



Optimization of ethylene oxychlorination fluidized-bed reactor using Differential Evolution (DE) method

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KEYWORDS

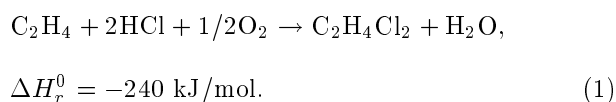
Ethylene dichloride;
 Ethylene
 oxychlorination;
 Fluidized-bed reactor;
 Optimization;
 Differential evolution.

Abstract. The present work aims to employ Differential Evolution (DE) algorithm to optimize ethylene oxychlorination process to produce 1,2-dichloroethane in a fluidized bed reactor as a feedstock of PVC production. A steady-state reactor model, based on two-phase theory of fluidization, was developed to investigate the effects of various parameters on C_2H_4 and HCl conversions. The model's results were compared favorably with the industrial data obtained from a pilot plant working in Italy. The feed temperature, pressure, HCl and O_2 molar flow rates, and cooling medium temperature were selected as decision variables to minimize the objective function subject to the environmental constraints. The highest performance was found at HCl/C_2H_4 and O_2/C_2H_4 molar ratios of 2 and 0.55, respectively; feed and cooling medium temperatures of 440 and 360 K, respectively; pressure of 367.6 kPa. The results show a decrease of 20°C in the feed temperature, which leads to saving energy and reducing the size of the pre-heater.

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1. Introduction

Oxychlorination of ethylene is a chemical reaction in which oxygen and hydrogen chloride react with ethylene in vapor phase over a supported copper chloride catalyst to produce ethylene dichloride (EDC or 1,2-dichloroethane) and water:



This reaction occurs at a temperature range of 473–573 K and a pressure of 0.4–0.6 MPa [1,2]. Since this reaction is highly exothermic, heat is removed by internal cooling coils submerged in the fluidized-bed.

EDC is a major chemical intermediate which belongs to a group of chemicals with the highest annual production rate. EDC is the precursor of Vinyl Chloride Monomer (VCM), which is polymerized to polyvinyl chloride (PVC). PVC polymer is utilized commercially in a wide variety of useful vinyl plastic products and appears in both rigid and flexible (plasticized) forms. These products include plastic pipe, vinyl house siding, flooring and wall covering, window frames, wire insulation, vinyl seat covers, recording discs, and many others.

Only a few papers in the literature are concerned with mathematical modeling of ethylene oxychlorination fluidized-bed reactor. Al-Zahrani et al. [3] investigated the effects of different parameters on the behavior of ethylene oxychlorination for EDC production in a fluidized-bed reactor. Prasad et al. [4] estimated the rate parameters of ethylene oxychlorination reaction by developing an unsteady-state model in a fixed-bed

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reactor while taking into account the change in catalyst composition, variation of temperature profiles, and exit gas-phase conversions with time. A two-step ethylene oxychlorination process of oxidation and reduction reactions was carried out in the fluidized-bed reactor by Go et al. [5]. They studied the effects of superficial gas velocity and gas composition on the reactivity and fluidization stability using an experimental set-up. Keshavarz Moraveji et al. [6] modeled a fluidized bed reactor for 1,2-dichloroethane production from ethylene oxychlorination by computational fluid dynamics. The effect of catalyst amount was considered carefully. They showed that the enhancement of catalyst up to 6 m (height of the bed) increases the products efficiency, especially 1,2-dichloroethane. Recently, Montebelli et al. [7] have presented a development and validation of a new kinetic model for the ethylene oxychlorination reaction, relying on 9 chemical reactions to describe the evolution of 12 species (including 6 major byproducts). They also reported two mathematical models of oxychlorination fluidized-bed reactors, namely the simple two-phase and the axially dispersed plug-flow models, as well as their comparative validation against industrial data.

To the best of our knowledge, the mathematical modeling of ethylene oxychlorination reactor has been carried out by a few researchers in order to achieve two goals: investigating the effects of operational parameters on the reactor performance and estimating the reaction kinetic parameters. Furthermore, no study has been found about the optimization of the ethylene oxychlorination reactor. To improve the reactor performance, economic feasibility, and safety, it is required to operate the reactor under optimal conditions.

In this work, a steady-state distributed mathematical model is developed for ethylene oxychlorination to produce EDC in a fluidized-bed reactor. A sensitivity analysis is carried out to indicate numerically the effects of various key operating variables on the performance of the reactor. Finally, the purpose of this study is to optimize the ethylene oxychlorination fluidized-bed reactor using a Differential Evolution (DE) algorithm as an exceptionally simple evolution strategy. The feed temperature, pressure, HCl and O₂ molar flow rates, and cooling medium temperature are considered as decision variables to minimize the defined objective function.

2. Mathematical modeling

The two-phase model, *bubbling bed model* proposed by Kunii and Levenspiel [8], which considers a fluidized bed as consisting of a bubble phase and a dense (or emulsion) phase, has been proven to be the most suitable model for incorporating recent findings in the hydrodynamics of fluidization. This model proposes a

separate governing equation for each phase and mass interchange between them.

2.1. Assumptions

The following assumptions are incorporated in the development of the mathematical model:

- i The bubble gas is devoid of solids and is in plug flow;
- ii The extent of reaction in the bubble-cloud phase is negligible. This assumption is justified by the experimental evidence reported by Toor and Calderbank [9] for small-sized particles and high flow rates;
- iii The dense phase is assumed to be perfectly mixed and uniform in temperature;
- iv An average value of the bubble size, and hence, an average value of the inter-phase exchange parameter are used for the whole bed. The effective bubble size is taken as that which exists at 40% of the expanded bed height [10];
- v The mass and heat transfer resistances between the particles and the dense-phase gas are negligible;
- vi The ideal gas law applies to the gas phase in both phases;
- vii The volumetric flow rate through the bubble phase is constant.

2.2. Mass and energy balances

The material balance of the i th component and the energy balance equations are developed for the bubble and dense phases at steady state, allowing for a change in volumetric flow rate in the dense phase gas. These equations followed by boundary conditions and ideal gas law equations are summarized in Table 1. Rearranging Eqs. (2) and (3), integrating them by using boundary conditions, and then substituting them into Eqs. (4) and (5), respectively, as well as ideal gas law equations result in the following equations:

$$N_{id} = x_{if} N_f \frac{Q_{df}}{Q_f} + \frac{P A_b u_b}{R} \left(\frac{x_{if}}{T_f} - \frac{x_{id}}{T_d} \right) (1 - e^{-\alpha_i H}) + V(1 - \delta)(1 - \varepsilon) \gamma_i r, \quad (9)$$

$$\begin{aligned} & \rho_g C_{pg} Q_{df} (T_f - 298) - \rho_g C_{pg} Q_d (T_d - 298) \\ & + u_b \rho_g C_{pg} A_b (T_f - T_d) (1 - e^{-\beta H}) \\ & + h_w A_w (T_w - T_d) + V(1 - \delta)(1 - \varepsilon) \\ & (-\Delta H_r) r = 0, \end{aligned} \quad (10)$$

where $\alpha_i = \frac{(K_{bd})_{ib}}{u_b}$ and $\beta = \frac{H_{bd}}{u_b \rho_g C_{pg}}$.

Table 1. Mass and energy balance equations and boundary conditions for the bubble and dense phases as well as ideal gas law equations [11].

Equation type	Equation	Equation no.
Mass and energy balances in bubble phase	$\frac{dN_{ib}}{dz} = A_b(K_{bd})_{ib} \left(\frac{N_{id}}{Q_d} - \frac{N_{ib}}{Q_b} \right)$	(2)
	$u_b \rho_g C_{pg} \frac{dT_b}{dz} = (H_{bd})_b (T_d - T_b)$	(3)
Mass and energy balances in dense phase	$N_{id} = N_{idf} + \int_0^H (K_{bd})_{ib} A_b \left(\frac{N_{ib}}{Q_b} - \frac{N_{id}}{Q_d} \right) dz + V(1 - \delta)(1 - \varepsilon)\gamma_i r$	(4)
	$\rho_g C_{pg} Q_{df} (T_f - 298) - \rho_g C_{pg} Q_d (T_d - 298) + \int_0^H (H_{bd})_b A_b (T_b - T_d) dz + h_w A_w (T_w - T_d) + V(1 - \delta)(1 - \varepsilon)(-\Delta H_r) r = 0$	(5)
Ideal gas law	$x_{id} P Q_d = N_{id} R T_d$	(6)
	$x_{if} P Q_f = N_{if} R T_f$	(7)
	$N_{idf} = x_{if} N_f \frac{Q_{df}}{Q_f},$	(8)
Boundary conditions at $z = 0, N_{ib} = N_{ibf} \quad T_b = T_f$		

2.3. Hydrodynamic and transport property correlations

Table 2 shows the hydrodynamic and transport property correlations used in this study.

2.4. Reaction kinetics

Several mechanism and kinetic studies have been reported in the literature for ethylene oxychlorination [18–20]. In this paper, a rate equation of the Hougen-Watson type, reported by Carrubba and Spencer [18], is used. This reaction rate model was based on the surface reaction of ethylene and oxygen, on the $\text{CuCl}_2\text{-Al}_2\text{O}_3$ based catalyst, to form an ethylene oxide intermediate as the rate-determining step. The reaction rate increases with increasing partial pressures of ethylene and oxygen, but it is independent of hydrogen chloride partial pressure. The reaction rate of EDC production has the following form:

$$r = \frac{k_r P_{\text{C}_2\text{H}_4} P_{\text{O}_2}^{1/2}}{\left[1 + 0.0017 P_{\text{C}_2\text{H}_4} + 0.0355 P_{\text{O}_2}^{1/2} + 0.0165 P_{\text{H}_2\text{O}} \right]^2}$$

$$k_r = 6.83 \times 10^{-7} \exp(-E/RT), \quad (11)$$

where k_r is the reaction rate constant; $P_{\text{C}_2\text{H}_4}$, P_{O_2} , and $P_{\text{H}_2\text{O}}$ are partial pressures of ethylene, oxygen, and water in millimeters of Hg, respectively; E is activation energy, 24.5 kcal/mol; the rate is expressed as moles of EDC per liter-second.

2.5. Numerical solution

The solution of the mass balance equations is followed by the calculation of the heat balance equation.

Eq. (9) consists of five simultaneous nonlinear algebraic equations involving five unknowns (the number of moles of the five components), and is thus amenable to numerical solution techniques. The equations are solved by a combination of the Newton-Raphson and the bisection methods, as described by Wgialla et al. [11].

In the calculation, it is supposed that the heat of reaction and heat capacity are dependent on temperature. The thermal conductivity, heat capacity, and density of gas mixture are predicted through linear combination of properties of the individual component gases.

3. Optimization

3.1. Differential Evolution (DE)

Over the last few years, Differential Evolution (DE) algorithm has been proposed for dealing with optimization problems. DE algorithm is a stochastic optimization method minimizing an objective function that can model the problem's objectives while incorporating constraints. This algorithm mainly has three advantages: finding the true global minimum regardless of the initial parameter values, fast convergence, and using a few control parameters. Other important features of DE algorithm include: (a) being simple, fast and easy to use; (b) very easily adaptable to integrand discrete optimization; (c) being quite effective in non-linear constraint optimization including penalty functions; and (d) being useful for optimizing multi-modal search spaces.

Different strategies can be adopted in DE algorithm depending upon the type of problem to which DE

Table 2. Hydrodynamic and transport property correlations.

Parameter	Theoretical or empirical expressions	Ref.
Bed voidage at minimum fluidization	$\varepsilon_{mf} = 0.586\varphi_s^{-0.72}Ar^{-0.029}\left(\frac{\rho_g}{\rho_p}\right)^{0.021}$ $Ar = \rho_g(\rho_p - \rho_g)g\frac{d_p^3}{\mu^2}$	Broadhurst and Becker [12]
Superficial velocity at minimum fluidization	$u_{mf} = \frac{(\varphi_s d_p)^2 g(\rho_p - \rho_g)}{150\mu} \frac{\varepsilon_{mf}^3}{1 - \varepsilon_{mf}}$	Kunii and Levenspiel [8]
Bubble diameter	$d_B = d_{BM} - (d_{BM} - d_{Bo})e^{-0.3z/D}$ $d_{BM} = 0.652[A(u_f - u_{mf})]^{0.4}$ $d_{Bo} = 0.00376(u_f - u_{mf})^2$	Mori and Wen [13]
Bubble rising velocity	$u_b = u_f - u_{mf} + 0.711(gd_B)^{0.5}$	Davidson and Harrison [14]
Fraction of bubble phase	$\delta = \frac{u_f - u_{mf}}{u_b}$	Kunii and Levenspiel [8]
Total feed volumetric flow rate	$Q_f = u_f A$	Kunii and Levenspiel [8]
Bubble-phase volumetric flow rate	$Q_b = (u_f - u_m)A$	Kunii and Levenspiel [8]
Dense-phase feed volumetric flow rate	$Q_{df} = Q_f - Q_b$	Kunii and Levenspiel [8]
Expanded bed height	$H = \frac{H_{mf}}{1 - \delta}$	Kunii and Levenspiel [8]
Overall mass transfer coefficient (bubble phase/dense phase) based on bubble volume	$\frac{1}{(K_{bd})_{ib}} = \frac{1}{(K_{bc})_{ib}} + \frac{1}{(K_{cd})_{ib}}$ $(K_{bc})_{ib} = 4.5\left(\frac{u_{mf}}{d_B}\right) + 5.85\left(\frac{D_{im}g^{0.25}}{d_B^{1.25}}\right)$ $(K_{cd})_{ib} = 6.78\left(\frac{\varepsilon_{mf}D_{im}u_b}{d_B^3}\right)^{0.5}$	Kunii and Levenspiel [8]
Overall heat transfer coefficient (bubble phase/dense phase) based on bubble volume	$\frac{1}{(H_{bd})_b} = \frac{1}{(H_{bc})_b} + \frac{1}{(H_{cd})_b}$ $(H_{bc})_b = 4.5\left(\frac{u_{mf}\rho_g C_{pg}}{d_B}\right) + 5.85\frac{(k_g \rho_g C_{pg})^{0.5} g^{0.25}}{d_B^{1.25}}$ $(H_{cd})_b = 6.78(k_g \rho_g C_{pg})^{0.5}\left(\frac{\varepsilon_{mf}u_b}{d_B^3}\right)^{0.5}$	Kunii and Levenspiel [8]
Heat transfer coefficient (bed-vertical tubes)	$h_w = 0.88\frac{k_g}{d_p}Ar^{0.213}$	Renz et al. [15]
Binary diffusivity	$D_{ij} = \frac{10^{-3}T^{1.75}(1/M_i + 1/M_j)^{0.5}}{P(V_i^{0.33} + V_j^{0.33})^2}$	Fuller et al. [16]
Diffusivity of component i in gas mixture	$D_{im} = \frac{1 - x_i}{\sum_{j=1}^n \frac{x_j}{D_{ij}}}$	Reid et al. [17]

is applied. The strategies can vary based on the vector to be perturbed, number of difference vectors considered for perturbation, and finally the type of crossover used. Ten different working strategies, proposed by Price and Storn [21], are as follows:

1. DE/best/1/exp;
2. DE/rand/1/exp;
3. DE/rand-to-best/1/exp;
4. DE/best/2/exp;
5. DE/rand/2/exp;
6. DE/best/1/bin;
7. DE/rand/1/bin;
8. DE/rand-to-best/1/bin;
9. DE/best/2/bin;

10. DE/rand/2/bin.

The general convention used above is DE/ $x/y/z$, in which DE stands for differential evolution, x represents a string denoting the vector to be perturbed, y is the number of difference vectors considered for perturbation of x , and z stands for the type of crossover being used (exp: exponential; bin: binomial).

Choosing population size (NP), scaling factor (F), and crossover constant (CR) depends on the specific problem applied, which is often difficult. But, some general guidelines are available. Normally, NP should be about 5-10 times the number of parameters in a vector. As for F , it lies in the range 0.4-1.0. Initially, $F = 0.5$ can be tried, then F and/or NP are increased if the population converges prematurely. A good first choice for CR is 0.1, but in general, CR should be as

Table 3. Strategy and parameters used for DE.

Strategy	DE/1/best/bin
Population size (NP)	100
Scaling factor (F)	0.8
Crossover constant (CR)	1.0

large as possible [22]. More details of basic version of DE (pseudo code), its strategies, and choosing of operating parameters were reported by Babu and Angira [23,24] and Babu and Munawar [22]. In this optimization, the strategies and parameters used for DE are presented in Table 3.

3.2. Optimization problem formulation

In this work, the goal of optimization is to find out the operating conditions, containing feed temperature, pressure, $\text{HCl}/\text{C}_2\text{H}_4$ and $\text{O}_2/\text{C}_2\text{H}_4$ molar ratios, and cooling medium temperature, that lead to the best performance of the reactor, i.e. objective function. For the best performance, four sub-functions are defined as follows:

- The first term: Maximize the ethylene conversion;
- The second term: Maximize the HCl conversion;
- The third term: Minimize the feed temperature. The main reason to develop this term is energy saving, reducing the size of the pre-heater, and also obtaining the highest conversion at the lowest possible temperature;
- The fourth term: Build up a logical relation between input flow rate and bed height; the residence time must be nearly 25 seconds.

Therefore, a suitable objective function is:

$$J = |X_{\text{C}_2\text{H}_4} - 1| + |X_{\text{HCl}} - 1| - \left(\frac{1}{T_f}\right) + |\tau - 25|. \quad (12)$$

In the commercial ethylene oxychlorination reactors, the reaction occurs at a temperature range of 473–573 K [1,2]. Therefore, the reactor temperature must not exceed 573 K. However, local hot spots may still remain, creating some problems. For example, copper chloride (CuCl_2) as a catalyst can be evaporated above 673 K, and it has been reported that the product distribution can change from high yields of 1,2-dichloroethane to a mixture of more highly chlorinated hydrocarbons such as 1,1,2-trichloroethane, trichloroethylene, vinyl chloride, and 1,2-dichloroethylene with increasing temperature [1,20]. Therefore, one constraint is considered as follows:

$$473 < T < 573 \text{ K}. \quad (13)$$

The optimization problem considered above is then reformulated so as to include the constraints.

Penalty function method is employed for handling constraints. Inequality constraint, Eq. (13), is incorporated into Eq. (12) using penalty function. This method involves penalizing the objective function in proportion to the extent of constraint violation (i.e., the penalty function takes a finite value when a constraint is violated and a value of zero when constraint is satisfied). In the present case, we used 10^7 as our penalty parameter, but this value depends on the order of magnitude of the variables in the problem; it may change from problem to problem.

Thus, the objective function considered for minimization, finally, is:

Minimize

$$\text{OF} = J + 10^7 \sum_{i=1}^2 G_i^2, \quad (14)$$

where:

$$G_1 = \max\{0, (473 - T)\}, \quad (15)$$

$$G_2 = \max\{0, (T - 573)\}. \quad (16)$$

The postulated optimization problem is solved with DE.

4. Results and discussion

4.1. Base case

In order to establish a reference point, simulation is carried out for a “base case”. The reactor design data as well as operating conditions for the base case are given in Table 4. The parametric sensitivity analysis is carried out to assess the impact of the variation of the following parameters on C_2H_4 and HCl conversions: height at minimum fluidization; feed temperature; pressure; cooling medium temperature; residence time; $\text{HCl}/\text{C}_2\text{H}_4$ and HCl/O_2 molar ratios.

4.2. Model validation

The fluidized-bed model of ethylene oxychlorination is validated against the pilot plant data, reported by Cavaterra [25], for pilot plant working in Italy under the design specifications and input data listed in Table 4. It is observed in Table 5 that the model performed satisfactorily well under special case of industrial conditions, and simulation data are in good agreement with the observed plant data.

4.3. Effect of residence time and bed height at minimum fluidization

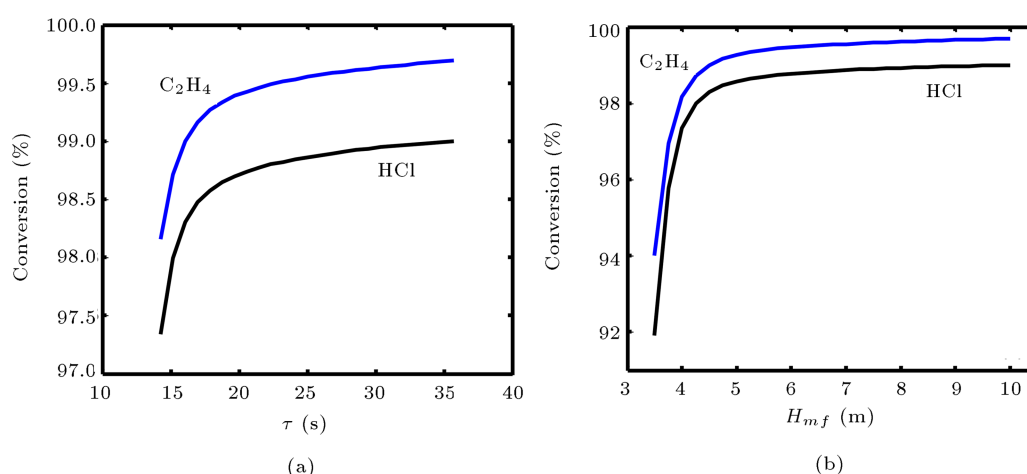
Figure 1(a) and (b) show the effect of residence time and bed height at minimum fluidization on C_2H_4 and HCl conversions, respectively. As the residence time increases, the superficial velocity and the bubble size decrease. When the bubble diameter decreases, the overall mass transfer area per unit bubble volume

Table 4. Design and operating conditions of pilot plant.

Parameter	Value
Bed height at minimum fluidization	7.0 m
Bed diameter	3.4 m
Density of solid particles	3075 kg/m ³
Catalyst particle diameter	80 μ m
Bed pressure	400 kPa
Feed temperature	460 K
Cooling medium temperature	360 K
Molar flow rate of HCl/C ₂ H ₄ /O ₂	64/31.85/21.5 mol/s
Residence time	25 s

Table 5. Comparison between model predictions and pilot plant data at the base case.

	Plant	Model	RE (%)
Outlet temperature (K)	498	497.79	0.04
C ₂ H ₄ conversion (%)	99.3	99.55	0.25
HCl conversion (%)	98.3	98.80	0.50

**Figure 1.** Effect of (a) residence time and (b) bed height at minimum fluidization on C₂H₄ and HCl conversions.

between bubble and dense phase increases; consequently, C₂H₄ and HCl conversions increase. It is very important to take care of the bubble diameter by selecting an appropriate reactant distributor in order to generate small bubbles. Furthermore, the reactor must be operated at sufficiently low superficial gas velocity. It is clear from Figure 1(a) that C₂H₄ and HCl conversions increase asymptotically until they reach a residence time of 20 s with C₂H₄ and HCl conversions of 99.4% and 98.6%, respectively; subsequently, the conversions increase slowly till the residence time of 35 s. At residence times in excess of 35 s, the conversions approach an equilibrium conversion. Therefore, $|\tau - 25|$ is considered as a sub-function in the objective function.

In Figure 1(b), increasing the bed height at minimum fluidization increases C₂H₄ and HCl conversions, because an increase in bed height at a constant

superficial velocity leads to an increase in residence time. This figure shows that small change of height at minimum fluidization, less than 5 m, has significant effect on C₂H₄ and HCl conversions, but increasing the bed height at minimum fluidization means increasing the amount of catalyst.

4.4. Effect of reactor pressure

The effects of total pressure on C₂H₄ and HCl conversions are illustrated in Figure 2. Increasing the reactor pressure from 250 to 500 kPa leads to an increase of C₂H₄ and HCl conversions from 96.9% to 99.8% and from 96.2% to 99.2%, respectively. As shown in this figure, increase of pressure above 400 kPa has slight effect on C₂H₄ and HCl conversions. Increasing the reactor pressure results in increasing the rate of reaction, and consequently, increasing C₂H₄ and HCl conversions.

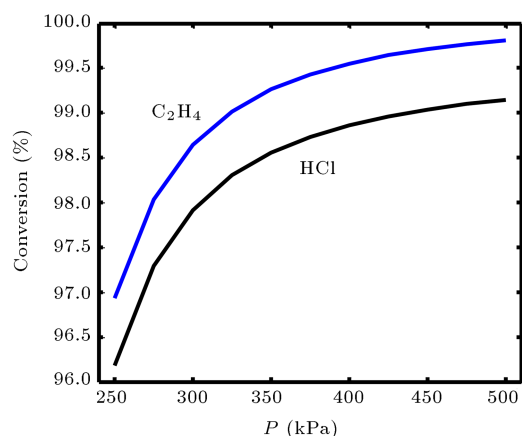


Figure 2. Effect of total pressure on C_2H_4 and HCl conversions.

4.5. Effect of feed temperature

Figure 3(a) and (b), respectively, show the influence of variation of feed temperature on C_2H_4 conversion and bed temperature. It is clear from this figure that

when the feed temperature increases from 360 to 440 K, the bed temperature increases from 377 to 498 K while C_2H_4 conversion increases from 0.09 to 0.99 as the rate of reaction increases. Also, the diffusivity of each component in the gas mixture increases as the feed temperature increases. Furthermore, the diffusivity of gas component affects the mass transfer coefficient. The variation of feed temperature above 440 K has very little effect on bed temperature and conversion. The feed temperature is selected as a decision variable for optimization, because the feed temperature has large effect on conversions.

4.6. Effect of cooling medium temperature

The effect of cooling medium temperature on C_2H_4 and HCl conversions and bed temperature is shown in Figure 4(a) and (b), respectively. When the cooling medium temperature increases from 360 to 440 K, C_2H_4 and HCl conversions and bed temperature increase 0.47%, 0.55%, and 14.5%, respectively. Therefore, the variation of cooling medium temperature

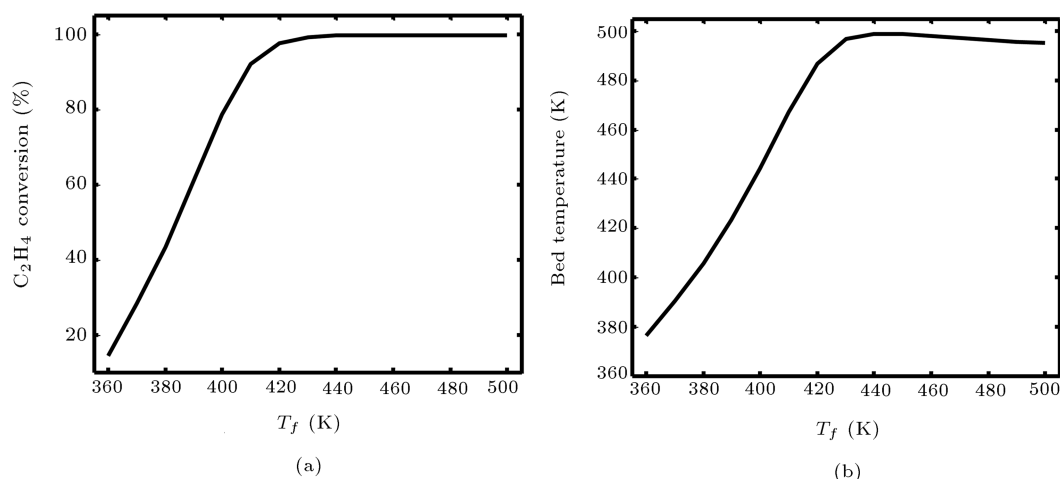


Figure 3. Effect of feed temperature on (a) ethylene conversion and (b) bed temperature.

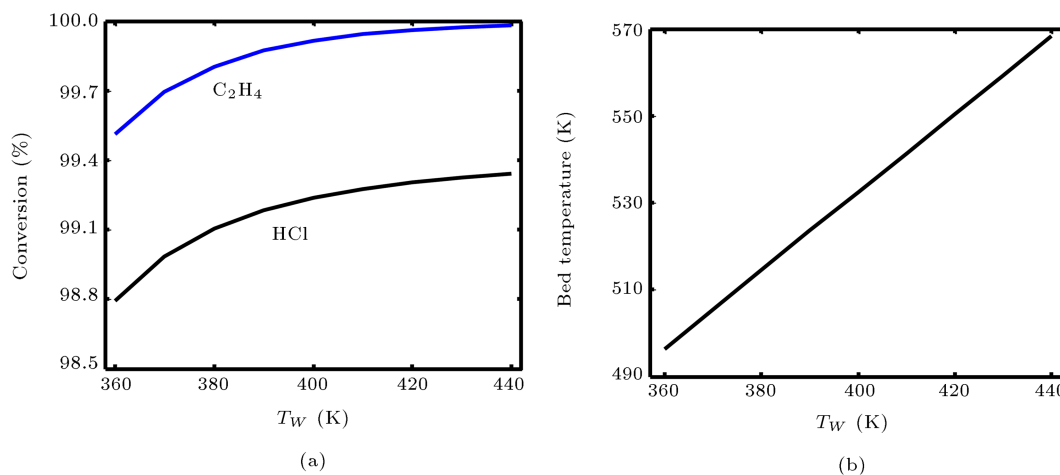


Figure 4. Effect of cooling medium temperature on (a) C_2H_4 and HCl conversions and (b) bed temperature.

Table 6. Minimal and maximal values as well as optimal values of decision variables.

Optimization variables	Minimal values	Maximal values	$\pm\alpha\%$	Optimal values
T_f (K)	400	510	$\pm 12\%$	440
T_w (K)	300	360	—	360
P (kPa)	200	600	$\pm 50\%$	367.6
HCl molar flow rate (mol/s)	40	80	$\pm 30\%$	63.57
O ₂ molar flow rate (mol/s)	5	35	$\pm 75\%$	17.42

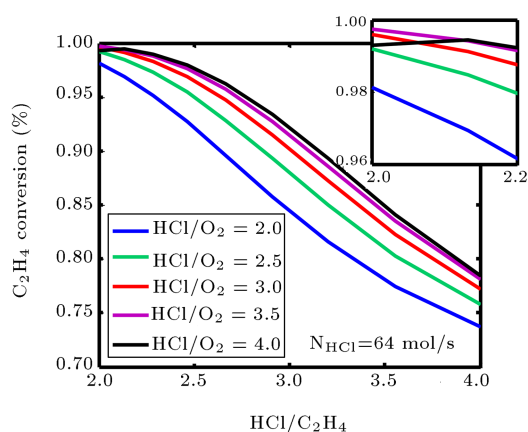
has little effect on the conversions, but large effect on the bed temperature. An increase in cooling medium temperature will decrease the heat transfer rate and increase the bed temperature. The cooling medium temperature must be maintained below 440 K in order for the temperature of fluidized-bed ethylene oxychlorination reactor not to exceed 573 K. This, in turn, prevents catalyst deactivation. Therefore, the cooling medium temperature plays an important role in this fluidized-bed reactor.

4.7. Effect of feed molar ratio

Figure 5 illustrates the variation of ethylene conversion versus HCl/C₂H₄ and HCl/O₂ molar ratios at constant HCl molar flow rate, 64 mol/s. Decreasing HCl/C₂H₄ molar ratio from 4 to 2 at constant HCl/O₂ molar ratio and increasing HCl/O₂ molar ratio from 2 to 4 at constant HCl/C₂H₄ molar ratio result in increasing C₂H₄ conversion. Totally, when the feed molar ratio shifts to the stoichiometry coefficient of ethylene oxychlorination reaction, the ethylene conversion will increase. It is clear from Figure 5 that at HCl/C₂H₄ = 2, C₂H₄ conversion at HCl/O₂ = 3.5 is higher than that at HCl/O₂ = 4. This is due to ethylene as the limiting reactant and the excess availability of oxygen.

4.8. Results of the optimization with DE

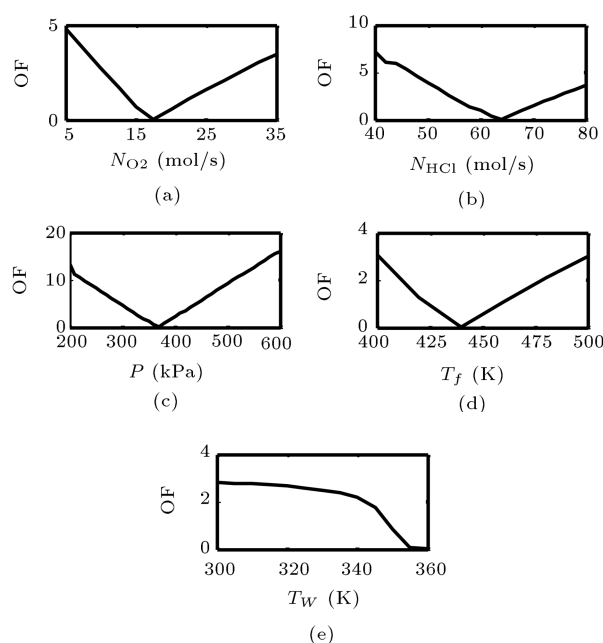
With due attention to parametric sensitivity analysis carried out in Sections 4.3–4.7, feed temperature, pressure, HCl and O₂ molar flow rates, and cooling medium temperature are selected as optimization decision vari-

**Figure 5.** Effect of HCl/C₂H₄ and HCl/O₂ molar ratio on ethylene conversion.

ables to minimize the objective function (Eq. (14)). C₂H₄ molar flow rate is considered equal to C₂H₄ molar flow rate of pilot plant working in Italy (31.85 mol/s), so that the results with the pilot plant data can be compared; it is not selected as a decision variable.

Minimal and maximal values of the decision variables are set, as shown in Table 6. The minimal and maximal allowed values of the decision variables were determined empirically based on reactor feed conditions, “base case”, presented in Table 4. As shown in Table 6, the minimal and maximal values of most decision variables are disturbed $\pm\alpha\%$ around “base case”. To ensure that the cooling water is in the liquid phase, the upper bound of cooling medium temperature is set at 360 K.

In order to optimize the reactor, the DE code is coupled with the non-linear mathematical model (Eqs. (2)–(10)). Figure 6(a)–(e) show variations of objective function in terms of (a) O₂ molar flow rate, (b) HCl molar flow rate, (c) pressure, (d) feed temperature, and (e) cooling medium temperature, respectively. As shown in these figures, the objective function is minimized in one point. These points, tabulated in

**Figure 6.** Variations of objective function versus (a) O₂ molar flow rate, (b) HCl molar flow rate, (c) pressure, (d) feed temperature, and (e) cooling medium temperature.

the last column of Table 6, are optimal operating conditions of the ethylene oxychlorination reactor. Under these conditions, $\text{HCl}/\text{C}_2\text{H}_4$ and $\text{O}_2/\text{C}_2\text{H}_4$ molar ratios are 2 and 0.55, respectively, which are in very good agreement with the stoichiometric coefficient of ethylene oxychlorination reaction (Eq. (1)). Residence time 25 s, bed temperature 510.2 K, HCl and C_2H_4 conversions 99.5% and 99.7%, respectively, are associated with the set of optimal operating conditions presented in Table 6. The results obtained, according to optimization, show an increase of 1.1% in the HCl conversion and a decrease of 8.1% and 18% in the pressure and $\text{O}_2/\text{C}_2\text{H}_4$ molar ratio, respectively. Also, decreasing feed temperature from 460 to 440 K leads to saving energy and reducing the size of the pre-heater.

5. Conclusion

Optimization of fluidized-bed ethylene oxychlorination reactor is studied by a steady-state mathematical model based on the two-phase theory of fluidization. A base case is generated considering similar operating conditions to pilot plant working in Italy. The model is validated against this pilot plant data, and good agreement is obtained. The effects of different operating variables on C_2H_4 and HCl conversions are numerically investigated. DE is used as a powerful optimization technique to determine the optimal reactor operating conditions. The feed temperature, pressure, $\text{HCl}/\text{C}_2\text{H}_4$ and $\text{O}_2/\text{C}_2\text{H}_4$ molar ratios, and cooling medium temperature are selected as decision variables to minimize the objective function. The results show that the obtained optimal operating conditions can increase HCl conversion by 1.1% as well as a decrease of 8.1% and 18% in the pressure and $\text{O}_2/\text{C}_2\text{H}_4$ molar ratio, respectively. Also, a decrease of 20°C is observed in the optimal feed temperature which results in energy saving. Also, the following key results are achieved:

- Increasing the height at minimum fluidization more than 5 m has no significant effect on C_2H_4 and HCl conversions. Therefore, above 5 m height, there is no economic justification for the extra capital investments on reactor volume and catalyst quantity;
- The residence time must be more than 20 s to achieve high conversion. This might occur by choosing a proper reactant distributor and regulating the superficial gas velocity;
- Increasing pressure and feed temperature above 400 kPa and 440 K, respectively, will have no significant effect on the conversion. An increase in temperature (above 440 K) causes loss of energy and enlargement of the size of the preheater;
- The cooling medium temperature should be less than 440 K to avoid catalyst deactivation;

- The optimum ethylene and HCl conversions (i.e., 99.5 and 99.7%) can be achieved by working at $\text{HCl}/\text{C}_2\text{H}_4$ and $\text{O}_2/\text{C}_2\text{H}_4$ molar ratios of 2 and 0.55, feed and cooling medium temperatures of 440 and 360 K, respectively, and pressure 367.6 kPa.

Nomenclature

A	Cross-sectional area of bed (m^2)
A_b	Cross-sectional area of bubble phase (m^2)
A_w	Area of heat transfer between coolant and bed (m^2)
C_{pg}	Gas heat capacity (J/kg K)
D	Bed diameter (m)
D_{ij}	Diffusivity of component i in component j (m^2/s)
D_{im}	Diffusivity of component i in gas mixture (m^2/s)
d_B	Bubble diameter (m)
d_p	Particle diameter (m)
g	Gravitational acceleration (m/s^2)
H	Bed height (m)
$(H_{bd})_b$	Inter-phase heat transfer coefficient between bubble and dense phases based on bubble volume ($\text{J/m}^3 \text{ s K}$)
$(H_{bc})_b$	Inter-phase heat transfer coefficient between bubble and cloud phases based on bubble volume ($\text{J/m}^3 \text{ s K}$)
$(H_{cd})_b$	Inter-phase heat transfer coefficient between cloud and dense phases based on bubble volume ($\text{J/m}^3 \text{ s K}$)
h_w	Bed to cooling surface heat transfer coefficient ($\text{J/m}^2 \text{ s K}$)
$(K_{bd})_{ib}$	Inter-phase mass transfer coefficient between bubble and dense phases based on bubble volume ($1/\text{s}$)
$(K_{bc})_{ib}$	Interphase mass transfer coefficient between bubble and cloud phases based on bubble volume ($1/\text{s}$)
$(K_{cd})_{ib}$	Interphase mass transfer coefficient between cloud and dense phases based on bubble volume ($1/\text{s}$)
k_g	Thermal conductivity of gas (J/K m s)
M	Molecular weight
N	Molar flow rate (mol/s)
OF	Objective Function
P	Reactor pressure (Pa)
Q	Volumetric flow rate (m^3/s)

R	Gas constant ($\text{m}^3 \text{ Pa/g mol K}$)
r	Kinetic rate of reaction ($\text{kg mol/m}^3 \text{ s}$)
T	Temperature (K)
u	Superficial gas velocity (m/s)
V	Volume of overall reactor (m^3)
x	Mole fraction
z	Distance along bed height (m)

Greek letters

γ_i	Stoichiometric coefficient of component i in reaction
δ	Fraction of bed consisting of bubbles
ΔH_i	Heat of reaction (J/kg mol)
ε	Bed void fraction
μ	Viscosity (kg/m s)
ρ_g	Density of gas (kg/m^3)
ρ_p	Density of solid particles (kg/m^3)
τ	Residence time (s)
φ_s	Sphericity of particles

Subscripts

b	Bubble phase gas
d	Dense phase gas
df	Inlet of dense phase gas
f	Fresh feed gas
i	i th component
mf	Minimum fluidization
w	Cooling medium

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