Optimal structure of reactive and non-reactive stages in reactive distillation processes

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We present a model for a reactive column, based on models by Almeida-Rivera (2005), shown in detail in Domancich *et al* (2006). It consists of pure separation stages combined with a reactive distillation sector, where both the reaction and the separation processes take place at the same time. A rigorous modeling of the column, with an equilibrium model for the reactive sector were employed. An example that shows the performance of a reactive distillation unit used for the MTBE production is presented. The economic optimization of the reactive distillation process is performed applying a MINLP algorithm and the cost of the resulting scheme is compared to the cost of the conventional process, considering that the reaction and the separation processes take place in different equipment.

1. Introduction

Reactive distillation columns constitute a clear example of process intensification. The significant improvement achieved by a process is what we call "process intensification". For example, the entire plant design is upgraded by reducing the number of units involved in a conventional process to obtain the same products.

However, reactive distillation is not suitable for every process where reaction and separation steps occur. Operating conditions, such as pressure and temperature of the reactive and separation processes and perhaps other requirements, must overlap in order to assure the feasibility of the combined process. This limitation can be overcome by fixing adequate operating conditions in the cases where it is possible to do so.

Reactive distillation has been presented as a multifunctional reactor, where the reactive and separation tasks are combined into a single unit, thus reducing investment costs. The advantages of this configuration have already been reported (Stankiewicz, 2003). Though a thorough review on the design methods for reactive distillation can be found in Almeida-Rivera *et al.* (2004), a systematic analysis of the performance of reactive distillation columns when structural variables are changed has not been presented yet.

2. Case study

The optimization problem consists of the minimization of the cost of a reactive distillation column, where methanol and isobutene are fed to the reactive sector in stoichiometric proportion. The reaction that takes place is the formation of MTBE.
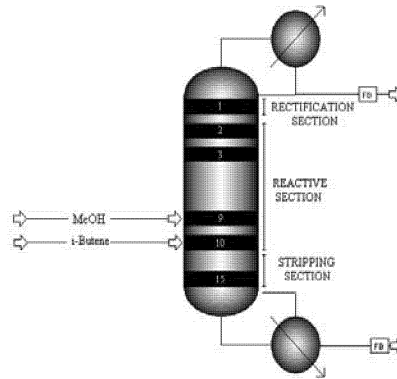
2.1 Column model and cost equations

The basic equations used for the modeling of the reactive column can be found elsewhere (Domancich *et al*, 2006). Some modifications, which are explained below, were made to this model so that it could reflect variations on the number of reactive and non-reactive stages. Other changes in the original model are that the total feed flow rate was increased in 30% and that the binary interaction parameters for Wilson´s equation were taken from Espinosa *et al* (1995) for all the species present.

For optimization purposes, geometry and cost equations were incorporated to the model. The geometry equations allow finding the size of the column (height and diameter, heat exchanger areas). The cost equations include a series of cost correlations (Douglas, 1988) in order to obtain the investment and operating costs. The investment cost was calculated from individual costs of shell, stages, catalyst, condenser and reboiler. The costs were updated to November 2006, by using Marshall & Swift cost indices *M&S* (Chem. Eng. 2006). The investment cost was annualized considering that the interest rate amounted to 10%, that the payout time (POT) was 5 years, and that the equipment operated 8000 hours a year. In this way, the total investment cost of the reactive column was obtained. The utilities for the condenser and reboiler were cooling water and low pressure steam, respectively related to the corresponding heat loads. All the equations used for cost evaluation are shown in Appendix A.

2.2 Formulation of the optimization problem

The following optimization problems are formulated:

$$
\begin{array}{ll}
\min \mathbf{TAC}\ (x,y) & \max \mathbf{PUR}\ (x,y) \\
\text{s.t. } g(x,y) \le 0 & \text{s.t. } g(x,y) \le 0 \\
\quad h(x,y) = 0 \quad \text{(P1)} & \quad h(x,y) = 0 \quad \text{(P2)} \\
\quad b^{L} \le x \le b^{U} & \quad b^{L} \le x \le b^{U} \\
\quad y \in \{0,1\} & \quad y \in \{0,1\}
\end{array}
$$

where

    x (continuous variables): bottom flow rate (F_B), tray catalyst mass (m_{cat}).

    y (discrete variables): associated to reactive or non-reactive tray factor (y_r) and feed locations (y_{MeOH}. for methanol feed and y_{iC4} for isobutene and inert feed)

    g (*x,y*): constraints on the required product composition and recovery

        MTBE conversion ≥ 0.95;   MTBE purity ≥ 88%w (80%)

    h (*x,y*): MESH equations and kinetic model for the reaction (Domancich *et al.* 2006), column geometry correlations

    b^L, b^U: lower and upper bounds on the optimization variable x

        180 mol/s $<F_B<$ 205 mol/s; 0 $< m_{cat,j} <$ 1000 Kg, $_{j}$=1, *Nt*; N_t=*15*

Two problems become necessary because the objective was to achieve the following two different goals: a) Minimizing the cost (Economic optimization). b) Maximizing the MTBE purity at the bottom of the column (Purity optimization).

The binary variables $y_{r,i}$ are assigned to all the stages, where we refer to the stage as reactive ($y_{r,i}$=1) or non-reactive ($y_{r,i}$=0), adding as constraints that all the reactive stages must be consecutive and that at least one non-reactive tray must appear above and below the section of reactive stages ($y_{r,1}$=0, $y_{r,n}$=0). Constraints, which impose that there is only one nonzero $y_{MeOH,j}$ and $y_{iC4,j}$, are set to define feed locations.

To avoid the product of integer-continuous variables, the Big-M formulation was implemented, using the upper bounds as parameters. The total number of trays selected, N_t=15, is considered constant. This value is not arbitrarily chosen, but selected from various optimizations performed using different total numbers of stages. It was seen that adding more trays does not improve the process significantly, and using less than 15 trays the performance of the column is poor. Reflux ratio was not considered as an optimization variable, because it is a key variable for the appearance of steady-state multiplicity. According to Singh *et al* (2005), it was taken as rr=7, a value that assures there is only one possible steady state. Both problems have 1173 continuous variables and 45 discrete variables. They were solved using GAMS.

3. Results and discussion

Results for both objectives are shown in Table 1. As expected, when performing the economic optimization, the composition of MTBE at the bottom reaches its lower limit. When maximizing this purity, the maximum value reached was 0.96, which is the composition of gasoline grade MTBE. In both cases the conversion reaches 0.98, a high value compared to the conversion obtained for the conventional MTBE production scheme of the reactor and separation sector constituted by 2 distillation columns operating at different pressures (Hoch *et al*, 2003), which only reaches 85%.

A comparison of the conventional process for obtaining gasoline grade MTBE vs. the Reactive distillation for the objective of purity maximization was performed. It was found that the investment and operating costs of the conventional process are higher than the same costs for the reactive distillation scheme. Results are shown in table 2. The difference is mainly due to the higher conversion obtained with the reactive distillation scheme (nearly 100%), because in the conventional process it only reaches 85%. Operating costs also decrease because a reactive distillation column has a favourable heat integration scheme, as the temperature of the reactive sector does not

reach 95°C, while refrigeration must be used to keep temperature below 95°C in the reactor of the conventional process in order to avoid catalyst deactivation.

Table 1: Results of the optimization for both alternatives.

rr =7	Purity optimization	Economic optimization
Conversion	0.984	0.985
MTBE purity (mass fraction)	0.96	0.88
Methanol feed tray	9	9
Isobutene and inert feed tray	10	10
F_B [kgmol/s]	180	205
Q_{reb} [kW]	10140	8157
A_{reb} [m^2]	286	230
Q_{cond} [kW]	23800	22022
A_{cond} [m^2]	873	805
Mass of catalyst/tray [kg]		
tray 1	0	0
trays 2 to 8	1000	1000
tray 9	1000	436
tray 10	887	758
trays 11 to 15	0	0
Total catalyst mass [kg]	8887	8194
Column shell cost [$]	1283810	1229238
Trays cost [$]	53350	50085
Catalyst cost [$]	766761	707200
Reboiler cost [$]	312840	271520
Condenser cost [$]	646404	613062
Total installed cost [$]	**3063165**	**2871105**
Water cost [$/year]	640702	590571
Steam cost[$/year]	1477191	1187925
Operating cost [$/year]	**2117893**	**1778496**
TAC	**2730526**	**2352717**

Table 2: Conventional MTBE production process costs

Equipment	Operating costs	Investment cost	
Reactor	$ 370000	**Reactor**	$ 400000
Column 1		**Catalyst**	$766761
Condenser	$500000	**Column 1** Shell	$860000
Reboiler	$2900000	Trays	$35000
Column 2		Condenser	$550000
Condenser	$40000	Reboiler	$500000
Reboiler	$220000	**Column 2** Shell	$450000
		Trays	$35000
		Condenser	$550000
		Reboiler	$500000
Total	**$4030000**	**Total**	**$3765361**

Reductions of 18% in investment costs and 47% in operating costs are achieved when using the reactive distillation scheme, instead of the conventional process. This is an important incentive for the development of reactive distillation systems.

4. Conclusions and future work

As shown in the Results section, reactive distillation is a promising alternative for the replacement of conventional schemes of production, where both the reaction and separation processes take place. Process intensification allows for saving costs, but, in return, control issues are more complex than when conventional schemes are used. The effect should be analyzed from the point of view of control-systems engineers, an issue that is currently under study.

Hoch *et al* (2003) also show the comparison between the cost of the separation sector when using two columns, and when using only one column and a pervaporation membrane. The latter alternative is being currently explored so as to pose a reactive distillation – pervaporation scheme that minimizes the total cost of the process.

Appendix A: Cost expressions used

Geometry Model (Douglas, 1988)

$$Hc = (\frac{2.3 N_t}{0.5}) * 0.348 \tag{A.1}$$

$$Dcol = 5.707 * 10^{-3} * \sqrt{\frac{F_V}{0.126}} (\frac{Mg}{Rho_V} * 16000)^{1/4} \tag{A.2}$$

$$Acond = \frac{Q_{cond}}{U_{cond} \Delta Tm_{\log cond}} \tag{A.3}$$

$$Acond = \frac{Q_{reb}}{U_{reb} \Delta Tm_{\log reb}} \tag{A.4}$$

Investment Cost (Douglas, 1988)

$$Ccol = (\frac{M \& S}{280}) * 101.9 * (D_{col} * f_{m-ft})^{1.066} * (H_c * f_{m-ft})^{0.802} * (2.18 + F_C) \tag{A.5}$$

$$Ctrays = (\frac{M \& S}{280}) * 4.7 * (D_{col} * f_{m-ft})^{1.55} * (H_t * f_{m-ft}) * (F_C) * N_t \tag{A.6}$$

$$Ccat = mt_{cat} * P_{cat} \tag{A.7}$$

$$Ccond = (\frac{M \& S}{280}) * 101.3 * (A_{cond} * f_{m2-ft2})^{0.65} * (2.29 + F_C) \tag{A.8}$$

$$Creb = (\frac{M \& S}{280}) * 101.3 * (A_{reb} * f_{m2-ft2})^{0.65} * (2.29 + F_C) \tag{A.9}$$

$$Cw = FV_w * P_w * 2.88e7 \tag{A.10}$$

$$Cs = FM_s * P_s * 2.88e7 \tag{A.11}$$

$$Cinst = C_{col} + C_{trays} + C_{cat} + C_{cond} + C_{reb} \tag{A.12}$$

$$Cop = C_w + C_s \tag{A.13}$$

$$TAC = \frac{C_{inst}}{POT} + C_{op} \tag{A.14}$$

Nomenclature

A: Area [m^2]

C$_{cat}$: Total catalyst cost [$]

C$_{col}$: Column shell cost [$]

C$_{cond}$: Condenser cost [$]

C$_{inst}$: Total installed cost [$]

C$_{op}$: Operating cost [$/year]

C$_{reb}$: Reboiler cost [$]

C$_s$: Steam cost [$/year]

C$_{trays}$: Total trays cost [$]

C$_w$: Water cost [$/year]

D$_{col}$: Column diameter [m]

F$_B$ bottom flow rate [kgmol/s]

Fc: Pressure and material correction factor

F$_V$: Vapor flowrate [m^3/s]

f$_{m-ft}$: Conversion factor

Hc: Column height [m]

Ht: Tray spacing [m]

Mg: Vapor molecular weight

M&S: Marshall and Swift cost index

mt$_{cat}$: Catalyst mass [Kg]

N$_t$: Number of trays

P$_{cat}$: Catalyst price [$/Kg]

P$_s$: Steam price [$/Kg]

P$_w$: Steam unit price or [$/m^3]

POT: Payout time [year]

PUR: MTBE purity (mass fraction)

Q$_{cond}$: Condenser heat duty [W]

Q$_{reb}$: Reboiler heat duty [W]

Rho : Molar density [mol/m^3]

rr: Reflux ratio

U: Global heat transfer coefficient [W/m^{2}K]

TAC: Total annual cost

X$_{ib}$: Isobutene conversion

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