

On the effect of inert gases in breaking the formic acid–water azeotrope by gas-gap membrane distillation

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Abstract

The effect of inert gases, such as helium, air, and sulfur hexafluoride, in breaking the formic acid–water azeotrope by gas-gap membrane distillation process is theoretically investigated under the process relevant operating conditions. A Stefan–Maxwell-based mathematical model that includes all necessary vapor–liquid equilibrium, heat, and mass relations is used for this purpose. According to the model predictions, heavy inert gases such as sulfur hexafluoride help more in breaking the azeotrope than lighter ones such as air and helium. This phenomenal behavior is discussed along with the effect of other associated process parameters. © 1999 Published by Elsevier Science S.A. All rights reserved.

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1. Introduction

Azeotropic mixtures that are impossible to separate by simple fractional distillation can be separated by a range of unit operations including those tested on an industrial scale such as azeotropic and extractive distillation and newer technologies showing promise in the laboratory such as pervaporation [1], adsorptive distillation [2], capillary distillation [3], diffusion distillation [4], and membrane distillation [5].

Membrane distillation, the process considered in this paper, is a hybrid of thermal distillation and membrane processing which can be configured as direct contact or gas-gap modules. In gas-gap membrane distillation a hydrophobic porous membrane is used to separate the feed mixture from a gas space which is bounded on the other side by a cooling surface (see Fig. 1). The hydrophobic nature of the membrane prevents the passage of liquid mixture while allowing for the passage of vapors. The process involves evaporation of water in the hot feed side, migration through the dry microsporous structure of the membrane and the additional gas-gap and finally condensation on a cooling surface.

The main advantage of membrane distillation over conventional distillation processes is that distillation takes place

at temperatures below the normal boiling point of the feed solutions. In addition, separation of the feed mixture is not only governed by vapor–liquid equilibrium relationships but also by the components diffusion rates in the inert gas which fills the membrane pores and the gap that separates the membrane from the condensing plate. Therefore, using gases other than air will affect the separation performance which is judged by both selectivity and flux. The major drawback of membrane distillation, however, is the danger of membrane wetting.

Other separation processes that rely on differences in diffusion rates across a gas layer include mass diffusion [6], sweep diffusion [7], and diffusion distillation [4]. The later process was proposed by Fullarton and Schlünder [4] to separate azeotropic mixtures such as a binary isopropanol–water mixture and a ternary isopropanol–water–methanol mixture. They found that in a wetted-wall column consisting of two concentric tubes with different inert gases and annular widths, a significant separation effect could be achieved. The use of membrane distillation for separating azeotropic mixtures such as propionic acid–water mixture and hydrochloric acid–water mixture was firstly proposed by Udriot et al. [5] who found that, at the azeotropic point, selectivities between 0.6 and 0.8 were achieved instead of unity as implied by VLE. Because of the higher fluxes obtained by membrane distillation than by pervaporation, they suggested the use of membrane distillation instead of

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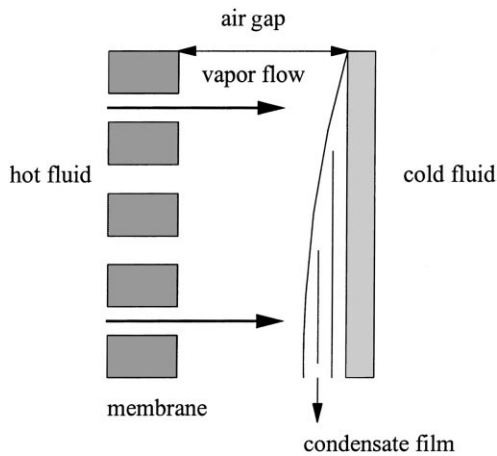


Fig. 1. Schematic drawing of gas-gap membrane distillation.

pervaporation for water rich azeotropes. Subsequently, Rivier and Stockar [8] used a plate and frame module with an air-gap of 4 mm to separate formic acid–water azeotrope. They found that integrating one membrane distillation unit with two rectification columns consumed approximately the same amount of energy required by the classical design. However, they suggested that if formic acid selectivities could be improved, then more efficient separation with better energy savings would be possible.

In an attempt to improve the process, a Stefan–Maxwell mathematical model is used to inspect the effect of inert gases; air, helium, and sulfur hexafluoride, in breaking the formic acid–water mixture azeotrope. The process performance is discussed in terms of fluxes and selectivities that can be achieved by using different inert gases. The effect of relevant process parameters, at the azeotropic point, are also discussed for the three selected inert gases.

2. Theory

The use of membrane distillation process for breaking the formic acid–water azeotrope is based on the preferential diffusion of certain gas-phase species through a nondiffusing inert gas. Obviously, this process is multicomponent, involving water, formic acid, and the stagnant gas. Diffusion in multicomponent ideal gas mixtures is accurately described by the Stefan–Maxwell equations. Exact analytical solutions of the Stefan–Maxwell equations with solution algorithms are recently presented by Taylor and Krishna [9].

Vapor migration from the feed side toward the cooling surface, in membrane distillation, results from the partial pressure gradient caused by a temperature difference across the unit. Mass transfer occurs in a consequence of three steps; movement of the transferring species from the liquid bulk toward the membrane surface, evaporation at the membrane gas–liquid interface, and transport through the membrane pores and the stagnant inert gas prior to con-

densation. However, the difference in diffusion rates between the transferring components results in the membrane-associated phenomenon; concentration polarization. Supplying the required latent heat of vaporization for the transferring species from the feed bulk creates a phenomenon known as temperature polarization. Calculation of the interfacial temperature and concentrations at the membrane surface is a pre-requisite for accurate vapor composition calculations.

The vapor compositions at the evaporating film and condensate film interfaces are calculated from the phase equilibrium.

$$y_i = \frac{\gamma_i x_i P_{0i}(T)}{P} \quad i = 1, 2, \dots, n \quad (1)$$

γ_i is the liquid activity coefficient calculated by Wilson's model and P_0 is the component vapor pressure calculated using Antoine's equation [10]. P is the total pressure. Once y_i are calculated, y_{n+1} , the mole fraction of the inert gas at the interface is calculated from the sum of mole fractions relation.

$$y_{n+1} = 1 - \sum_{i=1}^n y_i \quad (2)$$

The concentration of the permeating species at the membrane surface can be evaluated from the following mass balance relation:

$$x_{im} = x_{ip} - (x_{ip} - x_{ib}) \exp \left[\frac{N_t}{c_i k_{in}} \right] \quad (3)$$

whereas the temperature at the membrane and condensing surface, T_m , and T_p , respectively can be calculated from [11,12]

$$T_m = T_b - \frac{U_T}{h_h} \left((T_b - T_c) + \frac{\sum N_i \lambda_i}{h^*} \right) \quad (4)$$

$$T_p = T_c + \frac{U_T}{h_c} \left((T_b - T_c) + \frac{\sum N_i \lambda_i}{h^*} \right) \quad (5)$$

where

$$U_T = \frac{1}{(1/h_h) + (1/h^*) + (1/h_c)} \quad (6)$$

Details of the calculations of h_c , h_h , and h^* can be found elsewhere [12]. For a differential module length and under steady state conditions the condensate composition is

$$x_i = \frac{N_i}{\sum_{i=1}^n N_i} \quad (7)$$

It is assumed that mass transfer throughout the gas phase occurs purely by molecular diffusion; there is no transport by convection. Under steady state conditions, the equation of continuity of moles of species can be written as:

$$\frac{dN_i}{dz} = 0 \quad (8)$$

showing that N_i is z invariant. The molar fluxes N_i are made up of diffusive and convective terms:

$$N_i = J_i + y_i N_t$$

Krishna and Standart [13] developed a general matrix solution of the n differential Stefan–Maxwell equations to calculate the diffusion fluxes:

$$(N) = \frac{\varepsilon P}{RT} [\beta][E_m][k_{ym}](y_m - y_p) \quad (10)$$

ε corrects for the membrane open surface area, $[\beta]$ bootstrap matrix, $[E_m]$ matrix of high flux correction factors and $[k_{ym}]$ is the matrix of low flux mass transfer coefficients. For a ternary system, the elements of $[k_{ym}]$ can be explicitly written as:

$$\begin{aligned} k_{11} &= \frac{\kappa_{13}(y_{1m}\kappa_{23} + (1 - y_{1m})\kappa_{12})}{S} \\ k_{12} &= \frac{y_{1m}(\kappa_{13} - \kappa_{12})}{S} \quad k_{21} = \frac{y_{2m}\kappa_{13}(\kappa_{23} - \kappa_{12})}{S} \\ k_{22} &= \frac{\kappa_{23}(y_{2m}\kappa_{13} + (1 - y_{2m})\kappa_{12})}{S} \end{aligned} \quad (11)$$

where

$$S = y_{1m}\kappa_{23} + y_{2m}\kappa_{13} + y_{3m}\kappa_{12}$$

$$\kappa_{ij} = \frac{D_{ij}}{l}$$

$$l = \delta\tau + b$$

where δ is the membrane thickness, τ is the membrane tortuosity, b is the gas-gap width, l is the diffusion film thickness, and D_{ij} is the vapor phase diffusivity of binary gas pair i – j . The Fuller et al. [14] correlation, which is recommended by Reid et al [15], is used for calculating the diffusion coefficients. According to [14] correlation the diffusion coefficient can be related to temperature and pressure by

$$D_{ij(T,P)} = D_{ij(T_0,P_0)} \left(\frac{T}{T_0}\right)^{1.75} \left(\frac{P_0}{P}\right) \quad (12)$$

Other terms in Eq. (10) are fully described by [9] and [13]. The selectivity as defined by [5] and [8] is:

$$\alpha = \frac{x_p}{x_f}$$

Note that the interfacial temperatures and concentrations and the diffusion fluxes must be calculated iteratively.

3. Results and discussion

Rivier and Stockar mentioned that if the formic acid selectivity obtained by membrane distillation process could be improved then integrating membrane distillation modules with rectification columns would compete with other conventional distillation methods, from the economy per-

Table 1
Rivier and Stockar membrane module specifications [8]

Module	plate-and-frame
Membrane	flat PTFE membrane, Schleider and Schull TE 35 (0.2 μ m)
Area	0.04 m ²
Conditions	$T_h = 60^\circ\text{C}$, $T_c = 10^\circ\text{C}$
Gas-gap	4 mm

spective. The specifications of their membrane module are listed in Table 1. One of the possible modifications of the membrane distillation process is to replace the inert air which fills the space between the membrane and the coolant surface by another inert gas. Separation in membrane distillation occurs in a consequence of two steps, evaporation of the feed liquid at the membrane–liquid interface and diffusion through the gas-filled pores and the additional gas gap. The evaporation step is governed by the vapor–liquid equilibrium relationships and the diffusion step is limited by the speed of diffusion of the concerned components. Therefore, replacing air with other inert gases affects the diffusion step and, consequently, the overall separation.

Three different inert gases ranging from light to heavy are considered in this work. These are, in the order of lighter to heavier, helium, air, and sulfur hexafluoride. The hypothesis that underlies this work stems from the fact that the transport of volatile components, in membrane distillation, occurs virtually by molecular diffusion. As diffusion is a molecular process depending solely on the random motion of individual molecules, the rate of diffusion of the concerned components is, therefore, directly proportional to the average velocity of the transferring molecules. Owing to the well known fact that the average velocity becomes greater when light gases are used as a diffusion media, using different inert gases results in different diffusion rates. While heavy inert gases slow down the diffusion rates, light gases speed it up. The difference in diffusion rates of the concerned components is reflected directly on fluxes and, consequently, on selectivities. The use of heavy inert gas instead of light one acts as a filter with smaller pore size. Therefore, it is expected that by the use of heavy inert gases, selectivity will be better but at the expense of flux quantity. The inert gas filter notion is employed here to help in breaking the formic acid–water azeotrope. For the seek of the best operating conditions, the azeotropic mixture of formic acid–water is exposed to three different inert gas filters under different processes parameters. The effect of the considered inert gases is discussed below, along with the effect of appropriate process variables.

The effect of feed composition on the formic acid selectivity is shown in Fig. 2. As shown, when heavy gases such as SF₆ are used, the selectivity of formic acid is driven away from unity whereas when light gases such as helium are used the azeotropic point is only shifted from 77.5 to 84 wt.%. This behavioral difference is caused by the effect of the diffusion step on the overall process performance.

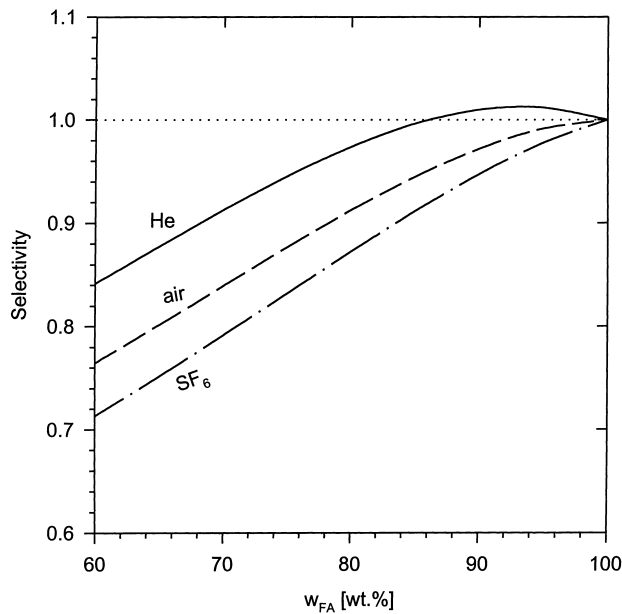


Fig. 2. Effect of formic acid composition on the formic acid selectivity ($T_h = 60^\circ\text{C}$, $T_c = 10^\circ\text{C}$, air-gap = 4 mm).

Since diffusion is molecular transport, the size and collision frequency of the molecules affect significantly their diffusion rates. Therefore, as expected and shown in Fig. 3 using light gases such as helium increases appreciably the total mass flux while using heavy gases such as SF_6 reduces it. This is a reminiscent of the gas filter notion. Notice that the lower the selectivity from unity the better the separation is. This is because the formic acid–water azeotrope is considered water poor azeotrope. The inert gas filter, specifically

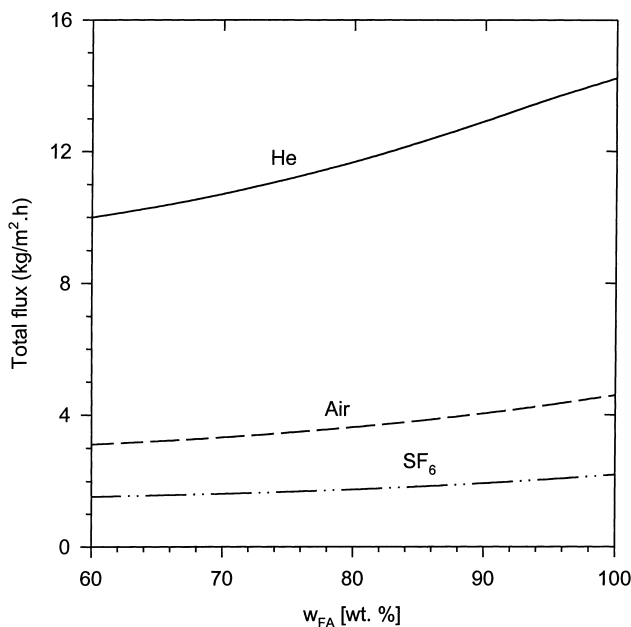


Fig. 3. Effect of formic acid composition on the total flux ($T_h = 60^\circ\text{C}$, $T_c = 10^\circ\text{C}$, air-gap = 4 mm).

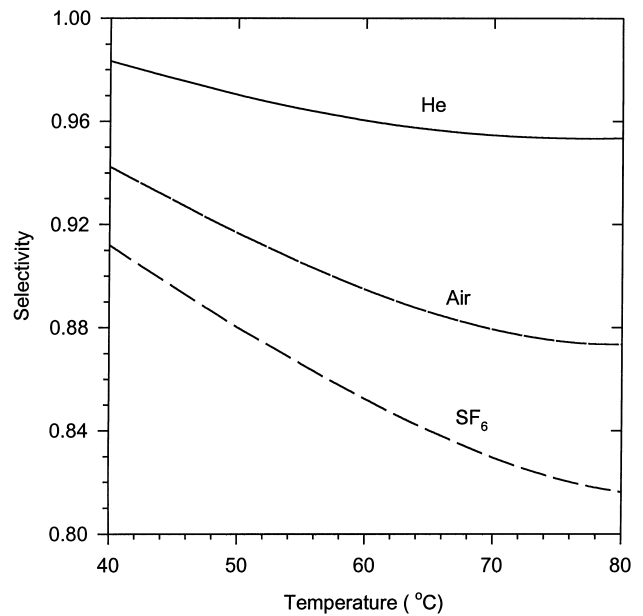


Fig. 4. Effect of feed temperature on the formic acid selectivity ($T_c = 10^\circ\text{C}$, air-gap = 4 mm, $w_{\text{FA}} = 77.5$ wt.%).

air, and SF_6 , preferentially passes water, thus, enriching the feed stream in formic acid. Therefore, using SF_6 gives the best results in terms of selectivity, however, this achievement is at the expense of flux reduction.

Fig. 4 shows the effect of feed temperature on selectivity at the azeotropic point for the three inert gases. As illustrated, operating at high feed temperatures gives better results in terms of selectivity than operating at low ones. The feed temperature increase doesn't only affect the vapor pressure of formic acid and water but also their diffusivities. As demonstrated in Eq. (12), the diffusion coefficients vary with the 1.75 power of the temperature. Since the components diffusion coefficients are welling to increase by increasing the feed temperature, more diffusion interactions are expected to take place and, consequently, the separation of the feed mixture will be more affected by the diffusion step as shown in Fig. 4. Again, SF_6 as a filling gas gives better selectivities for the whole investigated temperature range. The difference between attained selectivities by using the three inert gases is more pronounced at high feed temperatures than at lower ones.

The effect of coolant temperature at the azeotropic point on selectivity is elucidated in Fig. 5. Although, the coolant temperature is varied between 10 and 30°C no significant change in selectivity is perceived. The difference between the selectivity values remains approximately constant for all inspected gases over the whole coolant temperature range. This indicates that raising the coolant temperature steadily changes the ratio of molecular interactions between the concerned molecules.

The gas gap width is an important factor in determining the amount of flux of each component and, consequently, the process selectivity. Since the diffusion coefficients are only

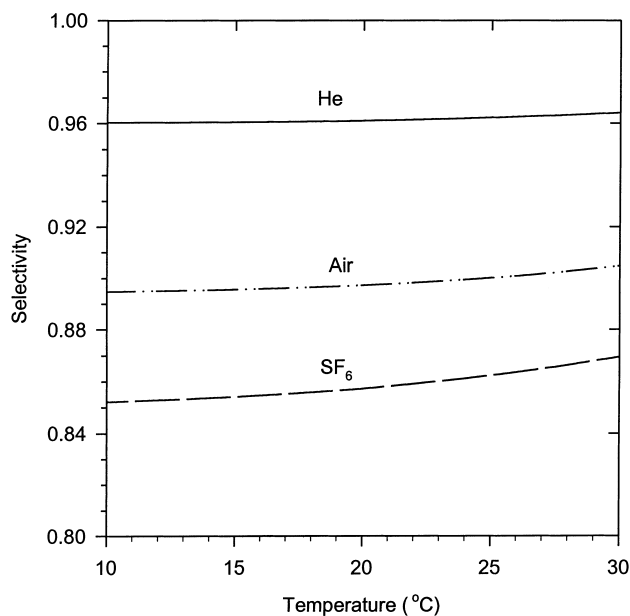


Fig. 5. Effect of coolant temperature on the formic acid selectivity ($T_h = 60^\circ\text{C}$, air-gap = 4 mm, $w_{\text{FA}} = 77.5$ wt.%).

dependent on temperature and pressure as elucidated in Eq. (12), the only effect of increasing the gap width is to reduce the formic acid and water fluxes. Assuming that species transfer occurs only by molecular diffusion i.e., no convection in the gas-gap, increasing the gap width increases the mass transfer resistance and inversely affects the flux. Eqs. (4) and (5), and Eq. (12) demonstrate the importance of the flux in relation to concentration and temperature polarization, respectively. However, the impor-

tance of temperature and concentration polarization are only significant at low feed concentrations [16]. In light of this, the influence of polarization phenomena on selectivity in the case of formic acid-water azeotropic mixture will be minimal. The selectivity, as shown in Fig. 6, is almost independent of the gas-gap width and the difference in the attained selectivities remains almost constant. This trend is compatible with [5,4] findings regarding the effect of gas-gap width on selectivity. Udriot et al. [5] found that the propionic acid selectivity remained constant when the air gap width was increased from 4 to 7 mm. Fullarton and Schlünder [4] reported that in the absence of any convective effect in the annular gap, the selectivity ought to be independent of the gap width. Owing to the fact that fluxes are inversely proportional to the diffusion path length, minimizing the gap width gives better results.

4. Conclusions

A Stefan–Maxwell mathematical model is used to study the effect of inert gases in breaking the formic acid–water azeotrope by gas-gap membrane distillation process. Based on simulation results, it was noticed that both the flux and selectivity of membrane distillation are not only governed by the vapor–liquid equilibrium relations but also by the different diffusivities in the inert gas. Under all studied conditions such as the hot and cold side temperatures, feed composition, and gap width, the heaviest inert gas SF6 gives the best selectivities but at the expense of flux reduction. The results showed that using such heavy gas eliminates totally the azeotropic point.

5. Nomenclature

b	gas-gap width (m)
c	molar concentration (mol/m^3)
D	Diffusion coefficient (m^2/s)
$[E]$	matrix of high flux correction factors (–)
h	heat transfer coefficient ($\text{W}/\text{m}^2 \text{K}$)
J	molar diffusion flux ($\text{mol}/\text{m}^2 \text{s}$)
k	mass transfer coefficient (m/s)
$[k_y]$	matrix of zero flux mass transfer coefficients [m/s]
l	diffusion film thickness (m)
N	molar flux ($\text{mol}/\text{m}^2 \text{s}$)
(N)	molar flux column matrix ($\text{mol}/\text{m}^2 \text{s}$)
P	total pressure (Pa)
P_0	(vapor pressure (Pa)
R	universal gas constant ($\text{J}/\text{mol K}$)
S	quantity defined in Eq. (11) (m/s)
T	absolute temperature (K)
U	overall heat transfer coefficient ($\text{W}/\text{m}^2 \text{K}$)
w	mass fraction (–)
x	mole fraction in the liquid phase (–)
y	mole fraction in the vapor phase (–)

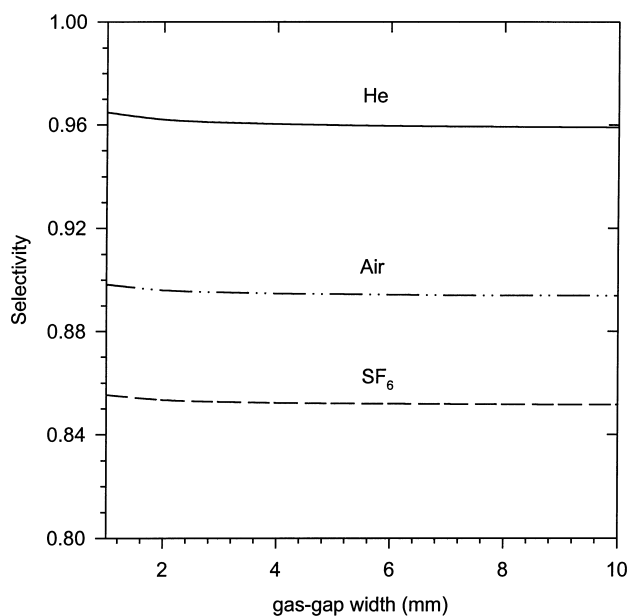


Fig. 6. Effect of gas-gap width on the formic acid selectivity ($T_h = 60^\circ\text{C}$, $T_c = 10^\circ\text{C}$, $w_{\text{FA}} = 77.5$ wt.%).

Greek symbols

α	selectivity (–)
$[\beta]$	bootstrap matrix (–)
γ	activity coefficient (–)
δ	membrane thickness (m)
ε	membrane porosity (–)
κ	Stefan–Maxwell mass transfer coefficient (m/s)
λ	latent heat of vaporization (J/mol)
τ	membrane tortuosity (–)

Subscripts and superscripts

b	bulk
c	cold side
h	hot region
i, n	indexes denoting component number
m	membrane
p	cooling plate side
T	total
*	air gap region

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