

A QUANTITATIVE COMPARISON OF STEADY-STATE DESIGNS FOR REACTIVE DISTILLATION AND CONVENTIONAL REACTOR/COLUMN/RECYCLE SYSTEM

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Abstract

Reactive distillation is an excellent example of recent advances in process intensification. It combines reaction and separation operations in one piece of equipment. This paper studies the steady-state economic optimum design of a chemical process with a generic exothermic reversible reaction $A+B\leftrightarrow C+D$ for two different process flowsheets: a conventional multi-unit reactor/separator/recycle structure and a reactive distillation column. Each system is optimized in terms of total annual cost (energy and capital). The effects of two parameters on the design of each flowsheet are studied: (1) the chemical equilibrium constants and (2) the temperature dependency of relative volatilities. The most fundamental difference between the two flowsheets is the ability in the conventional process to adjust reactor temperature and distillation column temperatures completely independently. This is not possible in the reactive distillation process.

Results show that reactive distillation is significantly less expensive than the conventional process for all values of the chemical equilibrium constant when relative volatilities are constant. However, when relative volatilities are temperature dependent and decrease significantly as temperatures approach those required for reasonable reaction rates, the reactive distillation column becomes more expensive than the conventional flowsheet.

Keywords

Reactive distillation, synthesis, chemical equilibrium constant

Introduction

Economic and environmental considerations have encouraged industry to focus on technologies based on process intensification. Stankiewicz and Moulijn (2000) define it as any chemical engineering development that leads to a substantially smaller and more energy efficient technology. An excellent example of process intensification is reactive distillation, which combines reaction and separation units in a single vessel. Reactive distillation can, in some systems, provide an alternative to

conventional multi-unit flowsheets, which typically include a reactor followed by a separation section with recycles back to the reaction section.

Although reactive distillation may be an attractive alternative to the conventional multi-unit processes, there is a fairly small class of chemical systems in which it can be effective because of some limitations. The relative volatilities of the reactants and the products should be such that the products can be removed from the reaction

zone of the column easily, while the reactants remain in the column. The temperatures of reaction and separation should be similar because both of these operations occur in the same unit simultaneously. Heats of reaction cannot be too large because of their impact on vapor and liquid rates throughout the reactive zone.

One of the most fundamental differences between reactive distillation and a conventional flowsheet is the selection of operation temperatures. In the conventional system, reactor temperature can be set at an optimum value, and distillation temperatures can be independently set at their optimum values (by adjusting column pressures). In reactive distillation, these temperatures are not independent.

As shown in the recent review by Taylor and Krishna (2000), the application of reactive distillation in the chemical and petroleum industries has increased rapidly in the last decade. Following the pioneering paper published by Agreda et al. (1990) discussing the methyl acetate reactive distillation process, many other papers and patents have explored its use for other chemical operations. A number of specific chemical systems have been studied in the literature. But only a few papers (Sirola, 1995, Chiang et al., 2002, Stitt, 2002) have appeared that compare reactive distillation flowsheets with other process flowsheets.

The purpose of this paper is to quantitatively compare the design of two different process flowsheets: (1) a conventional multi-unit reactor/separator/recycle structure, and (2) a reactive distillation column. This paper explores how the chemical equilibrium constant K_{EQ} and temperature dependency of relative volatilities α affect the design of both flowsheets for exothermic reversible reactions. Both of the flowsheets are designed to achieve the steady-state economic objective of minimum total annual cost. Systematic design procedures for both flowsheets are developed with some heuristic rules and engineering assumptions.

Process Studied

The basic process considered consists of a reversible liquid-phase reaction,



The forward and backward specific reaction rates, following the Arrhenius Law, are given by

$$k_F = a_F e^{-E_F/RT} \quad (2)$$

$$k_R = a_R e^{-E_R/RT} \quad (3)$$

respectively. Parameter values are given in Table 1. The forward reaction rate is specified as $0.008 \text{ kmol s}^{-1} \text{ kmol}^{-1}$ at 366 K.

Taking $(K_{EQ})_{366}$ equal to 2 as a base case, the reverse reaction rate at this temperature is varied by selecting a range of $(K_{EQ})_{366}$ values between 0.5 and 50.

$$(k_R)_{366} = \frac{(k_F)_{366}}{(K_{EQ})_{366}} \quad (4)$$

Both reaction rates are temperature dependent, and note that the ratio of k_F to k_R is not equal to $(K_{EQ})_{366}$ at temperatures different than 366 K due to the difference of activation energies.

Table 1. Physical Properties

Property	Value
Activation energy (cal/mol)	
forward	30,000
reverse	40,000
Specific reaction rate at 366 K ($\text{kmol s}^{-1} \text{ kmol}^{-1}$)	
forward	0.008
reverse	$0.008 / (K_{EQ})_{366}$
Heat of reaction (cal/mol)	-10,000
Heat of vaporization (cal/mol)	6,944

Constant and fairly large ($\alpha = 2$) relative volatilities are assumed to study the effects of chemical equilibrium constant. To study the effects of temperature dependency of relative volatilities, the relative volatilities between adjacent products and reactants (α_{CA} and α_{BD}) are kept constant (2) at 320 K and varied by selecting a range of values between 0.95 and 2 at 390 K. The vapor pressure coefficients of component A have been kept constant for all $(\alpha_{ij})_{390}$ cases. Then the coefficients of other components have been calculated to reduce the relative volatilities by taking the coefficients of A as reference for each $(\alpha_{ij})_{390}$ case. Table 2 gives the vapor pressure constants for all components.

Table 2. Vapor Pressure Constants

$(\alpha_{ij})_{390}$		A	B	C	D
0.95	A_{VP}	12.34	15.80	8.89	19.26
	B_{VP}	3862.00	5189.23	2534.77	6516.46
1.10	A_{VP}	12.34	14.99	9.71	17.62
	B_{VP}	3862.00	4927.86	2796.14	5993.72
1.50	A_{VP}	12.34	13.26	11.44	14.17
	B_{VP}	3862.00	4374.90	3349.10	4887.80
2.00	A_{VP}	12.34	11.65	13.04	10.96
	B_{VP}	3862.00	3862.00	3862.00	3862.00

Optimum Steady-State Design

The design objective is to obtain 95% conversion for fixed fresh feed flowrates (F_{0A} and F_{0B}) of 12.6 mol/sec and product purities of both components C and D of 95%.

Figure 1 gives a detailed flowsheet of the conventional multi-unit process. For this process, it is assumed that there is equimolal overflow, theoretical trays, saturated liquid feed and reflux, total condensers and partial reboilers in the columns and the reactor operates isothermally.

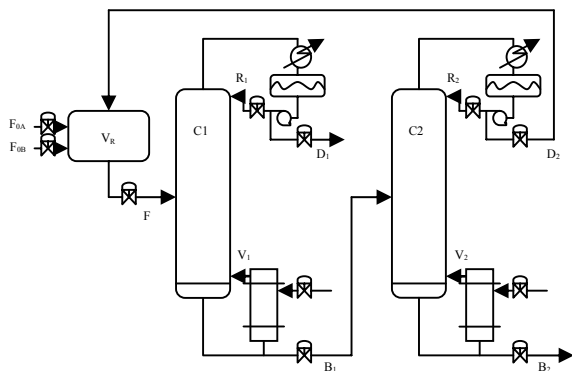


Figure 1. Conventional Process Flowsheet

Based on these specifications and simplifying assumptions, there are three optimization variables for the conventional multi-unit process: (1) molar holdup in the reactor V_R , (2) composition of the reactant B in the reactor z_B , and (3) reactor temperature T_R . A heuristic design procedure is used for the conventional multi-unit process by utilizing the material balances and specifying necessary variables. The column pressures are set using the vapor pressures P^S of pure components and liquid compositions in the reflux drum $x_{D,j}$ at 320 K (so that cooling water can be used in the condenser).

The reactive distillation alternative is shown in Figure 2. The column has a reactive zone between stripping and rectifying sections. The light reactant A is fed to the bottom tray of the reactive zone, while the heavy reactant B is introduced at the top of the reactive section.

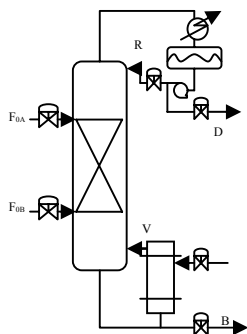


Figure 2. Reactive Distillation Column

The steady-state vapor and liquid rates are constant through the stripping and rectifying sections, since

equimolal overflow is assumed. But these rates change through the reactive zone because of the exothermic reaction. The heat of reaction vaporizes some liquid on each tray in that section; therefore the vapor rate increases up and liquid rate decreases down through the reactive zone. Reactive tray holdup is assumed to be 1000 mol.

For reactive distillation, there are three optimization variables for constant relative volatilities case: (1) the column pressure P , (2) the number of reactive trays N_{RX} , and (3) the number of the separating (equal stripping and rectifying) trays N_S . One more optimization variable (N_R) is needed for temperature dependent relative volatility case because tray numbers in both separation sections can not be assumed equal any more.

The relaxation method is used for solving the very large set of nonlinear and algebraic equations. The process is driven to the desired level of conversion and product purities by changing the vapor boilup and reflux flows. In this strategy, the reflux flowrate is varied by a PI feedback controller to drive the composition of component C in the distillate to its desired value of 95 mol %. This effectively sets the conversion at 95% and the purity of the bottoms product at 95 mol % component D. The vapor boilup V_S is manipulated by a P controller to control the level in the column base.

The design objective function is minimum total annual cost TAC, which includes both annual capital and energy costs assuming a payback period (β_{pay}) of three years. Total annual cost is defined as:

$$TAC = Energy\ Cost + \frac{Capital\ Investment}{\beta_{pay}} \quad (5)$$

Economic parameters and the basis of the equipment sizing calculations are taken from Kaymak and Luyben (in press) as the details of the assumptions, specifications and steady-state design procedures for both flowsheets.

The Effect of Chemical Equilibrium Constant on TAC

The effects of chemical equilibrium constants on the design parameters and total annual costs of both flowsheets are studied for a range of $(K_{EQ})_{366}$ between 0.5 and 50 by using constant relative volatilities $\alpha_{CA} = \alpha_{BD} = 2$. Table 3 gives optimization results of both flowsheets for four different $(K_{EQ})_{366}$ cases.

For the conventional process flowsheet, the optimum temperature of reactor increases as the value of $(K_{EQ})_{366}$ increases. Higher temperatures give smaller reactor holdup V_R and lower equilibrium constant K_{EQ} . However, low temperatures give small specific reaction rates, and therefore more reactant leaves the reactor with decreasing value of $(K_{EQ})_{366}$. Therefore lower values of $(K_{EQ})_{366}$ result in higher amounts of the recycle stream and vapor boilup in the columns to get the product streams with specified purities. Since product purities are specified and relative

volatilities are constant, tray numbers of columns do not alter with the change of $(K_{EQ})_{366}$ value.

Table 3. Optimization Results for Constant α_{ij}

$(K_{EQ})_{366}$	0.5	2.0	10.0	50.0
Conventional Process				
Design Variables				
T_R (K)	356.0	367.0	379.0	395.0
V_R (kmol)	222.5	102.5	60.0	25.0
z_B	0.275	0.225	0.150	0.110
Reactive Distillation				
Design Variables				
N_S & N_R	6	5	6	5
N_{RX}	18	9	4	3
P (bar)	5.5	8.0	11.0	16.0

For the reactive distillation flowsheet, there is an optimum pressure for each kinetic case that minimizes the vapor boilup. The higher K_{EQ} pushes the reaction to the right. The equilibrium constant K_{EQ} decreases with increasing temperature for an exothermic reaction. Therefore, the column can operate at higher pressures when $(K_{EQ})_{366}$ is larger. The higher $(K_{EQ})_{366}$ cases require less vapor boilup. The optimum number of separation stages does not change significantly, while the optimum number of reactive stages increases with decreasing values of $(K_{EQ})_{366}$ because there is a need of extra trays to achieve to the conversion in the reactive zone.

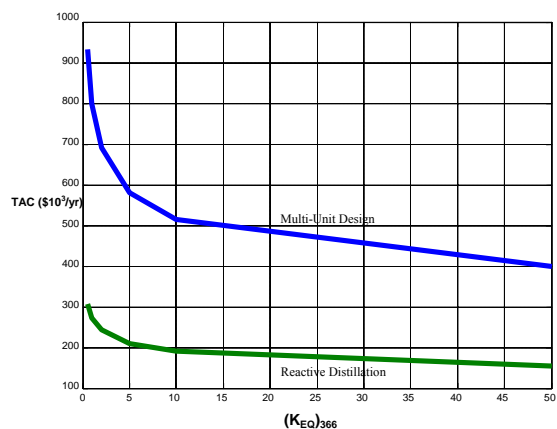


Figure 3. Comparison of TAC for Constant α_{ij}

The increase of vapor boilup with smaller $(K_{EQ})_{366}$ results in an increase of energy cost and capital costs of heat exchangers and columns for both design flowsheets. In addition, as $(K_{EQ})_{366}$ gets smaller, the increase of reactor size for the conventional system and total tray number for reactive distillation increase capital costs for both configurations. Thus, the total annual cost of both flowsheets increase with the decrease of $(K_{EQ})_{366}$ as seen in Figure 3.

The Effect of Relative Volatilities on TAC

The effects of temperature-dependent relative volatilities on the design parameters and total annual costs of both flowsheets are studied for a range of vapor pressure constants A_{VP} and B_{VP} using the base kinetic case $(K_{EQ})_{366} = 2$.

Optimization results of reactive distillation for temperature dependent α_{ij} case are summarized in Table 4. The optimum pressure of the column decreases as the value of α_{390} gets smaller. Operating at lower pressure and temperature has two advantages: (1) it gives higher equilibrium constant K_{EQ} and (2) it increases the relative volatilities.

Table 4. Results for Temperature-Dependent α_{ij}

α_{390}	0.95	1.10	1.50	2.00
Reactive Distillation				
Design Variables				
N_S	14	12	9	5
N_{RX}	68	41	13	7
N_R	3	4	6	5
P (bar)	3.75	4.50	7.00	8.50
V_S (mol/sec)	99.15	83.58	48.82	28.82
T_{RX} (K)	354.4	361.4	380.7	394.2
α at T_{RX}	1.34	1.37	1.56	2.00

The average relative volatilities in the reactive zone get smaller as the value of α_{390} decreases. The separation requires more column trays and energy consumption because the real relative volatilities get smaller with decreasing values of α_{390} . The optimum number of trays in the reactive distillation column increases as α_{390} gets smaller. The optimum number of trays in stripping section increases with the decrease of α_{390} , while there is a decrease in the optimum number of trays of rectifying section. But the impact of α_{390} on these two separation sections is not as significant as on the number of reactive zone trays. There is a big increase in the optimum number of reactive zone trays as the value of α_{390} is reduced. This increase is a result of the lower temperature in the reactive zone of the column, which reduces specific reaction rates and requires larger holdup (or catalyst). The separation is favored by lower temperatures, but the reaction is favored by higher temperatures. So a trade-off occurs. Naturally, reducing the value of α_{390} also increases the vapor boilup.

For the distillation columns in the conventional flowsheet, geometric mean values of the relative volatilities are used based on the temperatures at the top and the bottom of the columns. The operating pressure is fixed by specifying a reflux-drum temperature of 313 K so that cooling water can be used in the condenser. The liquid compositions are known in the column base, so the base temperature can be calculated.

Column base temperatures T_B and relative volatilities decrease as the α_{390} gets smaller for the conventional flowsheet. Thus, the average relative volatilities get

slightly smaller with decreasing the value of α_{390} , which results in a small increase of TAC for the conventional process flowsheet.

Figure 4 gives a direct comparison of the TAC of the two flowsheets. It should be remembered that the relative volatilities at the temperatures in the columns are never less than or equal to zero (the point at which no separation would occur).

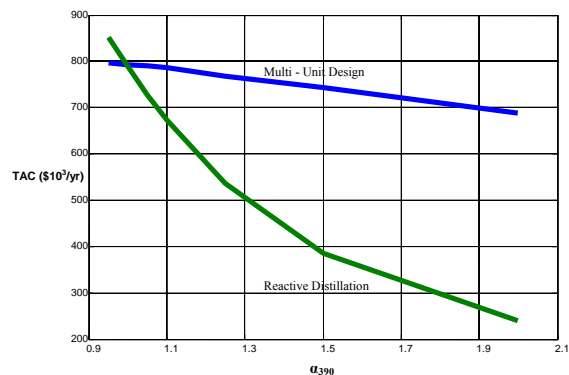


Figure 4. Comparison of TAC for Temperature-Dependent α_{ij}

Reducing the relative volatilities increases both capital and energy costs. The heat exchanger costs and energy costs increase because of the higher vapor boilup. The biggest economical impact occurs in the capital cost of column shell because of the large increase in the number of reactive trays.

Nomenclature

- a_F = preexponential factor for forward reaction, sec^{-1}
- a_R = preexponential factor for backward reaction, sec^{-1}
- E_F = activation energy of forward reaction, cal/mol
- E_R = activation energy of backward reaction, cal/mol
- k_F = specific reaction rate of forward reaction, sec^{-1}
- k_R = specific reaction rate of backward reaction, sec^{-1}
- K_{EQ} = equilibrium constant
- N_R = number of rectifying trays
- N_{RX} = number of reactive trays
- N_S = number of stripping trays
- P = column pressure, bar
- P^S = vapor pressure, bar
- R = perfect gas law constant, $\text{cal}/(\text{mol K})$
- T = temperature, K
- T_R = reactor temperature, K
- V_R = molar holdup of reactor, mol
- $x_{D,i}$ = distillate composition of component j in liquid
- z_B = mole fraction of component B in reactor
- α = relative volatility
- β_{pay} = payback period, year

Conclusions

The economic optimum steady-state designs of a conventional multi-unit reactor/column/recycle process and of a reactive distillation column have been quantitatively compared. First the effects of chemical equilibrium constants (K_{EQ})₃₆₆ over a range between 0.5 and 50 are studied with constant relative volatilities ($\alpha = 2$). As (K_{EQ})₃₆₆ becomes larger, the total annual cost TAC decreases for both configurations. Reactive distillation columns have much lower TAC than those of reactor/column/recycle because of the elimination of a reactor and a column with heat exchangers.

However, when the relative volatilities are made temperature dependent, the conventional process can be less expensive than the reactive distillation column. This occurs because of the inability to independently set temperatures for reaction and separation. Using the base kinetic case (K_{EQ})₃₆₆ = 2, there is a only small increase of TAC for the conventional flowsheet as relative volatilities are reduced at higher temperatures because distillation column temperatures can be independently set at their optimum values by adjusting column pressures. Since this is not true for reactive distillation, the impact of temperature dependent relative volatilities on reactive distillation is more important. As the α_{390} gets smaller, the TAC of reactive column increases significantly, which results in a more expensive steady-state design around $\alpha_{390} = 1$ compared to the TAC of conventional design.

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