

## Modeling and Simulation of Molecular Distillation Process for a Heavy Petroleum Cut

Zuñiga L., L. <sup>\*1</sup>; Lima, N. M. N. <sup>1</sup>; Wolf Maciel, M. R. <sup>1</sup>; Maciel Filho, R. <sup>1</sup>; Batistella, C. B. <sup>1</sup>; Manca, D. <sup>2</sup>; Manenti F. <sup>2</sup>; Medina, L. C. <sup>3</sup>

<sup>1</sup> Separation Process Development Laboratory (LDPS). School of Chemical Engineering. State University of Campinas, UNICAMP, Campinas-SP, Brazil.

<sup>2</sup> CMIC Dept. 'Giulio Natta'-Politecnico di Milano, Piazza Leonardo da Vinci, Italy

<sup>3</sup> CENPES/PDP/TPAP/PETROBRAS, Brazil.

E-mail: [lazuli@feq.unicamp.br](mailto:lazuli@feq.unicamp.br) and [wolf@feq.unicamp.br](mailto:wolf@feq.unicamp.br)

<sup>\*</sup>Corresponding author. Fax:+55 19 35213965

Modeling and simulation of molecular distillation to split of heavy petroleum cuts are proposed. A theoretical study of this problem is illustrated for a heavy petroleum cut divided into six pseudo-components. In the process simulation, a falling film is considered. The mathematical model comprises equations for the evaluation of the physicochemical properties, in order to characterize the distilled mixture. Heat and material balances on the liquid film are numerically solved by using a central finite-difference method. The simulation is carried out at the steady-state conditions, where the relevant process variables, such as film thickness, evaporation rate, film surface temperature, concentration profiles, and amount of distillate flow rate are computed. In molecular distillation, the concentration of the most volatile components shrinks in both axial and radial directions, especially due to the fast increase of the temperature in the falling film. As a consequence, the less volatile components of the liquid mixture undergoes a fast increase on the liquid interface, by clearly showing the potentialities of the molecular distillation process in separating heavy petroleum cuts. As the results show, the inlet variables such as the feed temperature and the feed flow rate largely influence the final composition of the condensate flow.

**Keywords:** Molecular distillation, mathematical modeling, heavy petroleum cuts, physicochemical properties.

### 1. Introduction

The molecular distillation is a method safe and suitable for separation and purification of thermally unstable materials for their special conditions of operation, as low pressure, low temperatures and short residence times. The internal structure of falling film molecular distillator is show in Figure 1. The main part of the equipment is constituted of an evaporator and a condenser. During the process are predetermined the feed temperature and feed flow rate, as well as the temperature of evaporator and the

temperature of condenser. The system pressure is constant (0.1 Pa). A new method based on short-path distillation, and developed on Separation Process Development Laboratory (LOPCA/UNICAMP) appears as one of the best alternative to separate and characterize cuts, atmospheric residue and heavy liquid petroleum fractions. Such a method allows exploring temperatures between 380°C – 700°C Atmospheric Equivalent Boiling Point (AEBP) and extending the True Boiling Point curve (Sbaite, 2006). The modeling and simulation of molecular distillation process play a fundamental role in supporting industries. Actually, the film surface temperature at the condensation surface is important to determine both the yield and the purity of the distilled product. Unfortunately, the direct measure of the temperature profile in the film is not an easy task. Consequently, a key issue is to build an appropriate inferentiation model describing the separation process as a function of the film profiles and, at the same time, supporting both the operation analysis and the process design. Also, the modeling and the simulation allow understanding how the process inlet variables, affect the process outlet variables. This paper describes the mathematical modeling and the numerical results of the molecular distillation process of a heavy petroleum cut (645 K to 1084 K AEBP) divided into six pseudocomponents. In the process simulation, a falling film, a heater and an extremely low pressure evaporator are considered, with centered internal condenser. The mathematical modeling by Kawala e Stephan (1989) and the boundary conditions introduced by Batistella (1996) were considered as a starting point to develop the particular modeling for heavy petroleum cuts. The mathematical model comprises equations for the evaluation of the physicochemical properties, which are formulated through the adjustment of experimental parameters such as molecular weight, specific heat, viscosity, and density, and expressed in terms of specific gravity and average boiling point of the pseudocomponents (ABP). Figure 2 reports the velocity profile in the liquid film.

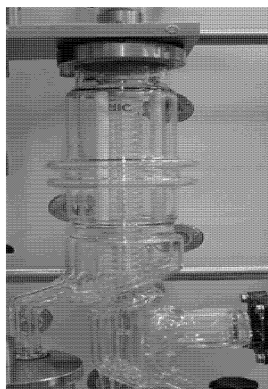


Figure 1. Internal structure of evaporator

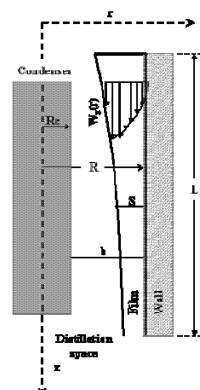


Figure 2. Velocity profile and film shape on the evaporator.

## 2. Mathematical Modeling

### 2.1 Thickness of the evaporating film

$$S = \left[ 3\eta_{\text{mis}} \left( \frac{\dot{m}_o}{2\pi g R \rho_{\text{mis}}^2} - \frac{1}{g \rho_{\text{mis}}^2} \int_{z_0}^z \dot{G}_g dz \right) \right]^{\frac{1}{3}} \quad (1)$$

### 2.2 Surface evaporation rate under vacuum

Equation 2 contains a factor  $(P/P_{\text{ref}})$ , introduced by Cruz e Gani (2006), to adjust the vacuum pressure,  $P$ .  $P_{\text{ref}}$  is the residual pressure generated by atmospheric air introduced into the system as a result of high vacuum.

$$\dot{G}_q = C_{qS} P_q^{\text{vap}} \left( \frac{M_q}{2\pi R_g T_S} \right)^{1/2} \left( \frac{P}{P_{\text{ref}}} \right) \left[ 1 - (1-F) \left( 1 - e^{-\frac{h}{k\beta}} \right)^n \right] \quad (2)$$

### 2.3 Temperature profile in the liquid film

$$W_z = \frac{\partial T}{\partial z} = \alpha_{\text{mis}} \left[ \frac{1}{r} \frac{\partial T}{\partial r} + \frac{\partial^2 T}{\partial r^2} \right] \quad (3)$$

$$T = T_o \quad \text{for } z = 0 \text{ and } (R-S) \leq r \leq R \quad (4)$$

$$T = T_w \quad \text{for } r = R \text{ and } 0 \leq z \leq L \text{ (Heated evaporator)} \quad (5)$$

$$\frac{\partial T}{\partial r} = - \frac{\sum_{q=1}^N (\dot{G}_q \Delta H_q^{\text{vap}})}{\lambda_{\text{mis}}} \quad \text{for } r = (R-S) \text{ and } 0 \leq z \leq L \quad (6)$$

### 2.4 Concentration profile in the liquid film

$$W_z \frac{\partial C_q}{\partial z} = D_q \left[ \frac{1}{r} \frac{\partial C_q}{\partial r} + \frac{\partial^2 C_q}{\partial r^2} \right] \quad q = 1, 2, \dots, N \quad (7)$$

$$C_q = C_{qo} \quad \text{for } (z = 0) \text{ and } R-S \leq r \leq R \quad (8)$$

$$\frac{\partial C_q}{\partial r} = 0 \quad \text{for } r = R \text{ and } (0 \leq z \leq L) \quad (9)$$

$$\frac{\partial C_q}{\partial r} = - \frac{\dot{G}_q - C_q M_q \left( \sum_{v=1}^N \frac{\dot{G}_v}{M_v} \right)}{\rho_{\text{mis}} D_q} \quad \text{for } r = R-S \text{ and } 0 \leq z \leq L, \text{ (Batistella, 1996)} \quad (10)$$

### 2.5 Overall distillate mass flow rate

$$D_z = \sum_{z=0}^L \dot{G}_{gz} A_z ; A_z = [2\pi(R-S)\Delta z] \quad (11)$$

### 3. Results And Analysis of Simulation

The partial differential equations 3 to 10 are represented in finite differences form by using the Crank-Nicolson method. The film thickness was discretized on 11 points, while the film length was discretized on 300 points. For the simulation, the split of a heavy petroleum cut (645 K to 1084 K AEBP) was considered, which was divided into six pseudocomponents: “a” (657.7 K AEBP) “b” (690.2 K AEBP), “c” (733.7 K AEBP) “d” (777.2 K AEBP) “e” (830.7 K AEBP) and “f” (976.7 K AEBP). Physicochemical properties (i.e.,  $\eta_{mis}$ ,  $\alpha_{mis}$ ,  $\rho_{mis}$ ,  $D_q$ ,  $\lambda_{mis}$ ), are calculated through temperature-dependent relationships. The operating conditions, 363 K of condenser temperature and 353 K of feed temperature were used. As shown in Figure 3, the temperature in film surface, ( $T_s$ ) increases gradually throughout the film length and it reaches a maximum in correspondence with the output region of evaporator. Also, the temperature  $T_s$  increases with the evaporator wall temperature ( $T_{evap}$ ), principally from the center region for output region of evaporator, where the evaporation of the most volatile pseudocomponents is the highest one. Figure 4 shows that the film thickness decreases continuously through the evaporator, from a maximum of  $2.2 \times 10^{-3}$  m in the inlet zone of the film, down to a minimum of  $1.7 \times 10^{-3}$  m in correspondence with the end zone of the film. Such a film decrease could be explained by the depletion of the most volatile pseudocomponents and the increase of the temperature in the liquid film, as well, caused by the heat exchange between the inner surface of evaporator and the falling film. Figure 5 shows that for the operating conditions of distillation were evaporated the “a”, “b” and part of “c” pseudocomponents. A gradually decrease of these pseudocomponents concentration is obtained in the liquid film. These pseudocomponents constitute the distillate flow. The “d”, “e”, and “f” pseudocomponents are not evaporated, and their concentration increase in the liquid film testifies it. This behaviour indicates that they remain unchanged during the process and that constitute the residue flow of molecular distillation. Figure 6 shows the concentration profile at the film surface of the “a” pseudocomponent (the most volatile). The rapid decrease of the concentration in the liquid film shows that the liquid phase is getting poorer in this pseudocomponent, which is faster when the temperature of evaporator rises. For “a” pseudocomponent the maximum concentration gradient is observed for the highest temperature. The evaporation rate and the overall distillate mass flow rate are both strongly affected by the temperature of evaporator. Figures 7 and 8 show that an increase in the temperature of evaporator for a fixed mass flow rate represents an increase in the evaporation rate and the distillation rate of 300 times with respect to the initial value.

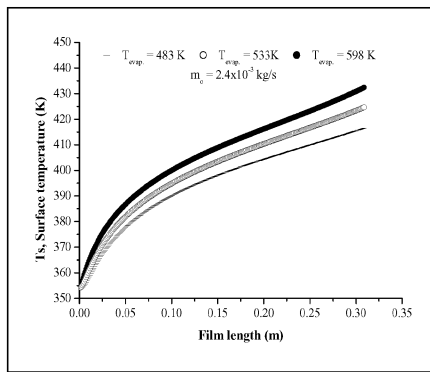


Figure 3. Temperature profile in surface of film.

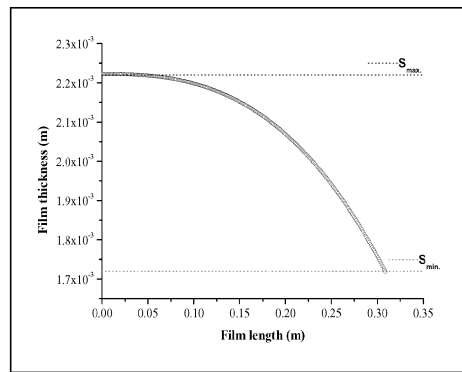


Figure 4. Thickness profile.

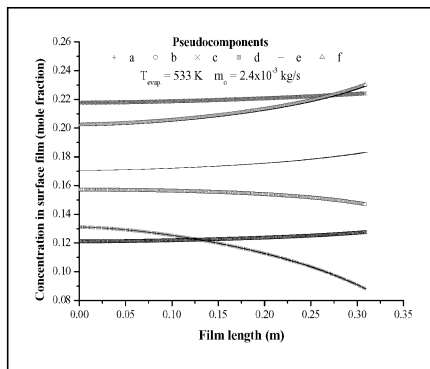


Figure 5. Concentration profiles of pseudocomponents in surface of film.

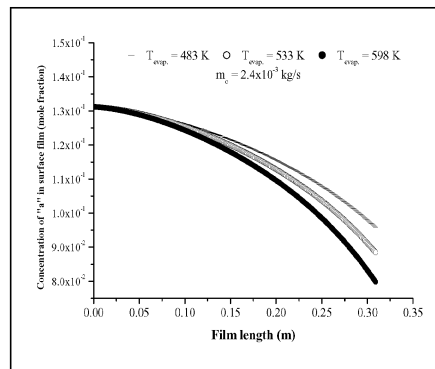


Figure 6. Concentration profiles of "a" pseudocomponent in surface of film.

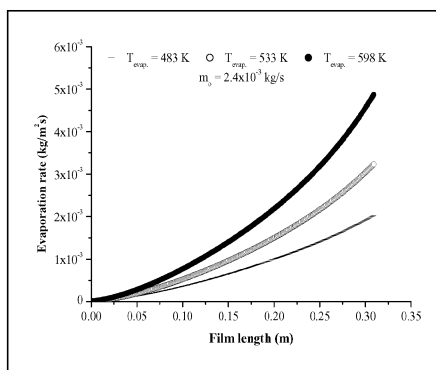


Figure 7. Evaporating rate profile.

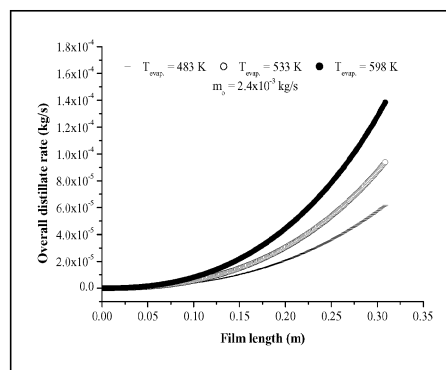


Figure 9. Overall distillate mass flow rate profile.

#### 4. Conclusions

From the simulation of molecular distillation process of a heavy residue cut using on falling film molecular distillator with heated evaporator were generated the profiles of the variables of interest to the process. The steady state process showed that the film surface temperature, the evaporation rate, and the overall distillate mass flow rate are strongly affected by the temperature of evaporator. During the distillation, the liquid film is getting poorer in its most volatile pseudocomponents, specifically, from the middle to outlet region of evaporator, where the temperature of the liquid film is the highest one. Consequently, the thickness of the film rapidly decreases in this region, whereas the concentration of the heaviest pseudocomponents continuously increases along the evaporator at the selected operating conditions. All the necessary heat for the evaporation process is provided through the wall of the evaporator and, for this reason, the temperature of film in the outlet region is considerably higher.

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#### References

- Batistella. C. B. and Maciel. M. R. W., 1996, Modeling, simulation and analysis of molecular distillators: centrifugal and falling film, *Comp. Chem. Eng.* 20, s19-s24.
- Kawala Z. and Stephan K., 1989, Evaporation rate and separation factor of molecular distillation in a falling film apparatus, *Chem. Eng. Technol.* 12, 406-413.
- Sales-Cruz M. and Gani R., 2006, Computer-aided modelling of short-path evaporation for chemical product purification. Analysis and design, *Chem. Eng. Res. Des.* 84(A7) 583-594.
- Sbaite P., Batistella, C. B., Winter A., Vasconcelos C. J, G., Wolf Maciel M. R., Maciel Filho R., Gomes A., Medina L., Kunert R., 2006, True boiling point extended curve of vacuum residue through molecular distillation, *Petrol. Sci. Technol.* 24, 265-274.

#### Notation

$A_z$ : Surface area element, m;  $C_q$ : Mole fraction;  $D_q$ : Diffusion coefficient,  $m^2s^{-1}$ ;  $D_z$ : Overall distillate mass flow rate,  $kg s^{-1}$ ;  $F$ : Surface ratio;  $g$ : Gravitational acceleration,  $ms^{-2}$ ;  $\dot{G}_q$ : Evaporation rate,  $kgm^{-2}s^{-1}$ ;  $\dot{G}_g$ : Global evaporation rate,  $kgm^{-2}s^{-1}$ ;  $k$ : Anisotropy of vapor;  $M_q$ : Molecular weight;  $\dot{m}_o$ : Feed rate,  $kg s^{-1}$ ;  $n$ : Collisions number;  $p_q^{vap}$ : Vapor pressure, Pa.;  $R_g$ : Universal gas constant,  $Jkmol^{-1}K^{-1}$ ;  $\alpha_{mis}$ : Temperature diffusivity,  $m^2s^{-1}$ ;  $\beta$ : Mean path of vapor molecule;  $\eta_{mis}$ : Viscosity, Pa s;  $\lambda_{mis}$ : Thermal conductivity,  $Wm^{-1}K^{-1}$ ;  $\Delta H_q^{vap}$ : Evaporation enthalpy,  $Jkg^{-1}$ ;  $\rho_{mis}$ : Density,  $kgm^{-3}$ .