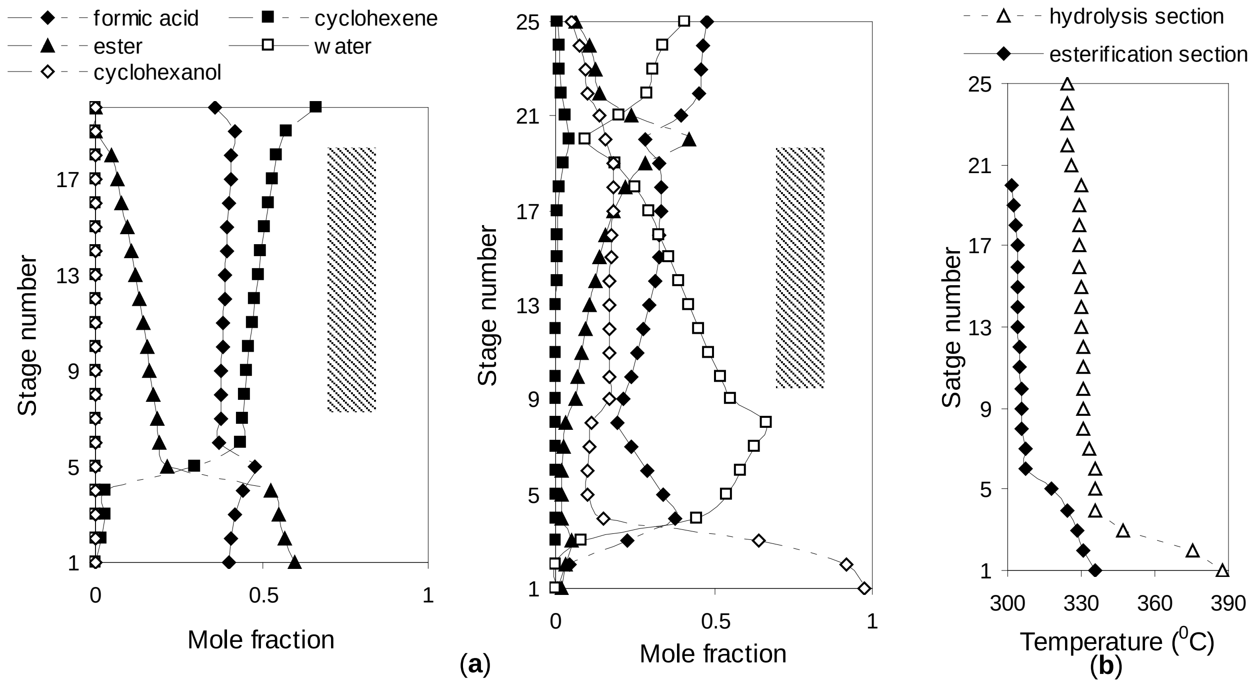


Figure 9. Effect of mole ratio on temperature profile of RDWDC

Table 2. Final *RDWDC* configuration

Basis : 9.8 mol/hr cyclohexanol production

	Esterification section	Hydrolysis section
Formic acid / cyclohexene	1.5	---
water / cyclohexene	-----	1
Rectifying stages	--	5
reactive stages	15	12
Stripping stages	5	5
Catalyst loading (kg)	1.2	1.1
Reboiler duty (kW)	0.2	0.4
Pressure	0.2 bar	0.2 bar



(**a**) (**b**)

Figure 10. RDWDC composition and temperature profile for Table 2

4. Conclusion

Performance of two step cyclohexanol process can be further increased by integrating two distillation columns in single unit i.e. *RDWDC*. Systematic analysis of different process parameters shows that cyclohexanol from cyclohexene in *RDWDC* is feasible and is the potential candidate. Process simulations are performed to obtain the feasible process operating parameters. *RDWDC* is only feasible when *RDWDC* is operated in excess formic acid.

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