

Optimization-Based Design of a Reactive Distillation Column for the purification process of cyclohexanone Using Rigorous Simulation Model and validated using an experimental packed column.

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Supporting Information

Supplementary Tables.

Table S1. Properties and abbreviations of compounds used in the RD model¹.

Component	Abbreviation	Formula	MW	CAS	Tb/K
Cyclohexanone	CX-ONE	C ₆ H ₁₀ O	98	108-94-1	428
2-Cyclohexen-1-one	CX-ENONE	C ₆ H ₈ O	96	930-68-7	443
2-(1-cyclohexen-1-yl)cyclohexanone	D2 ^a	C ₁₂ H ₁₈ O	178	1502-22-3	538.15
2-cyclohexylidencyclohexanone	D3 ^a	C ₁₂ H ₁₈ O	178	1011-12-7	538.15
[1,1'-bicyclohexyl]-2,2'-dione	C1 ^b	C ₁₂ H ₁₈ O ₂	194	32673-76-0	601±25.0
[1,1'-bicyclohexyl]-2,3'-dione	C2 ^b	C ₁₂ H ₁₈ O ₂	194	88974-62-3	601±25.0
Cyclohexanol	CX-OL	C ₆ H ₁₂ O	100	108-93-0	434

^a Lumped as DIMER with the properties of 2-(1-cyclohexen-1-yl)cyclohexanone.

^b Lumped as DIONE with the properties of [1,1'-bicyclohexyl]-2,2'-dione.

Appendix I. Thermodynamic properties estimation.

The vapour pressure of the pure compound i (P_i^{sat}) expressed in Eq. (S1), is calculated from Antoine constants in Eq (S1) which were taken from the NIST database² and are shown in Table S2.

$$\ln P_i^{sat} = A + \frac{B}{T + C} + D \cdot T + E \cdot \ln T + F \cdot T^G \quad (\text{S1})$$

Table S2. Parameter values used in Eq. to calculate the vapour pressures of pure compounds.

	CX-ONE	CX-OL	Water	CX-ENONE	DIMER	DIONE
A	73.91	177.68	62.14	46.82	63.33	72.83
B	-7944.4	-14337	-7258.2	-7241.8	-9770.61	-12977.3
C	0	0	0	0	0	0
D	0	0	0	0	0	0
E	-9.29	-24.15	-7.30	-5.01	-7.14	-8.16
F	5.00E-06	1.07E-05	4.17E-06	2.87E-18	2.06E-18	7.03E-19
G	2	2	2	6	6	6

The activity coefficients in Eq (6) can be calculated using the NRTL equation for a multicomponent mixture.

$$\ln \gamma_i = \frac{\sum_j \tau_{ij} G_{ji} x_j}{\sum_k G_{ki} x_k} + \sum_j \frac{x_j G_{ij}}{\sum_k G_{kj} x_k} \left(\tau_{ij} - \frac{\sum_k \tau_{kj} G_{kj} x_k}{\sum_k G_{kj} x_k} \right) \quad (\text{S2a})$$

where

$$\tau_{ij} = \frac{A_{ij}}{T \cdot R} \quad (\text{S2b})$$

$$G_i = \exp(-0.3 \cdot \tau_{ij}) \quad (\text{S2c})$$

being A_{ij} the binary interaction parameters obtained from experimental data fitting, and T the temperature in K. The binary interaction parameters are provided in Table S3³.

Table S3. NRTL binary interaction parameters A_{ij} , expressed in Eq. (S2b).

$i \backslash j$	CX-ONE	CX-OL	WATER	CX-ENONE
ONE	0	-262.77	279.95	-477.99
OL	368.3	0	108.9	258.74
WATER	845.731	1544.31	0	1491.2
CXENONE	791.01	-183.73	334.27	0

The enthalpies used in the energy balance can be calculated by Eq (S3).

$$\Delta H_i^L = \int_{T_{ref}}^{T_L} C p_i^L(T) \cdot dT \quad (S3)$$

where ΔH_i^L , in J/mol is the enthalpy of the pure component i at the temperature T_L in liquid state. T_{ref} is the reference temperature (in this work it is assumed as the temperature of the feed stream) and $C p_i^L(T)$ is the liquid heat capacity of the pure component i , whose coefficients are summarised in Table S3, expressed in Eq. (S4).

$$C p_i^L = +A + BT + CT^2 + DT^3 + ET^4 \quad (S4)$$

Table S3. Parameter values used in Eq.(S4) to calculate the liquid heat capacity of the pure component i .

	<i>CX-ONE</i>	<i>CX-OL</i>	<i>Water</i>	<i>CX-ENONE</i>	<i>DIMER</i>	<i>DIONE</i>
A	6.547E+05	1.160E+06	4.527E+05	3.006E+05	4.050E+05	5.579E+05
B	-5.625E+03	-1.171E+04	-4.117E+03	-2.326E+03	-2.838E+03	-3.405E+03
C	22.429	49.276	16.400	10.498	12.791	13.781
D	-3.736E-02	-8.379E-02	-2.883E-02	-1.787E-02	-1.931E-02	-2.004E-02
E	2.384E-05	5.116E-05	1.961E-05	1.155E-05	1.057E-05	1.069E-05

The enthalpy of the liquid stream is calculated with Eq. (S5).

$$\Delta H^L = \sum_{i=1}^{NC} x_i \cdot \Delta H_i^L \quad (S5)$$

The enthalpy of the vapour stream is also calculated from the enthalpy of the pure components.

$$\Delta H_i^V = \Delta H_i^L + \Delta_{vap} H_{m,i}^* \quad (S6)$$

where ΔH_i^V the enthalpy of the vapor phase of pure component i at temperature T , ΔH_i^L is the calculated enthalpy with Eq. (S3), and $\Delta_{vap} H_{m,i}^*$ is the enthalpy of vaporization of compound i at temperature T , calculated with the Eq.(S7), with the parameters presented in Table S4.

$$\Delta_{vap} H_{m,i}^* = A_i \cdot \left(1 - \frac{T}{T_{c,i}}\right)^{\left[B_i + C_i \cdot \frac{T}{T_{c,i}} + D_i \left(\frac{T}{T_{c,i}}\right)^2\right]} \quad (S7)$$

$$\Delta H^V = \sum_{i=1}^{NC} y_i \cdot \Delta H_i^V \quad (S8)$$

Table S4. Parameter values used in Eq. (S7) to calculate the enthalpy of vaporization of compound *i*.

	CX-ONE	CX-OL	WATER	CX-ENONE	DIMER	DIONE
A	17.810	17.253	17.805	18.054	18.310	18.592
B	0.025	-3.979	0.426	0.950	0.591	1.314
C	0.929	8.095	-0.323	-0.865	-0.061	-1.307
D	-0.628	-3.994	0.272	0.346	-0.959	0.472
Tci/K	664.9	647.1	647.1	693.0	769.0	801.0

Appendix II. Model tray equilibrium.

The nomenclature used is shown in Figure S1

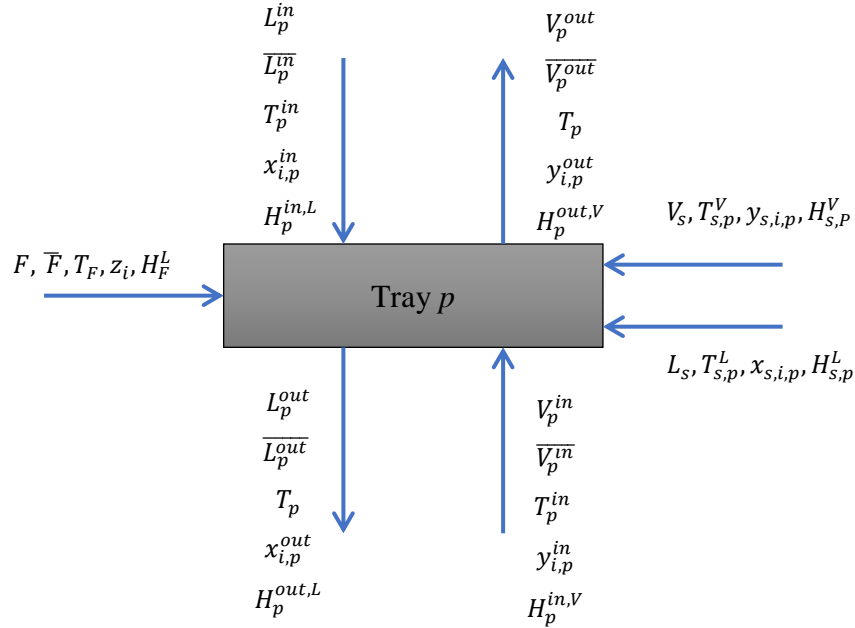


Figure S1. Nomenclature used to model an equilibrium tray. Total mass flows are highlighted with an overbar.

Mathematical model used for a distillation tray was based on the equilibrium-stage model using reaction kinetics. The vapour and liquid streams which leave each single step are in equilibrium. This means that their molar fraction compositions are related by Eq. (S9).

$$y_i^{out} P = x_i^{out} \gamma_i P_i^{sat} \quad (\text{S } 9)$$

This equation can be expressed as a function of the vapour-liquid distribution ratio of a pure component as given in Eq. (S10).

$$y_p^{out} = K_{i,p} \cdot x_p^{out} \quad (\text{S10})$$

where $K_{i,p}$ is the vapour-liquid distribution ratio of a pure component i in the stage p , calculated by Eq. (S10):

$$K_{i,p} = \frac{\gamma_i P_i^{sat}}{P} \quad (\text{S11})$$

The mole balance of each compound i ($i = CX - ONE, DIMER, H_2O, CX - ENONE, DIONE$), for every permanent tray is applied^{4, 5}:

$$0 = L_p^{in} \cdot x_{i,p}^{in} + V_p^{in} \cdot y_{p,1}^{in} - V_p^{out} \cdot y_{i,p}^{out} - L_p^{out} \cdot x_{i,p}^{out} + R_{i,p} \cdot M_t + a_f \cdot z_i \cdot F \quad (\text{S12})$$

The total molar balance in the tray can change due to the reaction term but the total mass balance is constant. The total mass flow for every permanent tray^{4, 5} is as follows

$$0 = \overline{L}_p^{in} + \overline{V}_p^{in} - \overline{L}_p^{out} - \overline{V}_p^{out} + a_f \cdot \overline{F} \quad (\text{S13})$$

The energy balance for each permanent tray is also included in the model:

$$0 = V_p^{in} \cdot H_p^{in,V} + L_p^{in} \cdot H_p^{in,L} - L_p^{out} \cdot H_p^{out,L} - V_p^{out} \cdot H_p^{out,V} \quad (\text{S14})$$

being $p = m = \{2, 3 \dots, NR\} \cup p = n = \{1, 2 \dots, NS - 1\}$. L, V are the molar flow rates of liquid and vapor streams in $mol \cdot h^{-1}$ respectively, which are feeding or leaving the stage p . The molar fraction of each stream is represented as y or x for the liquid or vapor stream, respectively. R_i is the production rate of compound i in $mol \cdot kg^{-1} \cdot h^{-1}$ and M_t is the total liquid hold-up expressed in kg . The chemical reaction is assumed to take place only at the liquid phase. The liquid holdup was calculated with the Billet and Schultes correlation for packed columns⁶. The H_p^L and H_p^V , are the enthalpies of stream liquid and vapor respectively and their values are calculated from the pure compound enthalpies provided in the appendix I. The value of a_f , is only equal to one for the feed tray. The temperature of reference used to calculate the enthalpies is the temperature of the feed stream.

The discrete decisions are modelled in gPROMS with GPD. The Boolean variable Y_p denotes the existence of a conditional tray. If a value of “true” is assigned for a tray p means that the liquid flow is fed to tray p in the rectification section or that the vapor stream is fed to a tray of the stripping section, and the VLE equations are applied to the tray p . The value of Y_p equal to zero means that either the liquid flow fed to a rectification tray or the vapor stream fed to a stripping tray are equal to zero, this tray is bypassed and the mass transfer between phases does not take place^{4, 7-9}.

$$\left[\begin{array}{l} Y_p = 1 \\ y_p^{out} = K_{i,p} \cdot x_p^{out} \\ K_{i,p} = f(T_p, x_{i,p}) \\ \sum_{i=1}^{NC} y_{i,p} = 1 \\ \sum_{i=1}^{NC} x_{i,p} = 1 \end{array} \right] \vee \left[\begin{array}{l} Y_p = 0 \\ y_p^{out} = y_p^{in} \\ x_{i,p}^{out} = x_{i,p}^{in} \\ V^{out} = V^{in} \\ L^{out} = L^{in} \end{array} \right] p \in m = (1,2..NR) \cup p \in n = (1,2..NS) \quad (S15)$$

The discrete decision modelled in gPROMS must be performed with the same number of equations in order to ensure that the degrees of freedom are satisfied.

Appendix III. Condenser model.

The implemented model assumes total condenser operation (vapour stream fed is condensed completely to liquid). The condenser temperature operation is assumed equal to the dew point of the mixture, (the equation used is summarized in Appendix II provided in the Supporting Information of this manuscript) In Figure S2, provided in the Supporting Information file, the model of the condenser used is summarised.

The operating temperature of condenser is calculated as the dew point of the vapour stream that is fed to the unit. The dew temperature is calculated using Eq.(S16)¹⁰.

$$\sum_{i=1}^{NC} y_{i,1} P_i^{sat} = 1 \quad (\text{S16})$$

where the vapor pressure of the pure compound i is calculated from Eq. (S1).

As can be seen in Figure S2, the composition of the streams V_1 , L_D and D is the same, so the total mass balance is the only equation required.

$$V_1 = D + L_D \quad (\text{S17})$$

$$x_D = y_{i,1} \quad (\text{S18})$$

The reflux rate is defined as the ratio of the molar flow rate L_D and D :

$$RR = \frac{L_D}{D} \quad (\text{S19})$$

The energy balance is used in order to calculate the heat flow that can be removed from the system in order to obtain a liquid stream at the bubble point temperature and the working pressure. This heat flow is represented as Q_{cond} in $kJ \cdot min^{-1}$ in Eq. (S20).

$$\frac{dH_p \cdot N_{i,p}}{dt} = V_1 \cdot H_1^V - D \cdot H_D^L - L_D \cdot H_{L_D}^L + Q_{cond} \quad (\text{S20})$$

As can be seen in Figure S2, the composition of the streams V_1 , L_D and D is the same, so the total mass balance is the only equation required.

$$V_1 = D + L_D \quad (\text{S21})$$

$$x_D = y_{i,1} \quad (\text{S22})$$

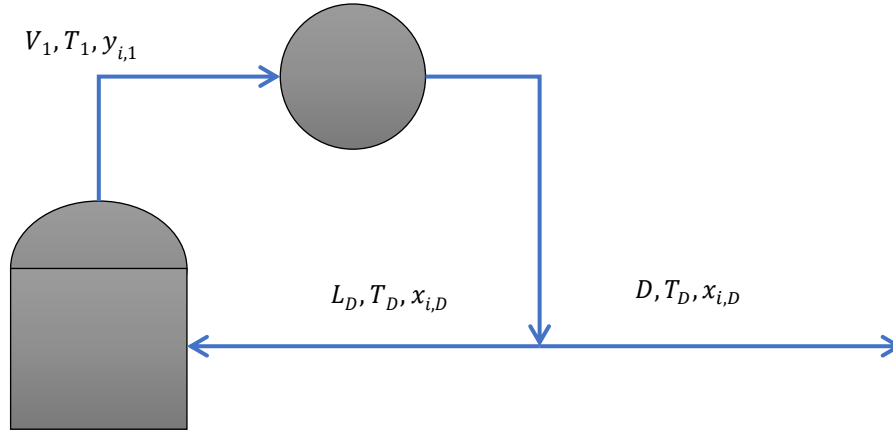


Figure S2. Schematic model of the total condenser where top stream (D) leaves the column in the RD model.

Appendix IV. Reboiler model.

The reboiler operation, represented in Figure S3, is taken as an equilibrium stage where total mass balance can be set as follows:

$$L_p = B + V_B \quad (S23)$$

where L_p is the molar flow rate that is fed from the last stage of the column, V_B and B are the ascending vapour phase and the liquid phase leaving the distillation column respectively.

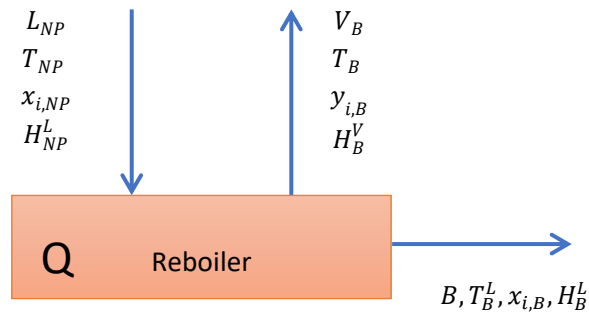


Figure S3. Schematic model of the reboiler where bottom stream (B) leaves the column in the RD model.

The mass balance for each compound is taken into account where the reaction is developed in the liquid phase:

$$\frac{dN_{i,p}}{dt} = L_{NP} \cdot x_{i,NP} - B \cdot x_{i,B} - V_B \cdot y_{i,B} + R_i \cdot M_t \quad (\text{S24})$$

Also, the heat flow required can be calculated from Eq. (S25):

$$\frac{dH_p \cdot N_{i,p}}{dt} = L_{NP} \cdot H_{NP}^L - B \cdot H_B^L - V_B \cdot H_B^V + Q_{reb} \quad (\text{S25})$$

Appendix V: Balance of total cost used to optimize the operation of RD column.

Diameter of distillation column. The column diameter can be determined assuming that the vapour velocity is between 60 and 80 per cent of the flooding velocity¹¹:

$$A = 0.621 (1 + RR) \cdot F_D \sqrt{\frac{M_D}{\rho_{m,D}}} \quad (\text{S26})$$

where:

- A = area in m^2
- RR = Reflux rate
- V_D = molar flowrate that leaves the top of the column in $\text{mol} \cdot \text{s}^{-1}$
- M_D = average molar weight of the distilled stream in $\text{mol} \cdot \text{kg}^{-1}$.
- $\rho_{m,D}$, is the molar density of distilled $\text{mol} \cdot \text{m}^{-3}$

$$M_D = \sum_{c=1}^{NC_D} x_{i,D} \cdot M_i \quad (\text{S27})$$

$$\rho_{m,D} = \frac{P_C}{8.314 \cdot T_C} \quad (\text{S28})$$

$$d_{col} = 2 \sqrt{\frac{A}{\pi}} \quad (\text{S29})$$

Height of distillation column. The column height is calculated assuming a tray spacing of 0.7 m, so the total height of the column can be calculated as:

$$h_{col} = 0.7 \cdot N_{total} \quad (S30)$$

The column shell and tray costs are estimated using the correlations proposed by Guthrie.³⁰ where M&S Index 2015 is the Marshall and Swift chemical equipment cost index for year 2015 (4th quarter),³¹ which allows costs to be updated from 1969 (when the M&S Index was 280); the cost is updated to current equipment cost using eq 10. The cost depends on the column material of construction and column operating pressure.

The column shell cost (CSC) can be estimated from the values of the height and diameter column, calculated with Eqs. (S28) and (S30) respectively from correlations proposed by Guthrie¹². The installed cost of the column shell, made of stainless steel, is estimated as^{11, 13, 14}:

$$CSC = \left(\frac{M\&S}{280} \right) 101.9 \cdot d_{col}^{1.066} \cdot h_{col}^{0.802} \cdot (c_{in} + c_m \cdot c_p) \quad (S31)$$

where $M\&S = 1625.9$ (the Marshal & Swift index for 2015) and the coefficients $c_{in} = 2.18$, $c_m = 3.67$ and $c_p = 1.2$ ¹⁴.

The tray cost can be calculated as follow:

$$TC = \left(\frac{M\&S}{280} \right) \cdot 4.7 \cdot d_{col}^{1.55} \cdot h_{col} \cdot (c_s + c_t + c_m) \quad (S32)$$

where the coefficients $c_s = 1$, $c_t = 0$ and $c_m = 1.7$ ¹⁴.

The total column cost is calculated as:

$$TCC = CSC + N \cdot TC \quad (S33)$$

The heat exchanger costs are a function of the heat transfer area (A) it is calculated from Eq. (S34) and (S35).

$$HEC_{reb} = \left(\frac{M\&S}{280} \right) \cdot 1799.00 \cdot A^{0.65} \quad (S34)$$

$$HEC_{cond} = \left(\frac{M\&S}{280} \right) \cdot 1609.13 \cdot A^{0.65} \quad (S35)$$

where the heat transfer area is straightforward from the design equation of an exchanger, which is function of the exchanged duty (Q), the difference of temperature between the output and input streams (ΔT) and the heat transfer coefficient (U).

$$A = \frac{Q}{U \cdot \Delta T} \quad (S36)$$

An overall heat transfer coefficient can be used in function of the type of used device, in this case the values chosen were $1200 \text{ W} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$ and $800 \text{ W} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$ for the reboiler and the condenser respectively ¹⁵.

The cost is updated to current equipment cost using the CEPCI value of 2017.

$$cost_{2017} = \frac{CEPCI_{2017}}{CEPCI_{2015}} \cdot cost_{2015} \quad (S37)$$

where $CEPCI_{2015} = 556.8$ and $CEPCI_{2017} = 567.5$ ¹⁶.

The total capital investment is the sum of the total costs of the column and the costs of both condenser and reboiler.

$$IC = TCC + HEC_{reb} + HEC_{cond} \quad (S38)$$

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