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MODELING THE CONFIGURATION CHARACTERISTICS AND OPERATING REGIMES OF A BINARY DISTILLATION COLUMN FOR CONTROL

MODELADO DE LAS CARACTERÍSTICAS DE CONFIGURACIÓN Y REGÍMENES DE OPERACIÓN DE UNA COLUMNA DE DESTILACIÓN BINARIA PARA SU CONTROL

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Abstract

This work describes a mathematical model for a distillation column which includes mass, composition, and energy balances, where the thermodynamic and equilibrium properties are represented by an equation of state. This model focuses on the specific configuration of the boiler (container plus boiling vessel) and the vertical condenser (with an external cooling jacket plus a helical pipe) and also on the effect of atmospheric and subcooling conditions in the condenser. For the sake of flexibility and to represent consistently the semi-continuous conditions during the startup, the equations are solved as a DAEs set. Results are compared with experimental data from a Methanol-Ethanol mixture in a 10-tray distillation column. The effects of configuration and operating conditions on the model fidelity are discussed. The model describes the semi-continuous hydraulics and the desired temperature profile that is expected to be used for process control.

Keywords: distillation column dynamics, condensate subcooling, model fidelity, distillation column configuration.

Resumen

Este trabajo describe un modelo matemático para una columna de destilación que incluye los balances de masa, composición, y energía, donde las propiedades termodinámicas y de equilibrio están representadas por una ecuación de estado. Este modelo se enfoca a la descripción específica del rehervidor (que tiene un contenedor más un tanque de ebullición) y el condensador vertical (con una chaqueta de enfriamiento externa, más un tubo helicoidal) y también los efectos de las condiciones atmosféricas y de sub-enfriamiento en el condensador. A fin de tener flexibilidad y para representar consistentemente las condiciones semi-continuas durante el arranque, las ecuaciones son resueltas como un conjunto de EAD. Los resultados son comparados con datos experimentales para una mezcla metanol-etanol en una destilación de 10-platos. Se discuten los efectos de la configuración y las condiciones de operación en la fidelidad del modelo. El modelo describe la hidráulica semi-continua y el perfil de temperaturas que se espera sea utilizado para control de procesos.

Palabras clave: dinámica de columnas de destilación, subenfriamiento de condensado, fidelidad de modelo, configuración de columna de destilación.

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1 Introduction

The starting aim of this work was the energy integration of a distillation column by a heat pump. For this aim the Aspen Plus was used (Martínez-Soria, 2001). During this work, it was observed that the interactions between the streams of equipment which are part of the thermodynamic cycle harden the convergence. Also Aspen models, as they are devised for general purpose, offer limited description of the configuration of equipment. Then, to obtain an adequate diagnosis of the performance, a home-grown distillation model was developed. Thus, the present work presents a detailed model for the distillation pilot plant located at the Mechatronics laboratory of CENIDET. The present work emphasizes the development of a model which considers the equipment configuration and the specific operating conditions. It has been observed that the configuration of this column is similar to other distillation columns available in several academic institutions (like the Chemical Department of Celaya Institute of Technology, Chemistry Faculty at UNAM, School of Chemical Engineering and Extraction Industries at IPN and Faculty of Chemical Sciences and Engineering at UAEM); thus, the improvement of this model will provide a better understanding of the behavior of similar columns. For this process, the basic mass and energy balances are known, thus most of the unknown parameters are related to the hydrodynamic equations and to the heat transfer parameters. In this work some of these parameters are evaluated by complementary techniques: experiments in the time domain. The used strategy consists in isolating as much as possible the effect of each parameter. The objective of improving the model fidelity is to enhance the control performance under disturbances.

1.1 Background

To synthesize a multivariable control for a given process objective, it is necessary to select measured and manipulated variables (inputs, u and outputs, y), which satisfy the basic criteria of control (observability, controllability, sensitivity). To predict the time variation of state variables and outputs, instead of using typical surface responses, model-based control uses a reference model. Predicted outputs are used to evaluate an objective function (which evaluates the difference between experimental outputs and their prescribed set trajectory) subject to process constraints. Finally, an optimizer minimizes for the increment of inputs, Δu, the summation during several sampling times of the squares of the objective function with weights W_y, $W_{\Delta u}$ (Rossiter, 2003).

$$\min_{\Delta u} W_y \left[r(t) - y(u) \right]^T \left[r(t) - y(u) \right] + W_{\Delta u} \Delta u^T \Delta u$$

(1)

Some of the obstacles to be dealt with in model-based control are a) tuning control variables (sampling time, predicting and control horizon) b) the representation of the effect of unmeasured disturbances and c) reducing model/plant mismatch. This work emphasizes the last issue. Yip and Marlin (2004) in their work comparing models with different fidelity have shown that the performance of Real Time Optimization to track the changing optimum relies on an accurate model to represent plant behavior.

Since the development of the simplified dynamic model of a distillation column was proposed by Wood and Berry (1973), several improvements have been made, for instance, models with composition and mass (Cingara and Jovanovic, 1990) and with energy and composition (Gani, *et al.*, 1986) have been developed. In a sequel of these works, Ruiz, *et al.* (1988), and Eden *et al.* (2002) found that the startup is composed by three stages: 1) a short discontinuous stage, where the pumps and the flow start while the heating is in progress; 2) a semi-continuous stage, where the hydraulic variables reach their steady state and the reflux changes from total to the desired reflux rate; 3) a final stage, where the column reaches the desired conditions.

Kister (2002) mentions that two of the major trouble spots for the development of a distillation model are the hydraulic prediction and reliable VLE data. Archambault *et al.* (1973) analyzed the operating conditions of the condenser. They showed that for a high ratio of cooling water flow to condensate flow, the condenser operates under subcooling conditions. Wittgens and Skogestad (2000) in their study on tray hydraulics concluded that models based on constant molar flows and linear tray hydraulics gave large deviations. Alpbaz (2002) studied the behavior of the specific configuration of a distillation boiler. In a

distillation column with similar characteristics, Gunter (2003) developed several tests to set some parameters of his dynamic model; but this model was used during warm start-up. Agachi *et al.* (2007), after comparing 5 models varying in modeling difficulty and computational complexity (from DAE models to Artificial Neural Networks) for an ethanol-water distillation column, conclude that fundamental models are attractive because they are globally valid and fewer parameters are required for their development. They also notice that when a model with high complexity is used, real-time feasibility for control requires an appropriate optimization strategy.

Furthermore, a project supported by OIT (DOE of USA; 2001) has been launched to develop fundamentals-based models for the distillation column operation and to establish the column internals. From the results of this project, large energy savings are expected by year 2020.

1.2   Objective

The objective of this work is to improve a general model for a distillation column in order to increase its fidelity from semi-continuous operation conditions to the required conditions at the specified purity.   The goal is to translate accurately the input variables: heat to the reboiler, cooling water flow and its cooling temperature to obtain a product with a desired flow-rate and composition.   An accurate measurement of the inputs plus a better phenomenological description produces better output descriptions. As it is evident in the mass and energy balances presented in Section 4.1, once the steady state is represented, the dynamic behavior depends on the initial conditions, the operating conditions, the physical properties of the fluid, and the available geometry of the equipment where the fluid travels (mass-high relationship in reboiler and condenser; weir, height and column diameter in trays). Lee (1998) has mentioned the requirements of an adequate model for control: *In nonlinear model predictive control a model should enable to predict accurately the effects of both, known and unknown changes on the system (output) behavior possibly in a closed-loop setting.*
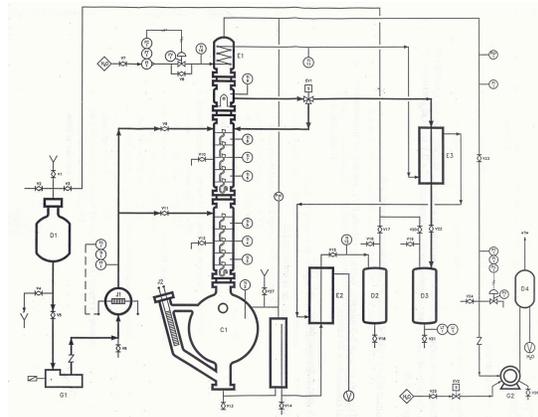

Fig. 1: Reference distillation column layout

2   Process description

The reference distillation column layout is presented in Fig. 1. The column was made in Pyrex crystal. The boiler section is composed by two vessels. The smaller vessel is used to heat a small part of the overall mixture volume by a heating coil, thus a fast response is obtained; the large vessel is used as a storage tank to compensate the evaporated fluid. The column is not insulated, i.e. the glass walls are exposed to the room temperature. The trays are perforated with the down comers located in the center of the tray, with a wide conic section (to reduce pressure drop and to avoid flooding) which ends in a "J" shape; then, the holdup is used as a liquid seal. To provide a complete and steady condensation the condenser has two cooling sections.   The inner section is located in the distillation chamber, where a helical pipe condenses the distillate; the outer section is an external cooling jacket. This configuration ensures total condensation of the distillate.

The dimensions of the column are presented in Table 1.

2.1   Related instrumentation

Reboiler.   The required heat is provided by an electric heating thermo-coil, while its instrumentation is formed by one Pt 100 RTD sensor and one electronic temperature indicator.
Trays.   The main body of the column has 6 temperature RTD Pt100 sensors and 6 electronic temperature indicators located at tray 2, 4, 5, 7, 9, 10 (consider boiler as number 1). Along the

Table 1. Geometric properties

Property	Value
Number of trays	10 (perforated)
Tray diameter	10 cm
Feed tray	6 from bottom
Condenser heat transfer area	0.5 m^2
Diameter of down comers	0.5 cm
Pitch from down comers	0.2 cm
Weir height	0.61 cm
Tray spacing	0.11 m
Tray diameter	0.10 m
Reboiler capacity	6 lt with a boiling vessel of 1 lt
Condenser capacity	1 lt
Condenser heat transfer area	0.5 m^2

column body, a differential pressure transmitter is used to monitor the difference of pressure between the top and the bottom of the column, a level indicator is used for the reboiler, and two flow meters measure the feeding flow and the cooling water flow of the condenser, respectively.

Feeding subprocess. The feeding mixture is stored in a deposit. Its temperature is controlled by a pre-heating electric thermo-coil. This deposit has one Pt 100 RTD temperature sensor, one electronic temperature indicator, and one temperature controller. The flow of the feeding mixture is regulated by the pulses of a feeding pump.

Condenser. The condenser has a differential pressure sensor. The cooling water has two Pt 100 RTD temperature sensors and two temperature indicators. An additional output condensate temperature was placed. The condenser has also one flow transmitter, one flow indicator, one flow controller and a 3-way reflux valve. An actuator regulates the reflux fraction by opening/closing pulses which are controlled by two timers. The condenser level is regulated by its geometric discharge outlet (see Appendix A).

Product. The distilled product is collected in a deposit which has a level transmitter.

Additional measurements were used to define more clearly the mass and energy balances in the condenser: the reflux temperature and the environmental temperature.

3   Methodology

The development stages start from the available experimental LVE data, and configuration of equipment, with high reliability, through the interaction between mass-energy, up to the conditions where there is high interaction between thermodynamic and hydraulic effects; thus, reliability of data is poor. So, specific experiments were designed. The following methodology was used to develop the distillation column model (modified from Dutta and Gualy, 2000):

1. Determine the parameters of a given equation of state to predict the physical properties of the liquid mixture.

2. Determine the *configuration* of the equipment in the distillation column.

3. Determine the *geometry* of the different sections of the distillation column.

4. Select a general model of a distillation column and modify it as required.

5. Define a set of experiments to obtain specific characteristics of the heat and mass transfer for the distillation column.

6. Execute specific experiments to fit the transfer-based parameters.

Static parameters were evaluated before the test, while *dynamic* parameters can be adjusted during the dynamic runs.

These steps are described in the following paragraphs

- The Stryjek-Vera-Peng-Robinson equation of state was used to represent the equilibrium and thermodynamic properties of the Methanol-Ethanol mixture in both phases. This mixture presents a slightly non ideal behavior due to hydrogen bonds interaction (Prausnitz *et al.*, 1967). Experimental data reported by Stephan & Hildwein (1987) were used to fit the interaction parameters (see Appendix B).

- The distillation model developed by Gani *et al.* (1986), which appears in Appendix A, was selected. After the comparison of experimental and simulated responses the configuration of the equipment was detected

as one of the reasons of discrepancy. Model enhancements are described in Section 4.

- Steady state experiments were executed to validate global balances.

- Specific experiments were defined and executed. The following operating conditions were selected to evaluate some model parameters:

  a) Without feeding. Under this condition the column operates as a batch column.

  b) Without condensation. This experiment is useful to estimate the heat losses to the environment.

4 Model enhancements

The different sections of the distillation column are: boiler, trays and condenser. The specific geometric characteristics are described in the following subsections.

4.1 Reboiler

Fig. 2 shows the geometric characteristics of the boiler. It is a thermosyphon composed by two vessels: a storage vessel and a small vessel where the heat is supplied.

The following model was developed to take into account the reboiler dynamics of this configuration.

Mass balance:

$$\frac{dM_b}{dt} = L_{Bb} - V_B \qquad (2)$$

Energy balance between vessels:

$$M_b \frac{dE_b}{dt} + M_B \frac{dE_B}{dt} = L_2\left(E_{l,2} - E_{l,b}\right) \qquad (3)$$
$$+ L_{Bb}\left(E_{l,B} - E_{l,b}\right) - V_B\left(E_{v,2} - E_{l,b}\right) + Q_B$$

The flow that communicates the storage vessel with the boiling vessel is obtained by the differential form of the communicating vessels $\left(\frac{dh_B}{dt} = \frac{dh_b}{dt}\right)$, with consistent initial conditions ($h_B = h_b$ at $t = 0$):

$$L_{Bb} = \frac{A_b\left(\frac{\rho_B}{\rho_2} L_2 - L_B\right) + A_B \frac{\rho_B}{\rho_b} V_b}{A_b + A_B} \qquad (4)$$
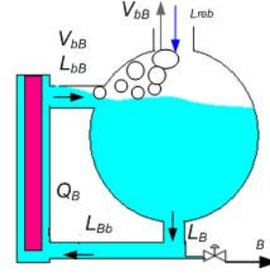

Fig. 2: Reboiler with a storage tank

If only a single vessel were taken into account, the boiling conditions would present at slower dynamics. Alpbaz *et al.* (2002) consider only the composition dynamics in the vessels, but the energy dynamics is also important. During the startup, there are high temperature differences in the storage and heating vessels which could produce diffusion effects in a direction opposite to the liquid flow.

4.2 Trays

Hydraulics

During the startup, when the vapor pressure is smaller than the environmental pressure, weeping occurs along the walls at some stages. A difficulty in representing a startup is that when the liquid arrives to its bubble point some vapor is released; thus, the liquid enthalpy decreases, and the vapor pressure presents sudden fluctuations.

This type of fluctuations occurs when the boiling heat is reduced suddenly, and the fluid stops boiling. Under these conditions $P_{atm} > P^*$, also there could be some reverse flow.

At every tray, the bottom pressure, P_f is evaluated as $P_f = P^* + \max\{0, \Delta P^*\} + \Delta P_h$, where $\Delta P^* = (P_{atm} - P^*)$, and $\Delta P_h = gM/A$. See Fig 3.

To preserve the consistency in the evaluation of the derivatives used to solve the continuation equations, the expression $\max\{0, \Delta P^*\}$ was approximated as $\approx 0.5\sqrt{(\Delta P^*)^2 + \varepsilon_p^2} + 0.5\Delta P^*$. The derivative of this equation is continuous with respect to P^* (Biegler *et al.*, 1997). Wang *et al.* (2003) use a discontinuous approach, but the actual process is semi-continuous. The proposed approach diminishes the restarting of the integration method.
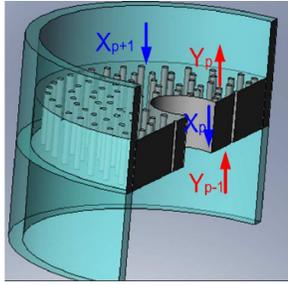
Fig. 3: p^{th} tray

At every tray, the vapor flow and its enthalpy depends upon the differential pressure through the tray.

$$\Delta P_v = P_f - P^* \qquad (5)$$

Then

$$\left\{ \begin{array}{l} \Delta P_v \geqslant 0, V = +\sqrt{\rho_v \Delta P_v / kv_v}, E_v = E_v^* \\ \Delta P_v < 0, V = -\sqrt{\rho_l |\Delta P_v| / kv_l}, E_v = E_l^* \end{array} \right. \qquad (6)$$

Heat losses along the column

Since the condenser operates at atmospheric conditions, and the boiler heat transfer area is small, the main heat losses occur along the column body. If the distillation column is heated until the condition that no-flow arrives to the condenser, then the heat supplied corresponds to the heat losses. A similar experiment was carried out by Gunter (2003).

Selective Condition

$$L_F = 0; \quad B = 0; \quad D = 0 \qquad (7)$$

From the cold start-up, the boiler heat was increased until the heat reached the tray before the condenser. At that condition, all the heat was spread in the environment; thus, an overall balance for all the trays produces

$$L_C E_{L,Cond} + V_B E_{V,B} = V_C E_{V,Cond}$$
$$+ L_{B+1} E_{L,B} + Q_B + Q_{Atm} \qquad (8)$$

In this expression Q_B is known; while the unknown Q_{Atm}, represents the heat losses to the environment. Then, when the Newton cooling equation is applied to the column body:

$$\frac{dQ_{Atm}}{dt} = \sum_{2}^{Np-1} K_{p,A}(T_p - T_{Atm}) \qquad (9)$$

Heat losses can be estimated at different operating conditions by evaluating $K_{p,A}$. This constant is humidity dependent.
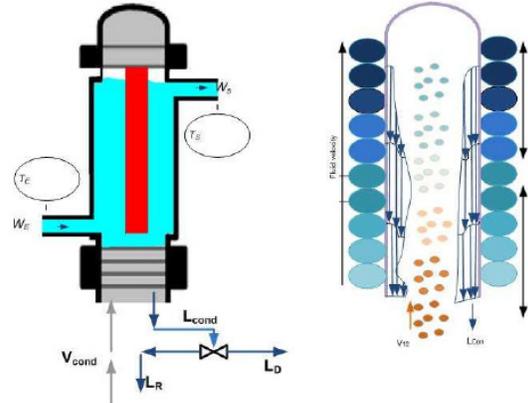

Fig. 4: Condenser of the distillation column

4.3 Condenser

The condenser has two sections. In the inner section of the condenser, the cooling water coming from the fresh water supply flows through a helical pipe counter currently with respect to the distillated flow, so that the behavior resembles a pipe with plug flow. In the outer section as soon as the cooling water reaches it, its temperature acquires the average temperature of the vessel, like a stirred tank (see Luyben, 2004). Finally, both cooling streams are merged (see Fig. 4).

Empirically some vibrations were observed in the early operations of this column, at small cooling flow, in spite of the 'o' rings provided in its structure. Once a higher level of cooling water was applied to the column, the vibrations were reduced. As a result, in fluids with low heat capacity and low flow of the top product, the distillate leaves the column at subcooling conditions (Archambault *et al.*, 1973). At industrial scale, distillation columns use subcooling to avoid cavitation in the reflow pumps of the condensate.

Evaluation of subcooling properties at the condenser. For the sub-cooling conditions in the condenser, there is an additional degree of freedom. The condenser pressure was selected as specification. Instead of Eqs. (A-5) and (A-8), the following conditions were used:

$$\Phi(T_b, P_C, x) = P_C(\sum_{1}^{n} K_i x_i^* - 1) = 0 \qquad (10)$$

$$E_L = E^{ig}(T_{sub}, x*) + E^{dep}(T_{sub}, P_C, x*) \qquad (11)$$

For the cooling water, the overall change in temperature is small, but the subcooling improves

purity of the distillate, at the expense of reducing its yield. Gorak (2008) recommends using some heating between the condensate and the reflow to reduce subcooling, since the behavior reduces distillation performance, in a similar way as when the feeding stream is placed at an incorrect temperature. The condenser equations are:

Mass balance

For a parallel array in the helical pipe and jacket sections, the flow is given by

$$Ww = W_{hl} + W_{jc} \tag{12}$$

$$\Delta P_{hl} = \Delta P_{jc} = k_{V1}\frac{W_{hl}^2}{\rho_{hl}} = k_{V2}\frac{W_{jc}^2}{\rho_{jc}} = \Delta P_T \tag{13}$$

$$W_{hl}^2 = \frac{k_{v1}}{k_{v2}}W_{shl}^2, \text{ then } W_{hl} = \sqrt{\frac{k_{v1}}{k_{v2}}}W_{jc} \tag{14}$$

Energy balance

$$W_w Cp(T_{w,out}-T_{ref}) = W_{hl}Cp(T_{hl,out} - T_{w,in}) + W_{sh}Cp(T_{jc,out} - T_{w,in}) \tag{15}$$

$$M_{hl}Cp_w\frac{dT_{hl,out}}{dt} = W_{hl}Cp_w(T_w - T_{hl,out}) + Q_{D-hl} - Q_{sh-hl} \tag{16}$$

$$M_{jc}Cp_w\frac{dT_{jc,out}}{dt} = W_{sh}Cp_w(T_{w,in}-T_{jc,out}) - Q_{jc-hl} \tag{17}$$

$$Q_{D-Hl} = UA_{hl}LMTD(T_{D,in}, T_{D,out}, T_{hl,in}, T_{hl,out}) \tag{18}$$

$$Q_{jc-hl} = UA_{sh}(T_{hl,ave} - T_{jc,ave}) \tag{19}$$

This dynamical model of the condenser provides a more accurate representation of the column. A heat transfer with two layers can be represented as in Lienhard and Lienhard, (2002):

$$K_1\frac{dT}{dt} = K_2 T + K_3 \tag{20}$$

then

$$\tau_2\frac{d^2 T_w}{dt^2} + \tau_1\frac{d^1 T_w}{dt^1} + \tau_3 T_w + \tau_4 = 0 \tag{21}$$

Thus, given the configuration of the condenser, the dynamics of the cooling water temperature has a 2nd order behavior, with two different negative eigenvalues, associated with the slow and fast dynamic in the cooling temperature.

The actual configuration provides not only an effective cooling (since the helical pipe provides a large heat transfer area, and a turbulent flow which increases the overall heat transfer coefficient U), but also gives a response which regulates sudden changes from the distillate flow (since there is a fast cooling flow in the helical pipe), and it maintains stability (since sudden changes in the input distillate are eventually compensated by the cooling jacket). This configuration is especially suited for sudden changes in the reflow rate which are caused by the opening/closing pulses of the reflow valve. For this vertical condenser, the output flow dynamics is highly dependent on the energy transferred and its geometry.

4.4 Structure of the differential algebraic equations

The differential variables x_d are mass, energy and composition per tray. The algebraic equations x_a are temperature and pressure per tray. See Appendix A. The general form for every tray, p is:

$$\frac{dx_d}{dt} = \mathrm{f}_{p,j}(t, x_d, x_a, u), \quad j = 1,..,3 \tag{22}$$

$$0 = \mathrm{g}_{p,j}(t, x_d, x_a, u), \quad j = 4,5 \tag{23}$$

4.5 Solution method for the differential algebraic equations

The system of Eqs. (22)-(23) is solved by the odes23t code of Matlab. This code is an implementation of the Gear method with variable time step, suited for a Differential-Algebraic Equations for moderate stiffness, required during column pressurization or pressure loss, which produce fluctuations in vapor flow. Maximum of 3rd order of approximation was specified. The Jacobian of this system of equations was evaluated numerically. Relative and absolute tolerances were used in the estimation of local error (10^{-4} and 10^{-6}). The steady state was obtained by regulating boiler and condenser levels in the distillation model. At every successful time step, the operating conditions were modified.

During the startup, or during sudden heat of the boiling at low reflux, trays holdup is small.

Table 2. Qualitative comparison with respect to other models

	Gani (1986)	Gunter (2003)	This Work
Equilibrium	Equation of state	Polynomial approximation, based on Van Laar activity coefficients	SVPR equation of state
Balance equations	Mass, composition, energy	Constant molar hold up. Constant vapor flow	Mass, energy, composition, Pressure with varying hold and liquid and vapor flow
Boiler	Geometry not specified	Geometry not specified	Boiling and storage vessels
Tray	General tray hydraulics	Francis equation Murphree efficiency	Francis equation Murphree efficiency
Condenser	Geometry not specified	Geometry not specified	Coil and Jacket section
Operating conditions	Continuous saturation	Continuous saturation	Semi-continuous and continuous. Saturation and subcooling
Environmental Conditions	Not specified	Estimated heat losses	Measured atmospheric and inlet conditions and Heat transfer modeled
Solution	ODE	ODE	DAE

When the holdup of a tray is small, its heat transfer is very fast, while pressure and vapor flow also changes fast; as a result, variable step methods use very small time steps.

Table 2 shows the qualitative comparison with respect to other models.

4.6 State space model

Given the set of measurements, Boiler Pressure, Tray Temperature,

$$y = h(t, x_a, x_d, u) \tag{24}$$

The state space model required for control is obtained by Taylor approximation of the DAE system (eqns. 22, 23), and eliminating the algebraic variables.

$$df = \left(\frac{df}{dx_d} - \frac{df}{dx_a} \left(\frac{dg}{dx_a} \right)^{-1} \frac{dg}{dx_d} \right) \Delta x_d$$
$$+ \left(\frac{df}{du} - \frac{df}{dx_a} \left(\frac{dg}{dx_a} \right)^{-1} \frac{dg}{du} \right) \Delta u$$

$$+ \left(\frac{df}{dv} - \frac{df}{dx_a} \left(\frac{dg}{dx_a} \right)^{-1} \frac{dg}{dv} \right) \Delta v \tag{25}$$

$$dh = \left(\frac{dh}{dx_d} - \frac{dh}{dx_a} \left(\frac{dg}{dx_a} \right)^{-1} \frac{dg}{dx_d} \right) \Delta x_d$$
$$+ \left(\frac{dh}{du} - \frac{dh}{dx_a} \left(\frac{dg}{dx_a} \right)^{-1} \frac{dg}{du} \right) \Delta u$$
$$+ \left(\frac{dh}{dv} - \frac{dh}{dx_a} \left(\frac{dg}{dx_a} \right)^{-1} \frac{dg}{dv} \right) \Delta v \tag{26}$$

df represents the linearized approximation for state variables, dh represents the linearized approximation for measurements, u represents the input vector (reflow, heat to the reboiler, cooling water flow to the condenser), and v represents the disturbances vector (environmental temperature).

This approximation relays in the assumption that the DAE is index 1. This is achieved by the structure of the DAE and the consistent initial conditions used. The numerical derivatives also require continuity which is achieved by the "smoothening" of the pressure drop term.

Table 3. Range of operating conditions

Property	Value
Atmospheric pressure	87.0 KPa
Atmospheric temperature	27.5 - 32.8 °C
Differential pressure	0 - 5.0 KPa
Composition in reboiler	0.59 mol (Methanol)
Feed flow	0
Heat supplied to reboiler	100-2500 W
Murphree efficiency	0.95-0.97
Cooling water flow	6.667 l/min
Boiler hold up	60.36- 80.85 mol (3.0 - 4. l)
Heating vessel hold up	10.05-17.00 mol (0.5-0.85 l)
Tray hold up	0.4 - 0.5 mol
Condenser hold up	0.4 - 5.0 mol

Finally, $\frac{\partial g}{\partial u} = 0$, for the manipulated variables in this model.

5   Dynamic experiments

Two experiments are present to corroborate the validity of the model. Feeding tests have been delayed due to a malfunction in the feeding heat system. Table 3 shows the range of the operating conditions used.

Test 5.1. Startup with further heat reduction

The behavior of the distillation model is tested using a change in the heat supplied to the boiler according to the profile shown in Table 4. Feeding flow is zero. Heating changes and their effects on tray temperatures are shown in Fig. 5.

Boiling starts shortly after the reboiler duty was applied. The time response of the model and the experimental data are similar, 1 min.

For the given composition in the reboiler the mixture bubble point is 64.4 °C, obtained by Aspen-Plus v7.1 (Aspen Technology, 2009). At the given load of heat to the reboiler, the time to arrive to this condition is 5.79 min, and 0.97 min if only the heating vessel is accounted.

Table 4. Profile of heat to reboiler

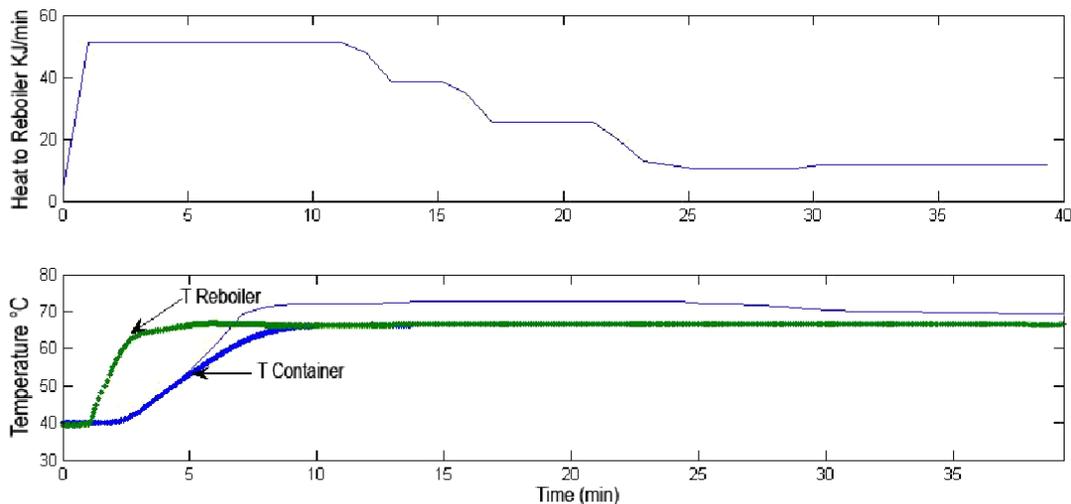| Time (min)	QB (J/ min)
1.01	51,200
12.10	38,400
17.14	25,600
22.18	10,200

Fig. 5: Temperature response of distillation column to heat supplied in boiler. a) Profile of heat supplied to the boiler b) Measured temperature (thin line), predicted temperature (thick line).

The trend of the steady state is different for computed and experimental results. This deviation in bubble temperature is possibly due to the location of the temperature sensor inside the boiler, or purity of mixture. An accurate prediction of temperature is particularly important when the composition is estimated from temperature measurements.

When the boiling heat is increased, the temperature of the boiling vessel is also increased until the mixture arrives to its bubble point. This temperature is maintained even if a heat reduction occurs at $t = 12.0$ min, because of the large holdup of the storage vessel. A further reduction of the heat reduces the vapor flow. During this transient the tray pressure and flow are oscillatory. A further reduction of the heat after $t = 25$ min reduces the temperature of the mixture and the boiling is stopped.

Test 5.2. Start-up distillate production and shut-down

The profile of the heat supplied to the reboiler is shown in Table 5. Fig. 6 shows the profile of the heat supplied to the reboiler and the fraction of the pulses for the reflow. The distillation column operates near to full reflow. After $t = 86$ min the fraction of reflow is set to 0.94, after $t = 127$, it is set to 0.88, and after $t = 179$ it is set to 0.79. The cooling water is kept within a range of 6.4-7.5 l/min. The environmental temperature was $30.3°C$ at the beginning of the test, and $26.1°C$ at the end of the test. No feeding flow is supplied.

Fig. 7 shows the experimental temperature profile along the column. Boiler starts at $t = 17$ min. As the vapor mixture ascends, other trays arrive to their bubble point condition. After the vapor arrives to the condenser, the reflow refreshes the trays. As the reflow is reduced, the temperature of the trays increases. After $t = 202$, when the heat to the reboiler is reduced, the trays become cooler; further reduction of heat to boiler at $t = 247$ stops boiling. After this condition the trays become cooler since they do not receive any steam.

Table 5. Profile of heat to reboiler

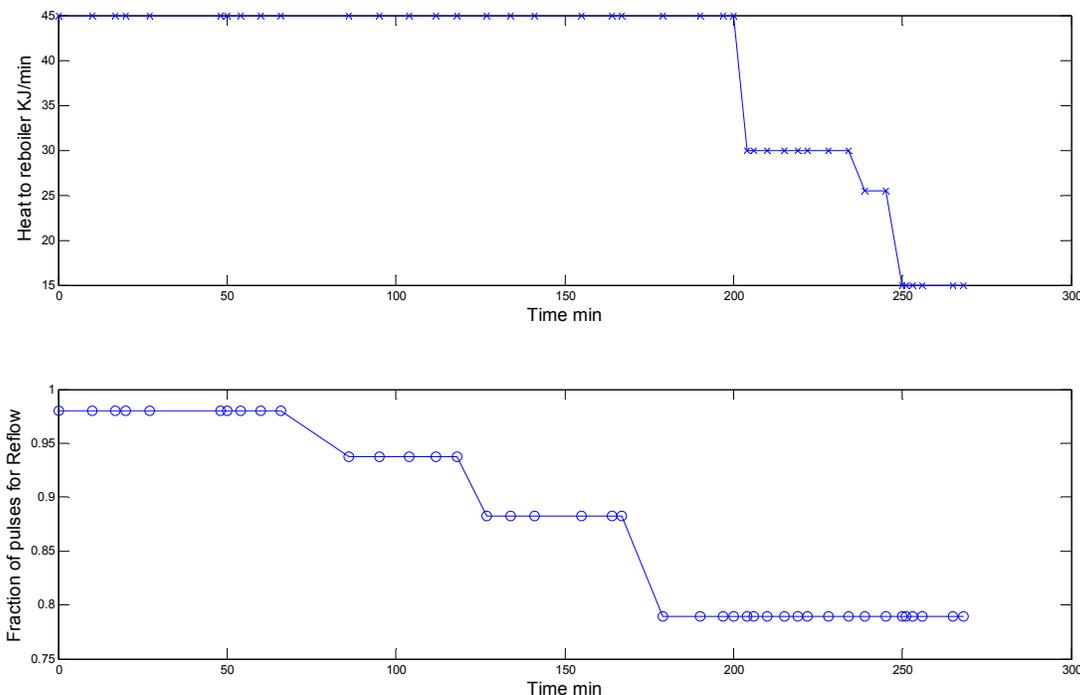| Time (min)	QB (J/ min)
0	45,000
202.1	30,000
236.9	25,740
247.3	15,020

Fig. 6: Heat supplied to reboiler and fraction of pulses for reflow in test 5.2
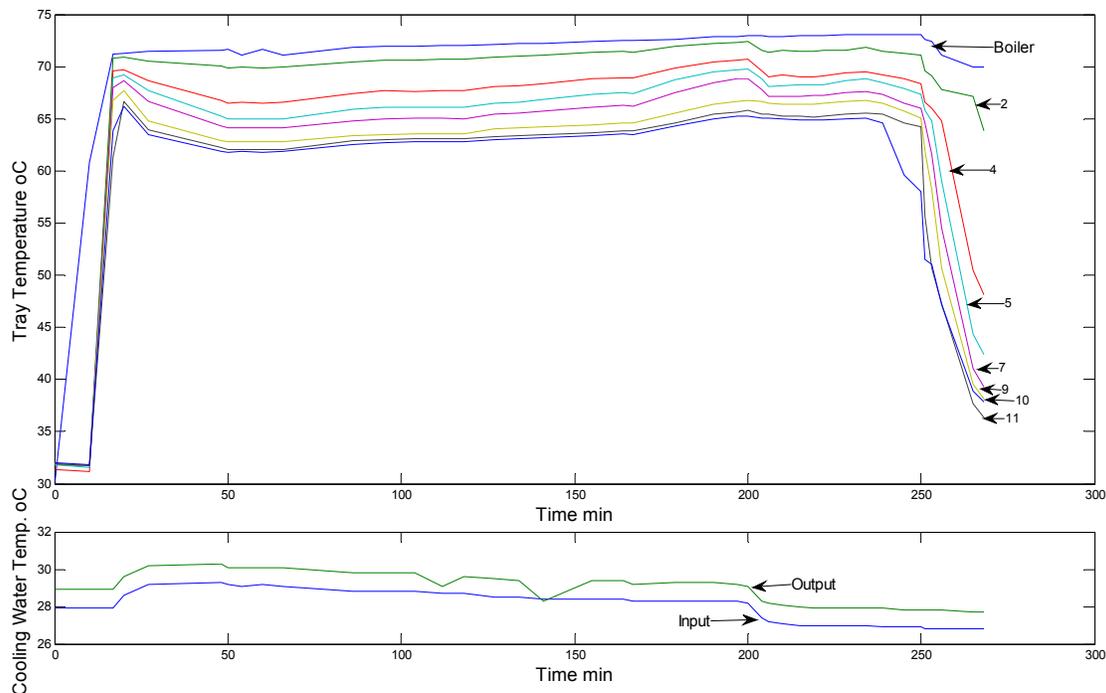
Fig. 7: Profile of temperatures along the distillation column. Top temperatures correspond to the Trays. Bottom Temperatures correspond to cooling water.
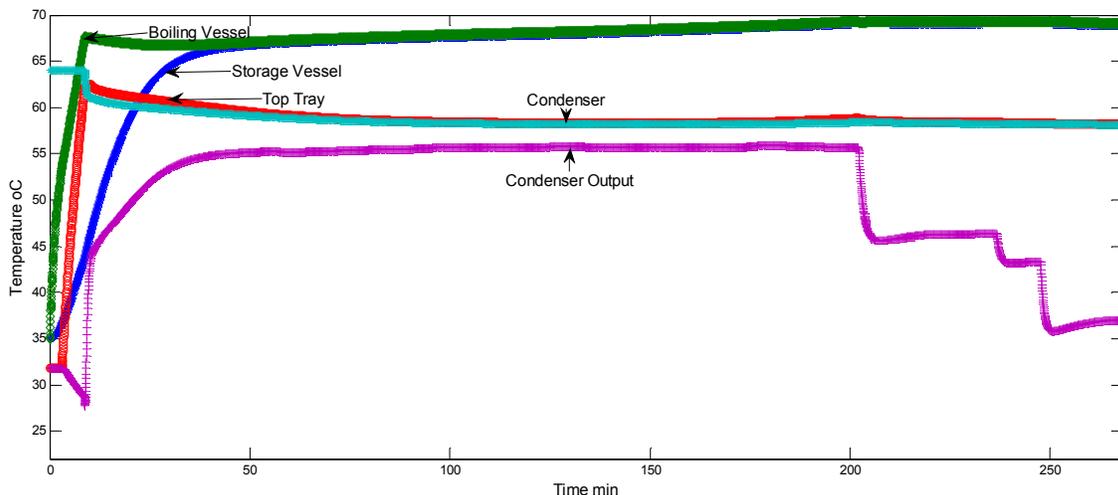

Fig. 8: Modeled profile of temperatures in the boiler and in the condenser.

In this figure, it is also observed that when steam arrives to the condenser, cooling water becomes warmer. The difference between input and output cooling water is around 1°C. As the reflow is reduced, output temperature is reduced, since the cooling stream receives less heat.

Fig. 8. presents the modeled temperature for: the boiler container, the storage vessel, the tray before the condenser, the condenser, and the condenser output. The estimated time for the boiling vessel is 12.5 min. The range of temperatures is similar to the experimental data,
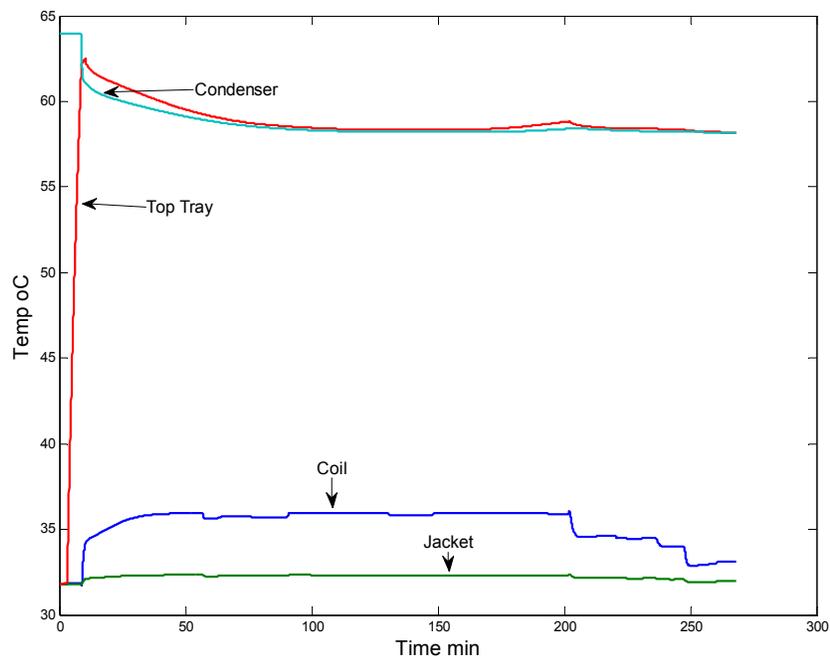
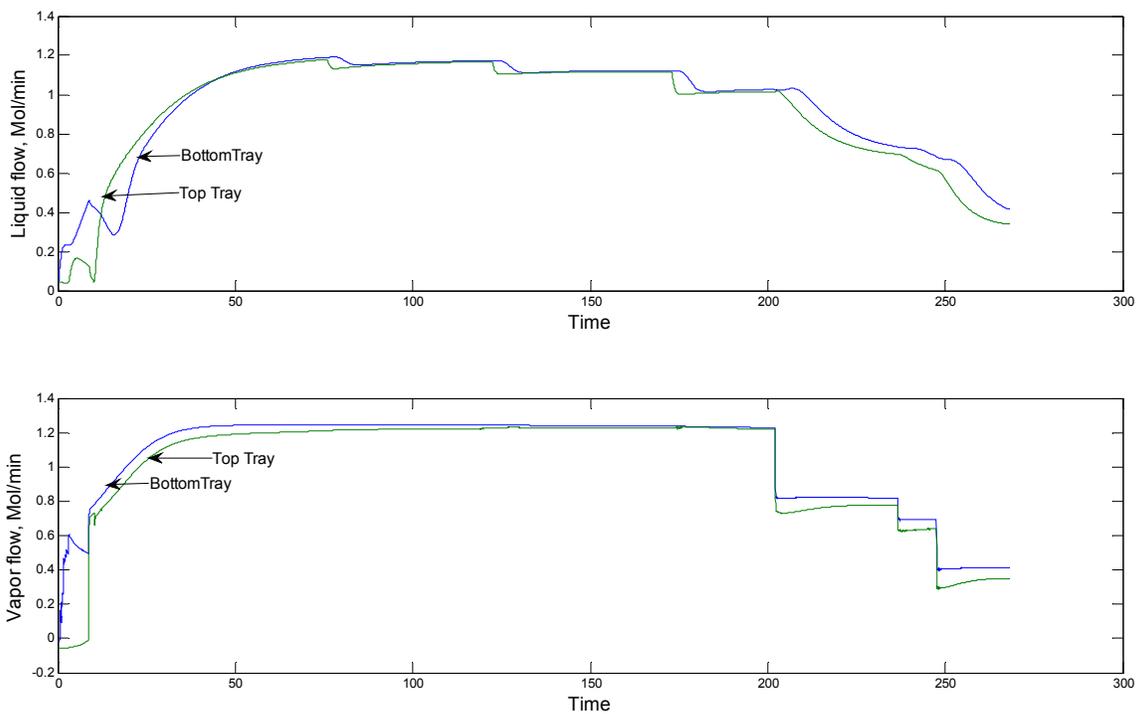Fig. 9: Modeled temperatures along the condenser, and cooling circuit.

Fig. 10: Modeled liquid and vapor flow behavior in top and bottom tray.

but the experimental results describe a faster cooling in the reboiler when the boiling heat is reduced. The condensate output temperature (only estimated) is very sensible to changes of heat reduction.

Fig. 9 presents the calculated profile of temperatures in the condenser and cooling water. The jacket temperature is cooler and more stable than the coil temperature. The effect heat reduction is appreciated more clearly after $t = 206$, when boiler heat is reduced.

Fig. 10 shows the calculated behavior of liquid and vapor flows at the bottom and at the top tray. The liquid flow increases from the initial conditions. The changes in the bottom tray are smoother than in the top tray. At $t = 10$ min the condenser receives vapor from the top tray. The vapor flow initially increases very fast. After $t = 40$ min the vapor flow increases steadily until $t = 200$ min, when the boiling heat decreases. At this condition, the vapor flow decreases. The response of the liquid flow to the boiling heat is slower, compared with the response of vapor flow, and it is also smoother.

We observed that the use of sub-cooling conditions provides a solution more stable than the use of saturation conditions in the condenser. When the same transient is executed including the sub-cooling, the oscillations are reduced.

6 Summary of results

The following paragraphs describe the quantitative results.

Boiler. The model of the boiler vessel and the storage vessel reduces the estimated boiling start-up time from 6-20 min to 1-6 min (according to the amount of reboiler heat). Adequate estimation of boiler holdup is important for the purity of the product, since higher boiling time drags the heavy components in the distilled product.

Column Body. The column model takes into account the heat losses. It has been found that 15 - 17% of the heat is lost in the environment for the given mixture.

Condenser. A model of a double section for the condenser was proposed. This array is represented by a second order. It promotes an agile response and, at the same time, it reduces oscillations in the condenser temperature of the distillation column. Models without this consideration require a large

mass-inertia to maintain stability under low loads of the column; but large mass-inertia causes a slow response. The cooling water changes around 1 °C; but it produces a subcooling of 15-18 °C at the given operating conditions. At these conditions the estimation of concentration from temperature represents a deviation of more than 10%.

Dynamic transients. The description of the semi-continuous stage is required for the consistent evaluation of the distillation process equations from start-up to continuous operation. These equations were solved by a DAE integrator.

Conclusions

A detailed model which takes into account the specific configuration of the boiler and the condenser was adapted to reduce plant/model mismatch of the distillation column. The configuration of the reboiler affects estimation of the vapor flow leaving from the reboiler. A model without this consideration has a narrow application, or it produces a time lead in its response.

To represent start-up and equilibrium conditions in trays, a formulation which preserves continuity and consistency of the solution of state variables was proposed. Stability is assured in the semicontinous range by the approximation of the pressure drop, and accuracy is assured in the continuous range by the description of the thermodynamic and configuration.

Monitoring additional operating conditions was relevant to improve the accuracy of the model.

Statistical analysis is required to tune some dynamics-related parameters to fit overall distillation column prediction; thus, this model becomes adequate for a model-based predictive control.

Acknowledgements

Nomenclature

A area
a parameter of the equation of state
B boiler container, boiler flow

B	parameter of the equation of state
C_p	heat capacity
D	distillated flow
E	energy
e	error
F	feed
f	fugacity
g	acceleration of gravity
h	height
K	constant, equilibrium constant
k	binary interaction parameter
K_v	valve constant
L	liquid flow
l	binary interaction parameter
M	mass hold up
M_w	molecular weight
P	pressure
Q	heat
r	prescribed trajectory of outputs
t	time
u	manipulated variable
U	overall heat transfer coefficient
V	vapor flow
W	control weights, cooling water flow
x	liquid composition
y	measured variables, vapor composition
z	feed composition, differential variables

Greek symbols

Δ	increment
ρ	density
φ	hold up effectiveness
η	Murphree tray efficiency
ε	small number
τ	dynamic related constant
Φ	function

Subscripts

a	algebraic
b	boiler vessel
B	bubble point
C	condenser
D	distillated
d	differential
Eff	effective
f	condition at the bottom of the tray
F	feeding
H	hydraulic
i	component
L	liquid
M	mixture
Jk	jacket

Hl	helical pipe
P	tray number
Sub	subcooling
v	valve
V	vapor
Wer	weir
$H2O$	water

Superscripts

$*$	equilibrium
Id	ideal gas
Dep	departure

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Appendix A. Model equations for the distillation column

Total mass

$$\frac{dM}{dt} = L_{p+1} + F_p - L_p - V_p + V_{p-1} \quad \text{(A.1)}$$

Component mass balance around tray p

$$\frac{d(Mx)}{dt} = L_{p+1}x_{p+1} + F_p z_p - L_p x_p - V_p y_p + V_{p-1}y_{p-1} \quad \text{(A.2)}$$

Total energy balance around tray p

$$\frac{d(M_p E_p)}{dt} = L_{p+1}E_{L,p+1} + F_p E_{F,p} - L_p E_{L,p}$$
$$- V_p E_{V,p} + V_{p-1}E_{V,p-1} + Q_p \quad \text{(A.3)}$$

The equilibrium equation is obtained by equating the liquid and vapor fugacities at the bubble point

$$f_{L,i}(T, P_b, x^*) = f_{V,i}(T, P_b, y^*) \quad \text{(A.4)}$$

$$\Phi(T, P, x) = P_b \left(\sum_1^n K_i x_i^* - 1 \right) = 0 \quad \text{(A.5)}$$

Also

$$\sum_i^n x_i = 1 \quad \text{(A.6)}$$

$$\sum_i^n y_i = 1 \quad \text{(A.7)}$$

$$E = E^{ig}(T, x^*) + E^{dep}(T, P, x^*) \quad \text{(A.8)}$$

Murphree tray efficiency

$$y_{p,i} = y_{p,i}^* \eta_V + (1 - \eta_V) y_{p-1,i}^* \quad \text{(A.9)}$$

Hydraulic equations for the trays. The liquid and vapor flow are evaluated by

$$L = \rho_L \frac{\sqrt{h_{eff}{}^3}}{K_{vL}} \quad \text{(A.10)}$$

$$h_{eff} = \max(0, h - h_{wer}) \quad \text{(A.11)}$$
$$h = M/A\rho_L$$

$$V = \frac{\sqrt{\Delta P \rho_V \text{Mw}_V}}{K_{vV}} \quad \text{(A.12)}$$

$$\Delta P = P_{p+1} + \varphi g h \rho_L - P_p \quad \text{(A.13)}$$

φ = two-phase factor suggested by Benett *et al.* (1983).

Condenser geometry:
To provide a small discharge at small volumes, and to avoid flooding, the condenser is built in such a way that flow increases rapidly as height increases. The following dependence of volume with respect to height was assumed:

$$V = V(h)_{cillinder} - V(h)_{Truncated\,volume}$$

$$V = \pi R^2{}_{cillinder} \left(h - \frac{h^{3/2}}{h_{ref}} \right) \quad \text{(A.14)}$$

Appendix B. Equation of state

$$P = \frac{\text{R} \cdot \text{T}}{\overline{\text{V}} - b} - \frac{a}{\overline{V}^2 + 2 \cdot b \cdot \overline{V} - b^2} \quad \text{(B.1)}$$

$$\text{a} = 0.45724 \frac{\text{R}^2 \cdot T_C^2}{P_C} \quad b = 0.077796 \frac{\text{R} \cdot \text{T}_C}{\text{P}_C} \quad \text{(B.2)}$$

The mixture properties are evaluated as:

$$a_M = \sum_{i=1}^N \sum_{j=1}^N x_i x_j a_{ij} \quad \text{(B.3)}$$

$$b_M = \sum_{i=1}^N \sum_{j=1}^N x_i x_j b_{ij} \quad \text{(B.4)}$$

Where

$$a_{ij} = \sqrt{a_i a_j}(1 - k_{ij}); \; \text{b}_{ij} = 0.5*(\text{b}_i + \text{b}_j)(1 - l_{ij}) \quad \text{(B.5)}$$

The value of the interaction parameters for this mixture minimize the deviation in the prediction of relative volatility, $k_{ij} = 0.01$; $l_{ij} = 0.017$

The compressibility factor $Z = \dfrac{P\bar{V}}{RT}$ is evaluated from the solution of:

$$Z^3 - (1 - B)Z^2 + (A - 2B - 3B^2)Z - (AB - B^2 - B^3) = 0 \quad \text{(B.6)}$$

$$A = \frac{a_M P}{R^2 T^2}; \quad B = \frac{b_M P}{RT} \quad \text{(B.7)}$$

The fugacity coefficient $\varphi_i = \dfrac{f_i}{x_i P}$ is obtained from

$$\ln \varphi_i = \frac{b_i}{b_M}(Z - 1) - \ln(Z - B)$$
$$- \frac{A}{2\sqrt{2}B} \left(\frac{2(x_1 a_{11} + x_2 a_{12})}{a_M} - \frac{b_1}{b_M} \right) \quad \text{(B.8)}$$
$$\ln \left[\frac{Z + (1 + \sqrt{2})B}{Z + (1 - \sqrt{2})B} \right]$$

The mixture enthalpy is obtained from

$$[E - E^*] = \int_v^\infty \left[-T\left(\frac{\partial P}{\partial T}\right)_v + P \right] dV + RT(Z - 1) \quad \text{(B.9)}$$

also

$$E^* = \left[\sum_{i=1}^N Cp_i (T_f - T_{ref}) x_i \right] - RT_{ref} \quad \text{(B.10)}$$