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# Dynamic modeling and simulation of an alembic pear wine distillation

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### ABSTRACT

In this research a phase equilibrium model to predict the recovery of several aroma compounds in spirits distilled in a traditional Charentais alembic has been developed. Due to the congeners' quasi-infinite dilution, the properties of the mixture are assumed to be dependent on the ethanol mole fraction only. Thus, the system is treated as a quasi-binary mixture; the ethanol recovery, the dynamics of the condensation and the heat transfer processes are modeled independently of the congener's concentration. The model was calibrated with laboratory data obtained during the elaboration of pear distillates. The concentration of ethanol and 15 congeners in the distillate were measured with gas chromatography during the experiments. Fitting just two parameters, one for heating power and one for heat loss, was sufficient to reproduce the experimental ethanol recovery curves. This allowed an accurate prediction of most of the congener's recovery curves. The prediction of five congeners, including acetaldehyde and methanol, are not significantly different from measured values. The prediction of the concentration of six congeners was biased but with relatively small errors (ranging between 8% and 25%). Significantly large prediction biases (more than 30%) were observed for ethyl hexanoate, ethyl decanoate and phenethyl alcohol.

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### 1. Introduction

Spirit beverages are produced around the world using a wide variety of raw materials through fermentation and subsequent distillation. Alembics are widely used for distillation in the production of various spirits, e.g., Brandy (Spain), Cognac (France), Whiskey (UK, Ireland), Cachaça (Brazil), Tequila (Mexico) and Pisco (Chile, Peru, Bolivia). Distillation is a method for separating substances of different volatility by evaporation and condensation. The spirits industry is undoubtedly capable of producing high quality beverages with the aid of its centuries-old experience. However, the global market demands new products, safer spirits, low prices and even higher quality favoring the presence of positive aromas while minimizing defects.

It is rather difficult to design new processes or products based on experience only. In turn, model based methods allow good designs in less time. Moreover, representative models are also useful to search for better operating strategies and to improve our understanding of the distillation process. Several models of spirits distillation with rectification columns either in batch (Osorio et al., 2004; Carvallo et al., 2011; Valderrama et al., 2012a,b) or continuous mode (Lora et al., 1992; Gaiser et al., 2002; Batista and Meirelles, 2011) have been published. However, modeling spirit distillation in a traditional alembic is a rare scientific subject. To the best of our knowledge, only

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### List of symbols

- $\dot{Q}_B$  net heat rate to the alembic bottom (boiler zone), W
- $N_B$  molar hold-up in the bottom, mol s<sup>-1</sup>
- $V_B \,$   $\,$  vapor flow from the bottom to the neck, mol  $s^{-1}$
- $\dot{Q}_C$  heat loss to the environment from the neck, W L liquid natural reflux flow from the neck to the
- bottom, mol s<sup>-1</sup>  $V_D$  vapor flow leaving the ascending part of the
- alembic neck (distillate flow), mol s<sup>-1</sup>
- $x_B$  ethanol molar fraction in the bottom liquid hold-up  $N_B$ , mol mol<sup>-1</sup>
- $y_B$   $$\ensuremath{\text{e}}$  ethanol molar fraction in the vapor flow  $V_B,$   $$\ensuremath{\text{mol}}\xspace{-1}$$
- $x_L$  ethanol molar fraction in the liquid reflux flow L, mol mol<sup>-1</sup>
- $\nu_B \qquad \ \ specific volume in the bottom liquid hold-up $N_B$, $m^3\,mol^{-1}$$
- $h_{\rm B}$  molar specific enthalpy in the bottom liquid hold-up N<sub>B</sub>, J mol<sup>-1</sup>
- $H_B$  molar specific enthalpy in the vapor flow  $V_B$ ,  $J \, mol^{-1}$
- $h_L$  molar specific enthalpy in the liquid reflux flow L, J mol<sup>-1</sup>
- $H_D$  molar specific enthalpy in the distillate flow  $V_D$ ,  $J \, mol^{-1}$
- $u_B$  molar specific internal energy in the bottom liquid hold-up N<sub>B</sub>, J mol<sup>-1</sup>
- P pressure, Pa
- k  $\,$  overall heat transfer coefficient, W  $m^{-2}\,K^{-1}$
- $k_B$  overall heat transfer coefficient between the boiling zone (bottom) and the environment,  $W\,m^{-2}\,K^{-1}$
- $k_C$  overall heat transfer coefficient between the condenser zone (neck) and the environment,  $W\,m^{-2}\,K^{-1}$
- A<sub>B</sub> surface area between boiling zone and ambient air, m<sup>2</sup>
- $A_C$  surface area between condenser zone and ambient,  $m^2$
- T<sub>B</sub> temperature in the boiling zone, K
- T<sub>C</sub> temperature in the condenser zone, K
- $T_{env}$  ambient temperature or temperature of the alembic's environment (laboratory), K
- $\alpha \qquad \qquad$ air side heat transfer coefficient, W $m^{-2}\,K^{-1}$
- $\lambda ~~$  thermal conductivity, W m  $^{-1}\,\text{K}^{-1}$
- Nu Nusselt number
- Gr Grashof number
- Pr Prandtl number
- Ra Rayleigh number, defined by  $Ra = Gr \cdot Pr$
- l characteristic length, m
- g gravity constant,  $m s^{-2}$
- $\nu$  kinematic viscosity, m s<sup>-2</sup>
- $\beta$  thermal expansion coefficient, K<sup>-1</sup>
- T<sub>0</sub> wall temperature, K
- a thermal diffusivity,  $m^2 s^{-1}$
- $\chi$  correction factor for condenser heat loss
- $\begin{array}{ll} x_{B,cong} & \mbox{ congener molar fraction in the bottom liquid} \\ & \mbox{ hold-up } N_B, \mbox{ mol} \mbox{ mol}^{-1} \end{array}$

УB,cong	congener molar fraction in the vapor flow $V_{\text{B}}\text{,}$ mol mol^{-1}
Х <sub>D,cong</sub>	congener molar fraction in the distillate flow $V_{\rm D},{\rm molmol^{-1}}$
K <sub>C,cong</sub>	congener partition coefficient in the condenser zone
K <sub>B,cong</sub> γcong	congener partition coefficient in the boiler zone congener activity coefficient
P <sup>LV</sup> <sub>0,cong</sub>	congener vapor pressure, Pa
$\overline{\overline{Q}}_{B}$	total (integrated) amount of energy that has
$\overline{\overline{V}}_{P}$	entered the alembic bottom, J total amount of vapor that has left the bottom
. <u>р</u>	from the beginning of the distillation, mol
V	transformed vapor flow rate, i.e., derivative of total amount of vapor that has left the bottom not with respect to time, but with respect to the delivered energy: $d\overline{V}_{R}(\overline{O}_{R})/d\overline{O}_{R}$
L <sup>*</sup>	transformed liquid natural reflux, i.e., deriva- tive of total amount of reflux that has entered the bottom not with respect to time, but with
V <sub>D</sub> *	respect to the delivered bottom energy $\overline{Q}_{B}$ , mol transformed distillate flow rate, i.e., derivative of total amount of distillate that has left the alembic neck not with respect to time, but with respect to the delivered bottom energy $\overline{\overline{Q}}_{B}$ , mol

one model has been published in the open literature regarding alembic distillation of Cachaça, a Brazilian sugar cane distillate (Scanavini et al., 2010, 2012).

To better understand the behavior of an alembic and provide guidance on how to operate it to maximize the spirit's quality and minimize toxic substances such as methanol and acetaldehyde (Carvallo et al., 2011; Lachenmeier and Sohnius, 2008), this article presents a simple model to predict the recovery of ethanol and several congeners in a traditional alembic.

### 2. Materials and methods

### 2.1. Experimental set up

The experimental distillation runs were performed in the copper Charentais alembic of 2L, shown in Fig. 1a. The raw material used in these distillations was 1.1L of pear distillate of 17.9%, v/v obtained from a prior first distillation. An electric heater was set to obtain an average distillation rate of 3 mL min<sup>-1</sup>. Three distillation runs were performed following the same procedure, where 600 mL of distillate was collected in successive samples; the first two of 25 mL and the rest of 50 mL. Once a distillation had finished, the alembic was allowed to cool down. Then, it was washed and left to dry before the next distillation was performed. Only one distillation was performed per day. For the analysis of the congener concentrations, the collected samples were mixed to larger fractions. Based on organoleptic analysis, the defined fractions are the following: head fraction (first 25 mL), heart fraction (25-300 mL), two tail fractions (tail 1 from 300 to 450 mL and tail 2 from 450 to 600 mL) and the residue (undistilled rest collected from the alembic bottom). The laboratory temperature was regulated between 23  $^\circ\text{C}$  and 24  $^\circ\text{C}$  and thus assumed

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Fig. 1 – Charentais alembic. (a) Photography of the 2L copper Charentais alembic used for the experimental distillation runs and (b) schematic representation of the basic alembic model.

23.5 °C in the simulations. Further details are given by Garcia-Llobodanin et al. (2007, 2011).

### 2.2. Analytical characterization

The different fractions – head, heart, tail 1, tail 2 and residue – were analyzed by gas chromatography (GC) to determine and quantify their main aromatic compounds and their ethanol content. The equipment employed was an Agilent 6890 series with a Flame Ionization Detector and an automatic injector appropriately attached to a HP Chemstation software (Agilent, Waldbron, Germany) for the data analysis. The detail of the method is described in Garcia-Llobodanin et al. (2007, 2011). The compounds determined were acetaldehyde, methyl acetate, acetal, ethyl acetate, methanol, 2-butanol, 1-propanol, 2-methyl-1-propanol, 1-butanol, ethyl hexanoate, 2-methyl-1-butanol, 3-methyl-1-butanol, furfural, ethyl decanoate and phenethyl alcohol.

### 2.3. Data validation

For the different collected samples, the mass and the alcoholic degree were measured. The transformation of these data to weight fractions reveals that the raw data does not comply with the total and ethanol component mass balances. The total mass balance error can be explained by a remaining liquid film at the inside of the alembic wall. The balance difference in the ethanol mass is assumed to be caused by external perturbations in the composition measurement (GC). Consequently, the experimental values are corrected to reconciled values which comply with the ethanol balance. The reconciled data results from an optimization algorithm where the compliance of the ethanol balance is imposed as an equality constraint whereas the alteration with respect to the raw data is minimized (Albuquerque and Biegler, 1996). Here, the data reconciliation is based on a mass balance, where the measured total masses are assumed to be exact and the mass fraction values (calculated from experimental volume fractions) are

corrected. The resulting optimization problem represents a least square minimization with linear constraints and is suitably performed with Matlab's *lsqlin* routine. Since the true values should comply with the material balances, the reconciled values are statistically more probable to represent the true ethanol mass fractions. The corrected mass fractions are converted to reconciled mole fractions and are further used to calculate the molar amount of the samples.

### 2.4. Modeling

#### 2.4.1. Model assumptions

The distillation is represented by two equilibrium stages as illustrated in Fig. 1b: alembic bottom (or boiler) and neck (or condenser). Due to the heat rate  $\dot{Q}_B$  (W), the liquid in the bottom N<sub>B</sub> (mol s<sup>-1</sup>) evaporates to produce a vapor flow V<sub>B</sub> (mol s<sup>-1</sup>) that ascends and contacts the neck where it is partially condensed due to a heat loss  $\dot{Q}_C$  (W) to the environment. The condensed liquid *L* (mol s<sup>-1</sup>) returns downwards as a reflux to the bottom, whereas the remaining vapor V<sub>D</sub> (mol s<sup>-1</sup>) passes to the descending part of the neck where it is totally condensed and collected as distillate.

The bottom  $N_B$  and the material streams  $V_B$ , L,  $V_D$  have ethanol molar fractions  $x_B$ ,  $y_B$ ,  $x_L$ ,  $y_D$  and specific enthalpies  $h_B$ ,  $H_B$ ,  $h_L$ ,  $H_D$  (J mol<sup>-1</sup>) respectively.

The model includes material and energy balances in the boiler and condenser (swan neck of the still). Since the holdup in the condenser is very small compared with the boiler holdup, its dynamics is neglected applying a pseudostationary approximation to the condenser balances. The influence of the congener concentrations on the energy balance is also neglected, i.e., the enthalpy of the distillate is approximated by the enthalpy of the water–ethanol mixture. Hence, the congener calculations have no effect on the integration of the set of energy and ethanol–water material balance equations. This subset of equations therefore represents a *quasi-binary* model of an ethanol–water system which is solved independently of the congeners.

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The vapor liquid equilibrium (VLE), in turn, is predicted from Raoult's law, where the gas phase is considered to behave ideally and UNIFAC is used to model the congener's concentrations in the liquid and vapor phases. The pressure in the system has been considered constant (1 atm), since the pressure drop in the alembic is negligible.

## 2.4.2. Quasi-binary equations (energy and ethanol–water material balances)

As a result of the assumptions described above, the set of energy and ethanol–water material balances is independent of the congener equations. The following three differential equations describe the boiler dynamics:

$$\frac{dN_{\rm B}}{dt} = L - V_{\rm B} \tag{1}$$

$$\frac{d(N_B x_B)}{dt} = L x_L - V_B y_B \tag{2}$$

$$\frac{d(N_B u_B)}{dt} = Lh_L - V_B H_B + \dot{Q}_B$$
(3)

Due to the pseudo-stationary approximation, the condenser is represented by three algebraic equations:

$$0 = V_B - L - V_D \tag{4}$$

$$0 = V_B y_B - L x_L - V_D y_D \tag{5}$$

$$0 = V_B H_B - L h_L - V_D H_D - \dot{Q}_C$$
(6)

This system of equations is written in a simplified form using the following relations:

$$\frac{dx_{\rm B}}{dt} = \frac{1}{N_{\rm B}} (L(x_{\rm L} - x_{\rm B}) - V_{\rm B}(y_{\rm B} - x_{\rm B})) \tag{7}$$

$$u_{\rm B} = h_{\rm B} - v_{\rm B} P \approx h_{\rm B} \tag{8}$$

$$\frac{dh_{B}(\mathbf{x}_{B}, T_{B}(\mathbf{x}_{B}))}{dt} = \frac{\partial h_{B}}{\partial \mathbf{x}_{B}} \frac{d\mathbf{x}_{B}}{dt} + \frac{\partial h_{B}}{\partial T_{B}} \frac{\partial T_{B}}{\partial \mathbf{x}_{B}} \frac{d\mathbf{x}_{B}}{dt}$$
$$= \frac{d\mathbf{x}_{B}}{dt} \left(\frac{\partial h_{B}}{\partial \mathbf{x}_{B}} + \frac{\partial h_{B}}{\partial T_{B}} \frac{\partial T_{B}}{\partial \mathbf{x}_{B}}\right)$$
(9)

It should be noticed that in Eq. (3) energy is balanced and not enthalpy, which is not a conservative quantity. This is why the time derivative of the systems internal energy is found on the left hand side. The enthalpy flows on the right hand side represent energy flows that comprise the transport of internal energy and compression work. Eq. (8) is the definition of enthalpy which relates it to the specific internal energy  $u_B$ . Since for liquids the specific volume v is very small, the term v P can be neglected. Consequently, the internal energy and enthalpy are approximately equal, which is often assumed for liquids when energy balances are formulated in the literature.

The resulting equation system is formed by Eqs. (1), (4)–(7) and the following Eq. (10):

$$(L(x_L - x_B) - V_B(y_B - x_B)) \left( \frac{\partial h_B}{\partial x_B} + \frac{\partial h_B}{\partial T_B} \frac{\partial T_B}{\partial x_B} \right) = L(h_L - h_B)$$
  
- V\_B(H\_B - h\_B) +  $\dot{Q}_B$  (10)

This system includes two differential equations and four algebraic equations. The differential algebraic equation system (DAE) is solved with Matlab's solver *ode*15s and solving the algebraic variables in terms of the differential variables ( $x_B$ ,  $N_B$ ) at each time step. For the variable  $x_L$  (liquid composition in condenser) this is only possible with an iterative procedure since the thermodynamic VLE equations depend on  $x_L$  ( $H_D$ ,  $h_L$ ,  $y_D$ ).

Specifically, the four algebraic equations are reduced to one equation. The three algebraic variables  $V_D$ ,  $V_B$  and L are expressed as explicit functions of  $x_L$  using Eqs. (4)–(6):

$$V_{\rm B}(x_{\rm L}) = \frac{\dot{Q}_{\rm c}((H_{\rm D} - h_{\rm L})/(x_{\rm L} - y_{\rm D}))}{(h_{\rm B} - H_{\rm D}) + ((y_{\rm B} - y_{\rm D})/(x_{\rm L} - y_{\rm D}))(H_{\rm D} - h_{\rm L})}$$
(11)

$$L(x_{\rm L}) = \frac{-\dot{Q}_{\rm c}((H_{\rm D} - h_{\rm B})/(y_{\rm B} - y_{\rm D}))}{(h_{\rm L} - H_{\rm D}) + ((x_{\rm L} - y_{\rm D})/(y_{\rm B} - y_{\rm D}))(H_{\rm D} - h_{\rm B})}$$
(12)

$$V_D(x_L) = V_B(x_L) - L(x_L)$$
 (13)

Using Eqs. (11)–(13),  $V_D$ ,  $V_B$  and L are substituted in Eq. (10) to give a single equation, which implicitly contains one algebraic unknown  $x_L$ . This equation is solved iteratively using Matlab's *fsolve* routine to calculate  $x_L$  with the given differential unknowns  $x_B$  and  $N_B$ . With the found liquid composition  $x_L$ , the remaining three algebraic variables are calculated using Eqs. (11)–(13).

The model also includes the heat transfer rates  $\dot{Q}_B$  and  $\dot{Q}_C$ , which could not be directly measured. For the treatment of this heat transfer two model variations are used as explained next.

### 2.4.3. Heat transfer model

Two model variations are considered that differ in the representation of the heat transfer rates  $\dot{Q}_C$  and  $\dot{Q}_B$ .

- Constant heat rates (Model 1): both the net heat rate to the boiling zone  $\dot{Q}_B$  and the heat losses in the neck  $\dot{Q}_C$  are simply held constant and represent two fitting parameters.
- Predicted heat rates (Model 2):  $\dot{Q}_B$  is the net heat flow to the boiler which is the difference between the constant heat flow from the electric heater,  $\dot{Q}_{B,const}$  (W), and the boiler heat loss to the environment. The heat loss in the condenser (neck) and the boiling heat both vary in time due to the changing liquid level and driving temperature differences. The corresponding expressions for the heat rates are:

$$\dot{Q}_{B} = \dot{Q}_{B,const} - k_{B}A_{B}(T_{B} - T_{env})$$
(14)

$$\dot{Q}_{C} = k_{C}A_{C}(T_{C} - T_{env}) \tag{15}$$

where  $k_B$ ,  $k_C$ ,  $A_B$ ,  $A_C$ ,  $T_B$ ,  $T_C$  and  $T_{env}$  are respectively the heat transfer coefficient in the boiling zone (W m<sup>-2</sup> K<sup>-1</sup>), heat transfer coefficient in the condenser zone (W m<sup>-2</sup> K<sup>-1</sup>), boiler area (m<sup>2</sup>), condenser area (m<sup>2</sup>), boiler temperature (K), condenser temperature (K) and ambient temperature (K).

In the predictive model both the heat exchange areas and the heat transfer coefficients depend on the alembic geometry, which is why a detailed analysis of the geometry was done. As shown in Fig. 2 the alembic shape is divided into

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Fig. 2 – Scale drawing of the geometric model used for the area and heat exchange calculations (all length specifications in mm). The dotted lines represent the assumed inclinations of the heat exchange areas.

seven basic geometrical sections: two spheroidal (sections II and IV), one cylindrical (section III), and three conical segments (sections I, V and VI) and one bent cylindrical (section VII). These are further subdivided into 16 heat exchange areas of different inclination angles. According to this geometry, at each time step the magnitudes of both the bottom area  $A_B$  and the condenser area  $A_C$  are recalculated, as the liquid level is decreasing in time. Likewise, the heat transfer coefficients are recalculated at each time step, because they depend on the varying temperature according to natural convection correlations. Neglecting the heat transfer resistance inside the alembic and the copper wall, the heat transfer coefficient *k* is equal to the air side heat transfer coefficient *a* (W m<sup>-2</sup> K<sup>-1</sup>):

$$k = \alpha = \frac{\operatorname{Nu}\lambda}{l} \tag{16}$$

where l (m) is the overflow length and  $\lambda$  (W m<sup>-1</sup> K<sup>-1</sup>) is the thermal conductivity. The Nusselt number (Nu) is calculated by the correlations in Table 1 that depend on the geometrical

shape and inclination angle of each area (VDI-Wärmeatlas, 2006, chapter F).

The Nusselt number (Nu) is a function of the Grashof (Gr) and Prandtl (Pr) numbers and of the surface angle ( $\phi$ ). The Grashof number is defined by:

$$Gr = \frac{gl^3}{\nu^2}\beta(T_0 - T_{env})$$
(17)

with the gravity constant g (m s<sup>-2</sup>), characteristic length l (m), kinematic viscosity v (m s<sup>-2</sup>), thermal expansion coefficient  $\beta$ (1/K), wall temperature  $T_0$  (K) and the ambient temperature  $T_{env}$  (K).

The Prandtl number is defined by the ratio between the thermal diffusivity  $a (m^2 s^{-1})$  and the kinematic viscosity v:

$$Pr = \frac{a}{v} \tag{18}$$

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Table 1 – Correlations of the Nusselt number used for the different geometries taken from VDI-Wärmeatlas (2006, chapter F).					
Geometry	Correlation	Areas applied			
Plate with heat flowing downwards and inclination angle $0^{\circ} \le \phi \le 60^{\circ}$ , includes vertical plates and vertical cylinders	Nu = $(0.825 + 0.387(Gr \cdot cos(\phi)Pr \cdot f_1(Pr))^{1/6})^2$ where $f_1(Pr) = (1 + (0.492/Pr)^{9/16})^{-16/9}$	2ª, 3, 7, 8, 9, 13, 14, 15, 16			
Inclined plate with heat flowing upwards and $0^\circ \le \phi \le 60^\circ$	IF Ra = Gr Pr > Ra <sub>crit</sub> ( $\phi$ ) THEN turbulent flow: Nu = 0.56(Ra <sub>crit</sub> cos( $\phi$ )) <sup>1/4</sup> + 0.13(Ra <sup>1/3</sup> <sub>crit</sub> + Ra <sup>1/3</sup> ) where the critical Rayleigh number is log Ra <sub>crit</sub> = 3.888 - 0.00346 $\phi^{1.5}$ - 0.000375 $\phi^2$ + 0.00547 $\phi^{0.5}$ with $\phi$ in rad. ELSE laminar flow: calculate like plate with heat flowing downwards	2ª, 4, 5, 6, 10, 11, 12			
Horizontal cylinder	Nu = $(0.752 + 0.387(Gr \cdot \cos(\phi)Pr \cdot f_3(Pr))^{1/6})^2$ where $f_3(Pr) = (1 + (0.559/Pr)^{9/16})^{-16/9}$	1			

<sup>a</sup> Area 2 represents an inclined cylinder. Since no correlation for this geometry was found in literature, Area 2 was further subdivided into subareas representing different inclined plates.

Given that the theoretical estimation of heat transfer coefficients has a degree of significant uncertainty, heat transfer coefficients are multiplied by a constant correction factor  $\chi$ :

$$k = \chi \cdot (k)_{\text{predicted}} \tag{19}$$

Hence, the equations for the predicted heat rates assume the form:

$$Q_{B} = Q_{B,const} - \chi \cdot k_{B,predicted}(t)A_{B}(t)(T_{B} - T_{env})$$
(20)

 $Q_{C} = \chi \cdot k_{C, predicted}(t) A_{C}(t) (T_{C} - T_{env})$ (21)

and contain the two parameters  $Q_{B,const}$  and  $\chi$ .

#### 2.4.4. Binary model parameter fitting

Both model variations contain parameters which are fitted to the (reconciled) experimental ethanol recovery data obtained according to Section 2.3. That is, with a given set of parameters the models generate theoretical ethanol recovery time curves. With Matlab's optimizer *fminsearch* parameters are found such that the difference between model predictions and experimental data are minimized using the following objective function:

$$f_{obj} = \sum \frac{(y_{D,i} - y_{D,i}^{exp})^2}{\bar{y}_D^2} + \sum \frac{(N_{D,i} - N_{D,i}^{exp})^2}{\bar{N}_D^2}$$
(22)

where  $y_{D,i}^{exp}$ ,  $N_{D,i}^{exp}$ ,  $y_{D,i}$ ,  $N_{D,i}$  are respectively the experimental and simulated ethanol molar fraction and the total molar amount of the ith sample of the distillation run. The sum of squared differences is weighted with the mean distillate mole fraction  $\bar{y}_D$  and mean sample molar amount  $\bar{N}_D$ .

Here it has to be pointed out that the predicted distillate flow concentrations  $y_{D,i}$  are not the instant distillate concentrations at the experimental times where distillate samples were withdrawn (as explained in Section 2.1). Each experimental concentration corresponds to one of the withdrawn distillate samples. It thus represents an average concentration of the distillate flow leaving the system at the corresponding time interval where the sample was collected. Thus  $\boldsymbol{y}_{\text{D},i}$  is calculated as

$$y_{D,i} = \frac{\Delta N_{D,eth}}{\Delta N_D} = \frac{N_{D,eth}(t_{exp,i}) - N_{D,eth}(t_{exp,i-1})}{N_D(t_{exp,i}) - N_D(t_{exp,i-1})}$$
(23)

with the total collected distillate amount  $N_D$  and the total collected distillate ethanol amount  $N_{D,eth}$ . In the simulations the predicted ethanol amount is calculated by adding to the system another two differential equations:

$$\frac{d(N_D)}{dt} = V_D \tag{24}$$

$$\frac{d(N_{D,eth})}{dt} = y_D V_D$$
(25)

where  $N_D$  and  $N_{D,eth}$  are integrated as two additional differential variables.

#### 2.4.5. Congener modeling equations

As explained above, given the extremely low concentrations of the congeners, it is assumed that they do not influence the equilibrium temperature, enthalpy or any other physical property of the mixture. Therefore, the energy balance is not changed and the quasi-binary ethanol–water system is integrated independently of the congeners. The simulation of each congener is just added to the model through the respective mass balance.

The boiler component balance is:

$$\frac{d(N_B x_{B,cong})}{dt} = L x_{L,cong} - V_B y_{B,cong}$$
<sup>(26)</sup>

and the condenser component balance is:

$$0 = V_B y_{B,conq} - L x_{L,conq} - V_D y_{D,conq}$$
(27)

where  $x_{B,cong}$ ,  $y_{B,cong}$  and  $x_{D,cong}$  are the congener's molar fraction in the bottom, vapor stream  $V_B$  and the distillate stream  $V_D$  respectively.

The thermodynamic equilibrium relationships are:

$$y_{D,cong}(x_{L,cong}) = K_{C,cong} x_{L,cong}$$
<sup>(28)</sup>

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Fig. 3 – Ethanol recovery curves: experimental ethanol molar fraction ( $\bigcirc$ ), experimental distillate molar amount ( $\triangle$ ), simulation with constant heat rates (dashed line: - - -), simulation with predicted heat rates (solid line: —). The position of the ethanol molar fractions on the time axis is the middle of the time interval corresponding to the respective collected sample.

and

$$y_{B,cong}(x_{B,cong}) = K_{B,cong}x_{B,cong}$$
<sup>(29)</sup>

with the partition coefficient in the condenser  $K_{C,cong}$  and in the bottom  $K_{B,cong}$ . Eqs. (26) and (27) can be transformed using the total mass balance (1) and the equilibrium relations (28) and (29) to yield

$$\frac{dx_{B,cong}}{dt} = \frac{1}{N_B} \left( L \left( \left. x_{L,cong} \right|_{x_{B,cong}} - x_{B,cong} \right) - V_B \left( \left. y_{B,cong} \right|_{x_{B,cong}} - x_{B,cong} \right) \right)$$
(30)

and

$$x_{L,cong} = \frac{V_B K_{B,cong} x_{B,cong}}{L + V_D K_{C,cong}}$$
(31)

Hence, with each congener one more differential variable,  $x_{B,cong}$ , is added to the system and integrated by one additional differential Eq. (30). All additional variables are calculated by explicit algebraic equations.

#### 2.4.6. Congener equilibrium relationship

The equilibrium constant is calculated by the extended Raoult's law:

$$y_{cong}P = x_{cong}P_{0,cong}^{LV}\gamma_{cong}.$$
(32)

Thus, the partition coefficient is

$$K_{cong} = \frac{y_{cong}}{x_{cong}} = \frac{P_{0,cong}^{LV} \gamma_{cong}}{P}.$$
(33)

Activity coefficients were calculated using the UNIFAC group contribution method. Since activity coefficients in

general are a property of the mixture, the quasi-binary assumption also applies here: the activity coefficient only depends on the ethanol concentration; it assumes the value of infinite dilution in a water–ethanol mixture rendering the partition coefficient as a function of only the ethanol fraction:

$$K_{cong} = \frac{y_{cong}}{x_{cong}} = \frac{P_{0,cong}^{LV}(x_{Eth})\gamma_{cong}(x_{Eth})}{P} = K_{cong}(x_{Eth})$$
(34)

### 3. Results and discussion

#### 3.1. Quasi-binary models

Fig. 3 represents the experimental values of the total molar amount distilled and the ethanol molar fractions for the three runs as well as the respective fitted curves of the two heat transfer models explained in Section 2.4.2. Table 2 shows the fitted parameters and the objective function values for both binary models for each experimental distillation run.

#### 3.1.1. Heat ratio

Let the heat ratio be defined as the ratio between the boiler and condenser heat:

$$r_{\rm Q} \equiv \frac{\dot{Q}_{\rm C}}{\dot{Q}_{\rm B}} \tag{35}$$

The basic model inherently implies that distillations with the same heat ratio will produce the same ethanol recovery curves, as explained below.

Let  $\overline{Q}_B$  be defined as the total amount of energy that has entered the alembic bottom from the beginning of the distillation; its derivative is the bottom heat rate  $d\overline{\overline{Q}}_B/dt = Q_B$ . Since the heat rate is always greater than zero throughout the distillation,  $\overline{\overline{Q}}_B(t)$  is a strictly monotonous function of time; hence, the inverse function  $t(\overline{\overline{Q}}_B)$  and derivative  $dt/d\overline{\overline{Q}}_B$  exist. Conse-

Table 2 – Objective function values and fitted parameters for the two models and each distillation run.							
Model	Constant heat rates				Predicted heat rates		
Run #	Objective function	Boiling heat rate $Q_B$ (W)	Neck heat losses Q <sub>C</sub> (W)	Neck/boiler heat rate ratio $r_Q = Q_C/Q_B$	Objective function	Boiling heat rate $Q_B$ (W)	Correction factor $\chi$
1	0.031	119.7	27.0	0.225	0.0310	132.2	0.662
2	0.038	121.7	26.5	0.218	0.0210	135.8	0.671
3	0.022	99.6	23.4	0.234	0.0044	112.3	0.597

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quently, the whole set of Eqs. (1), (4)–(7), (10), (24) and (25) can be multiplied by  $dt/d\overline{Q}_B$ . This has the effect that the independent coordinate, time, is eliminated and the equation system is based on a new independent coordinate in terms of the delivered bottom energy  $\overline{Q}_B$ . Specifically, one can define  $\overline{\overline{V}}_B(t)$ as the total amount of vapor that has left the bottom from the beginning of the distillation and hence V<sub>B</sub> is its derivative  $d\overline{\overline{V}}_B/dt$ . In the new equation system, this term becomes a transformed mass flow V<sub>B</sub><sup>\*</sup> related to the new independent coordinate  $\overline{\overline{Q}}_B$ :

$$V_{B} \cdot \frac{dt}{d\overline{\overline{Q}}_{B}} = \frac{d\overline{\overline{V}}_{B}}{dt} \cdot \frac{dt}{d\overline{\overline{Q}}_{B}} = \frac{d\overline{\overline{V}}_{B}}{d\overline{\overline{Q}}_{B}} \equiv V^{*}$$
(36)

With analogous definitions of  $L^*$  and  $V_D^*$  the transformed equation system assumes the following form:

$$\frac{dN_B}{d\overline{Q}_B} = L^* - V_B^* \tag{37}$$

$$\frac{d(x_B)}{d\overline{\overline{\mathbb{Q}}}_B} = \frac{1}{N_B} (L^*(x_L - x_B) - V_B^*(y_B - x_B))$$
(38)

$$\begin{aligned} \left(L^*(x_L - x_B) - V_B^*(y_B - x_B)\right) \left(\frac{\partial h_B}{\partial x_B} + \frac{\partial h_B}{\partial T_B}\frac{dT_B}{dx_B}\right) &= L^*(h_L - h_B) \\ &- V_B^*(H_B - h_B) + 1 \end{aligned}$$
(39)

$$0 = V_B^* - L^* - V_D^*$$
 (40)

$$0 = V_B^* y_B - L^* x_L - V_D^* y_D$$
(41)

$$0 = V_B^* H_B - L^* h_L - V_D^* H_D - r_Q$$
(42)

$$\frac{dN_D}{d\bar{Q}_B} = V_D^* \tag{43}$$

$$\frac{dN_{\rm D,eth}}{d\bar{\bar{Q}}_{\rm B}} = y_{\rm D} V_{\rm D}^* \tag{44}$$

In the bottom energy balance (39) the heat transfer term becomes a constant equal to one and in Eq. (42) the condenser heat rate  $\dot{Q}_{\rm C}$  becomes the heat ratio  $r_{\rm Q}$ , which is the only heat transfer parameter influencing the solution of the model. Therefore, it is clear, that any distillation with the same heat ratio will give the same ethanol fraction versus distillation amount profiles.

#### 3.1.2. Constant heat rates (Model 1)

Despite its simplicity, Model 1 shows a good representation of the data (Fig. 3). In the distillate-time curves  $N_D(t)$  of the three runs (Fig. 3) it can be seen that run 3 is slower than runs 1 and 2 due to a smaller heating power. The heat loss in the neck  $\dot{Q}_C$  depends on the system temperature which should be similar in the three runs. Hence, it should be expected that the heat loss rate would be the same, resulting in distinct heat ratios and distinct ethanol recovery curves (as explained in the previous Section 3.1.1). However, the ethanol recovery curves are very much alike (see Fig. 4), therefore, heat ratios are the same (Table 2) and  $\dot{Q}_C$  for run 3 is smaller. We explain this behavior below.



Fig. 4 – Ethanol recovery curves over the distillate amount: run #1 ( $\bigcirc$ ), run #2 (+) and run #3 ( $\Diamond$ ).

#### 3.1.3. Predicted heat rates (Model 2)

Model 2 (Fig. 3 and Table 2) is more accurate than Model 1, since it considers the effect of temperature in the heat transfer prediction. As the less volatile component, water, is enriched in the bottom during the distillation, temperature increased over time. Consequently, the heat loss and reflux increase, lowering the distillation rate (see Fig. 3). This behavior can be reproduced by Model 2 only. In addition, larger reflux rates produce higher ethanol concentrations in the distillate. The discrepancy between the models regarding this behavior can be observed in the ethanol molar fraction of the distillate from about 60 min of distillation, where Model 2 achieves a better representation. In the distillation run 1, the difference between the models is smaller (similar values of objective functions), because the electric heater had a less stable heat supply.

The correction factors of 66%, 67% and 60% for the runs 1, 2 and 3 (see Table 2) indicate that the real heat loss is lower than suggested by the natural convection correlations. A possible explanation on the discrepancy could be that the plate of the electric heater warmed up the effective ambient temperature around the alembic. Hence, the correction factor in fact corrects the temperature difference:

$$\Delta T_{effective} = \chi (T_o - T_{env}) \tag{45}$$

This also explains why the heat loss  $\dot{Q}_C$  for the slower run 3 is smaller, since lower heating powers induce lower convective air streams around the alembic, reducing the heat transfer.

Further experiments have to be done in order to investigate this complex heat exchange behavior, where the goal should be to eliminate the correction factor as an adjustable parameter and consequently enhance the predictability of the model.

### 4. Congener prediction

Here, Model 2 is used since it more accurately fits the ethanol recovery curves. Fig. 5 shows a comparison of the simulated congener concentration curves and the experimental data for run 1; the curves of the other runs are similar. The profiles of the congener concentrations in the different fractions (head, heart, tail 1, tail 2 and residue) are correctly predicted for most



Fig. 5 – Congener concentrations (distillation run 1): predicted values (■) and experimental data (□) in the fractions: head (HD), heart (HT), tail 1 (TL1), tail 2 (TL2) and residue (RES). The position on the distillate axis is the middle of the distillate interval that corresponds to the respective fraction.

congeners and most fractions. The head fraction presents the greatest discrepancy between experimental and simulated values. In turn, as seen in Table 3, the heart fraction predictions are quite accurate. Table 3 also shows the results of a two-tailed t-test with critical t-values (at a 5% significance level) assuming unequal variances (Matlab's ttest2 function) and interpreting the three runs as a triple replicate.

Five predictions are not significantly different from measured values, acetaldehyde, acetal, methanol, ethyl hexanoate and 3-methyl-1-butanol. For high alcohols, such as 1-propanol, 2-methyl-1-propanol, 2-methyl-1-butanol and 1-butanol, the observed biases are statistically significant although relatively small (ranging between 9% and 25%). Other important compounds that negatively affect spirits quality – methyl acetate, ethyl acetate and furfural – are also predicted with relatively small errors: 8%, 23% and 20% respectively. Significantly large prediction biases (more than 30%) are observed for ethyl hexanoate, ethyl decanoate, phenethyl alcohol and 2-butanol. However, the latter is not distilled in the heart, and the model correctly predicts that its concentration is extremely low.

An important result of the simulation is that the trend of the different type of aromas is correctly reproduced, where some congeners show maximum concentration in the head

Table 3 – Average mole fractions in the heart fraction (25–300 mL) of the three distillation runs compared to the predicted values.								
Congeners	Experimental		Simulation		Degrees of freedom	t-Value	Critical t-value (two tail)	Deviation (%)
	Average (mol/mol)	StandDev (mol/mol)	Average (mol/mol)	StandDev (mol/mol)				
Acetaldehyde	1.27E-04	2.03E-05	1.73E-04	4.21E-06	2	3.8	4.3	27
Methyl acetate	8.18E-06	5.14E-07	1.07E-05	2.70E-07	3	7.6	3.2	24
Acetal	4.03E-06	8.29E-07	5.50E-06	1.45E-07	2	3.0	4.3	27
Ethyl acetate	2.61E-05	9.89E-07	2.83E-05	7.70E-07	4	3.1	2.8	8
Methanol	4.96E-03	1.45E-04	4.90E-03	8.03E-05	3	-0.6	3.2	-1
2-Butanol	0.00E+00	0.00E+00	7.94E-08	2.07E-09	2	66.4	4.3	100
1-Propanol	1.03E-04	1.59E-06	1.38E-04	3.27E-06	3	16.5	3.2	25
2-Methyl-1-propanol	1.09E-04	3.74E-06	1.20E-04	3.15E-06	4	3.9	2.8	9
1-Butanol	6.30E-06	2.97E-07	7.26E-06	1.75E-07	3	4.8	3.2	13
Ethyl hexanoate	4.74E-07	1.15E-07	1.93E-07	1.01E-08	2	-4.2	4.3	-145
2-Methyl-1-butanol	6.08E-05	2.17E-06	6.75E-05	1.80E-06	4	4.1	2.8	10
3-Methyl-1-butanol	3.30E-04	1.21E-05	3.53E-04	9.30E-06	4	2.6	2.8	6
Furfural	2.13E-06	1.00E-07	1.80E-06	1.26E-08	2	-5.6	4.3	-18
Ethyl decanoate	1.15E-07	7.26E-09	5.44E-08	3.19E-09	3	-13.3	3.2	-112
Phenethyl alcohol	8.55E-07	1.59E-08	3.56E-06	3.25E-08	3	129.5	3.2	76

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fraction and others in the heart fraction (e.g., furfural). Hence, the model not only gives answers to quantitative questions but also answers to qualitative questions such as whether some operating decisions favor one or another aroma. Thus, the simulation of this model is useful to explore operating strategies to tailor the aroma composition of pear spirits. However, the VLE models of some congeners should be studied further in order to achieve even more reliable predictions. The alembic model above and that presented in Scanavini et al. (2010) consider two equilibrium stages: heat loss by natural convection and negligible hold-up in the neck. However, Scanavini et al. (2010) measured the amount of total distillate recovered over time and used it as input for the simulations, which is an indirect way of specifying the varying heating power. In turn, in Scanavini et al. (2012) an insulated alembic was used and a fixed average heat input and no reflux was considered in the simulations. By contrast, in our model, the varying heating power is predicted. In Scanavini et al. (2010, 2012), seven congeners were measured and simulated, which except for acetic acid are also included here. With our model six of these components (1-propanol, methanol, ethyl acetate, acetaldehyde, 2-methyl-1-propanol and 3-methyl-1-butanol) were predicted more accurately. Both our model and those of Scanavini et al. (2010, 2012) achieve more accurate predictions for the heart fractions, whereas the uncertainty in the head and tail fraction were larger. Methanol was not detected in the heart in Scanavini et al. (2010), while in Scanavini et al. (2012) methanol predictions in the heart showed deviations up to 50%. In turn, our predictions of methanol were accurate. This is an important outcome, since methanol is a crucial substance regarding spirit safety.

### 5. Conclusions

The results obtained show that the models developed correctly reproduce pot still distillation. In addition, the simplifying assumptions introduced were verified to be reasonable (two equilibrium stages, quasi-binary mixture, negligible condenser hold-up). The models presented could be useful to design new spirit products and enhance alembic operations to increase energy efficiency and improve spirit safety and flavor.

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