

OPERATING STRATEGIES TO MINIMISE THE METHANOL CONTENT IN DISTILLATES OBTAINED IN ALEMBICS

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ABSTRACT

The aromatic composition of fruit distillates not only depends on the raw material, but also on the distillation system and its operating conditions. One of the several compounds recovered during distillation is methanol, which is toxic for human consumption. In this paper, a multi-objective optimal control problem is formulated to minimise methanol's recovery and maximise ethanol's recovery in a batch distillation system, by adapting the heating trajectory. The dynamic optimisation problem is solved using orthogonal collocation on finite elements. Compared with a standard operation policy, the optimal heating trajectory reduced the methanol concentration in the distillate by 50%, without significantly affecting the ethanol recovery.

Keywords: aroma distillation, methanol, multi-objective optimisation, spirits.

1. INTRODUCTION

Distilled alcoholic beverages are produced worldwide from a wide variety of fruits and cereals, for example, Whisky (UK, Ireland), Cachaça (Brazil), Tequila (Mexico), Cognac/Brandy (France, Spain) and Pisco (Peru, Chile), to name a few. In the case of Pisco, the fermented juice is made from Muscat grapes containing 94-98% v/v of a mixture of water and ethanol, where the rest is comprised of hundreds of volatile compounds (Thorngate 1998; Voilley & Lubbers 1998). These minority volatile compounds are called congeners and essentially define the quality of the fruit distillates. The preparation of many of these distillates goes through several stages, and distillation is the most relevant in the final composition of the spirit. For distillation, Charentais copper alembics are the most frequently used in small scale production facilities. This system is operated in batch mode, recovering three cuts, head, heart and tail, where the heart cut gives rise to the final product. Although the operation of this alembic is

relatively simple, its operation is exposed to many disturbances that generate variability in the composition of the final product.

Nowadays, consumers are more demanding, asking for new products that are safe and aromatically distinctive. Therefore, the distillate should be rich in positive aromas as well as free from off-flavours and toxic compounds. Moreover, these products should keep their quality from year to year.

In this study, we focus on minimising the methanol content of the distillates, which is recovered in the three cuts. Methanol is slowly metabolized in the human body, producing formaldehyde and formic acid which are extremely toxic in high concentrations. Excessive intake of methanol generates various ailments such as fatigue, thirst, headache, stomach pains, nausea, vomiting, sensitivity to light and noise, lack of concentration and attention, tremors, excessive sweating and hypertension (Swift & Davidson 1998). Hence, in many countries, methanol content in alcoholic beverages is regulated. In Chile, methanol concentration must be less than 1.5 g/L of absolute alcohol (L.a.a).

Mathematical models have been developed for exploring new operating strategies in food and chemical processes, in order to obtain reproducible products with a predefined composition. Several phenomenological models have been presented in the literature for wine batch distillation, for example, in plate rectification columns (Osorio et al., 2004), packed rectification columns (Carvallo et al., 2011) and alembics (Scanavini et al 2010; Scanavini et al., 2012; Sacher et al., 2013). In addition, several numerical techniques have been applied to design dynamic optimization strategies for batch distillation. These techniques approach the design

as an optimal control problem, where the goal is to optimise a specific performance index (minimum time, maximum distillate, maximum quality or maximum profit) by searching for the best control path. For example, for a plate column batch distillation system, Osorio et al. (2005) solved the optimal control problem finding the trajectory of the cooling flow rate in the partial condenser. The objectives were to maximise the terpene recovery and minimise the fatty acid recovery in a Muscat wine distillate. The process model was very complex, with many differential and implicit algebraic equations; therefore, the formulation solution of a full optimisation problem is extremely difficult. To simplify the numerical solution of the optimisation problem, the cooling flow rate was established as a predefined smooth function of time, derived from previous experiences. The optimisation resulted in the parameters of the predefined function that maximised a multi-objective cost function. The optimal strategy obtained was validated in lab scale experiments. De Lucca et al. (2013) explored various operating policies, with a simulator of a packed bed column, to minimise the methanol content in the distillate. They used the same predefined function with adjustable parameters of Osorio et al. (2005) to find an optimal cooling flow rate trajectory. In these studies, the predefined function restricted the cooling flow rates to a sub-optimal solution space.

In this paper, a full optimal control problem is formulated and solved for a Charentais alembic distillation. The aim is to minimise the methanol recovery and maximise the ethanol recovery in the distillate in a fixed operation time, by manipulating the heating power trajectory. A ternary version of a previous alembic model (Sacher et al., 2013) was used in the optimisation.

2. MATERIALS AND METHODS

2.1. Distillation system

The distillation system is an automatic controlled Charentais copper alembic (Figure 1) which has the following features and elements:

- 4.8 L capacity
- Total condenser
- Three Pt100 sensors to measure the temperature in the boiler, partial condenser and surroundings
- Electrical resistance inside the kettle (1200 W)

- A Programmable Logic Controller (PLC) receives data from the temperature sensors and sends the control signal to the electrical resistance in the boiler.

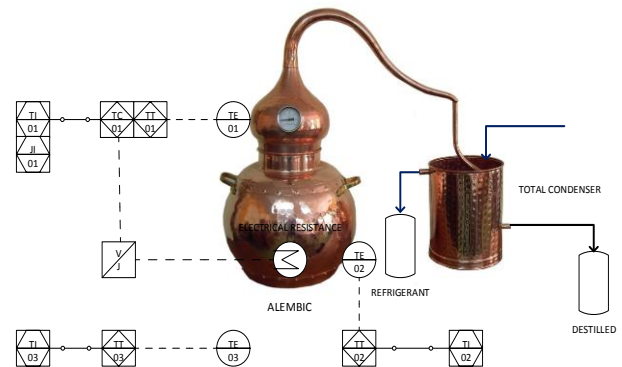


Figure 1: P&ID of the distillation system.

2.2. Experimental conditions

The Muscat wine was approximated as a synthetic ternary mixture of 13% v/v of ethanol and 1.5 g/L.a.a. of methanol (Osorio et al. 2004). The alembic was initially loaded with 1.8 L, and the ambient temperature was constant at 24 °C.

2.3. Modelling

To simplify, the liquid-vapour (L/V) equilibrium was considered to be a non-ideal "quasi binary" mixture of ethanol/water plus a congener (Sacher et al., 2013). The model includes mass and energy balances for the two equilibrium stages, the boiler and the partial condenser. The congeners' L/V equilibrium depends on ethanol concentration only, due to the assumption of "quasi binary" mixture. Activity coefficients were calculated using the UNIFAC group contribution method.

The mathematical model used in this paper is a simplified version of Sacher et al. (2013), which only considers a mixture of water, methanol and ethanol.

Mass (total, ethanol, methanol) and energy balances in the boiler,

$$\frac{d(M_B)}{dt} = L - V_B \quad (1)$$

$$\frac{d(M_B \cdot x_B^e)}{dt} = L \cdot x_L^e - V_B \cdot y_B^e \quad (2)$$

$$\frac{d(M_B \cdot x_B^m)}{dt} = L \cdot x_L^m - V_B \cdot y_B^m \quad (3)$$

$$\frac{d(M_B \cdot u_B)}{dt} = L \cdot h_L - V_B \cdot H_B + \dot{Q}_B \quad (4)$$

Mass (total, ethanol, methanol) and energy balances in the partial condenser (negligible liquid holdup),

$$V_B - L - V_D = 0 \quad (5)$$

$$V_B \cdot y_B^e - L \cdot x_L^e - V_D \cdot y_D^e = 0 \quad (6)$$

$$V_B \cdot y_B^m - L \cdot x_L^m - V_D \cdot y_D^m = 0 \quad (7)$$

$$V_B \cdot H_B - L \cdot h_L - V_D \cdot H_D - \dot{Q}_C = 0 \quad (8)$$

Thermodynamic equilibrium ethanol-water

The mole fraction of ethanol vapour (y_B^e, y_D^e), equilibrium temperatures and enthalpies ($H_{B,D}, h_L$) are calculated from empirical correlations (Sacher et al., 2013). These equations depend on the ethanol mole fraction in the liquid phase (x_B^e, x_L^e) only.

Thermodynamic equilibrium relationships for methanol,

$$y_D^m = K_C^m \cdot x_L^m \quad (9)$$

$$y_B^m = K_B^m \cdot x_B^m \quad (10)$$

$$K_{B,C}^m(x_B^e, x_L^e) = \frac{y_{B,D}^m}{x_{B,L}^m} = \frac{P_m(x_B^e, x_L^e) \cdot \gamma_m(x_B^e, x_L^e)}{P} \quad (11)$$

The activity coefficient for methanol γ_m is estimated using the UNIFAC contribution groups method. Given the assumption of a quasi-binary mixture, the activity coefficient only depends on the ethanol concentration since an infinite dilution of methanol in a mixture of water-ethanol is assumed.

Heat transfer model

$$\dot{Q}_B = \dot{Q}_{cal} - U \cdot A \cdot (T_B - T_{amb}) \quad (12)$$

$$\dot{Q}_C = U \cdot A \cdot (T_C - T_{amb}) \quad (13)$$

where \dot{Q}_{cal} and T_{amb} are input variables corresponding to the control variable and disturbance of the system, respectively. This model has only one empirical

parameter, $U \cdot A$, which can be easily fitted with data normally available in commercial distillation facilities (Pérez-Correa et al., 2013).

Simulation

To simulate the model, a reordering of equations is convenient. The distillate molar flow rate is obtained from mass and energy balances in the partial condenser (Eqs. 5, 6 and 8).

$$V_D = \frac{\dot{Q}_C}{(H_B - H_D) + \frac{(y_B^e - y_D^e)}{(x_L^e - y_D^e)} \cdot (H_D - h_L)} - \frac{-\dot{Q}_C}{(h_L - H_D) + \frac{(x_L^e - y_D^e)}{(y_B^e - y_D^e)} \cdot (H_D - H_B)} \quad (14)$$

To calculate the volume of distillate, an empirical correlation which calculates the density of the mixture from ethanol composition is used (Neuburg & Perez-Correa 1994),

$$\rho_L = \frac{x_D^e \cdot PM_E + (1 - x_D^e) \cdot PM_W}{\phi \cdot x_B^e + (1 - x_B^e) \cdot PM_W / \rho_W} \quad (15)$$

$$\phi = f(x_B^e, T_D) \quad (16)$$

Finally to calculate the composition of ethanol in the partial condenser, a rearrangement of the energy balance (Eq. 4) from mass balances in the boiler (Eqs. 1 and 2) is required,

$$(L(x_L^e - x_B^e) - V_B(y_B^e - x_B^e)) \left(\frac{\partial h_B}{\partial x_B} + \frac{\partial h_B}{\partial T_B} \frac{dT_B}{dx_B} \right) = L(h_L - h_B) - V_B(H_B - h_B) + \dot{Q}_B \quad (17)$$

This equation is an implicit function that depends on the value of x_L^e . This equation was solved in the AMPL code (see appendix) as a constraint in the optimisation problem.

2.4. Optimisation

The multi-objective weighted cost function considers methanol (main objective of this study) and ethanol recoveries in the distillate. The weight defines the priority in the respective distillation. Then, the objective function is,

$$\min_u J(u) = \alpha Rec_{met}(tf) - (1 - \alpha) Rec_{et}(tf) \quad (18)$$

$$0 \leq \alpha \leq 1 \quad (19)$$

where the recoveries are,

$$Rec_k = \frac{\int_{t_0}^{t_f} (D(t) \cdot x_k(t)) dt}{M_0 \cdot x_k(t_0)} \quad (20)$$

α is the adjustable weight, Rec_k is the recovery of compound k (met = methanol, et = ethanol), $D(t)$ is the molar flow rate of distillate, x_k is the mole fraction of compound k , M_0 is the initial mass, and finally, t_0 and t_f are the initial and final distillation times respectively.

A common practice in the fruit distillates industry is to use the cooling rate in the partial condenser to control the reflux rate. In the alembic used in this study, the reflux rate is given by natural condensation and is not directly controllable. Hence, we manipulated the heating power in the alembic boiler instead. The optimisation process must find an optimal heating power path that minimises methanol recovery and maximises ethanol recovery in the distillate. We applied the simultaneous simulation-optimisation method (direct transcription), using orthogonal collocation on finite elements (Biegler, 2010), which has been shown to be useful in tackling large scale optimisation problems. Only one cut was considered in computing the cost function (Eq. 18), corresponding to the heart/tail cut that was set at 2 h. Additional optimisation constraints are: (i) the heating power varies between 0 and 1100 W; (ii) the minimum distillate flow rate is 2 mL/min.

The optimal control problem in its discrete form can be expressed as:

$$\min_u J(u) \quad (21)$$

subject to

$$\forall i = 1 \dots ne, j = 1 \dots ncp$$

$$x_{i,j} = x_{i-1} + h_i \sum_{j=1}^{ncp} \Omega_j(\tau_j) \cdot \frac{dx}{dt_{i,j}} \quad (22)$$

$$g(x_{i,j}, y_{i,j}, u_{i,j}, \theta) = 0 \quad (23)$$

$$u_L \leq u_{i,j} \leq u_U \quad (24)$$

$$x_L \leq x_{i,j} \leq x_U \quad (25)$$

$$\theta_L \leq \theta \leq \theta_U \quad (26)$$

$$\frac{dx}{dt_{i,j}} = f(x_{i,j}, y_{i,j}, u_{i,j}, \theta) \quad (27)$$

where ne is the number of finite elements, ncp is the number of collocation points, x are differential state variables, y are algebraic state variables, u are control variables and θ are model parameters. Equation 22 corresponds to the discrete approximation of the differential state variables. h_i corresponds to the length of the finite element, which is given by the total process time divided by the number of finite elements; τ represents the normalised time in the finite element. Finally Ω are the interpolation polynomial functions in each finite element. In this study, we used 3 Radau collocation points (Biegler, 2010). The optimisation problem was coded in AMPL and solved using IPOPT (Biegler, 2010). Figure 2 shows the flowchart of the simultaneous simulation-optimisation method, using the orthogonal collocation on finite elements strategy used in this work.

3. RESULTS AND DISCUSSION

The optimisation was solved in a Samsung Intel core i7 laptop using the student version of AMPL. Therefore, we considered only 5 finite elements, since the maximum number of variables and constraints allowed were 300. We also tried using the NEOS web interface, but the optimisation problem did not converge with any solver available.

Different values of the weight α were tried, but the solver only found solutions for $0.5 \leq \alpha \leq 1$. For values below 0.5 the cost function took high negative values, resulting in a degenerated optimization problem; hence, some constraints were not met. Table 1 shows the cost function (J), the distillate alcohol grade (GA_d), the relative methanol concentration in the distillate (Met_d), the ethanol recovery (Rec_{et}) and the methanol recovery (Rec_{met}) for different values of α .

Table 1: Optimization results for different values of α .

α	J (-)	GA_d (%)	Met_d (g/L.a.a)	Rec_{et} (%)	Rec_{met} (%)
0.5	-8,1	46.0	1.37	64.8	48.7
0.6	1,8	52.4	1.16	59.8	42.9
0.72	31	78.5	0.75	58.3	41.2
0.8	22	52.4	1.16	59.8	42.9
0.9	31	78.5	0.75	58.3	41.2
1	41	53.5	1.09	58.3	41.0

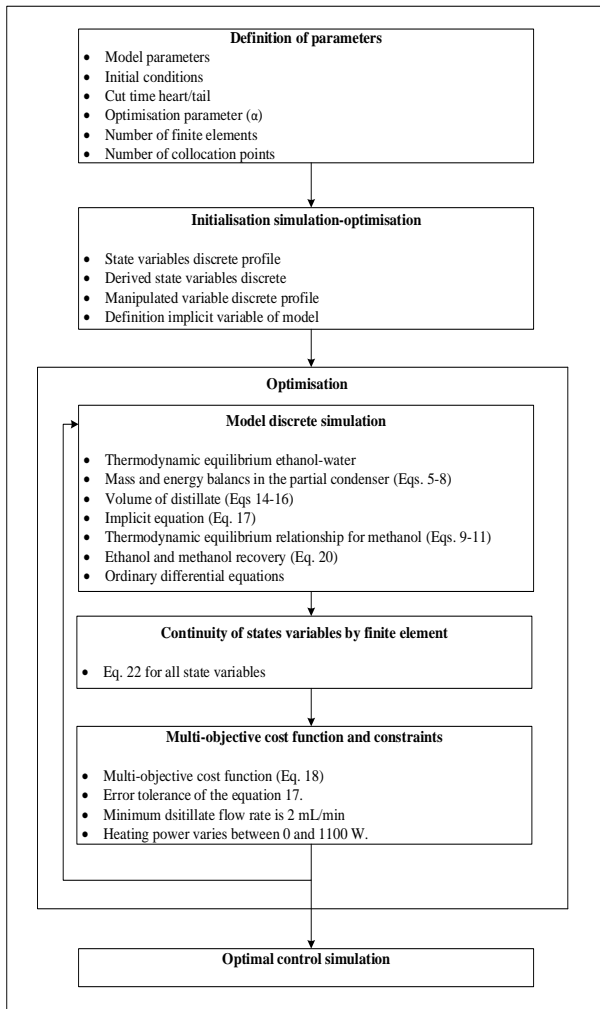


Figure 2: Flowchart of the simultaneous simulation-optimisation method.

It is important to highlight that for values of $\alpha = 0.75$ and 0.9 , a very low relative concentration of methanol in the distillate was obtained. These optimal trajectories reduce the relative concentration of methanol by 50% compared with the initial wine. In previous research (Luna et al., 2014) relative concentration of methanol were reduced by only 29%. In turn, for $\alpha = 0.5$, the highest methanol recovery was obtained. We observed that lower methanol relative concentrations were obtained when the distillates were more concentrated in ethanol and less total volume was recovered.

Figure 3 shows optimum trajectories of the heating power for the extreme cases ($\alpha = 0.5$ and $\alpha = 0.9$). To obtain a distillate with a low concentration of methanol ($\alpha = 0.9$), a high heating power is required at the beginning of the distillation and a low heating power at the end. In turn, if a low heating power is applied at the beginning and a high heating power at the end ($\alpha = 0.5$), a distillate with high methanol concentration will be obtained.

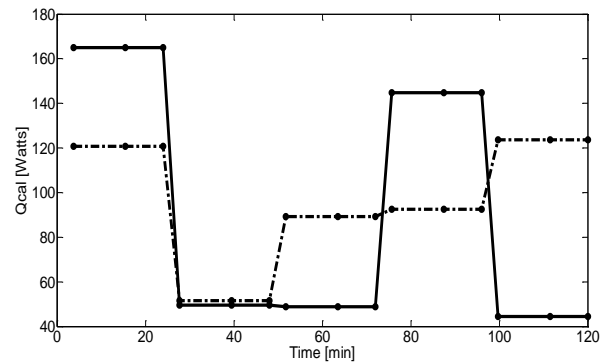


Figure 3: Heating power vs. time. Dashed line: $\alpha = 0.5$; Solid line: $\alpha = 0.9$.

4. CONCLUSIONS AND FUTURE WORK

This is the first study that apply a direct transcription method to minimise methanol content in Charentais alembic spirit distillations. Our results indicate that by properly managing the heating power in the boiler, significant reductions in the distillate methanol concentrations can be achieved. We have previously applied several operating strategies, and never achieved such low methanol concentrations as shown in this work. We expect that by testing more robust cost-functions, improving the method for solving the implicit algebraic constraint, and using more finite elements, we will be able to attain smoother heating power trajectories and even lower methanol concentrations.

Future work consider experimental validation, addition of more congeners in the distillation model, develop more complex cost-functions, and including cut times as decision variables.

Results shown here are general, therefore these can be applied to reduce methanol content in any fruit distillate obtained in alembics of any size.

APPENDIX

AMPL Code

```
# This program minimises the concentration of
methanol (Cmet) and maximises recovery of ethanol
(ETR) for the batch distillation process in a copper
Charentais, with a fixed operating time (tf) and less than
or equal final concentration of 1.5 g methanol/L.a.a. To
achieve this goal, heating power (Qcal) was handled
during distillation with a constant room temperature.
The model was published in its first version in Sacher et
al. 2013.
```

```
# First version: Ricardo Luna 14/01/2015.
```

```
# Process parameters or constants
```

```
param UAb := 0.3196778; # Coefficient and heat
transfer area of the boiler
```

```
param UAc := 0.3333333; # Coefficient and heat
transfer area of the condenser
```

```

param Tamb := 24+273.15; # Room temperature [k]
param MWe := 46.07; # Ethanol Molecular weight
param MWw := 18.0153; # Water Molecular weight
param MWmet := 32.04; # Methanol Molecular weight
param rhow := 1; # Water density [g/mL]
param time := 7200; # Final time [hours]
param alpha := 1; # Weight of function multi-purpose
# Initial conditions for differential variables
param x1_init := 91.789; # Boiler initial moles (Mb)
param x2_init := 0.0437; # Ethanol molar fraction in boiler (xb)
param x3_init := 0; # Distilled initial volume (V)
param x4_init := 0; # Moles of distilled ethanol (M_etd)
param x5_init := 0.000116; # Methanol molar fraction in boiler (xb_met)
param x6_init := 0; # Moles of distilled methanol (M_metd)
param t_init := 0; # Initial time (seg)
# Indexes, number of placement points and number of finite elements
param nfe >= 1 integer;
param ncp >= 1 integer;
let nfe := 5; # Finite element numbers
let ncp := 3; # number of placement points
set fe := 1..nfe; # Finite element index
set cp := 1..ncp; # placement points index
param h{fe} := (time/nfe); # length of a finite element
# Matrix of Radau placement coefficient (implicit Runge-Kutta)
param a{cp,cp};
let a[1,1] := 0.19681547722366;let a[1,2] := 0.39442431473909;
let a[1,3] := 0.37640306270047;let a[2,1] := -0.06553542585020;
let a[2,2] := 0.29207341166523;let a[2,3] := 0.51248582618842;
let a[3,1] := 0.02377097434822;let a[3,2] := -0.04154875212600;
let a[3,3] := 0.11111111111111;
# Discrete profiles of state variables and time
var x1 {fe,cp} >= 0 := x1_init ;
var x2 {fe,cp} >= 0, <=1, := x2_init ;
var x3 {fe,cp} >= 0 := x3_init ;
var x4 {fe,cp} >= 0 := x4_init ;
var x5 {fe,cp} >= 0, <=1, := x5_init ;
var x6 {fe,cp} >= 0 := x6_init ;
var t {fe,cp} >= 0 := t_init ;
# Discrete derivative of state variables and time
var x1dot {fe,cp} ;
var x2dot {fe,cp} ;
var x3dot {fe,cp} ;
var x4dot {fe,cp} ;
var x5dot {fe,cp} ;
var x6dot {fe,cp} ;
var tdot {fe,cp} ;
# Discrete profiles of control variables
var Qcal {fe} >= 0, <= 1000, := 300; # Watt
# Declaration of implicit variable of the model

```

```

var xL {fe,cp} >=0, <=1, := 1.1*x2_init; # Reflux liquid mole fraction L
# Constitutive equations (explicit algebraic)
# Liquid/vapor equilibrium in the boiler
# Steam mole fraction in boiler
var yb {i in fe,j in cp} = -59.6868501+-89.4037240*x2[i,j]+-39.8552042*x2[i,j]^1.5+81.47664393*exp(x2[i,j])-21.7897938*exp(-x2[i,j]);
# Boiler temperature
var Tb {i in fe,j in cp} = 273.15+(-0.02214517+-0.05785120*x2[i,j]^1.5+0.032146591*exp(x2[i,j]))^-1;
# Liquid enthalpy [J/gmol]
var hb {i in fe,j in cp} = (55.678*x2[i,j]+75.425)*Tb[i,j]-15208.44*x2[i,j]-20602.34;
# Gas enthalpy [J/gmol]
var Hb {i in fe,j in cp} = 36172.03-2919.83*yb[i,j]+(31.461-11.976*yb[i,j])*Tb[i,j]+(4.063*10^-4+0.0734*yb[i,j])*Tb[i,j]^2;
# dhb/dxb partial derivative
var dhbdxb {i in fe,j in cp} = 55.678*Tb[i,j]-15208.44;
# dhb/Tb partial derivative
var dhbdTb {i in fe,j in cp} = 55.678*x2[i,j]+75.425;
# dTbdxb partial derivative
var dTbdxb {i in fe,j in cp} = -(1.5*-0.05785120*x2[i,j]^0.5+0.032146591*exp(x2[i,j]))/(-0.02214517+-0.05785120*x2[i,j]^1.5+0.032146591*exp(x2[i,j]))^2;
# Total derivative
var DhbDxb {i in fe,j in cp} = dhbdxb[i,j]+dhbdTb[i,j]*dTbdxb[i,j];
# Liquid/vapor equilibrium in condenser
# Steam mole fraction in boiler
var yD {i in fe,j in cp} = -59.6868501+-89.4037240*xL[i,j]+-39.8552042*xL[i,j]^1.5+81.47664393*exp(xL[i,j])-21.7897938*exp(-xL[i,j]);
# Condenser temperature
var Tc {i in fe,j in cp} = 273.15+(-0.02214517+-0.05785120*(xL[i,j]^(1.5))+0.032146591*exp(xL[i,j]))^-1;
# Liquid enthalpy [J/gmol]
var hL {i in fe,j in cp} = (55.678*xL[i,j]+75.425)*Tc[i,j]-15208.44*xL[i,j]-20602.34;
# Gas enthalpy [J/gmol]
var Hd {i in fe,j in cp} = 36172.03-2919.83*yD[i,j]+(31.461-11.976*yD[i,j])*Tc[i,j]+(4.063*10^-4+0.0734*yD[i,j])*Tc[i,j]^2;
# Stationary mass balances in the condenser
# Molar flow of vapor ascending
var Vb {i in fe,j in cp} = UAc*(Tc[i,j]-Tamb)/((Hb[i,j]-Hd[i,j])+(yb[i,j]-yD[i,j])/(xL[i,j]-yD[i,j]))*(Hd[i,j]-hL[i,j]);
# Molar flow of liquid reflux

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```

var L {i in fe,j in cp} = -UAc*(Tc[i,j]-Tamb)/((hL[i,j]-
Hd[i,j])+(xL[i,j]-yD[i,j])/(yb[i,j]-yD[i,j]))*(Hd[i,j]-
Hb[i,j]));
# Molar flow of distillate
var D {i in fe,j in cp} = Vb[i,j]-L[i,j];
# Calculation of volumetric flow of distillate
# Molecular weight of the mixture
var MWm {i in fe,j in cp} = MWe*yD[i,j]+(1-
yD[i,j])*MWw;
# Apparent molal volume for mixing [m3/kmol]
var oa {i in fe,j in cp} = 5.1214e-2+6.549e-
3*yD[i,j]+7.406e-5*(Tc[i,j]-273.15);
# Mixture density [g/mL]
var rhom {i in fe,j in cp} =
MWm[i,j]/(oa[i,j]*1000*yD[i,j]+(1-
yD[i,j])*MWw/rhow);
# Distillate volume [mL]
var Vd {i in fe,j in cp} =
D[i,j]*MWm[i,j]*(1/rhom[i,j]);
var tiempo {i in fe,j in cp} = t[i,j]/60;
var Flujo {i in fe,j in cp} = x3[i,j]/tiempo[i,j];
# Implicit algebraic constitutive equation
# Left side of the equation
var g1 {i in fe,j in cp} = (L[i,j]*(xL[i,j]-x2[i,j])-
Vb[i,j]*(yb[i,j]-x2[i,j]))*(DhbDxb[i,j]);
# Right side of the equation
var g2 {i in fe,j in cp} = L[i,j]*(hL[i,j]-hb[i,j])-
Vb[i,j]*(Hb[i,j]-hb[i,j])+(Qcal[i]-UAb*(Tb[i,j]-Tamb));
# Error definition of the equation
var e {i in fe,j in cp} = (g1[i,j]-g2[i,j])^2;
# Calculation of properties and methanol balances
var Kmetanolb {i in fe,j in cp} = -
407274.016707888*x2[i,j]^5+137084.909351167*x2[i,
j]^4-
19714.4353078579*x2[i,j]^3+1757.07481156027*x2[i,
j]^2-125.445056947666*x2[i,j]+7.99009392867259;
var Kmetanolc {i in fe,j in cp} = -
407274.016707888*xL[i,j]^5+137084.909351167*xL[i,
j]^4-
19714.4353078579*xL[i,j]^3+1757.07481156027*xL[i,
j]^2-125.445056947666*xL[i,j]+7.99009392867259;
# Mole fraction of methanol vapor in the boiler
var ybmet {i in fe,j in cp} =
Kmetanolb[i,j]*x5[i,j]*x5_init; # Multiply by x5_init to
return to the original value # Liquid mole fraction in the
gooseneck
var xLmet {i in fe,j in cp} =
(Vb[i,j]*ybmet[i,j])/(L[i,j]+D[i,j]*Kmetanolc[i,j]);
# Vapor mole fraction in the gooseneck
var yDmet {i in fe,j in cp} = xLmet[i,j]*Kmetanolc[i,j];
# Alcoholic strength
var GLb {i in fe,j in cp} = -
38.950116015168470*x2[i,j]^6+231.0609445800233*x
2[i,j]^5-
548.2530421230588*x2[i,j]^4+704.8795688586179*x2
[i,j]^3-
570.0321285089950*x2[i,j]^2+321.3122048471700*x2
[i,j]+0.001131244289002;
var GLd {i in fe,j in cp} = -
38.950116015168470*yD[i,j]^6+231.0609445800233*

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yD[i,j]^5-
548.2530421230588*yD[i,j]^4+704.8795688586179*y
D[i,j]^3-
570.0321285089950*yD[i,j]^2+321.3122048471700*y
D[i,j]+0.001131244289002;
# Methanol concentration [gmetanol/L.a.a]
var Cmet {i in fe,j in cp} =
x6[i,j]*MWmet*1000/((x3[i,j]*(GLd[i,j]/100))+0.0000
0001);
# Ethanol recovery [%]
var Etr {i in fe,j in cp} = x4[i,j]*100/(x1_init*x2_init);
# Methanol recovery [%]
var Mtr {i in fe,j in cp} = x6[i,j]*100/(x1_init*x5_init);
# Differential equations
# Moles balance in the kettle
odex1 {i in fe,j in cp}: x1dot[i,j] = L[i,j]-Vb[i,j];
# Ethanol balance in the kettle
odex2 {i in fe,j in cp}: x2dot[i,j] =
1/x1[i,j]*(L[i,j]*(xL[i,j]-x2[i,j])-Vb[i,j]*(yb[i,j]-
x2[i,j]));
# Distillate volume in time
odex3 {i in fe,j in cp}: x3dot[i,j] = Vd[i,j];
# Moles of distilled ethanol in time
odex4 {i in fe,j in cp}: x4dot[i,j] = D[i,j]*yD[i,j];
# Methanol balance in the kettle
# Normalized equation to x5_init (to avoid tolerance
error)
odex5 {i in fe,j in cp}: x5dot[i,j] =
(1/x1[i,j]*(L[i,j]*(xLmet[i,j]-x5[i,j]*x5_init)-
Vb[i,j]*(ybmet[i,j]-x5[i,j]*x5_init)))/(1/x5_init);
# Moles of distilled methanol in time
odex6 {i in fe,j in cp}: x6dot[i,j] = (D[i,j]*yDmet[i,j]);
# Operating time
odet {i in fe,j in cp}: tdot[i,j] = 1;
# Declaration of real variable (denormalization of x5)
var X5 {i in fe,j in cp} = x5[i,j]*x5_init;
# Continuity of the states through finite element and its
definition in the placement points for finite element
i=2, nfe
# Moles in the kettle
fecolx1 {i in fe diff {1},j in cp}: x1[i,j] = x1[i-1,ncp]
+h[i]*sum{k in cp} a[k,j]*x1dot[i,k];
# Ethanol fraction in the kettle
fecolx2 {i in fe diff {1},j in cp}: x2[i,j] = x2[i-1,ncp]
+h[i]*sum{k in cp} a[k,j]*x2dot[i,k];
# Distillate volume
fecolx3 {i in fe diff {1},j in cp}: x3[i,j] = x3[i-1,ncp]
+h[i]*sum{k in cp} a[k,j]*x3dot[i,k];
# Moles of distilled ethanol
fecolx4 {i in fe diff {1},j in cp}: x4[i,j] = x4[i-1,ncp]
+h[i]*sum{k in cp} a[k,j]*x4dot[i,k];
# Methanol in the kettle
fecolx5 {i in fe diff {1},j in cp}: x5[i,j] = x5[i-1,ncp]
+h[i]*sum{k in cp} a[k,j]*x5dot[i,k];
# Moles of distilled methanol
fecolx6 {i in fe diff {1},j in cp}: x6[i,j] = x6[i-1,ncp]
+h[i]*sum{k in cp} a[k,j]*x6dot[i,k];
# tiempo
fecolt {i in fe diff {1},j in cp}: t[i,j] = t[i-1,ncp]
+h[i]*sum{k in cp} a[k,j]*tdot[i,k];

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# Continuity of the states through finite element and its
definition in the placement points for the first finite
element
# Moles in the kettle
fecolx10{i in 1..1,j in cp}: x1[i,j] = x1_init
+h[i]*sum{k in cp} a[k,j]*x1dot[i,k];
# Ethanol fraction in the kettle
fecolx20{i in 1..1,j in cp}: x2[i,j] = x2_init
+h[i]*sum{k in cp} a[k,j]*x2dot[i,k];
# Distillate volume
fecolx30{i in 1..1,j in cp}: x3[i,j] = x3_init
+h[i]*sum{k in cp} a[k,j]*x3dot[i,k];
# Moles of distilled ethanol
fecolx40{i in 1..1,j in cp}: x4[i,j] = x4_init
+h[i]*sum{k in cp} a[k,j]*x4dot[i,k];
# Methanol in the kettle
fecolx50{i in 1..1,j in cp}: x5[i,j] = x5_init/x5_init
+h[i]*sum{k in cp} a[k,j]*x5dot[i,k];
# Moles of distilled methanol
fecolx60{i in 1..1,j in cp}: x6[i,j] = x6_init
+h[i]*sum{k in cp} a[k,j]*x6dot[i,k];
# Time
fecolt0{i in 1..1,j in cp}: t[i,j] = t_init
+h[i]*sum{k in cp} a[k,j]*tdot[i,k];
# Objectives
var J1 = alpha*Mtr[nfe,ncp];
var J2 = (1-alpha)*Etr[nfe,ncp];
var Jt = J1+J2;
# Objective Function
Minimize fcosto: alpha*Mtr[nfe,ncp]-(1-
alpha)*Etr[nfe,ncp];
# Constraints
subject to r1 {i in 1..nfe,j in 1..ncp} :
e[i,j]<=0.0000001; # Error tolerance in the implicit
equation
subject to r2 : Etr[nfe,ncp] <=100;
subject to r3 : Mtr[nfe,ncp] <=100;
subject to r4 {i in 1..nfe,j in 1..ncp} : Flujo[i,j]>=2;
subject to r5 : Mtr[nfe,ncp] >=0;
subject to r6 : Etr[nfe,ncp] >=0;

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