CHEMICAL ENGINEERING TRANSACTIONS
VOL. 92, 2022
A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.cetjournal.it
Guest Editors: Rubens Maciel Filho, Eliseo Ranzi, Leonardo Tognotti

ISBN 978-88-95608-90-7; **ISSN** 2283-9216
DOI: 10.3303/CET2292091

Biolubricant Production: from the Acknowledgment of Experimental Plant using Molecular Distillation as Downstream Process, the Development of a Unit Operation into Aspen Plus®

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Biolubricant is a lubricant that can decompose naturally, helping to reduce the number of harmful chemicals such as petrochemical oils released into the environment. This is a promissory product with features similar to mineral oils. Currently, the replacement of energy sources from petroleum by biofuels is being hardly studied, but for other applications such as lubricants, there are still many opportunities to be developed. Conventional downstream separators to achieve high levels of yield and purity of biolubricants have to operate upon high-temperature conditions. The higher the temperature the higher the degradation ratio of molecules. Molecular distillation (MD) is an effective alternative and operates with lower pressure and, consequently, lower temperature. However, this tool is not able to be used in the Aspen Plus® to predict large-scale demands as well as to carry out simulations for optimization. Hence, this paper aims to propose the development of a general procedure to emulate a falling film molecular distillation in the commercial simulator Aspen Plus®. The contribution of this paper was to define and model a suitable unit operation in the commercial simulator. This work was supported by the experimental unit already designed and implemented in the lab (LDPS). The simulation data computing efficiency elements were according to experimental results, indicating it as a high potential tool to emulate MD. This study supports the idea of a cost-effective biolubricant design since these results are relevant to predict large-scale demands as well as to carry out simulations integrated with other unit operations.

1. Introduction

Lubricants are the essential components of mechanical devices. They avoid breakage due to the friction of moving parts, cover from corrosion, and block the heating up process (Cecilia et al., 2020). At present, they are produced from mineral oil, fomenting ecological problems. In this context, Europe and the USA have devoted energy and time to developments in biolubricants (Fernández-Silva et al., 2021). Deriving from vegetable oils rather than mineral oils, they have great attributes in terms of biodegradability, lubricity, and toxicity (Encinar et al., 2020).

Castor oil and fusel alcohols are potential commodities to biolubricant processes (Vo et al., 2021). Castor oil crop has been increasing in South American countries and fusel alcohols are a residue from sugar mills. They show competitive prices and could promote the commercial and financial situation of these local areas. Being a sustainable product should have achievements in environmental, economic, and social matters; otherwise, the product would not have a sustainable stamp on the market.

Biolubricants from vegetable oils and branched alcohols have some technical challenges set apart the final product due to their high viscosity and solubility of reactants.

Molecular distillation (MD) is a highly efficient separation process of multicomponent mixtures, which could be attached to the separation process to achieve high quality of the final product in a faster way. The equipment

Paper Received: 14 January 2022; Revised: 12 March 2022; Accepted: 19 April 2022
Please cite this article as: Lista A.E., Quintero H.I., Batistella C.B., Wolf Maciel M.R., 2022, Biolubricant Production: from the Acknowledgment of Experimental Plant Using Molecular Distillation as Downstream Process, the Development of a Unit Operation Into Aspen Plus®, Chemical Engineering Transactions, 92, 541-546 DOI:10.3303/CET2292091

operates at low-pressure values from one atmosphere to high vacuum (<1 mbar). At these conditions, high boiling point substances are recovered under no thermal decomposition.
The high efficiency of the evaporation part of the equipment is achieved by spreading a thin film of feed stream onto a uniform heated surface; the higher the surface contact the higher the evaporation rates and, consequently, a shorter heating time is reached (Engy et al., 2021).
The distance gap between the evaporator and the condenser has a great effect on this separation process efficiency. The distillation gap is around the mean free pathway of the molecules; hence, they reach the condenser without being swerved by other molecules or returning to the evaporating surface (Engy et al., 2021). Molecular distillation is therefore a non-equilibrium process with high-efficiency separation under no thermal decomposition.
This equipment was developed in (LDPS) lab and the experiments showed a promising separation operation for biolubricants (Perez, 2012). However, this unit operation is not available in the commercial simulator Aspen Plus® to predict large-scale demands as well as to carry out simulations integrated with other unit operations or even for doing optimization of process variables.
Researchers have developed some specific simulation models to represent MD processes. Batistella and Maciel (1996), from the same research group of this paper, developed the DISMOL simulator to predict the mechanism of MD process. In recent years, Mallmann et al. (2009) emulated the MD process into the Aspen Plus® for the same binary components used by Batistella and Maciel (1996) and compared with the DISMOL simulator. They found interesting results and Tehlah et al. (2017) used the same methodology proposed by Mallmann et al. (2009) for oleic acid recovery. However, biolubricant research has been dedicated mostly to lab-scale studies.
In this context, the goal of this paper was to define a suitable model to represent molecular distillation for the biolubricant separation in the commercial simulator Aspen Plus®. A single flash vessel through an efficiency factor was selected to represent MD operation and supported it with experimental data obtained by the expertise of the authors of this work. This study contributes to the idea of a cost-effective biolubricant design; the results turn possible to explore different process variables and evaluate the product stream's outcomes into a commercial simulator.

2. Molecular Distillation Operation: Simulator Development

The simulation of a single flash (Figure 1) has been adopted to represent MD in some previous studies (Mallmann et al., 2009; Tehlah et al., 2017 and Komesu et al., 2016). Since an MD process is non-equilibrium, this paper has adopted an efficiency factor consideration with the operating temperature as the analyzed parameter (Mallmann et al., 2009).The simulation was validated through distillation mass ratio (F/D – feed; distillate flow) and mass fraction of distillate stream (Mallmann et al., 2009).

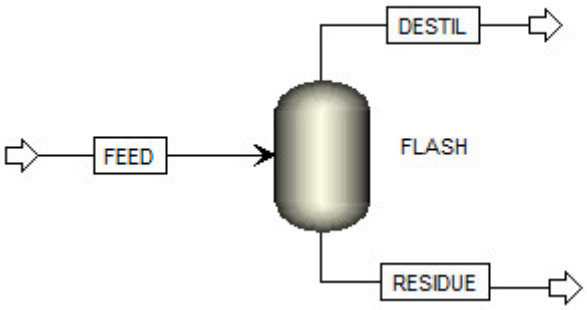

Figure 1: Molecular distillation emulation in the commercial software Aspen Plus®.

During the simulations, T_{FLASH} was varied and the distillation mass ratio (distillate/feed) was monitored. The final T_{FLASH} was found when the distillation mass ratio was equivalent to the experimental data. The distillate mass fraction obtained from the flash was corrected by efficiency considerations, which represented the differences between equilibrium and non-equilibrium operations (Mallmann et al., 2009).
Firstly, the authors of this paper have used Eq. (1) proposed by Mallmann et al. (2009) to calculate efficiency in which T_{FLASH} is the temperature inside the Flash vessel and T_{MD} is the evaporator temperature using molecular distillation.

$$\eta = \frac{T_{flash}(K)}{T_{MD}(K)} \quad (1)$$

The authors have proposed another efficiency equation (Eq. 4) to represent the equilibrium considerations. Although the equation Eq. (1) was suitable for previous studies, other factors such as the rate of surface evaporation, equation Eq. (2), may influence the prediction of efficiency (Batistella and Maciel, 1996).

$$E_i = P_i^{sat}\left(\frac{M_i}{2\pi \cdot R \cdot T_s}\right)^{1/2} \quad (2)$$

In this paper, efficiency was considered as the rate of surface evaporation (Eq. 3) between flash and molecular distillation.
Calculating efficiency as the rate of surface evaporation instead of temperature ratio (Eq. 1), Eq. (4) was obtained.

$$\eta = \frac{E_{flash}}{E_{MD}} \quad (3)$$

$$\eta = \frac{\sqrt{T_{flash}(K)}}{\sqrt{T_{DM}(K)}} \quad (4)$$

3. Simulation Approach Validation

The objective of this section is the validation of the efficiency factor considering the rate of surface evaporation. The developed tool (Eq. 4) should fit the Aspen Plus® outputs using the flash vessel to the experimental data by molecular distillation.
In this preliminary investigation, simulated and experimental data from binary system glycerin and propylene glycol (Martinello et al., 2003) were compared to the emulated results into the Aspen Plus® from this study.
Previous researches using Matlab 5.3 by Martinello et al. (2003) studied the same equimolar binary system. They used a flow rate of 1 ml/min at 318.15 K to feed the flash vessel at 0.001 mbar and adopted UNIFAC to calculate the thermo-physical properties. In addition, they analyzed the distillation mass ratio and mass fraction of the distilled component (propylene glycol - PP). Their experimental study was performed in a molecular distillation UIC KDL4 and they used the same operational conditions described above.
To compare with them, the authors of this study have analyzed the same streams (Table 1) and simulated them under the same operating conditions. In this work, there are three simulated outputs from the flash vessel into the Aspen Plus®: with no efficiency correction; corrected using Eq. (1) proposed by Mallmann et al. (2009), and corrected using Eq. (4) proposed by this work (Table 1).

Table 1: Experimental and simulation data (Matlab; DEST-BIOLUB and Aspen Plus®)

Parameter	Experimental Martinello (2003)	Matlab 5.2 Simulation Martinello (2003)	Aspen Plus® (This work)	Aspen Plus® adjusted Eq. (1) (This work)	Aspen Plus® adjusted Eq. (4) (This work)
Operating temperature (K)	323.00	323.00	266.68	266.68	266.68
Distillation mass ratio (D/F) %m/m	37.40	40.50	37.10	37.10	37.10
Distillation PP %m/m	91.12	90.46	99.70	82.30	90.60

The flash vessel simulation required lower values of operation temperature (Table 1) to achieve the similar experimental distillation mass ratio (D/F) by Martinello et al., 2003. This is because flash vessel occurs at an equilibrium phase at 100% efficiency while molecular distillation is ruled by mass transfer ratio with some

efficiency limitations demanding high temperatures. Since the pressure is very low (0.001 mbar), the bubble point is close to -7°C which explains the low flash operation temperature.
Such temperature and equilibrium differences between flash and MD were taken into account using Eq. (5) by Mallmann et al. (2009) and Eq. (6) proposed by this work to adjust the higher mass distilled fraction results from the flash vessel (Table 1). The efficiency factors were 82.5% and 90.9%, respectively.

$$\eta = \frac{266.68}{323} = 82.5\% \quad (5)$$

$$\eta = \frac{\sqrt{266.68}}{\sqrt{323}} = 90.9\% \quad (6)$$

Equation 4 to convert the flash result into MD better agreed to the experimental results (Table 2). Regarding the distillation of PP mass fraction, Aspen Plus® predictions with the efficiency factor proposed are within ±1% of that obtained experimentally by Martinello et al. (2003), which validate the use of this tool as an efficiency factor to represent the separation difference between the unit operations.
Either the distillation mass ratio (D/F) or distillation mass fraction deviation using Aspen Plus® were the lowest simulated values (Table 2), which means that using the commercial software with the efficiency factor proposed is more accurate to predict large-scale process demands.

Table 2: Simulation deviation results

Parameter	Matlab 5.2 Simulation Martinello (2003)	Aspen Plus® (This work)	Aspen Plus® adjusted Eq. (1) (This work)	Aspen Plus® adjusted Eq. (4) (This work)
Distillation mass ratio (D/F) %m/m deviation	8.28	0.80	0.80	0.80
Distillation PP %m/m deviation	0.72	9.42	9.71	0.59

Although the equation Eq. (1) was suitable for previous studies (Mallmann et al., 2009; Tehlah et al., 2017 and Komesu et al., 2016), other factors such as the rate of surface evaporation, may influence the prediction of efficiency (Batistella and Maciel, 1996). Thus, the developed flash process tool adjusted by Eq (4) can be applied to the biolubricant separation considered in this work.

4. Biolubricant Process Simulation

The approach validated in the previous section was used for the simulation of biolubricant separation in a flash vessel into the Aspen Plus®. The feed stream of the process (Table 3) was consisted of a binary system made up by isoamyl ricinoleate (biolubricant) and monoricinoleine (Perez, 2012).
A flow rate of 4.2E-7 Kmol/s at 363.15 K was fed to the flash vessel at 0.001 mbar and adopted UNIFAC to calculate the thermo-physical properties (Perez, 2012).
The flash vessel simulation required lower values of operation temperature (Table 4) as predicted by the previous simulation with glycerin and propylene glycol. The thermodynamic equilibrium difference between the unit operations was adjusted using Eq. (1) and Eq. (4). The efficiency factors were 83.0% and 91.1%, respectively.

Table 3: Composition of biolubricant separation and its properties in the feed stream

Component	Mole fraction	Molar mass	Formula
Isoamyl ricinoleate	0.86	368.59	$C_{23}H_{44}O_3$
Monoricinoleine	0.14	372.54	$C_{21}H_{40}O_5$

Table 4: Experimental and simulation for Biolubricant separation

Parameter	Experimental Perez (2012)	Aspen Plus® (This work)	Aspen Plus® adjusted Eq. (1) (This work)	Aspen Plus® adjusted Eq. (4) (This work)
Operating temperature (K)	418.0	347.2	347.2	347.2
Distillation mass ratio (D/F) %m/m	34.0	32.1	32.1	32.1
Distillation Biolubricant %m/m	89.7	95.9	79.6	87.4

The simulated values (using Aspen Plus corrected with Eq. 4 in Table 5) were similar to the experimental results obtained by Perez (2012). Although the distillation mass fraction deviation was greater when compared to the previous binary system (Table 5), it is a still low value (within ± 3%) close to some previous studies in the literature (Mallmann et al., 2009; Tehlah et al., 2017 and Komesu et al., 2016).
Considering the rate of surface evaporation (Eq. 4), the distilled mass fraction values better represented molecular distillation than values using Eq. (1), which confirms that Eq (4) is suitable to model the performance between the flash vessel and molecular distillation.

Table 5: Simulation deviation results

Parameter	Aspen Plus® (This work)	Aspen Plus® adjusted Eq. (1) (This work)	Aspen Plus® adjusted Eq. (4) (This work)
Distillation mass ratio (D/F) %m/m deviation	5.4	5.4	5.4
Distillation Biolubricant %m/m deviation	6.9	11.2	2.6

5. Conclusions

A new efficiency factor coupled to a flash vessel in the commercial software Aspen Plus® is proposed to emulate the molecular distillation operation. This new efficiency factor considers the rate of surface evaporation to represent molecular distillation (non-equilibrium) into a flash vessel (equilibrium) operation. The results showed good agreement with experimental data either to glycerin/propylene glycol or biolubricant system. During both binary simulations, considering the rate of surface evaporation, the corrected distillate mass fraction values

better represented molecular distillation than simulated corrected values using just the temperature ratio, which confirms that this new efficiency factor coupled to a flash vessel in the Aspen Plus®, is suitable to model the performance between the flash vessel and molecular distillation.

Nomenclature

M_i – molecular weight, Da
P_{sat}^i –saturated pressure, Pa
T_s – Surface temperature, K
T_{flash} – flash temperature, K
T_{MD} – evaporator temperature using molecular distillation, K
η – efficiency factor, -

Acknowledgments

The authors would like to thank grant #2015/20630-4 São Paulo Research Foundation (FAPESP).

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