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PURIFICATION OF CRUDE GLYCEROL BY SHORT PATH EVAPORATION. THEORETICAL AND PRACTICAL ANALYSIS OF PROCESS PARAMETERS

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ABSTRACT. Crude glycerol, the by-product from biodiesel production process, increased drastically as rapid growth of biodiesel industry. This by-product contains many impurities such as water, soaps, free fatty acids, esters etc. This paper presents a process development based on molecular distillation or short path evaporation, for glycerol purification up to 99%. Several experiments and theoretical analysis have been carried out to identify the effect of important parameters (mean free path, Knudsen number, evaporation rate, feed flow rate and evaporation temperature) which determine the performance of the molecular distillation process. The purified glycerol is collected in the distillate while the residue is enriched in higher molar mass components. High performance liquid chromatography (HPLC) was employed to determine the purity of glycerol.

Keywords: *glycerol, molecular distillation, mean free path*

INTRODUCTION

The glycerol market is currently undergoing radical changes, driven by very large supplies of glycerol arising from biodiesel production, because the production of 10 kg of biodiesel by the transesterification process yields about 1 kg of crude glycerol as co-product [1-3]. The crude glycerol contains many impurities such as water, organic and inorganic salts, soaps, alcohol, traces of mono- and diglycerides and vegetable colours. High purity glycerol is still required as it is an important industrial feedstock for applications in food, cosmetic, pharmaceutical industries or other uses [4]. In this study the molecular distillation process has been studied as a technique for glycerol purification.

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Characteristics of the molecular distillation process are: the small distance between the evaporator and condenser, low temperatures, short residence times and low pressure in the distillation gap. In contrast to the conventional distillation, molecular distillation does not occur at any well-defined temperature, as long as there is a thermal gradient between the condenser and the evaporator. Consequently, the distilling vapour molecules pass directly from the vaporizing surface to the condensing surface and no equilibrium exists between the vapor and the liquid phases. Ideal distillation conditions are attained when the rate of evaporation is equal to the rate of condensation and no vapour molecules returning to the liquid phase [5-8]. The condition for the molecular distillation is that the mean free path (λ) for the light molecules to be greater than the distance between the evaporator and the condenser [9-10]. In contrast, the heavy molecules can not reach the condenser and return to the evaporator [11]. Schematic representation of molecular distillation is shown in Figure 1.

The objective of this paper is the estimation of the molecular distillation parameters for glycerol evaporation.

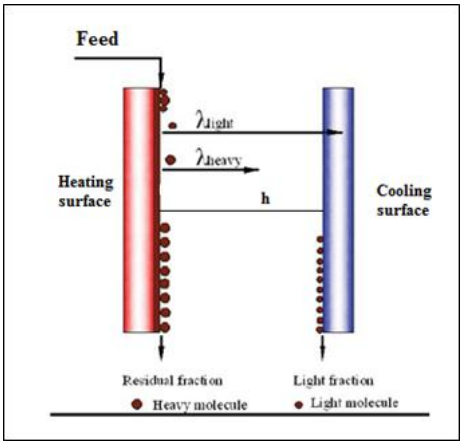


Figure 1. Schematic representation of molecular distillation process [12]

RESULTS AND DISCUSSION

(1) The mean free path [7]

$$\lambda = 2.3 \cdot 10^{-20} \frac{T}{p\sigma^2}, [cm]$$

where: T-temperature (K); p- gas pressure (torr); σ- molecule diameter (cm).

The mean free path was calculated at pressures below 1mmHg at different temperatures in order to select the operating parameters of the process because the mean free path must be higher than 0.8 cm, which is the distance between the evaporator and condenser, for the equipment used and presented in Figure 7. The mean free path of the glycerol molecules at different temperatures is shown in Figure 2.

The glycerol molecules can reach the cooling surface at pressure below 0.3 mmHg. The mean free path of the impurities (such as methyl ester, free fatty acid, mono-, di- and triglycerides) is smaller and the distance between the evaporator and condenser and can be separated effectively due to the difference between mean free paths and molar masses.

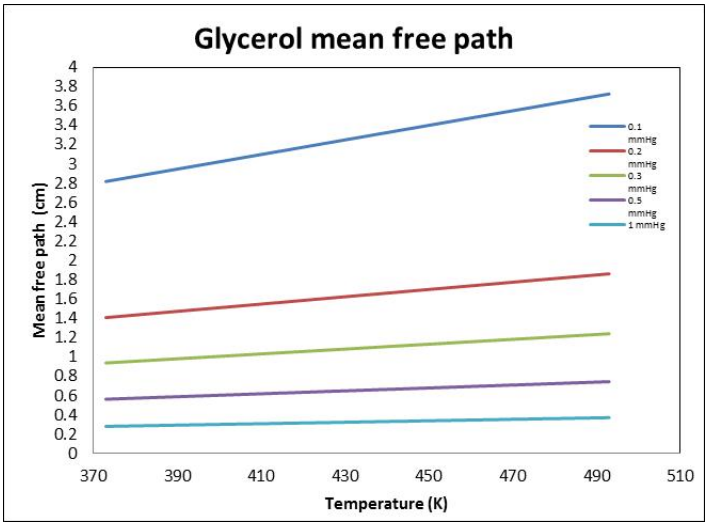


Figure 2. Effect of temperature on glycerol mean free path

(2) The Knudsen number [13]:

$$Kn = \frac{\lambda}{h}$$

where: λ- the mean free path (cm); h- distance between the evaporator and condenser (cm).

The distillation at 0.3 mmHg is in the intermediate range (0.05<Kn<10) and it is a proper distillation rate, see Figure 3. The thermal decomposition of glycerol in these conditions is reduced.

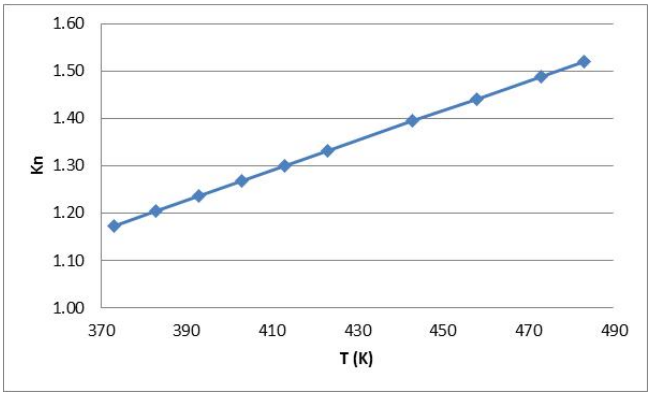


Figure 3. Effect of temperature on Knudsen number

(3) ***The relative evaporation rate [7]***

$$M_0 = 5.83 \cdot 10^{-2} \cdot p \left(\frac{M^0}{T}\right)^{1/2}, \ [g \cdot cm^{-2} \cdot s^{-1}]$$

where: p- vapour pressure (torr); T-temperature (K); M^0- molecular mass (g.mol).

(4) ***The effective evaporation rate [7]***

$$M_r = 5.83 \cdot 10^{-2} \cdot f \cdot p \left(\frac{M^0}{T}\right)^{1/2}, \ [g \cdot cm^{-2} \cdot s^{-1}]$$

where f is the efficiency factor, determined with the formula

$$f = F + (1 - F)(2 \cdot e^{-N} - e^{-2N}) \ [9]$$

F is the surface ratio

$$F = \frac{A_{evap}}{A_{evap} + A_{cond}} \ [9]$$

$$N = \frac{h}{k \cdot \lambda} \ [9]$$

$$\log k = 0{,}2 \cdot F + 1{,}38(F + 0{,}1)^4 \ [9]$$

The effect of temperature on evaporation rate is shown in Figure 4. An increased heat supply to the evaporated liquid causes its temperature to rise and thus induces the rise of saturated vapor pressure and distillation rate increase. The efficiency factor f is 0.98, the difference between the relative and effective evaporation rate is very small.

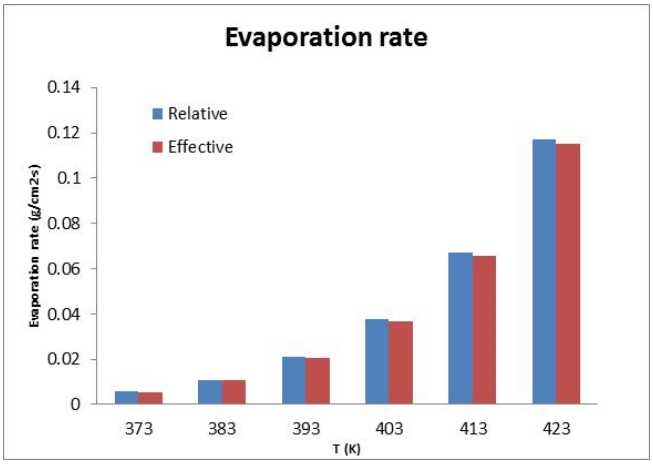


Figure 4. Effect of temperature on evaporation rate

The purity obtained for glycerol was about 99% (98.6-99.24%) in the temperature range of 373K-423K.

At 423 K, the maximum quantity of separated glycerol, was at feed flow rate of 90 ml/min and then decreased, as shown in Figure 5. This can be explained by the thickness of the evaporating falling film. At higher feed flow rates, the thickness of the film is larger, the velocity of the film is bigger and the contact with the heated surface is not enough for evaporation. At 90 ml/min, the glycerol yield is 80%, at a purity of about 99%. This is very important, because the yield we obtained by classical distillation was no higher than 58.85 %.

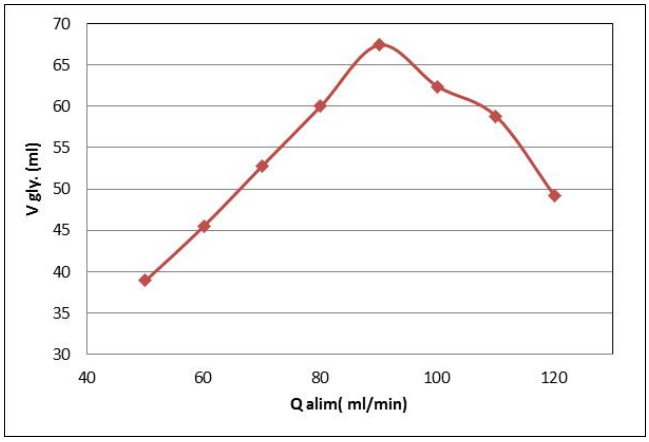


Figure 5. Effect of feed flow rate on distillate volume of glycerol

CONCLUSIONS

Molecular distillation is an effective tool to purify glycerol up to 99%, after the water and the volatiles were removed. The purification is possible due to the differences between mean free path, molar mass and volatilities of glycerol and impurities. The low residence time and using a higher vacuum in molecular distillation process, increased the glycerol yield and productivity.

EXPERIMENTAL SECTION

Materials

The material used to make the study is crude glycerol obtained from the biodiesel plant of SC EXPUR Slobozia, with the following composition:

Table 1. Crude glycerol (EXPUR) characteristics

Crt.	Properties	Specifications
1	Glycerol content (%)	84.6
2	Water (%)	9.1
3	MONG	1.5
4	Alcalinity (meq/100g)	1.8
5	Methanol (%)	0.04
6	Ash (%)	4.8

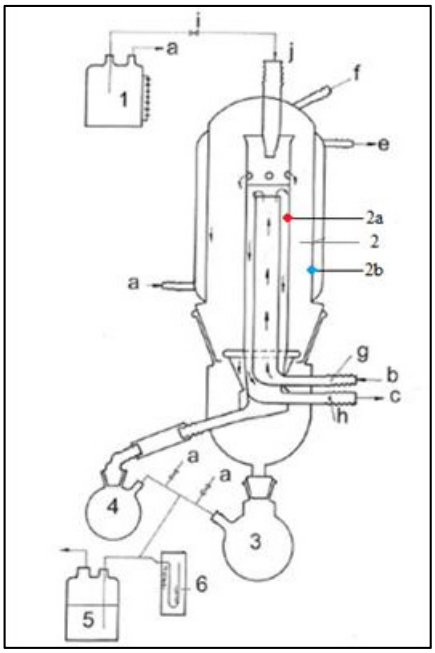
This glycerol has already been pre-treated, the methanol was recovered and the soap and free fatty acids were removed, because the MONG content is reduced. After the water was removed by conventional batch distillation (T=373 K and 40 mmHg), the glycerol was distillated by molecular distillation. The glycerol content after water removal was 92.28%.

Equipment

The distillation was performed using a laboratory falling film type molecular distillation column, shown in Figure 2, made of four concentric cylindrical Pyrom glass tubes, that allows the visual inspection of the distillation process. The thermal agent (silicon oil) is introduced into the central tube, through the connection hose-b and it comes back from the column to the thermostat, by connection hose-c. The raw glycerol solution is degased and is introduced from the tank-1 connected to the column by the inlet hose-j and it is uniformly distributed on the external surface of the second tube, which acts as evaporator, through the inlet holes. The solution passes through the surface of the second tube in a falling film and the volatiles components evaporate. The

vapors condensate on the internal surface of the third tube and the condensate is collected in the round flask- 3. The heavier components are collected in the round flask-4. The fourth tube is for the cooling agent, and it has two connection hoses – inlet/outlet. The whole installation is connected to a vacuum pump through the connection hose -f.

The distance between the evaporation and cooling surface is 0.8 cm. The surface area of the evaporator is 0.097968 m^2 and the area of the condenser is 0.158256 m^2. The operational temperature was up to 150°C and the pressure of the system was kept constant to 0.3 mmHg.



1- feeding tank
2- column body
2a-evaporator surface
2b- condenser surface
3- heavy molecule solution
4- light molecules condensate
5- trap
a – cooling agent (water) inlet
b- Thermal agent (silicon oil) inlet
c- Thermal agent (silicon oil) outlet
e – cooling agent (water) outlet

Figure 7. Laboratory falling film distillation column

Analytical procedures

For the glycerol concentration determination, HPLC analyses were carried out on a Jasco Chromatograph (Japan) equipped with an intelligent HPLC pump (Model PU-980), a ternary gradient unit (Model LG-980-02), an intelligent column thermostat (Model CO-2060 Plus), an intelligent reflex index detector (Model RI-2031 Plus) and an injection valve equipped with a 20 μL sample loop (Rheodyne). Samples were manually injected with a Hamilton Rheodyne Syringe (50 mL). This system was controlled and data were processed with the ChromPass software.

The separation was achieved on a Carbosep Coregel 87H3 column (300 x 7.8 mm) at temperature of 70 ºC. The mobile phase was a sulphuric acid 0.01 M solution. The flow rate was 1 mL min^{-1} and the injection volume was 20 µL. All samples and standards were filtered through PVDF 0.45 µm syringe filters (Teknokroma) and manually injected into the HPLC system. Each run was completed within 14 min.

ACKNOWLEDGMENTS

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