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# UPTODATE REVIEW OF COUPLED HEAT AND MASS TRANSFER MODELS AND APPLICATIONS OF THE THERMODYNAMIC OF IRREVERSIBLE PROCESSES IN FALLING FILM ABSORBERS

Mahamoudou A. \*, Ramousse J. and Le Pierrès N.

\*Author for correspondence

LOCIE Laboratory, CNRS UM5271,  
Savoie Mont-Blanc University,  
Le Bourget-du-Lac, 73370,  
France,

E-mail: [arnat.mahamoudou@univ-smb.fr](mailto:arnat.mahamoudou@univ-smb.fr)

## ABSTRACT

As a key component of the absorption machines, this paper focuses on the absorber to review the different analytical and numerical approaches used to analyse the thermal, mass and hydrodynamic phenomena occurring in falling films for both smooth and wavy laminar regimes. As nowadays, researches used the Thermodynamic of Irreversible Processes (TIP) to identify, to locate and to quantify the entropy generation sources, this paper also presents results of the application of the TIP on these absorber.

## INTRODUCTION

Absorption machines are environmentally friendly systems widely used for cooling and heating. These machines work with four main components: a desorber, a condenser, an evaporator and an absorber, and require two fluids: an absorbent and a refrigerant. The choice of the absorbent-refrigerant couple is based on many criteria [1]–[3]. The working couples can be classified as a function of their refrigerant:  $\text{NH}_3$ ,  $\text{H}_2\text{O}$ , alcohol, halogenated hydrocarbon and other mediums [4]–[6]. The most common ones are the lithium bromide/water (LiBr/  $\text{H}_2\text{O}$ ) and the water/ ammoniac ( $\text{H}_2\text{O}$  /  $\text{NH}_3$ ) couples [3].

The performance of the absorption machine is affected by many factors such as the design [7], [8], the operating conditions [9], [10] and the working fluids [11], [12] but also by the component efficiencies [13]. Researches show that the performance of the absorber has a direct impact in optimizing the Coefficient of Performance (COP) of the system. As a result, it is considered as a key component of these machines [14], [15]. Different configurations of absorbers, namely: plates, membranes, vertical and horizontal tubes for different absorption modes: falling film, spray and bubbles, have been studied with the aim of improving its performance [16].

The objective of this paper is to provide a comprehensive review of falling film absorbers because of their compactness, the high heat transfer coefficients they can achieve, their flexibility and suitability for different applications and their relatively low cost [17]. In their critical review of the different assumptions and methods of solving the absorber problems, [18] shows that despite the significant progress made from 1977 to 2000, work remains to be done. The aim of this paper is to update

the conclusions of [18] by focusing on the studies made after 2000. Thus, this paper is divided in two main parts. First, the theoretical approaches used to find the temperature and concentration distributions over a falling film are reviewed for both smooth and wavy laminar falling liquid film. Experimental studies at local scale are also mentioned. Then, the application of the Thermodynamic of Irreversible Processes (TIP) to these absorbers is presented.

## NOMENCLATURE

$D$	[m <sup>2</sup> /s]	Diffusion coefficient
$Ha$	[W/ m <sup>2</sup> ]	Surface heat of absorption
$ha$	[J/(kg. m <sup>2</sup> )]	Specific heat of absorption
$j$	[mol/(m <sup>2</sup> .s)]	Molar flux
$k$	[W/K. m]	Thermal conductivity
$\dot{m}$	[kg/s]	Flow rate
$p$	[Pa]	Pressure
$\dot{q}$	[W/m]	heat flux per wall unit length
Re	[-]	Reynolds number
$\dot{S}_{gen}'''$	[W/(K. m <sup>3</sup> )]	Volumic entropy generation rate
$T$	[K]	Temperature
$V$	[m/s]	velocity
$Y$	[-]	Mass fraction

### Greek characters

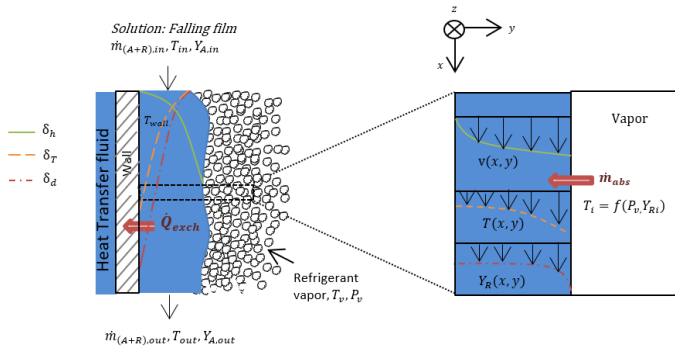
$\gamma$	[J/mol]	Chemical potential
$\delta$	[m]	Film thickness
$\rho$	[kg/m <sup>3</sup> ]	density
$\tau$	[Pa]	Shear stress tensor

### Subscripts

A	Absorbent
A + R	Absorbent+Refrigerant
abs	Absorbed
d	Diffusive
exch	Exchanged
h	Hydrodynamic
i	Interface
in	inlet
out	outlet
R	Refrigerant
s	solution
T	Thermal
vap	Vapor
w	Wall

## PROBLEM DESCRIPTION

The improvement of the falling film absorber efficiency requires understanding the phenomena encountered in these absorbers. Figure 1 shows the flow of a solution over a vertical plate and in contact with vapor refrigerant. Due to the chemical potential difference at the solution – vapor interface, a mass transfer process is induced from the vapor to the solution by absorption. This exothermic absorption rises the falling film temperature. These phenomena lead to the formation of the concentration  $\delta_d$ , thermal  $\delta_T$  and hydrodynamic  $\delta_h$  boundary layers in the solution showing the evolution of the absorption phenomenon impact into the falling film. Although, some researchers affirm that the interaction between the mass and the heat transfer is negligible and so that they could be studied independently [19], others studies shows that the falling films are the seat of thermal and mass phenomena strongly coupled to the falling film hydrodynamics [20].



**Figure 1** Schematic description of heat and mass transfer in falling film absorbers

The coupling between these phenomena is realized through two boundary conditions: the vapor pressure equilibrium – equation (1) – and the energy balance at the interface – equation (2) [18].

$$\begin{cases} T_{s,i} = T_{vap,i} \\ P_{vap} = f(T_{s,i}, Y_i) \end{cases} \quad (1)$$

$$H_a = h_a \dot{m}_{abs} = k_s \left( \frac{\partial T}{\partial y} \right)_i \quad (2)$$

To improve the absorber performance, the absorption phenomenon has been studied at local scale by solving the momentum, energy and mass conservation equations. Seven general assumptions are made in most of the studies [21]–[23]:

- The falling film solution is Newtonian and incompressible;
- All thermo-physical properties of the liquid and vapor are assumed constant and independent of temperature and concentration;
- The Dufour and Soret effects are neglected: The Dufour effect implies an energy flux due to a chemical potential gradient. The Soret effect is its reciprocal and it implies a gradient of concentration due to a temperature gradient;
- Transfer phenomena in the  $z$  direction is negligible (figure 1): side effects are neglected (2D resolution);

- Vapor pressure equilibrium exists between the vapor and the liquid at the interface;
- Steady-state regime is fully developed;
- Finite or infinite dilution.

The dilution is said to be infinite if the absorbed flow is very low compared to the solution flow. In this case, equation (3) gives the absorbed flow rate at the interface [20]:

$$\dot{m}_{abs} = \left[ -\rho D_{R-A} \frac{\partial Y_R}{\partial y} \right] \quad (3)$$

However, in real cases, it is not the case and so, at the interface equation (4) has to be used [22]:

$$\dot{m}_{abs} = \left[ -\rho \left( \frac{D_{R-A}}{1 - Y_R} \right) \frac{\partial Y_R}{\partial y} \right] \quad (4)$$

The next paragraphs summarize the analytical and numerical models developed to solve the problem of coupled heat and mass transfers in smooth and in wavy laminar falling films on plates, horizontal and vertical tube absorbers.

## FREE FALLING FILM SURFACE IN LAMINAR REGIME

In a smooth laminar regime, the fluid layers are linear and slide in parallel with no disruption between them.

### Flat Plate Absorbers

Flat plate heat exchanger technologies are widely used in the industry because of their compactness, excellent heat transfer efficiency and low cost [24]. Many authors developed analytical solutions for these kinds of exchangers. The first study was carried out by [25] for a smooth laminar LiBr/H<sub>2</sub>O falling film by considering uniform and constant velocity. However, this velocity assumption leads not only to a deviation in the heat and mass transfer coefficients but also to a wrong estimation of the necessary distance for boundary layer development [20]. The same conclusion was found for an adiabatic absorber whatever the Lewis number for the LiBr/H<sub>2</sub>O couple [27].

The recent works are solved using numerical approaches. Through a numerical resolution, [28] found that the hypothesis of constant properties for the LiBr/H<sub>2</sub>O leads to an increase of 5% of the total mass absorbed for an absorber length of 10 meters. By considering an additional differential heat of solution released within the bulk due to the growth of the concentration boundary layer in the streamwise direction, [29] found that the effect of variable properties remain low for couples with high transport properties. By introducing the thermal and mass boundary layer, [30] highlighted a ‘semi-established’ and an ‘established’ zones in order to emphasize the importance of coupling the thermal and mass phenomena at the interface. For volatile absorbents such as NH<sub>3</sub>/H<sub>2</sub>O, the impact of the absorbent desorption on the refrigerant absorption near the inlet could be significant [31] and the liquid phase controls the mass transfer resistance while the heat fluid transfer controls the heat transfer resistance [32]. Authors like [33] studied the phenomena on the vapor phase and concluded that a part of the energy released at the interface is transferred to the vapor phase.

## Vertical Absorbers

Vertical tube absorbers problem resolution is quite similar to that of flat plate absorbers. In its model, [34] solved the problem by making the same assumptions as those made by [35] for the horizontal tube case. [34] compared the results obtained when considering uniform and linear velocity profile. As [20], [34] found that the absorption rate is overestimated and leads to a deviation is of about 30% when uniform velocity is considered. By studying the temperature and concentration profiles on the streamwise direction and by considering the same hypothesis as [36], [37] confirm the result saying that thermal boundary layer develops faster than the diffusive boundary layer.

Many numerical resolutions of vertical tube absorbers are encountered in the literature. By considering the same assumptions than [20] and adding the inter-diffusion term in the thermal equation, [38] showed that the absorbed flow over 1-meter length is 6.5% greater when the falling film properties are assumed constant. The difference found here is higher than that of [28] – 5% for 10 meters. The introduction of both inter-diffusion and Soret-Dufour effects on a LiBr/H<sub>2</sub>O problem resolution leads to an increase in the average heat flow and in the average absorbed mass of 9.5% and 4% respectively [39]. By considering the convective heat and mass transfer coefficients between the liquid and the wall but also between the liquid and the interface, [40] found that the energy released near the entrance of the absorber due to the exothermic absorption is five times greater than at the outlet.

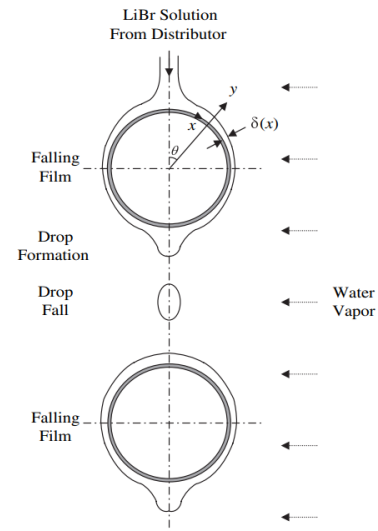
## Horizontal Absorbers

In the following, researches that studied horizontal tube absorbers are mentioned and analysed. These kinds of absorbers offer high heat and mass transfer coefficients [41].

Most of the numerical resolution carried out on horizontal tubes divided the LiBr/H<sub>2</sub>O flow in three different regimes: falling film in contact with tube, drop formation at the bottom of the tube and drop fall between the tubes [42], [43] (figure 2). Adiabatic absorption is assumed during the drop formation and the drop fall. [44] investigated the possibility of reducing the absorber size by using the understanding of these three regimes and found that for the same heat transfer area, the cooling capacity is 30% higher when using tubes with a diameter of 6.35 mm than conventional tubes (19.5mm).

The investigation of partial wetting, by considering the shape of the cylinder, at reduced mass flow rates on the absorption rate is carried out analytically by [45]. They found that the partial wetting reduces the total mass transfer over the whole surface. By extending the previous work, [46] concluded that both heat and mass transfer coefficients are impacted by the partial wetting.

Depending on the LiBr/H<sub>2</sub>O flow rate and the wetting ratio, almost 50% of the total absorption occurs in the droplets (figure 2) [42]. [47] concluded that the absorption in droplets represents 74% to 77% of the absorption process when the inlet temperatures of cooling water and poor solution are 28°C and 41.25°C respectively. [47] studied the LiBr/H<sub>2</sub>O in the same conditions as [43] and by considering an empirical expression for the mass enthalpy.



**Figure 2** Description of the three different flow regimes for a horizontal tube absorber [43]

## WAVY-LAMINAR FLOW REGIME

[48] affirms that there are three distinct flow regimes depending on the Reynolds number (table 1). 20 years later, [49] affirmed that there are waves for all Reynolds numbers due to hydrodynamic instabilities. They may be classified in capillary or inertial laminar waves (rolls waves) [50].

Type of flow	Reynolds number
Laminar flow without rippling of the free surface	$Re < 13$
Laminar flow without rippling (wavy) of the free surface	$13 < Re < 500$
Turbulent flow	$500 < Re$

**Table 1** Type of flows [48]

Although hydrodynamics of falling liquid film plays a major role in heat and mass transfers, only few works have been carried out to investigate the effect of waves on the transfer phenomena and only one was found after 2000. In a sinusoidal regular wave film flow, the absorption rate is higher than in a laminar flow with smooth surface [51], [52]. This improvement is due to the transverse component velocity (y axis) – which misses in smooth flows – and the convection associated with it in falling film plate absorbers [53] and in vertical absorber [54]. By focusing on inertial waves with recirculation of steam absorption in falling film of LiBr aqueous solution, [55] showed that the recirculation of the solution play an important role in the absorption phenomenon. They explained that at the entrance of the absorber, the absorption rate is a little bit higher in a smooth film than in a wavy one as the waves are in developing stage. Afterwards, the recirculation of the solution due to the waves brings to the interface the cold and salt concentrated solution which favors the absorption of water: the absorption becomes more important in the wavy film. However, given the low diffusivity of the absorbent, for the couple LiBr/H<sub>2</sub>O, the transfer of vapor into the

film is limited and consequently the absorption rate decreases. The recirculation, in this region, allows to increase the absorption by removing the heat from the interface.

## EXPERIMENTAL STUDIES

Using image processing, [56] showed that waves increase the transfer. [57] used a video camera and a display monitor to measure the thickness, wave amplitude and frequency of a LiBr/H<sub>2</sub>O falling film that flows over a vertical tube. They found that the wave amplitude is affected by the flow rate of the falling film and the outer diameter of the tube. In the same conditions as [57], [58] found that the average film thickness is 10-25% less than the value calculated by using Nusselt equations but also that the film thickness increases with the increase of the Reynolds number and the decrease of the Kapitza number. By analyzing the impact of the three different regimes – falling film, droplet formation and droplet fall – on the LiBr/H<sub>2</sub>O absorption phenomena over horizontal tube banks using high-speed flow visualization, image analysis, and computations, [59] also underlined the importance of the solution flow rate and the diameter of the tube. Indeed, depending on these parameters, the droplet can be detached or not before it hits the next tube. This phenomenon is very interesting because the impact of the droplet on the next tube causes waves and oscillations. Moreover, they found that the relative fractions of absorption in the droplet formation and falling film modes depend significantly on the solution flow rate.

## THERMODYNAMIC APPROACH

Over the years, different approaches that use the TIP were developed and applied to evaluate and optimize thermodynamic systems. The most popular are the entropy generation analysis (EGA) and the entropy generation minimization (EGM) [60]. The latter explained that the EGA is the method of identification and reduction of thermodynamic irreversibility while the EGM is the method of minimizing the losses of a system by respecting constraints. The EGM was introduced by [61] and widely used to optimize different type of heat exchangers. The idea was to find the optimal operating conditions or dimensions that gives the lower entropy generation rate. More recently, authors started to apply the second law of analysis on absorption machines and showed that for each component of these machines, there are avoidable and unavoidable irreversibilities, but also irreversibilities due to the inefficiency within the component itself – endogenous – and irreversibilities due to the operating conditions – Exogenous. Most of the exergy destruction is concentrated in the absorber and in the desorber and is mainly endogenous and unavoidable for the case of a single-effect LiBr/H<sub>2</sub>O absorption refrigeration cycle [62]. As a result, some researchers decided to focus on the absorber and to understand how the local entropy generation is created.

The entropy generation in an absorber is due to different phenomena: the heat transfer, the mass transfer, the hydrodynamic of the falling film and the coupling due to Soret and Dufour effects. Nevertheless, most of the thermodynamic studies in the literature neglected the Soret and Dufour effects and studied the local entropy generation rate ( $S''_{gen}$ ) by using equation (5) [63]:

$$\dot{S}'''_{gen} = \vec{q} \cdot \vec{\nabla} \left( \frac{1}{T} \right) + \frac{\vec{v} : \vec{\nabla}(\vec{V})}{T} - \frac{1}{T} \vec{j}_v \cdot \vec{\nabla}(y_v) \quad (5)$$

The first term on the right-side is the entropy generation due to heat transfer; the second term is due to viscous flow and the third term, to mass transfer.

At local scale, there are not a lot of articles that applied the TIP approach to falling film absorbers because of their complexity. In the following paragraphs, the works that applied this approach on plate and tube absorbers are analyzed.

### Flat Plate Absorbers

The study of the CO<sub>2</sub> absorption at constant temperature and pressure by water that flows down over an adiabatic vertical plate showed that the mass flux transferred by convection is much greater than that transferred by diffusion [64]. Furthermore, the entropy generation is due to the mass phenomena near the liquid – vapor interface and to the viscosity near the wall. [65] also considered that the absorption is made at constant temperature and so there is no heat irreversibility. The results showed that the viscous entropy generation increases with the film temperature. This irreversibility is zero at the interface and maximum at the wall as shown in [64]. In the diffusive boundary layer, the mass transfer irreversibility increases with the increase of the film thickness and of the temperature. These two previous works do not apply to an absorption machine absorber but provide a thermodynamic analysis of the absorption process.

In the case of an adiabatic absorber with the NH<sub>3</sub>/H<sub>2</sub>O couple, the entropy generation due to the heat and mass coupling caused by the thermodynamic equilibrium at the interface is almost 200 times the heat transfer irreversibility [66]. Moreover, the higher the difference of temperature between the liquid – vapor interface and the wall, the higher the total entropy generation but the effect of the temperature gradient on the viscous irreversibilities is very low.

### Tube Absorbers

The study of the water absorption in a LiBr/H<sub>2</sub>O solution over a horizontal cooled tube showed that the total entropy generation is dominated by the heat irreversibilities and that the diffusion mass transfer and viscous irreversibilities are negligible for Reynolds between 4 to 28 [67]. The total entropy generation increases with decreasing the tube diameter, inlet flow temperature and solution mass flow rate [67]. Furthermore, there is a Reynolds at which the entropy generation per unit of width film (length tube) is minimum [68].

## CONCLUSION

This paper describes a number of researches carried out on falling film absorbers. Although some authors solved the coupled heat and mass transfers analytically, many of them solved the equations in a numerical way because of the complexity of the coupling at the liquid – vapor interface. The lack of local investigation for volatile absorbent couple due to the presence of both absorbent and refrigerant on both liquid and vapor phases is still to be performed. Smooth laminar flows and wavy laminar flows were also studied. All authors agree that the absorbed mass flux is higher when considering the wavy flow

regime compared to the smooth flow. The lack of experimental validation for the temperature and the concentration profiles at local scale remains; efforts must be done in this area for the future works. More recently, researchers showed the importance of the second law of thermodynamics on the absorber studies. This approach allows a better understanding of the different phenomena that occur in the absorber. Researchers agree that the local entropy generation rate is the sum of thermal, viscous, convective and diffusive irreversibilities.

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