
Dynamic Modeling of a Sub-zero, Fed-batch, Packed Distillation Column to Produce TetrafluoroethyleneJohannes I. Espach^{1,*}Paul W. Sonnendecker¹Prof. Philippus L. Crouse¹

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Abstract

Equilibrium and rate-based dynamic models are proposed for a laboratory scale, fed-batch, packed distillation column that operates at sub-zero temperatures. The purpose of the column is to separate tetrafluoroethylene from a ternary mixture that also contains hexafluoropropylene and octafluorocyclobutane. The simulation results for both models indicate second-order type responses, with either increases or decreases from the expected steady-state values. It is recommended to build a start-up routine into the simulations. Experimental validation should also form part of future work.

Keywords: distillation, hexafluoropropylene, octafluorocyclobutane, dynamic modeling, tetrafluoroethylene

1 Introduction

Polytetrafluoroethylene (PTFE) is regarded as one of the most important industrial polymers, due to its high melting point, low frictional coefficient and its high resistance to chemical attack. However, PTFE has a very high melt viscosity which does not allow it to be processed by typical thermoplastic processing methods. Instead, PTFE products are produced by subtractive manufacturing methods, which produce considerable amounts of waste. This waste is not biodegradable and the incineration of PTFE in the presence of oxygen produces toxic gases. Numerous works have, therefore, been published that deal with the depolymerization of PTFE through pyrolysis to produce its monomer, tetrafluoroethylene (TFE), as the first step in a chemical recycling process [1–4].

During the pyrolysis process, tetrafluoroethylene undergoes secondary reactions to produce hexafluoropropylene (HFP) and octafluorocyclobutane (OFCB) at temperatures higher than 948.15 K and pressures above 40 kPa, in the absence of a carrier gas [1]. The next step in the recycling process is to separate TFE from the ternary mixture, to serve as feedstock to a polymerization reactor. This should typically be achieved through distillation at sub-zero temperatures. Previous examples of distillation columns that have been used to separate TFE-HFP-OFCB ternary mixtures include a Podbielniak column [2] and a packed, batch distillation column [5].

Continuous separation faces a technical problem. The normal boiling point for pure TFE is 348.77 K [6], while the freezing point of OFCB is 232.95 K [7]. This means that it is not possible to feed the ternary mixture as a fully condensed liquid. A two-phase mixture is possible but at the cost of acquiring an expensive cryogenic pump. Furthermore, it is also not possible to increase the pressure of the mixture, such that the dew point is higher than OFCB's freezing point, as it poses the risk of TFE autopolymerizing. Therefore, the recommended phase for the feed should be a gaseous mixture. Since the normal boiling points of OFCB and HFP are 267.17 K [7] and 243.75 K [8], a feed mixture that is stored at an average temperature of 296.15 K can be regarded as a superheated vapor.

Superheated vapor feed mixtures are usually introduced near or at the bottom of a column, such as in enriching-only columns where the reboiler is absent. Enriching-only columns are capable of producing a high purity distillate product, at the expense of the total fractional recovery of the light key component [9]. However, this may be a viable option for laboratory systems to cut out the need for acquiring an expensive cryogenic pump, especially if the main goal is producing a pure distillate product.

The column presented in this work is unconventional, as it has a batch style reboiler that is empty at start-up, with the feed introduced as the superheated vapor. The reasoning behind this configuration is to have a single column-system to separate the components. This saves on both capital and running costs for a laboratory system, especially since special refrigeration equipment needs to be acquired to provide utility fluid to both the condenser and reboiler. Naturally, this configuration creates an interesting modeling problem.

Dynamic mathematical models offer insight to the internal operation of column and usually prove valuable when designing and implementing the column's control system. One of two modeling approaches can be taken, either equilibrium or rate-based modeling [10]. Both approaches will be explored in this work.

2 Column Set-up

A process flow diagram of the laboratory system under investigation, is shown in Fig. 1. A gas pump draws the feed mixture from a cylinder and introduces it to the top part of the reboiler, to ensure the feed enters from the bottom of the column. At start-up, the reboiler will be empty. The bottoms product will accumulate in the reboiler, which will be kept at a lower temperature to prevent excessive boil-up. After TFE has been purified during the fed-batch mode of operation, the HFP-OFCB binary mixture can be separated through batch distillation.

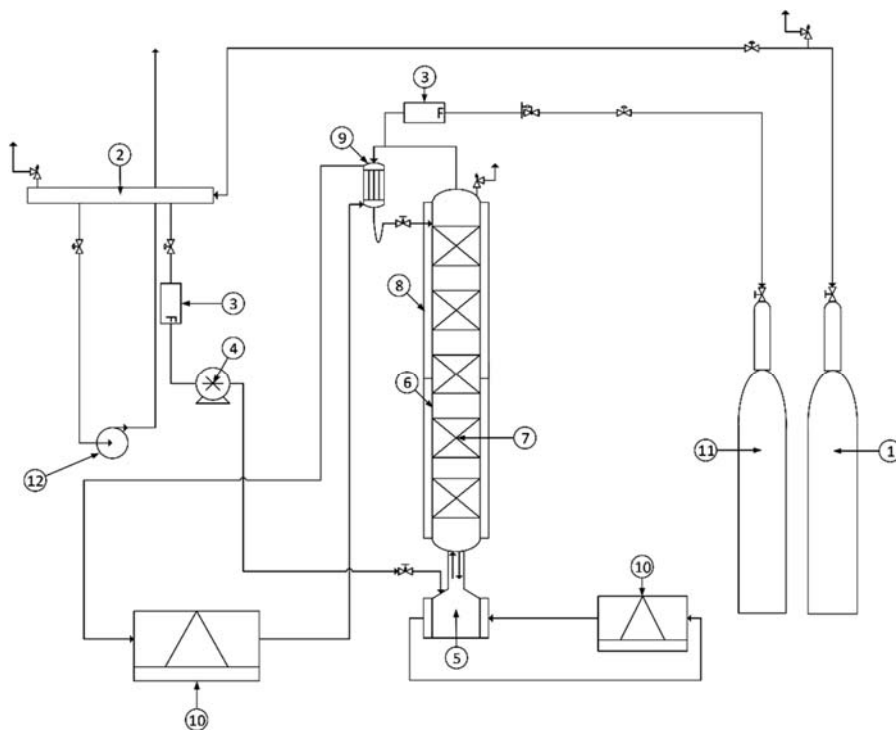


Figure 1. Process flow diagram for the distillation system: (1) feed cylinder, (2) distribution manifold, (3) mass flow meters, (4) feed pump, (5) jacketed reboiler, (6) distillation column, (7) packed section, (8) cooling jacket (for start-up), (9) condenser, (10) Julabo refrigeration units, (11) distillate product cylinder, (12) vacuum pump.

2.1 Column

The column consists of five individual packed sections, with copper shavings used as packing material. Each packed section has a height of around 150 mm, while the packing material has an approximate particle diameter of 5 mm and an approximate length to diameter ratio of 1. Furthermore, the column has a total height of 1450 mm and an internal diameter of 20 mm.

2.2 Condenser

The condenser consists of a bundle of six tubes that are 100 mm in length and have an inside diameter of 4.6 mm and a wall thickness of 0.95 mm. The column top product enters from the top of the tubes, while the utility fluid enters from the bottom of the condenser on the shell side. Methanol is used as the utility fluid, that is cooled and circulated by a Julabo refrigeration unit [11]. The distillate product is drawn off from a headspace in the condenser, above the tubes.

The condensate drains into a reflux line that is bent into an inverted siphon, before being returned to the column as reflux. This design is analogous to reflux drums in larger columns, with the purpose to facilitate reflux accumulation to ensure a continuous reflux flow into the column.

2.3 Reboiler

The cylindrical inner cavity of the batch-style reboiler has a diameter of 104 mm, a height of 118 mm and a wall thickness of 4 mm. The reboiler jacket has an inner diameter of 165 mm and a height of 152 mm. A second Julabo provides a thermofluid as utility to the reboiler. The column, condenser, reflux tube and reboiler are all well insulated.

3 Modeling

Packed columns may either be modeled using partial differential equations or by dividing the packed sections into a number of theoretical stages and applying the mass and energy balances as would be done for a tray column [12, 13]. Both the equilibrium and rate models were built on the assumption that each packed section will behave as a theoretical stage.

3.1 Equilibrium-based Modeling

The equilibrium-based model was built on the following additional assumptions, as well as on the work presented in [12]:

- The vapor and liquid streams leaving a packed section are in thermodynamic equilibrium;
- Vapor hold-ups on packed sections are negligible;
- The operating pressure is well controlled and remains constant.

Furthermore, stage numbering will commence from the bottom of the column, starting with the first packed section. The equilibrium-based dynamic mass and energy balances are summarized below.

3.1.1 Balances around the reboiler:

The component mole balance for the reboiler is defined by Eq. (1)

$$\frac{d(M_{\text{reb}}x_{i,\text{reb}})}{dt} = x_{i,1}L_1 - y_{i,\text{reb}}V_{\text{reb}} \quad (1)$$

where M_{reb} and $x_{i,\text{reb}}$ denote the liquid molar hold-up and mole fractions in the reboiler, L_1 and $x_{i,1}$ denote the liquid molar flow and mole fraction from the first packed section and V_{reb} and $y_{i,\text{reb}}$ are the vapor flow and mole fraction coming from the reboiler. The energy balance for the reboiler is defined by Eq. (2)

$$\frac{d(M_{\text{reb}}h_{\text{reb}})}{dt} = L_1h_1 + Q_{\text{reb}} - V_{\text{reb}}H_{\text{reb}} \quad (2)$$

here, h_{reb} and H_{reb} are the liquid and vapor enthalpies for the reboiler denominated fluids, h_1 is the enthalpy of the liquid flow coming from the first packed section and Q_{reb} is the heat duty for the reboiler. The total liquid molar hold-up in the reboiler is calculated by the summation of Eq. (3)

$$M_{\text{reb}} = \sum M_{\text{reb}}x_{i,\text{reb}} \quad (3)$$

after which the mole fractions of the vapor leaving the reboiler is calculated using the equilibrium coefficient, $K_{i,\text{reb}}$

$$y_{i,\text{reb}} = K_{i,\text{reb}}x_{i,\text{reb}} \quad (4)$$

Finally, both the vapor and liquid mole fractions must sum to unity, as shown in Eq. (5) and Eq. (6)

$$\sum x_{i,\text{reb}} = 1 \quad (5)$$

$$\sum y_{i,\text{reb}} = 1 \quad (6)$$

3.1.2 Balances around the feed section:

The same format is followed for the mass and energy balances on the packed sections. The first packed section is where the feed flowrate, F , with mole fractions, z_i , is introduced

$$\frac{d(M_1x_{i,1})}{dt} = z_iF + y_{i,\text{reb}}V_{\text{reb}} + x_{i,2}L_2 - y_{i,1}V_1 - x_{i,1}L_1 \quad (7)$$

$$\frac{d(M_1h_1)}{dt} = FH_F + V_{\text{reb}}H_{\text{reb}} + L_2h_2 - V_1H_1 - L_1h_1 \quad (8)$$

$$M_1 = \sum M_1x_{i,1} \quad (9)$$

$$y_{i,1} = K_{i,1}x_{i,1} \quad (10)$$

$$\sum x_{i,1} = 1 \quad (11)$$

$$\sum y_{i,1} = 1 \quad (12)$$

3.1.3 Balances around packed sections $n = 2$ to $n = 4$

$$\frac{d(M_nx_{i,n})}{dt} = y_{i,n-1}V_{n-1} + x_{i,n+1}L_{n+1} - y_{i,n}V_n - x_{i,n}L_n \quad (13)$$

$$\frac{d(M_nh_n)}{dt} = V_{n-1}H_{n-1} + L_{n+1}h_{n+1} - V_nH_n - L_nh_n \quad (14)$$

$$M_n = \sum M_nx_{i,n} \quad (15)$$

$$y_{i,n} = K_{i,n}x_{i,n} \quad (16)$$

$$\sum x_{i,n} = 1 \quad (17)$$

$$\sum y_{i,n} = 1 \quad (18)$$

3.1.4 Balances around packed section 5

$$\frac{d(M_5x_{i,5})}{dt} = y_{i,4}V_4 + x_{i,\text{refl}}L_{\text{refl}} - y_{i,5}V_5 - x_{i,5}L_5 \quad (19)$$

$$\frac{d(M_5h_5)}{dt} = V_4H_4 + L_{\text{refl}}h_{\text{refl}} - V_5H_5 - L_5h_5 \quad (20)$$

$$M_5 = \sum M_5x_{i,5} \quad (21)$$

$$y_{i,5} = K_{i,5}x_{i,5} \quad (22)$$

$$\sum x_{i,5} = 1 \quad (23)$$

$$\sum y_{i,5} = 1 \quad (24)$$

3.1.5 Balances around the condenser

Since there are no hold-ups associated with the condenser, the condensate delivered from the condenser, L_{cond} , can be calculated by a steady-state energy balance

$$L_{\text{cond}}(h_{\text{cond}} - H_5) = Q_{\text{cond}} \quad (25)$$

after which the distillate flow rate, D , can be calculated from the mass balance over the condenser

$$D = V_5 - L_{\text{cond}} \quad (26)$$

Finally, since the distillate is drawn off from the vapor coming from the last packed section, the distillate and condensate have the same composition

$$x_{i,\text{cond}} = y_{i,D} = y_{i,5} \quad (27)$$

3.1.6 Balances around the reflux line

$$\frac{d(M_{\text{refl}}x_{i,\text{refl}})}{dt} = x_{i,\text{cond}}L_{\text{cond}} - x_{i,\text{refl}}L_{\text{refl}} \quad (28)$$

$$\frac{d(M_{\text{refl}}h_{\text{refl}})}{dt} = L_{\text{cond}}h_{\text{cond}} - L_{\text{refl}}h_{\text{refl}} \quad (29)$$

$$M_{\text{refl}} = \sum M_{\text{refl}}x_{i,\text{refl}} \quad (30)$$

3.2 Rate-based Modeling

The same assumptions that were made for the equilibrium-based model can be made for the rate-based model, except for the assumption that the vapor and liquid streams leaving a packed section is in vapor-liquid equilibrium. This assumption is replaced by the Maxwell-Stefan mass transfer model, which is based on the two-film theory [10, 13, 14]. Furthermore, the reboiler is treated as an equilibrium contact and has the same modeling equations as shown in Sect. 3.1. The modeling equations for the condenser and reflux line are also the same as in Sect. 3.1 and will not be repeated below.

3.2.1 Balances around the feed section:

The mass and energy balances for the rate-based model are split according to the two phases. For the liquid phase, the mass and energy balances are defined by Eq. (31) and Eq. (32)

$$\frac{d(M_1x_{i,1})}{dt} = x_{i,2}L_2 - x_{i,1}L_1 + N_{i,1} \quad (31)$$

$$\frac{d(M_1h_1)}{dt} = L_2h_2 - L_1h_1 + E_{i,1} \quad (32)$$

where the terms N_i and E_i in the rate-based model denote the interphase mass and energy transfer rates. These terms are calculated using the Maxwell-Stefan diffusion model. The application of this model to distillation modeling is well documented in the literature and will not be covered here.

Instead, the reader is encouraged to peruse the references [10, 13 – 16] for more information. The vapor phase mass and energy balances are defined by Eq. (33) and Eq. (34)

$$0 = z_iF + y_{i,\text{reb}} - y_{i,1} - N_{i,1} \quad (33)$$

$$0 = FH_F + V_{\text{reb}}H_{\text{reb}} - V_1H_1 - E_{i,1} \quad (34)$$

$$M_1 = \sum M_1x_{i,1} \quad (35)$$

The thermodynamic and summation equations are omitted here, as they are used by the Maxwell-Stefan model to calculate the mass and energy transfer rates.

3.2.2 Balances around packed sections $n = 2$ to $n = 4$

$$\frac{d(M_n x_{i,n})}{dt} = x_{i,n+1} L_{n+1} - x_{i,n} L_n + N_{i,n} \quad (36)$$

$$\frac{d(M_n h_n)}{dt} = L_{n+1} h_{n+1} - L_n h_n + E_{i,n} \quad (37)$$

$$0 = y_{i,n-1} V_{n-1} - y_{i,n} V_n - N_{i,n} \quad (38)$$

$$0 = V_{n-1} H_{n-1} - V_n H_n - E_{i,n} \quad (39)$$

$$M_n = \sum M_n x_{i,n} \quad (40)$$

3.2.3 Balances around packed section 5

$$\frac{d(M_5 x_{i,5})}{dt} = x_{i,\text{refl}} L_{\text{refl}} - x_{i,5} L_5 + N_{i,5} \quad (41)$$

$$\frac{d(M_5 h_5)}{dt} = L_{\text{refl}} h_{\text{refl}} - L_5 h_5 + E_{i,n} \quad (42)$$

$$0 = y_{i,4} V_4 - y_{i,5} V_5 - N_{i,5} \quad (43)$$

$$0 = V_4 H_4 - V_5 H_5 - E_{i,n} \quad (44)$$

$$M_5 = \sum M_5 x_{i,5} \quad (45)$$

3.3 Auxiliary Models

3.3.1 Thermodynamic Model

The vapor-liquid equilibrium model used consists of the nonrandom two-liquid (NRTL) activity coefficient model to describe the liquid phase. The vapor phase is described by the Peng-Robinson equation of state that utilizes the Mathias-Copeman alpha constant and the Wong-Sandler mixing rules. Fitted data for the three binary systems were obtained from the literature [17 – 19].

3.3.2 Physical Properties

The pure component physical properties for the three species were obtained from multiple references, as well as for the mixing rules used. Tab. 1 presents a summary of where the physical properties were found.

Table 1. Physical properties list of references.

Property	Reference
Critical properties	[17 – 19]
Density	[20, 21]
Diffusivity	[20, 22]
Enthalpy	[23]
Liquid surface tension	[21]
Thermal conductivity	[24, 25]
Vapor pressure	[6, 8, 17 – 19]
Viscosity	[21]

3.3.3 Reboiler, Condenser and Pressure Drop Models

Design heat transfer models were used to calculate the reboiler and condenser heat duties [26], while the Robbins-method was used to calculate pressure drop on each packed section [20].

3.3.4 Reflux Line Model

The reflux line outflow was characterized by calculating the volumetric flowrate through the needle valve that is installed in the line. The equation in question is the design equation for a control valve, as shown in Eq. (46)

$$\dot{v} = C_V f(x) \sqrt{\frac{\Delta P_{CV}}{SG}} \quad (46)$$

where \dot{v} denotes the volumetric flowrate through the valve, C_V is the valve coefficient, $f(x)$ is the valve characteristic equation, ΔP_{CV} is the pressure-drop over the valve and SG is the fluid's specific gravity. A needle valve that exhibits linear valve characteristics is installed in the reflux line, therefore, $f(x)$ is equal to the valve's stem position. The pressure-drop over the control valve can be calculated by performing a mechanical energy balance over the reflux line, as shown in Eq. (47)

$$\Delta P_{CV} = -\frac{\rho g \Delta s}{1000} - \frac{f' L_e \rho u^2}{d \cdot 2000} \quad (47)$$

here, ρ is the mixture's density, g is the gravitational acceleration constant, Δs is the change in height of the liquid in the tube, f' is the friction factor, L_e is the equivalent length of the tube, d is the inside diameter of the tube and u denotes the linear velocity of the fluid flow. Due to the empirical nature of Eq. (46), \dot{v} should be calculated in units of US gpm, with ΔP_{CV} in units of psi [27].

4 Simulation Results

The two models were initialized to the operating conditions listed in Tab. 2. Dynamic responses of the two models were tested by introducing a 50 % step increase in the feed flowrate. The reflux valve's stem position was kept constant at 30 % open, as this position provided a constant simulated liquid flow to keep the packed sections wet (a higher liquid flow would empty the reflux line). The simulated responses that take place on the first packed section are presented in Fig. 2 to Fig. 4, as this is the section that is directly affected by a change in the feed flowrate.

Table 2. Initial operating conditions before the introduction of a disturbance.

Variable	Value
Operating pressure [kPa]	160
Condenser temperature [K]	206.15
Reboiler temperature [K]	253.15
Feed temperature [K]	296.15
Feed flowrate [kmol s ⁻¹]	2.96×10 ⁻⁷
Z_{TFE}	0.6
Z_{HFP}	0.3
Z_{OFCB}	0.1
$f(x)$	0.3

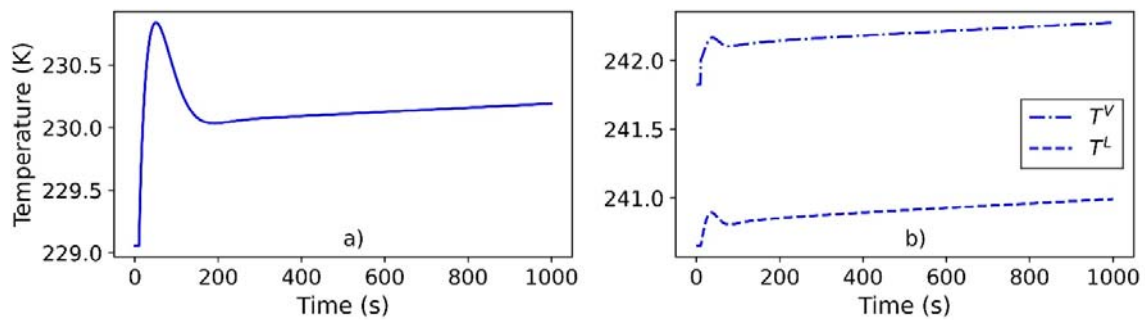


Figure 2. Temperature comparison between the (a) equilibrium-based model and the (b) rate-based model.

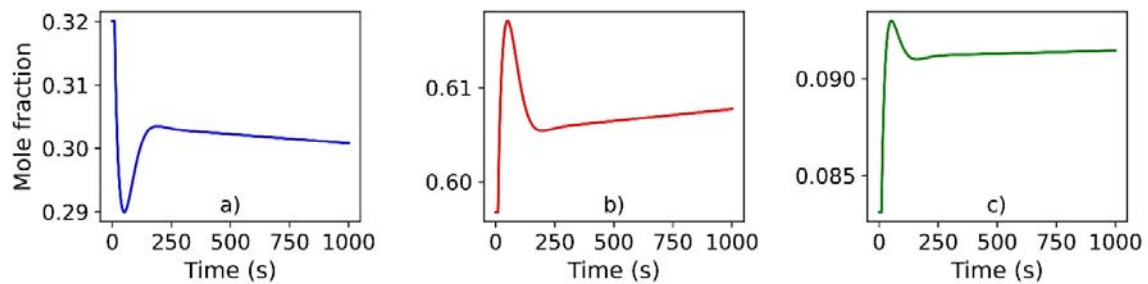


Figure 3. Equilibrium-based dynamic response for the liquid fraction of (a) TFE, (b) HFP and (c) OFCB on the first packed section.

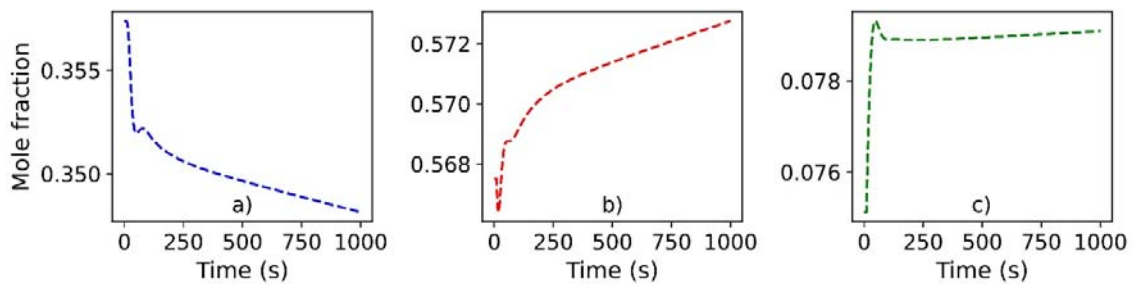


Figure 4. Rate-based dynamic response for the liquid fraction of (a) TFE, (b) HFP and (c) OFCB on the first packed section.

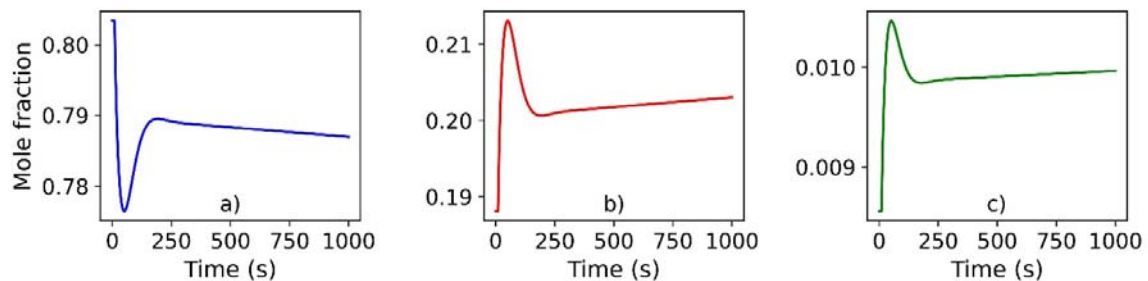


Figure 5. Vapor mole fraction responses of (a) TFE, (b) HFP and (c) OFCB on the first packed section for the equilibrium-based model.

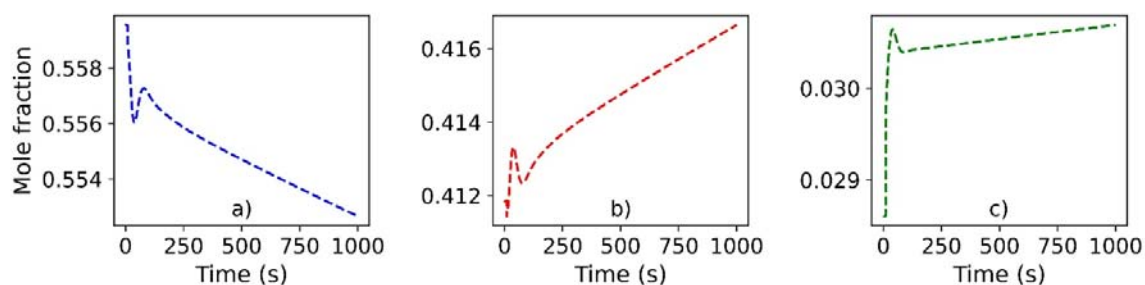


Figure 6. Vapor mole fraction responses of (a) TFE, (b) HFP and (c) OFCB on the first packed section for the rate-based model.

The responses produced by the equilibrium-based model represent the second-order dynamics that are typical of distillation systems. The responses seem to level off to a new steady-state as can usually be expected. However, closer inspection reveals that the values do tend to either increase or decrease past the expected steady-states. This is a result of the fact that the model represents a semi-batch system, which should not reach a continuous steady-state. This kind of response is accentuated by the rate-based model, which seems to drastically move past the expected steady-state. The apparent unstable response of the rate-based model, in comparison to the equilibrium model, can be attributed to the diffusion effects that governs the rate-based model's mass and energy transfer. However, it is important to note that the magnitude with which the values change is small. This is a result of the initialization of the model, which created large liquid hold-up values relative to the feed and internal flows. The result is that the large hold-ups absorb the change in feed flowrate with little effect. A possible solution to this is to include a start-up routine in the simulation. In practice, the column's operation would be continuously dynamic, and a start-up routine would add value to the simulation.

Future work requires the simulation results to be validated against experimental data, especially due to the column's unconventional set-up. At this time no previous experimental or dynamic simulation data exists for the separation of ternary mixtures of TFE, HFP and OFCB in either continuous, batch or, semi-batch columns that the authors know of.

5 Conclusion

Equilibrium and rate-based modeling approaches were explored to simulate the operation of a fed-batch, packed distillation column that is used to separate mixtures of tetrafluoroethylene hexafluoropropylene and octafluorocyclobutane at sub-zero temperatures. It was found that the sensitivity of the models to changes in the feed flowrate is dampened, which is a result of the high liquid molar hold-ups generated by the model initialization. This issue can possibly be circumvented by adding a start-up routine to the simulations. The models should also be validated against experimental data to prove their usefulness.

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Symbols used*Symbols*

C_v	[-]	control valve characteristic coefficient
d	[m]	inside diameter
D	[kmol s ⁻¹]	distillate flowrate
E	[W]	interphase heat transfer rate
$f(x)$	[-]	inherent valve characteristic
f'	[-]	friction factor
F	[kmol s ⁻¹]	feed flowrate
g	[m s ⁻²]	gravitational acceleration
h	[J kmol ⁻¹]	liquid molar enthalpy
H	[J kmol ⁻¹]	vapor molar enthalpy
K	[-]	vapor-liquid equilibrium coefficient
L	[kmol s ⁻¹]	internal liquid flowrate
L_e	[m]	equivalent length
M	[kmol]	liquid molar hold-up
N	[kmol s ⁻¹]	interphase mass transfer rate
P	[kPa (psi)]	pressure
Q	[W]	heat duty
s	[m]	height
SG	[-]	specific gravity
t	[s]	time
u	[m s ⁻¹]	linear flow velocity
\dot{v}	[m ³ s ⁻¹ (gpm)]	volumetric flowrate
V	[kmol s ⁻¹]	internal vapor flow
x	[-]	liquid mole fraction
y	[-]	vapor mole fraction
z	[-]	mole fraction in feed

Greek letters

Δ	[-]	change in a property
ρ	[kg m ⁻³]	density

Subscripts

cond	condenser
F	feed
i	component

n packed section number

reb reboiler

refl reflux

Abbreviations

HFP hexafluoropropylene

NRTL nonrandom two-liquid

OFCB octafluorocyclobutane

PTFE polytetrafluoroethylene

TFE tetrafluoroethylene

References

- [1] A. Bezuidenhoudt, P. W. Sonnendecker, P. L. Crouse, *Polym. Degrad. Stab.* **2017**, *142* (1), 78–88. DOI: 10.1016/j.polymdegradstab.2017.05.025
- [2] E. E. Lewis, M. A. Naylor, *J. Am. Chem. Soc.* **1947**, *69* (8), 1968–1970. DOI: 10.1021/ja01200a039
- [3] E. Meissner, A. Wróblewska, E. Milchert, *Polym. Degrad. Stab.* **2004**, *83* (1), 163–172. DOI: 10.1016/S0141-3910(03)00259-3
- [4] I. J. Van Der Walt, O. S. L. Bruinsma, *J. Appl. Polym. Sci.* **2006**, *102* (3), 2752–2759. DOI: 10.1002/app.24399
- [5] F. J. Conradie, *Batch separation of tetrafluoroethylene, hexafluoropropylene and octafluorocyclobutane*, M.Eng. Thesis, University of Pretoria **2011**.
- [6] G. T. Furukawa, R. E. McCoskey, M. L. Reilly, *J. Res. Natl. Bur. Stand.* **1953**, *51* (2), 69–72. DOI: 10.6028/jres.051.007
- [7] G. T. Furukawa, R. E. McCoskey, M. L. Reilly, *J. Res. Natl. Bur. Stand.* **1954**, *52* (1), 11–16. DOI: 10.6028/jres.052.003
- [8] C. Coquelet, D. Ramjugernath, H. Madani, A. Valtz, P. Naidoo, A. H. Meniai, *J. Chem. Eng. Data* **2010**, *55* (6), 2093–2099. DOI: 10.1021/jc900596d
- [9] P. C. Wankat, *Separation process engineering: includes mass transfer analysis*, 3rd ed., Pearson Education International, Cape Town **2012**.
- [10] R. Krishnamurthy, R. Taylor, *AIChE J.* **1985**, *31* (3), 449–456. DOI: 10.1002/aic.690310312
- [11] www.julabo.com/en/downloads/catalogs (Accessed on February 09, 2020)
- [12] S. Skogestad, in *Selected Papers from the 3rd IFAC Symp.* (Ed: J. G. Balchen), Pergamon, New York **1993**.
- [13] R. Krishnamurthy, R. Taylor, *Ind. Eng. Chem. Process Des. Dev.* **1985**, *24* (3), 513–524. DOI: 10.1021/i200030a001
- [14] R. Krishnamurthy, R. Taylor, *AIChE J.* **1985**, *31* (3), 449–456. DOI: 10.1002/aic.690310313
- [15] M. F. Powers, D. J. Vickery, A. Arehole, R. Taylor, *Comput. Chem. Eng.* **1988**, *12* (12), 1229–1241. DOI: 10.1016/0098-1354(88)85073-7
- [16] R. Taylor, R. Krishna, *Multicomponent Mass Transfer*, 1st ed., Wiley Series in Chemical Engineering, Vol. 2, John Wiley & Sons, New York **1993**.

- [17] F. J. Conradie, P. L. Crouse, X. Courtial, I. J. van der Walt, D. Ramjugernath, *J. Chem. Eng. Data* **2012**, *57* (7), 1978–1983. DOI: 10.1021/je300217x
- [18] F. J. Conradie, P. L. Crouse, X. Courtial, W. M. Nelson, I. J. van der Walt, D. Ramjugernath, *J. Chem. Eng. Data* **2014**, *59* (1), 82–88. DOI: 10.1021/je400828j
- [19] F. J. Conradie, P. L. Crouse, X. Courtial, W. M. Nelson, I. J. van der Walt, D. Ramjugernath, *J. Chem. Eng. Data* **2015**, *60* (3), 966–969. DOI: 10.1021/je501047e
- [20] D. W. Green, R. H. Perry, *Perry's Chemical Engineers' Handbook*, 8th ed., McGraw-Hill, New York **2008**.
- [21] C. L. Yaws, *Yaws' Thermophysical Properties of Chemicals and Hydrocarbons (Electronic Edition)*, Knovel, New York **2010**.
- [22] C. R. Wilke, P. Chang, *AIChE J.* **1955**, *1* (2), 264–270. DOI: 10.1002/aic.690010222
- [23] C. L. Yaws, *Yaws' Handbook of Thermodynamic Properties for Hydrocarbons and Chemicals (Electronic Edition)*, Knovel, New York **2009**.
- [24] C. L. Yaws, *Yaws' Handbook of Thermodynamic and Physical Properties of Chemical Compounds (Electronic Edition)*, Knovel, New York **2003**.
- [25] C. L. Yaws, *Yaws' Transport Properties of Chemicals and Hydrocarbons (Electronic Edition)*, Knovel, New York **2010**.
- [26] R. K. Sinnott, *Chemical Engineering Design*, 4th ed., Coulson & Richardson's Chemical Engineering Series, Vol. 6, Elsevier Butterworth-Heinemann, Oxford **2005**.
- [27] I. L. Greeff, W. Skinner, *Piping System Design*, 1st ed., University of Pretoria, Pretoria **2000**.

Entry for the Table of Contents

Research Article: Equilibrium and rate-based dynamic modeling approaches are employed to study a fed-batch, packed distillation column that is used to separate gaseous mixtures of tetrafluoroethylene, hexafluoropropylene and octafluorocyclobutane. This research forms part of a process to chemically recycle polytetrafluoroethylene and is preceded by a vacuum pyrolysis step.

Dynamic Modeling of a Sub-zero, Fed-batch, Packed Distillation Column to Produce Tetrafluoroethylene

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