1
2
3
4
5
6
7 **Three-Dimensional Simulation of Rivulet and Film Flows over an Inclined**
8 **Plate: Effects of Solvent Properties and Contact Angle**

9 Rajesh K. Singh^{1,2,*}, Janine E. Galvin¹ and Xin Sun³

10 ¹Computational Science and Engineering Division, National Energy Technology Laboratory,
11 Albany, Oregon 97321, United States

12 ²ORISE Postdoctoral Fellow, National Energy Technology Laboratory,
13 Albany, Oregon 97321, United States

14 ³Fundamental Computational Sciences Directorate, Pacific Northwest National Laboratory,
15 Richland, Washington 99352, United States

16 *Corresponding author: rajesh-kumar.singh@netl.doe.gov; rajeshsingh.175@gmail.com

ABSTRACT

We numerically investigated the film flow down an inclined plate using the volume of a fluid (VOF) method. The flow simulations have been systematically carried out for a wide range of parameters, such as inlet size, inclination angle, contact angle, flow rates and solvent properties (viscosity and surface tension). Based on the simulation results, scaling theory is being proposed for both interfacial area and for film thickness in terms of the Kapitza number (Ka). The Kapitza number is advantageous because it depends only on solvent properties. The Kapitza number decreases with increased solvent viscosity and is fixed for a given fluid. To investigate the effects of solvent properties on interfacial area a small inlet cross-section was used. The interfacial area decreases with increased value of Ka and scaling for interfacial area in terms of Ka is proposed. The time to reach pseudo-steady state of rivulet is also observed to increase with decreasing Ka . For a fixed flow rate, the inlet cross-section has marginal effect on the interfacial area; however, the developed width of the rivulet remains unchanged. In addition to inlet size, flow rate and solvent properties, the impact of contact angle on film thickness and interfacial area was also investigated. The contact angle has negligible effect for a fully wetted plate, but it significantly affects the interfacial area of the rivulet. A scaling theory for interfacial area in terms of the contact angle and Ka is presented.

Keywords:

VOF, Film flow, Rivulet flow, Interfacial area, Structure packing and Contact angle

1. Introduction

Carbon dioxide (CO_2) is a major contributor (about 72% globally) to greenhouse gas emissions that are responsible for global warming [1]. Fossil-fueled power plants account for 40% of the total CO_2 emissions [2]. Because fossil-fueled power plants play a major role in fulfilling current energy demands, CO_2 emissions from power plants must be mitigated to control global warming. Post-combustion carbon capture based on chemical absorption via reaction with amine solvents in a packed column is considered efficient and economical. The absorption is carried out in a packed column with countercurrent gas-liquid flow, wherein the gas flows up and the liquid falls down. The column is filled with a packing material that provides enhanced surface area for gas-liquid contact. Structured packing consists of corrugated sheets arranged in a crisscrossing fashion to form a single layer of packing material. Structured packing offers superior performance [3] with a large surface area per unit volume for mass transport and a high absorption efficiency while minimizing pressure drop [4]. Structured packed columns are also widely used in other chemical processing technologies such as distillation and liquid-liquid extraction [5-7]. The accurate design of such columns requires knowing essential hydrodynamic characteristics, such as, pressure drop and liquid holdup of the packing element [8].

Solvent absorption columns are characterized by length scales of several meters with diameters that range from 5–10 m and column heights from 20–30m [9, 10]. In contrast, the characteristic dimensions of structured packing are much smaller with the length scale of a typical layer of corrugated structured packing on the order of 20 centimeters. Finally, the dimension of liquid film thickness is typically less than a millimeter. These scales cannot be resolved simultaneously within a single computational model. That is, it is computationally infeasible to run computations at large scales while taking into account the local gas-liquid interactions at liquid film level and real geometry of the packing. In this context, gravity-driven film flow down an inclined plate provides the simplest configuration for better understanding the hydrodynamics through structured packing.

Flow down an inclined plate can exhibit a range of flow patterns, namely, full film, rivulet, and droplet. These features are dependent upon various flow parameters (e.g., liquid and gas flow rates),

1 packing characteristics (e.g., plate surface texture, plate inclination angle, etc) and physical properties.
2 The falling film is probably the most recognized flow regime for flow down an inclined plate, and it is
3 characterized by a gravity-driven thin layer liquid with typical thickness of order of a millimeter or less. A
4 thin film facilitates heat transfer between the wall and liquid, while large interfacial areas that are
5 generated, even at small flow rates, promote mass transfer between the gas and liquid. Accordingly,
6 computation of the film thickness is critical. In the early 20th century, Nusselt derived an expression for
7 film thickness for the case of a flat, smooth gas-liquid interface [11], however, a falling film also often
8 exhibits wavy in nature. Since then, a number of experimental [12-16], theoretical [17, 18], and numerical
9 [19-23] studies on the dynamics of film flow have been conducted, with many of these works
10 concentrating on the average and local variation of the film thickness with flow rate. In this case, liquid
11 enters as smooth laminar flow which develop a wavy at downstream of inlet due to growth of surface
12 instability caused by gravity, viscosity and surface tension effects [24]. For example, transition to wavy
13 laminar flow from pure laminar occurs at intermediate Reynolds number (> 60) [25]. A wavy interface
14 will enhance the interfacial area as compared to that smoother one and in turn promote both the heat and
15 mass transfer between the phases. Theoretical studies show that, due to ripples on the interface, the time-
16 averaged film thickness is reduced by approximately 8% compared to smooth interface [26].

17 As noted earlier, plate configuration and solvent properties will influence the resulting film
18 thickness and interfacial area. The actual geometry of the packing material highly influences how the
19 wetted area evolves and perpetuates. Structured packing may be characterized by a specific large scale
20 corrugation structure as well as a small scale surface structure (e.g., embossed, perforated). Cross-stream
21 plate texture was shown to enhance solvent spreading by preventing flow channeling and thereby
22 improving interfacial area/mass transfer area [27, 28]. However, Sebastia-Saez et al [23] observed a
23 reduction in wetted area for cross-stream plate texture compared to that of smooth plate. The inclination
24 angle also alters the effect of gravity so film thickness decreases with increased inclination angle, owing
25 to an enhanced film velocity [29, 30]. This trend is also evident in Nusselt's formula. While the effect of

changing inclination angle is pronounced at lower angles, it becomes marginal beyond 60° [31]. Film thickness has also been reported to increase with solvent viscosity[21], which is consistent with the Nusselt formula [11]. Consequently, an increase in solvent viscosity may lead to enhanced liquid holdup and increased pressure drop in the packed column. Recently, experimental studies [6] have shown a complex dependency of liquid holdup in structured packings on solvent viscosity, in conjunction with liquid load. Specifically, for a highly viscous liquid ($\mu \geq 20\text{mPas}$) the film flow liquid holdup showed non-monotonic variation, i.e. first increases then decreases, with increasing liquid load, while for a low viscous liquid the holdup always increased with increased liquid load.

Inertia (or flow rate) may also change the overall flow pattern observed. With increasing inertia, the flow pattern progresses from droplet to rivulet and finally to full film [32, 33]. Accordingly, a number of experimental [34-36] and numerical [31, 37] studies on the hydrodynamics of rivulet flow have been conducted. Rochelle and coworkers [35, 36] have conducted experiments for calculation of film thickness and interfacial area in structured packing. The solvent viscosity has a negligible effect on either of these quantities, whereas surface tension marginally affects the interfacial area. However, studies were limited to small range of viscosity (<10 mPas). In contrast, other experimental studies have observed a significant effect of the viscosity on the film behavior. In particular, increased liquid holdup [38-40] and interfacial area [38] were observed with increasing viscosity. Numerical studies later confirmed this behavior [23, 37]. In particular, higher viscous forces act against gravity and make the film more stable [34], consequently, rivulet width increases. In contrast [38], the experimental study of Nicolaiewsky et al [41] reported a decrease in wetted area with increased liquid viscosity.

Besides viscosity, surface tension also affects the interfacial and wetted area. Indeed, values of the surface tension and viscosity are interrelated, and a highly viscous solvent exhibits lower value of surface tension [42]. In fact, surface tension is a dominant property influencing the value of the contact angle [43]; therefore, surface wettability alters with change in the value of surface tension. Lowering the

surface tension leads to increased interfacial area and the effects are more pronounced at low surface tension ($\leq 30 \text{ mN/m}$) [36].

As evident, the impact of different parameters on various aspects related to wetting phenomena have been investigated and reported in the literature. To the best of our knowledge, however, no one has made an attempt to explain the hydrodynamics of film flow as a single dimensionless number accounting for all physical properties. Also, data for viscous fluids that are more representative of the type of solvents found in industry is lacking. Finally, the effect of contact angle on interfacial area has not been extensively explored. In this view, a scaling theory for film thickness and interfacial area in terms of the Kapitza number and the contact angle is presented. The advantage of the Kapitza number is that it only depends on the physical properties of the liquid and is independent of the flow parameters. Accordingly, it is fixed for each fluid.

In this effort, VOF simulations are used to investigate full film flow down an inclined plate followed by rivulet flow. The mathematical formulation is briefly outlined in Section 2. Section 3 describes the problem setup, numerical scheme, and solvent properties. In Section 4, simulation results are first compared with experimental studies for film down an inclined plate. Then, the effects of solvent properties on the film thickness are studied. Rivulet flow is examined next. The results for film thickness and interfacial area of rivulet flows for a wide range of parameters are analyzed. In the last section, the present work is summarized.

2. Mathematical Formulation

Volume of fluid (VOF) [44] multiphase flow simulations are used to investigate film flow down an inclined plate. It is well adapted for stratified flow as liquid film in packings. This method is explained in the manual of the commercial CFD code ‘Ansys Fluent 14.0’ [45], and a brief sketch is provided here. In this approach the entire flow field is treated as a single phase. Therefore, the governing equations are solved for a single shared field among phases:

$$\nabla \cdot \mathbf{u} = 0, \quad (1)$$

$$\frac{\partial(\rho \mathbf{u})}{\partial t} + \nabla \cdot (\rho \mathbf{u} \mathbf{u}) = -\nabla p + \mu \nabla \cdot (\nabla \mathbf{u} + (\nabla \mathbf{u})^T) + \rho \mathbf{g} + \mathbf{F}, \quad (2)$$

where $\mathbf{u}$ is the velocity, ρ the density, p the pressure, μ the viscosity, and $\mathbf{F}$ represents additional forces depending on the problem.

In the system, the additional force is due to the interfacial surface tension which is distributed over a thin interfacial layer. The continuum surface force (CSF) [46] has been employed to model surface tension. The surface tension force, which produces a jump in the normal traction across the interface, is expressed as a singular force

$$\mathbf{F} = \sigma \frac{\rho \kappa \nabla f}{\frac{1}{2}(\rho_g + \rho_l)} \quad (3)$$

where σ is the interfacial tension, κ is the local curvature of the interface, and ∇f shows the direction vector.

The interface between the phases is tracked by solving an additional transport equation (4) of scalar f . Note that the value of f varies from 0 to 1 (0 corresponds to cells with all gas, and 1 corresponds to all liquid).

$$\frac{\partial f}{\partial t} + \mathbf{u} \cdot \nabla f = 0 \quad (4)$$

The advantage of two phase flow simulation is that Equation (4) is solved only for the secondary phase, and volume fraction of the primary phase is computed by satisfying the constraint $\sum_{i=1}^n f_i = 1, i=1,2$.

3. Problem Setup

We investigated wetting of an inclined smooth flat plate due to downward film flow. A schematic of the simulation setup is presented in Figure 1. The domain consists of an inclined flat plate having the dimensions $60 \times 50 \text{ mm}^2$. The depth of the domain was specified as 7 mm. Similar configurations have been used because of the availability of experimental results for validation [15]. A liquid enters the domain at the top and exits the bottom in the presence of gravity. Air was considered as a stagnant gas phase at 25°C and 1 atm.

The bottom and side boundaries (i.e., smooth walls) were set to no-slip walls with a static contact angle. The outlet and top boundaries were set to a pressure outlet with zero gauge pressure. The liquid inlet was defined as a uniform film flow given by a constant velocity perpendicular to the boundary. Unless otherwise said, the dimension of the liquid inlet was given by the width of the plate (50 mm) and the depth of the domain (7 mm). For studying rivulet flow, inlet size was always made smaller than the entire face. In such cases, the remaining part of the inlet cross section was specified as a pressure outlet with zero gauge pressure. Turbulence is not taken into account since the range of the Reynolds number of the liquid flow indicates laminar flows.

Meshing is a critical step that dictates the convergence, stability, and accuracy of the simulations. To capture the film flow dynamics accurately and with greater efficiency the flow domain was discretized with a very fine non-uniform hexahedral mesh. Accordingly, the mesh density inside the liquid film and near the interface is finer than the region adjacent to the surrounding gas (see Figure 2(a)). To account for the characteristics of rivulet flow the center of the flow domain was meshed with a very fine grid. A grid independence study was also conducted to determine a reasonable mesh while maintaining grid independent predictions. Temporal evaluations of the specific wetted area $A_{wn} = A_w / A_p$, where A_w and A_p are wetted and total areas of plate respectively, are presented in Figure 2(b) for three grid resolutions. While simulations with grid resolution of 1.37M and 1.52M elements show differences in wetted area at intermediate time interval, they predict the same value once pseudo-steady state is achieved (defined later). In addition, they show the same interface shape (Figure 2(c)). Hence, a resolution consisting of 1.37M elements was selected as an optimum mesh, which falls within the range reported by similar numerical studies [20, 23].

The isothermal transient flow simulations were carried out using Ansys Fluent 14.0 [45]. The partial differential equations are solved using a segregated solver. The Second Order Upwinding scheme was used in discretization of the momentum equation. Coupling between velocity and pressure was established by the PISO (Pressure Implicit with Split of Operators) scheme [19] and the PRESTO!

(PREssure STaggering Option) method was used for the pressure interpolation. The Geo-Reconstruct scheme that utilizes a piecewise linear interface calculation (PLIC) is used to discretize the interface. The stability of the simulation was ensured by enforcing the CFL condition with the value of Courant number of 0.50. Accordingly, very small time step (Δt) variations from 10^{-5} – 10^{-4} were needed to satisfy the CFL condition. The simulation was considered to reach pseudo-steady state when the solvent mass outflow and the wetted area of the plate were approximately constant. The simulation and wall time required to achieve pseudo-steady state varied case by case (0.50 – 5.0 sec). For example, simulations with highly viscous solvents required more simulation time. In addition, simulations with low contact angles (corresponding to high surface wettability) also demand more wall time due to smaller Δt . Regardless, these simulations were computationally expensive and so each case was run using 128 cores in parallel. Overall, the simulation wall time varied to 24 –144 hours.

4. Solvent Properties

A number of alkanolamine-based solutions are used as solvents in structured packing columns for post-combustion carbon capture [47]. Although monoethanolamine (MEA) is still the preferred solvent, an alternative amine may result in better performance. In this view, simulations were conducted with various aqueous alkanolamines. These include MEA [48-50], 2-aminomethylpropanol (AMP) [51], N-methyldiethanolamine (MDEA) [52], and 1-methylepiperazine (MPZ) [53] at different concentrations to cover a wide range of solvent properties (μ_l : 0.9–37 mPas and σ : 30–73 mN/m) (see Table 1). The value of the contact angle (γ) corresponding to each solvent was not readily available in the literature. Therefore, a value of 70°, corresponding to water on steel was used in the preliminary simulations. Note that a given solid surface may exhibit different γ values depending on the surface tension of the liquid. Moreover, the contact angle also varies with change in solid surface for a given liquid [54]. Given the importance of contact angle on wettability, the effect of varying contact angle was also systematically investigated.

1

Table 1: Physical properties of the solvents at 25°C and 1atm

Solvent	μ_l (mPa/s)	ρ_l (Kg/m ³)	σ (mN/m)	Ka
Water	0.89	997.0	72.80	3969
20%MEA	1.18	996 [48]	57.8 [49]	2173
30% MEA	2.52	988 [48]	55.0 [49]	750
26.73% AMP [51]	2.70	995.8	43.01	534
40% MEA	3.71	979 [48]	54.80 [49]	450
0.073xMPZ [53]	5.56	1005.3	54.42	258
48.8% MDEA	9.25	1016.6	47.56	117
0.10x MPZ[53]	10.75	1000.9	47.25	93
0.51x MPZ [53]	13.36	946.41	34.37	50
0.41x MPZ [53]	23.48	962.20	35.89	25
0.31x MPZ [53]	36.42	981.31	38.40	15
$Ka = \sigma_l (\rho_l / \mu_l^4 g)^{1/3}$ <p>?: Percentage by weight, x: mole fraction</p>				

2 5. Results and Discussion

3 The wetting phenomenon of an inclined plate is dictated by many parameters, such as, solvent
4 properties (μ_l and σ_l), flow rate (Q), plate inclination angle (θ) and contact angle (γ). In addition for film
5 and rivulet flow down an inclined plate four forces dominate: inertia, surface tension, viscous and
6 gravitational. Therefore, identifying representative dimensionless groups for this problem is useful. Such
7 dimensional analysis has already been covered in the literature for this system and so is not covered here
8 (e.g. [33, 55, 56]). In this paper, two dimensionless numbers, the Kapitza number (Ka) and the film
9 Weber number (We) are chosen to explain the behavior of full film flows. The Weber number is
10 advantageous for evaluating the flow transition in full film flow. For studying the hydrodynamics of
11 rivulet flow, bulk Reynolds number (Re) is used over the film Weber number as consistent with previous
12 works [57]. The simulations for rivulet flow were conducted at a fixed flow rate, and the value of
13 Reynolds number is not same for all solvents. Here forward, the film Weber number and the bulk

Reynolds number will be addressed as the Weber number and the Reynolds number respectively. The formulation of these dimensionless numbers will be explained in the relevant section(s) below.

5.1 Comparison with Experiment

For validation of the simulation method, the predicted results are first compared with the results from experiments [15] and later with Nusselt film theory [11]. Hoffmann et al [15] conducted experiments of film flow down a flat plate that was inclined 60° to the horizontal using water (Table 1) and air at 25°C ($\rho_g = 1.18 \text{ kg/m}^3$ and $\mu_g = 0.018 \text{ mPas}$). Note that the value of the contact angle in the experiment was not mentioned. However, as noted earlier, it is considered as 70° in these simulations, which corresponds to a water-liquid and steel substrate system. The impact of solvent flow rate, characterized by the Weber number, on the wetted area was studied. The Weber number represents the ratio of inertia to surface tension forces and is often used to characterize film flow. Here it is formulated based on Nusselt theory for computation of film thickness of a uniform film flowing down over a flat incline plate having smooth gas-liquid interface [11]:

$$\text{We} = \frac{\rho_l V_{\text{in}}^2 \delta_N}{\sigma_l} \quad (5)$$

where δ_N is Nusselt film thickness: $\delta_N = (3\mu_l Q / \Delta\rho g W \sin\theta)^{1/3}$, $\Delta\rho = \rho_l - \rho_g$, ρ_g is density of the gas, V_{in} is Nusselt film velocity: $V_{\text{in}} = Q / W \delta_N$ and W is width of the plate. Using these relations the We is expressed in terms of fluid properties and flow rate as follows:

$$\text{We} = \frac{\rho_l}{\sigma} \left(\frac{Q^5 \Delta\rho g \sin\theta}{3W^5 \mu_l} \right)^{1/3} \quad (6)$$

The wetted area of the plate was computed for different We values. In the experiment the plate was found to be fully wetted for $\text{We} > 0.90$. Figure 3(a) shows snapshots of the interface for different Weber numbers. A value of volume fraction (f) of 0.50 is used to define the liquid–gas interface [31]. At very low Weber numbers (< 0.05), a liquid droplet is seen and droplet detached and rivulet evolve. Here

surface tension dominates over the inertial force. Further increase in the flow rate corresponds to rivulet flow. At higher flow rates, increased inertia gives rise to a fully wetted plate ($We = 1.10$).

The areas are compared with those from experiments in Figure 3(b). Here the wetted area is normalized by the actual area of the plate ($A_{wn} = A_w/A_p$). As evident the simulation results match well with experiment validating the use of the current VOF simulations for conducting further study of film flow over an inclined plate. Also included in the figure are the results from a separate numerical simulation by the same group, which systematically under predicts the wetted area [32]. The underprediction in the wetted area might be due to coarse meshing and discretization schemes. Regardless, the VOF method has been successfully used in two phase flow investigation [5, 28, 31, 32, 58].

5.2 Effect of the Solvent Properties

Apart from inertia, the hydrodynamics of the film flow down an inclined plate also depends on the physical properties of the solvent. In this section, the effect of fluid properties is studied in terms of the Kapitza number (Ka) to get a collective effect of all fluid parameters. Historically, the Kapitza number has been used for explaining the dynamics of wavy falling film flow [56, 59, 60]. Here it is used as a dimensionless number representative of fluid and given below. In addition, it reduces dimensionless number required for investigating the film flow [55]. Note that the cubic of Kapitza number (Ka) has been referred to as the cubic root of Film number (Fi) used in the falling film flow [27, 61].

$$Ka = \sigma_l \left(\frac{\rho_l}{\mu_l^4 g} \right)^{1/3} \quad (7)$$

The effect of Weber number and Kapitza number on the wetted area of the plate is examined first. For a given solvent (i.e., fixed Ka number), the Weber number is varied by changing the flow rate. The solvent flow rate is derived from rearranging Equation (6) as given in Equation (8):

$$Q = W \left(\frac{\sigma_l We}{\rho_l} \right)^{3/5} \left(\frac{3\mu_l}{\Delta\rho g \sin\alpha} \right)^{1/5} \quad (8)$$

As indicated, solvents having different physical properties cannot have the same flow rate at a fixed We value. Figure 4(a) shows the variation in the specific wetted area with Ka for five We values at $t=0.50$ sec. The figure reveals a non-monotonic variation of A_{wn} with Ka for a fixed We , that is, it first increases and then decreases with increased Ka . Similar behavior was also reported by Rizzuti and Brucato [62], specifically, the effective interfacial area increases and then decreases with increasing viscosity. Note that the wetted and interfacial areas are related; the wetted area is equal to the normal projection of the interfacial area on the plate. In contrast, the VOF study by Sebastia-Saez et al [23] only observed an increase in wetted area with viscosity. However, their studies were restricted to a small viscosity ($\mu_l < 3.7 \text{ mPaS}$) and low flow rates ($We \leq 0.87$) wherein the wetted area is observed to increase with increased viscosity. As discussed below, the data in Figure 4(a) does not necessarily correspond to pseudo-steady state for all solvents in regard to wetted area. The pseudo-steady state results ($t > 2.0$ s) are given in Figure 4(b). As shown, the specific wetted area increases with decreased Ka (increased viscosity), and the plate is fully wetted for $Ka \leq 50$ and $We \geq 0.47$. At low Ka , viscous effects overcome surface tension, so the plate becomes fully wetted. It is also worth noting that at low Ka numbers surface waves are absent so that the interface becomes smooth except for meniscus near the walls due to capillary effects

Previous VOF studies [20, 23] on film flow down an inclined plate reported that wetted area of film achieved a pseudo-steady state after $t = 0.25$ sec. However, these studies used water as the liquid ($Ka = 3969$). In this study, a highly viscous solvent (lower Ka) was found to be characterized by a slower wetting rate; therefore, requiring more time to achieve pseudo-steady state. Black and Coninck [63] also reported that a highly viscous solvent wets the surface more slowly than one with low viscosity. To quantify this observation the time required for 99.50% wetted plate (t_w) was computed and further normalized by the capillary time scale $t_c = \mu_l^3 / \sigma_l^2 \rho_l$. The normalized time scale becomes $t_w^* = t_w / (\mu_l^3 / \sigma_l^2 \rho_l)$. It would be worthwhile to note that a viscous time scale $t_v = (\nu_l / (g \sin \theta)^2)^{1/3}$ is often used when examining full film flow. However, surface tension also plays a significant role during

the intermediate transient flow structures, such as rivulet and droplet, prior to the plate becoming fully wetted. Therefore, the capillary time scale was found more suitable as it is a function of both μ and σ .

The normalized time scale t_w^* varies as $Ka^{7/4}$ as shown in Figures 4(c) at $We = 1.50$ and 1.10 , wherein the plate becomes fully wetted for the range of Kapitza number studied. Although t_w^* increases with increasing Ka the absolute value of t_w decreases. A high Ka , t_c has very small value. For example, water at 25°C has a small t_c of 1.33×10^{-10} sec compared to a highly viscous solvent with low Ka , such as 0.31m aqueous solution of MPZ which has a t_c of 3.34×10^{-5} sec. Similar scaling also holds for the time required to achieve other fractions of the wetted plate (not presented for sake of brevity). From scaling analysis presented in the Figure 4(c), the wetted time (t_w) can also be deduced in dimensional form and presented as $t_w \sim Ka^{-7/4} \sim \mu_l^{2/3} / (\sigma_l^{1/4} \rho_l^{5/12} g^{7/12})$. For comparison, Nusselt theory predicts $t_w \sim (\mu_l / \Delta \rho g)^{2/3}$, which is based on a 1D film analysis assuming steady uniform film. Film flow over a plate, however, exhibits 3D transient features and wave formation (figures not presented) before achieving fully wetted conditions, such as, rivulets, fingering phenomena and partially wetted film. Surface tension plays an important role in the intermediate flow structure and it is accounted in the present computation of t_w through use of the Kapitza number.

Next the effects of Ka on the film thickness (δ) was examined and compared with Nusselt theory as a further validation of the simulation results. The flow rates and simulation time were chosen in such a way that the plate becomes fully wetted for all solvents. The average film thickness was computed and further normalized by viscous length scale as $\delta^* = \delta / (v^2 / g)^{1/3}$ [64]. An excellent match is observed with a very small over-prediction by simulation (see Figure 5). The differences are primarily attributed to meniscus at the side walls in the simulation that result in slightly higher film thickness. The excellent agreement between simulation and theory indicates that surface tension does not play a significant role in the computation of mean film thickness for a fully wetted condition as one might expect. It is worth

noting that slight differences are seen at high Ka values (>2000), where a wavy interface due to surface tension affects the film thickness. Interfacial surface tension also plays an important role during the transient flow structure where droplet, rivulet, and partial film may evolve before the plate becomes fully wetted. Variation of the film thickness with Kapitza number was also repeated for higher Weber numbers. The film thickness for different We values converges onto a single curve, with scaling $\delta^* \sim \text{Ka}^{1/4} \text{We}^{1/5}$ as presented in the inset of Figure 5.

5.3 Interfacial Area of Rivulet

Variation of interfacial area with solvent properties is not revealed in the setup used above, wherein the entire width of the domain was specified as the inlet. In this section, a smaller inlet was used which leads to rivulet flow [see Figure 6(a)] rather than fully wetted film flow. Unless otherwise stated the dimension of the reduced inlet area is 2 mm in height and 4 mm in width. For this case, flow rate is fixed at $Q=2 \times 10^{-6} \text{ m}^3/\text{sec}$ (corresponding to Re (defined below) ranging from 5 to 204). Again, the simulations were conducted for a sufficiently long time (t_s) as to achieve pseudo-steady values of the wetted area. The value of t_s was observed to increase with decreasing values of Ka, so that a highly viscous solvent takes more time to achieve a pseudo-steady state. As presented in Figure 6(b), the specific interfacial (A_m) and wetted (A_{wm}) areas decrease with increased Ka. The inset of Figure 6(b) clearly shows that the rivulets become wider with increased Ka (reduced viscosity). This observation is consistent with experimental studies of Shi and Mersmann [38] who also observed an increase in rivulet width (thereby interfacial area) with increased solvent viscosity (1 – 21 mPas), corresponding Ka (40 – 3388), for a wide range of flow rate ($10^{-8} - 10^{-5} \text{ m}^3/\text{sec}$). In contrast, Nicolaiewsky et al [41] observed a decrease in rivulet width with increasing viscosity (0.75–125 mPas) for flow rates ranging from 4.17×10^{-6} to $2.17 \times 10^{-5} \text{ m}^3/\text{sec}$. Given the active role of interfacial area in heat and mass transfer and chemical reaction, only variation in the interfacial area is discussed here on, however, the variation in wetted area follows a similar trend as interfacial area.

To ensure the observed behavior was independent of inlet size, the size of the inlet was varied at the same flow rate. Specifically, the height of the inlet was kept constant as 2mm while the width was varied. The shape and developed width of the interface for $Ka=15$, a highly viscous solvent, is presented in Figure 7(a) for the four inlet sizes. The inlet area does not have a significant effect, and the interfacial area marginally increases with increasing inlet size due to entrance effects (see Figure 7(b)). The wider inlet needs more longitudinal distance to become a fully developed rivulet, but the developed width of the rivulet approximately the same. More quantitatively, value of the developed width are also approximate same ($\leq 7\%$) as presented in the Figure 7(a) for all inlets at $Ka=15$. More extensive, the normalized developed interfacial area divided by the longitudinal distance, APL, is compared for all inlets in inset of Figure 7(b). The developed interfacial area is the corresponding interfacial area at which point the rivulet is fully developed. As evident the APL does not significantly change with inlet size. Finally, Figure 7(b) also confirms that the interfacial area decreases with increased value of Ka (Figure 6(b)) regardless of the inlet size and holds the scaling relation as $A_m \sim 1/Ka^{1/2}$.

In the above the effects of the solvent properties on the wetted area was studied at a fixed flow of $2 \times 10^{-6} \text{ m}^3/\text{sec}$. Since the flow rate affects the film thickness and interfacial area, the influence of flow rate for fixed inlet size ($2 \times 20 \text{ mm}^2$) was also studied. Further, effects of the flow rate were explained by Reynolds number and defined as $Re = 4Q/P_{in}\nu_l$, where P_{in} is the perimeter of the inlet. This formulation was also adopted for studying the hydrodynamics of the rivulet flow [57]. The flow rate was varied from 10^{-6} to $10^{-5} \text{ m}^3/\text{sec}$ which corresponds to range of Re 3 to 815 depending on the solvent properties. Only few data points lie above Reynolds number greater than 300, but it is in laminar flow regime. The fully turbulent film is found to occur after $Re > 1600$ [65]. As expected, the interfacial area increases with increased flow rate at all Ka . Further analysis, provided in Figure 8(a), shows the scaling relation given below:

$$A_m \sim Re^{2/5}/Ka^{1/2} \quad (9)$$

In addition to flow rate, the effect of plate inclination angle (θ) on the hydrodynamics of rivulet flow was also examined as it is a key factor affecting the flow distribution in the structure packing and, subsequently, the absorption efficiency of the column. In structured packing the corrugated sheets are arranged side-by-side with opposing channel orientations. The channels are then orientated with an inclination angle from the horizontal that typically varies from 45 to 60° [58]. In this view, the inclination angle was varied from 20° to 75° for a fixed flow rate of $Q=2 \times 10^{-6} \text{ m}^3/\text{sec}$. Figure 8(b) depicts variation of the interfacial area as a function of Ka for different θ values. As expected, the interfacial area decreases with increasing θ value. Changing the inclination angle alters the effects of gravity so that an increased value of θ corresponds to higher film velocity, and as a result, interfacial area decreases. Furthermore, the change in the interfacial area is more pronounced at low Ka values (higher viscosity). Scaling for the variation of interfacial area with inclination angle is presented in the inset of Figure 8(b) that shows a relation:

$$A_m \sim 1/\sin^p \theta$$

$$p = 0.35; \quad \text{Ka} < 100$$

$$= 0.20; \quad \text{Ka} > 100$$
(10)

where the value of the exponent p depends on the Kapitza number. One can also see from this relationship or Figure 8(b) that the change in interfacial area is not significant beyond an inclination angle of 60° for the range of Ka studied (i.e., the gravitational effect $g \sin \theta$ does not vary much between 60 - 90°).

5.4 Effect of Contact Angle

So far the flow simulations were restricted to $\gamma = 70^\circ$ because values for the contact angle corresponding to each aqueous solvent were not available. However, the contact angle is an important component of the system that indicates the degree of wetting when a liquid and solid interact. Young's equation [66] reveals a relationship between contact angle and interfacial surface tensions, however, in practice the observed contact angle is not equal to that defined by Young's equation [67]. Nevertheless, the contact angle is still considered a characteristic for a solid-liquid systems in a specific environment

[68]. That is, a given solvent shows different wetting behavior (i.e., different contact angle) depending on the solid surface. For a given surface (solid), the measured contact angles do not vary randomly upon the testing liquid. The value of $\cos \gamma$ and σ were observed to follow in a linear trend for a homogenous series of liquids. In this view, lower values of σ yields to a smaller contact angles [54]. Contact angle hysteresis has also been noted, which is generally considered to result from either surface roughness or heterogeneity of the surface [69, 70]. In this effort, however, the value of contact angle is considered static. In this view, extensive simulations were conducted to investigate the effects of contact angle on the wetting phenomena of both a fully wetted and a partially wetted plate. From simulation results, an empirical theory capable of explaining the interfacial areas for any solvent and contact angle is proposed.

The fully wetted flow simulations were conducted for three γ values at $Q=1.05 \times 10^{-5} \text{ m}^3/\text{sec}$ ($We = 0.81 - 1.50$). For the fully wetted plate the solid boundaries restrict the outer surface of the film so that, the contact angle does not play a significant role on the shape of the surface. Specifically, the contact angle has a minor effect on the meniscuses at the sidewalls and the ratio between the meniscus height and the distance between the side walls is very large. In this case, the contact angle has negligible impact on the film thickness, and it remains unchanged for all values of γ (figure not presented). Conversely, the contact angle does affect the wetting speed, particularly at low Ka (high viscosity). Figure 9 shows the temporal evolution of normalized wetted area where the time t_w is normalized by the capillary time scale as $t_w^* = t_w / (\mu_l^3 / \sigma_l^2 \rho_l)$ (recall Figure 5(c) and corresponding text). Two wetting regimes become apparent with a solid vertical line included for demarcation. Initially the bulk of the liquid moves in the longitudinal direction and this period is marked as Regime I where the effect of contact angle is negligible. Once the bulk leaves the domain, Regime II, the effect of the contact angle is pronounced. As expected, spreading of the solvent decreases, or the time needed to achieve a 99.5% of fully wetted plate

(t_w) increases, with increased contact angle. The wetted time scales with contact angle as $t_w^* \sim \cos^{1/2} \gamma$ (inset of Figure 9). Finally, coupling the scaling of t_w with both Ka and γ leads to $t_w^* \sim Ka^{7/4} \cos^{-1/2} \gamma$.

The effect of contact angle on the hydrodynamics of a partially wetted plate was also investigated. Unlike the fully wetted plate, the contact angle determines the outer surface shape of the rivulet. Flow simulations were conducted for a range of contact angles (20–80°) at $Q = 2 \times 10^{-6} \text{ m}^3/\text{sec}$ ($Re = 5\text{--}204$). In Figure 10(a), the gas–liquid interfaces is presented for $Ka=15$. The shape of the interface changes from diverging to converging with increasing contact angle, corresponding to reduced surface wettability and interface size. For the same solvent, Figure 10(b) shows the variation of the wetted and interfacial areas with the contact angle. As expected, both areas decrease with increased γ values, because surface wettability decreases with increasing contact angle. Furthermore, variation of the wetted area with the contact angle is steeper than that of the interfacial area. Accordingly, the difference between the wetted and interfacial areas increases with increasing contact angle. This development corresponds to increasing rivulet thickness presented in Figure 10(a), and may, in part, be understood by considering that as the contact angle increases the curvature of the interface also increases.

In the inset of Figure 11(a) the interfacial area is plotted as a function of the contact angle for six values of the Kapitza number. For all cases the interfacial area decreases with increasing contact angle, but two regimes of variation are revealed depending upon the Ka value. To elucidate this behavior, the interfacial area is renormalized by the interfacial area at $\gamma = 70^\circ$ (A_{70}). As a result, the top three and bottom three curves merge, and two regimes of solvent are clearly visible depending on the value of the surface tension. As noted earlier the contact angle and surface tension are related. Nicolaiwsky and Fair [43] observed surface tension played dominant role on the estimation of contact angle while viscosity only had a marginal effect. In this effort, those with low surface tension ($\sim 35 \text{ mN/m}$; lower Ka) show steeper variation of interfacial area with contact angle, while solvents having medium ($\sim 50 \text{ mN/m}$) and higher surface tension respond more slowly with contact angle. However, in both cases, the interfacial

area shows a scaling relation $A \sim (1 - \cos \gamma)^{-m}$. Furthermore, the value of the exponent m is larger at smaller values of σ .

$$A_m \sim 1/(1 - \cos \gamma)^m$$

$$m = 0.46; \quad \sigma < 50 \text{ mN/m}$$

$$= 0.35; \quad > 50 \text{ mN/m}$$
(11)

The scaling for specific Interfacial area (A_m) with contact angle is shown in Figure 12(b) as a function of $(1 - \cos \gamma)^{-m}$ for two solvents ($Ka=26$ and 783). Shi and Mersmann [38] showed a strong impact of the contact angle on the wetted area as $A_m \sim 1/(1 - 0.93 \cos \gamma)$ while Nicolaiewsky et al [41] found mild effect of the contact angle on the film width (thereby wetted area) as $B \sim 1/(1 - \cos \gamma)^{0.264}$. Similar to these studies, the contact angle is found to clearly influence the wetting behavior; however, the present study observes two values of the exponent (m) depending on the surface tension of solvent. Previous studies [71, 72] have also invoked a critical value of surface tension (σ_{ref}) that marks two regimes for variation of the interfacial area.

The specific interfacial and wetted areas were shown to vary as $A \sim 1/Ka^{1/2}$ for a fixed contact angle $\gamma = 70^\circ$ (see Figure 9(b)). As demonstrated in the Figure 12(a), this scaling relation was also found to hold for all contact angles. Note that a lower value of interfacial area was noted for the combination of small Ka ($Ka \leq 25$) and small contact angle ($\gamma = 20^\circ$ & 25°). In these cases, the value of the interfacial area fall slightly below the scaling line but they still follow the scaling $A \sim 1/Ka^{1/2}$. It is worth noting that the rate of surface wetting for these systems was extremely slow. All curves collapse when the expressions for the interfacial area as a function of the Reynolds and Kapitza numbers (equation 9), the inclination angle (equation 10) and contact angle (equation 11) are combined. The following phenomenological correlation is obtained. As shown in Figure 12(b):

$$A_m = \frac{0.3075 \times Re^{2/5}}{Ka^{1/2} (1 - \cos \gamma)^m \sin^p \theta}$$
(12)

A small scatter is observed at low Ka corresponds to highly viscous solvent in the Figure 12(b). Further, the slow wetting speeds of the highly viscous solvent at low contact angles resulted in a lower slope and consequently a finite intercept at the ordinate is observed. The Figure 12 (b) clearly shows that Interfacial area increases with Reynolds number. A very high value of R^2 ($=0.9913$) shows a strong hold of the correlation presented in equation(12), and it can be used to compute the interfacial area of rivulet.

6. Summary

We have conducted three Dimensional multiphase flow simulations for film flow down an inclined plate using the VOF method. The behavior of the liquid film is a key aspect to the overall efficiency of a structured packed column utilized in distillation and absorption processes. In this view, extensive CFD simulations were conducted for parameters influencing the hydrodynamics of the film flow, specifically, film thickness and interfacial area. The simulation results for wetted area of the plate matched well with the experimental results of Hoffman et al [15]. A scaling analysis for film thickness and interfacial area in terms of Kapitza number was proposed. The Kapitza number is fixed for a given solvent with the Kapitza number decreasing with increasing solvent viscosity. The results show that for a fully wetted plate, the film thickness (δ) decreases with increasing Kapitza number. Besides this, wetted area of the plate shows non-monotonic variation with Kapitza number i.e. first increase and then decreases with Kapitza number for a fixed Weber number.

For a partially wetted plate, the interfacial area of the rivulet flow was found to decrease with increasing Kapitza number, and scaling shows the relationship $A_{in} \sim 1/Ka^{1/2}$. The developed width of the rivulet was found independent of inlet size and strongly influenced by flow rate for given solvent. The effect of plate inclination angle was also investigated. The interfacial area decreases with increased inclination angle, however the effect is not significant beyond an angle of 60° .

The contact angle is a key factor dictating the wetting dynamics, and so the effect of varying contact angle on the hydrodynamics was also studied. The contact angle had negligible impact on the film thickness for a fully wetted plate; however wetting speed is influenced. In particular the wetting time of

the plate shows two regimes and once the initial transients have passed it increases with increased contact angle. For rivulet flow, the interfacial area decreases with increasing contact angle whereas height of the rivulet increases. It shows two regimes for the variation of interfacial area with contact angle. A scaling analysis shows the relationship $A_m \sim (1 - \cos \gamma)^{-m}$, where the value of the exponent m shows two values depending on the Kapitza number. By combining these analyses a phenomenological correlation for wetted/interfacial area is derived in terms of the Reynold's number, contact angle, inclination angle, and solvent physical properties given in terms of the Kapitza number.

Acknowledgement

This research was supported in part by an appointment to the National Energy Technology Laboratory Research Participation Program, sponsored by the Office of Fossil Energy, U.S. Department of Energy, through Carbon Capture Simulation Initiative (CCSI) and administered by the Oak Ridge Institute for Science and Education. Authors would also like to thank Prof. Sankaran Sundaresan, Princeton University, for his valuable inputs and discussion on the project.

References

1. IEA, *CO₂ Capture and Storage: A Key Carbon Abatement Option*. 2008, Paris, France: OECD Publishing. 53.
2. Chu, S., *Carbon Capture and Sequestration*. Science, 2009. **325**(5948): p. 1599-1599.
3. Nawrocki, P.A., Z.P. Xu, and K.T. Chuang, *Mass transfer in structured corrugated packing*. The Canadian Journal of Chemical Engineering, 1991. **69**(6): p. 1336-1343.
4. Wang, G.Q., X.G. Yuan, and K.T. Yu, *Review of Mass-Transfer Correlations for Packed Columns**. Industrial & Engineering Chemistry Research, 2005. **44**(23): p. 8715-8729.
5. Xu, Y.Y., et al., *Portraying the Countercurrent Flow on Packings by Three-Dimensional Computational Fluid Dynamics Simulations*. Chemical Engineering & Technology, 2008. **31**(10): p. 1445-1452.
6. Bradtmöller, C., et al., *Influence of Viscosity on Liquid Flow Inside Structured Packings*. Industrial & Engineering Chemistry Research, 2015. **54**(10): p. 2803-2815.
7. Pangarkar, K., et al., *Structured Packings for Multiphase Catalytic Reactors*. Industrial & Engineering Chemistry Research, 2008. **47**(10): p. 3720-3751.
8. Heymes, F., et al., *Hydrodynamics and mass transfer in a packed column: Case of toluene absorption with a viscous absorbent*. Chemical Engineering Science, 2006. **61**(15): p. 5094-5106.
9. Raynal, L., F. Ben Rayana, and A. Royon-Lebeaud, *Use of CFD for CO₂ absorbers optimum design : from local scale to large industrial scale*. Greenhouse Gas Control Technologies 9, 2009. **1**(1): p. 917-924.
10. Raynal, L. and A. Royon-Lebeaud, *A multi-scale approach for CFD calculations of gas-liquid flow within large size column equipped with structured packing*. Chemical Engineering Science, 2007. **62**(24): p. 7196-7204.
11. Nusselt, W., *Die Oberflächenkondensation des Wasserdampfes*. Zeitschrift des Vereines Deutscher Ingenieure 1916. **60**(27): p. 541-546.
12. Moran, K., J. Inumaru, and M. Kawaji, *Instantaneous hydrodynamics of a laminar wavy liquid film*. International Journal of Multiphase Flow, 2002. **28**(5): p. 731-755.
13. Camur, H., K. Balasubramanian, and O.E. Peremeci, *Determination of free surface flow characteristics of free falling fluid over an inclined plate by opto-coupler arrangement*, in *IEEE Instrumentation and Measurement Technology Conference*. 2001.
14. Decre, M.M.J. and J.-C. Baret, *Gravity-driven flows of viscous liquids over two-dimensional topographies*. Journal of Fluid Mechanics, 2003. **487**: p. 147-166.
15. Hoffmann, A., et al., *Fluid dynamics in multiphase distillation processes in packed towers*. Computers & Chemical Engineering, 2005. **29**(6): p. 1433-1437.
16. Roy, R.P. and S. Jain, *A study of thin water film flow down an inclined plate without and with countercurrent air flow*. Experiments in Fluids, 1989. **7**(5): p. 318-328.
17. Ruyer-Quil, C. and P. Manneville, *Improved modeling of flows down inclined planes*. The European Physical Journal B - Condensed Matter and Complex Systems, 2000. **15**(2): p. 357-369.
18. Trifonov, Y.Y., *Spreading of a viscous liquid film over the corrugated surface and the heat and mass transfer calculations*. Journal of Engineering Thermophysics, 2008. **17**(4): p. 282-291.
19. Dou, H.S., et al., *Simulation of front evolving liquid film flowing down an inclined plate using level set method*. Computational Mechanics, 2004. **34**(4): p. 271-281.
20. Cooke, J.J., et al., *Gas-liquid flow on smooth and textured inclined planes*. World Academy of Science, Engineering and Technology, 2012. **6**(8): p. 1449-1457.
21. Gu, F., et al., *CFD Simulation of Liquid Film Flow on Inclined Plates*. Chemical Engineering & Technology, 2004. **27**(10): p. 1099-1104.
22. Valluri, P., et al., *Thin film flow over structured packings at moderate Reynolds numbers*. Chemical Engineering Science, 2005. **60**(7): p. 1965-1975.

23. Sebastia-Saez, D., et al., *3D modeling of hydrodynamics and physical mass transfer characteristics of liquid film flows in structured packing elements*. International Journal of Greenhouse Gas Control, 2013. **19**(0): p. 492-502.
24. Oron, A., S.H. Davis, and S.G. Bankoff, *Long-scale evolution of thin liquid films*. Reviews of Modern Physics, 1997. **69**(3): p. 931-980.
25. Drosos, E.I.P., S.V. Paras, and A.J. Karabelas, *Characteristics of developing free falling films at intermediate Reynolds and high Kapitza numbers*. International Journal of Multiphase Flow, 2004. **30**(7-8): p. 853-876.
26. Portalski, S., *Studies of falling liquid film flow Film thickness on a smooth vertical plate*. Chemical Engineering Science, 1963. **18**(12): p. 787-804.
27. Kohrt, M., et al., *Texture influence on liquid-side mass transfer*. Chemical Engineering Research and Design, 2011. **89**(8): p. 1405-1413.
28. Iso, Y., et al., *Numerical and Experimental Study on Liquid Film Flows on Packing Elements in Absorbers for Post-combustion CO₂ Capture*. Energy Procedia, 2013. **37**(0): p. 860-868.
29. Podowski, M.Z. and A. Kumbaro, *The Modeling of Thin Liquid Films Along Inclined Surfaces*. Journal of Fluids Engineering, 2004. **126**(4): p. 565-572.
30. Zhou, D.W., T. Gambaryan-Roisman, and P. Stephan, *Measurement of water falling film thickness to flat plate using confocal chromatic sensing technique*. Experimental Thermal and Fluid Science, 2009. **33**(2): p. 273-283.
31. Lan, H., et al., *Developing Laminar Gravity-Driven Thin Liquid Film Flow Down an Inclined Plane*. Journal of Fluids Engineering-Transactions of the Asme, 2010. **132**(8).
32. Hoffmann, A., et al., *Detailed investigation of multiphase (gas-liquid and gas-liquid-liquid) flow behaviour on inclined plates*. Chemical Engineering Research & Design, 2006. **84**(A2): p. 147-154.
33. Iso, Y. and X. Chen, *Flow Transition Behavior of the Wetting Flow Between the Film Flow and Rivulet Flow on an Inclined Wall*. Journal of Fluids Engineering-Transactions of the Asme, 2011. **133**(9): p. 091101.
34. Ataki, A. and H.J. Bart, *Experimental and CFD simulation study for the wetting of a structured packing element with liquids*. Chemical Engineering & Technology, 2006. **29**(3): p. 336-347.
35. Tsai, R.E., et al., *Influence of Surface Tension on Effective Packing Area*. Industrial & Engineering Chemistry Research, 2008. **47**(4): p. 1253-1260.
36. Tsai, R.E., et al., *Influence of viscosity and surface tension on the effective mass transfer area of structured packing*. Energy Procedia, 2009. **1**(1): p. 1197-1204.
37. Ataki, A. and H.J. Bart, *The use of the VOF-model to study the wetting of solid surfaces*. Chemical Engineering & Technology, 2004. **27**(10): p. 1109-1114.
38. Shi, M.G. and A. Mersmann, *Effective interfacial area in packed columns*. German chemical engineering, 1985. **8**(2): p. 87-96.
39. Zakeri, A., A. Einbu, and H.F. Svendsen, *Experimental investigation of liquid holdup in structured packings*. Chemical Engineering Research & Design, 2012. **90**(5): p. 585-590.
40. Rendtorff Birrer, F. and U. Böhm, *Gas-liquid dispersions in structured packing with high-viscosity liquids*. Chemical Engineering Science, 2004. **59**(20): p. 4385-4392.
41. Nicolaiewsky, E.M.A., et al., *Liquid film flow and area generation in structured packed columns*. Powder Technology, 1999. **104**(1): p. 84-94.
42. Pelofsky, A.H., *Surface Tension-Viscosity Relation for Liquids*. Journal of Chemical & Engineering Data, 1966. **11**(3): p. 394-397.
43. Nicolaiewsky, E.M.A. and J.R. Fair, *Liquid Flow over Textured Surfaces. 1. Contact Angles*. Industrial & Engineering Chemistry Research, 1998. **38**(1): p. 284-291.
44. Hirt, C.W. and B.D. Nichols, *Volume of fluid (VOF) method for the dynamics of free boundaries*. Journal of Computational Physics, 1981. **39**(1): p. 201-225.
45. *ANSYS Fluent Theory Guide*. 2011.
46. Brackbill, J.U., D.B. Kothe, and C. Zemach, *A continuum method for modeling surface tension*. Journal of Computational Physics, 1992. **100**(2): p. 335-354.

47. Yang, H., et al., *Progress in carbon dioxide separation and capture: A review*. Journal of Environmental Sciences, 2008. **20**(1): p. 14-27.
48. Maham, Y., et al., *Volumetric properties of aqueous solutions of monoethanolamine, mono- and dimethylethanolamines at temperatures from 5 to 80 °C I*. Thermochimica Acta, 2002. **386**(2): p. 111-118.
49. Tahery, R. and H. Modarress, *A new and a simple model for surface tension prediction of water and organic liquid mixtures*. Iranian Journal of Science and Technology Transaction B-Engineering, 2005. **29**(B5): p. 501-509.
50. Yu, C.H., H.H. Cheng, and C.S. Tan, *CO₂ capture by alkanolamine solutions containing diethylenetriamine and piperazine in a rotating packed bed*. International Journal of Greenhouse Gas Control, 2012. **9**: p. 136-147.
51. Murshid, G., et al., *Thermo physical analysis of 2-amino-2-methyl-1-propanol solvent for carbon dioxide removal*. Chemical Engineering Transactions, 2011. **25**: p. 45-50.
52. Muhammad, A., et al., *Viscosity, Refractive Index, Surface Tension, and Thermal Decomposition of Aqueous N-Methyldiethanolamine Solutions from (298.15 to 338.15) K*. Journal of Chemical & Engineering Data, 2008. **53**(9): p. 2226-2229.
53. Rayer, A.V., et al., *Physicochemical properties of {1-methyl piperazine (1) + water (2)} system at T = (298.15 to 343.15) K and atmospheric pressure*. The Journal of Chemical Thermodynamics, 2011. **43**(12): p. 1897-1905.
54. Zisman, W.A., *Relation of the Equilibrium Contact Angle to Liquid and Solid Constitution, in Contact Angle, Wettability, and Adhesion*. 1964, American Chemical Society. p. 1-51.
55. Kalliadasis, S., et al., *Falling Liquid Films*. 1 ed. Applied Mathematical Sciences. 2012, London: Springer-Verlag London.
56. Meza, C.E. and V. Balakotaiah, *Modeling and experimental studies of large amplitude waves on vertically falling films*. Chemical Engineering Science, 2008. **63**(19): p. 4704-4734.
57. Towell, G.D. and L.B. Rothfeld, *Hydrodynamics of rivulet flow*. AIChE Journal, 1966. **12**(5): p. 972-980.
58. Raynal, L., C. Boyer, and J.-P. Ballaguet, *Liquid Holdup and Pressure Drop Determination in Structured Packing with CFD Simulations*. The Canadian Journal of Chemical Engineering, 2004. **82**(5): p. 871-879.
59. Chang, H., *Wave Evolution on a Falling Film*. Annual Review of Fluid Mechanics, 1994. **26**(1): p. 103-136.
60. Argyriadi, K., M. Vlachogiannis, and V. Bontozoglou, *Experimental study of inclined film flow along periodic corrugations: The effect of wall steepness*. Physics of Fluids, 2006. **18**(1): p. 012102.
61. Alekseenko, S.V., et al., *Wave Flow of Liquid Films*. 1994: Begell House.
62. Rizzuti, L. and A. Brucato, *Liquid viscosity and flow rate effects on interfacial area in packed columns*. The Chemical Engineering Journal, 1989. **41**(1): p. 49-52.
63. Blake, T.D. and J. De Coninck, *The influence of solid-liquid interactions on dynamic wetting*. Advances in Colloid and Interface Science, 2002. **96**(1-3): p. 21-36.
64. Dukler, A.E. and O.P. Bergelin, *CHARACTERISTICS OF FLOW - IN FALLING LIQUID FILMS*. Chemical Engineering Progress, 1952. **48**(11): p. 557-563.
65. Ishigai, S., et al., *Hydrodynamics and Heat Transfer of Vertical Falling Liquid Films : Part 1, Classification of Flow Regimes*. Bulletin of JSME, 1972. **15**(83): p. 594-602.
66. Young, T., *An Essay on the Cohesion of Fluids*. Philosophical Transactions of the Royal Society of London, 1805. **95**: p. 65-87.
67. Neumann, A.W., *Contact angles and their temperature dependence: thermodynamic status, measurement, interpretation and application*. Advances in Colloid and Interface Science, 1974. **4**(2-3): p. 105-191.
68. Snoeijer, J.H. and B. Andreotti, *A microscopic view on contact angle selection*. Physics of Fluids (1994-present), 2008. **20**(5): p. -.

- 1 69. Schwartz, L.W. and S. Garoff, *Contact angle hysteresis and the shape of the three-phase line*. Journal
2 of Colloid and Interface Science, 1985. **106**(2): p. 422-437.
- 3 70. Johnson, R.E. and R.H. Dettre, *Contact Angle Hysteresis. III. Study of an Idealized Heterogeneous*
4 *Surface*. The Journal of Physical Chemistry, 1964. **68**(7): p. 1744-1750.
- 5 71. Rocha, J.A., J.L. Bravo, and J.R. Fair, *Distillation columns containing structured packings: a*
6 *comprehensive model for their performance. 1. Hydraulic models*. Industrial & Engineering
7 Chemistry Research, 1993. **32**(4): p. 641-651.
- 8 72. Gualito, J.J., et al., *Design Method for Distillation Columns Filled with Metallic, Ceramic, or Plastic*
9 *Structured Packings*. Industrial & Engineering Chemistry Research, 1997. **36**(5): p. 1747-1757.

10

Nomenclature

A	: Area
CO	: Courant number
D	: Hydraulic diameter
$\mathbf{F}$	: Surface tension force per unit volume
f	: Volume fraction
$\mathbf{g}$	: Gravitational acceleration
Ka	: Kapitza Number
$\mathbf{n}$	: Unit normal vector
p	: Pressure
Q	: Solvent flow rate
Re	: Reynolds number
t	: Time
$\mathbf{u}$	: Velocity vector
W	: Plate width
We	: Weber number
x	: Mole fraction

Greek symbols

δ	: Film thickness
γ	: Contact Angle
∇	: Gradient operator
Δt	: Time step
κ	: Interface curvature
μ	: Dynamic viscosity
ν	: Kinematic viscosity
θ	: Inclination angle
ρ	: Density
σ	: Surface tension

Subscripts

g	: Gas
In	: Normalized interfacial
in	: Inlet
l	: Liquid
wn	: Normalized wetted

1 w : Wetted

2 P : Total

3 N : Nusselt

4 **Superscripts**

5 $*$: Normalized value

6 T : Transpose

7 **Abbreviations**

8 CFL : Courant–Friedrichs–Lewy

9 CSF : Continuum surface force

10 AMP : 2-aminomethylpropanol

11 MDEA : N-methyldiethanolamine

12 MEA : Monoethanolamine

13 MPZ : 1-methylepiperazine

14 PISO : Pressure implicit with dplit of operators

15 PLIC : Piecewise linear interface calculation

16 VOF : Volume of fluid

List of Figures

- Figure 1:** Schematic of the computational flow domain showing that plate is 60° inclined to the horizontal. The solvent is flowing down from top on the inclined smooth plate.
- Figure 2:** (a) Discretization of the flow domain showing meshing scheme used in the simulation. Near the plate, fine mesh is used in order to resolve the film flow dynamics. The center of the domain is also meshed very fine to capture the rivulet flow behavior. (b) Temporal evaluation of the normalized wetted area ($A_{wn} = A_w/A_p$) for three grid resolutions at $A_{wn} = A_w/A_p = 0.24$. The wetted area is normalized by the actual area of the plate. (c) Shape of the Interface for two grid resolutions at $We=0.24$ also confirm the grid independent results.
- Figure 3:** (a) Effect of the inertia on the flow pattern for downward film flow over an inclined plate. Film is entering from the top of the plate as shown in the figure. The Flow develops from droplet to rivulet and finally full film. (b) Comparison of the predicted normalized wetted area (A_{wn}) with experimental results of Hoffman et al (2005) at different Weber numbers for water ($Ka=3969$), $\gamma=70^\circ$ and $\theta=60^\circ$.
- Figure 4:** Variation of the normalized wetted area of the plate with Ka at different Weber numbers at (a) $t=0.5$ sec and (b) 2 sec for pseudo-steady dynamics of film flow. (c) Scaling for normalized time ($t_w^* = t_w / (\mu_l^3 / \sigma_l^2 \rho_l)$) to achieve 99.50% of the final steady state value of A_{wn} with Ka shows $t_w^* \sim Ka^{7/4}$ at both Weber numbers. The plate becomes fully wetted at both We values for all Ka tested.
- Figure 5:** (a) Comparison of the predicted normalized film thickness (δ^*) with Nusselt theory for fully wetted plate at a fixed flow rate ($Q=1.05 \times 10^{-5}$ m³/sec) and different Kapitza numbers (Ka). This agreement verifies nearly uniform film behavior for highly viscous solvents. Inset shows the scaling of normalized film thickness (δ^*) with Weber number (We) and Kapitza number (Ka) as a relation $\delta^* \sim Ka^{1/4} We^{1/5}$ at a given inclination angle (60°).
- Figure 6:** Schematic of the flow domain used for the study of rivulet flow. (b) Variation of the interfacial and wetted areas with Ka at a $Q=2 \times 10^{-6}$ m³/sec and $\theta=60^\circ$. Inset shows the interface ($f=0.50$) for indicated solvents. Recall at a fixed flow rate, solvents have different Reynolds numbers.
- Figure 7:** (a) Shape of the interface ($f=0.50$) for different inlet sizes at a flow rate $Q=2 \times 10^{-6}$ m³/sec, $\theta=60^\circ$, and $Ka=15$. The developed rivulet width (~ 8.75 mm) is insensitive to inlet size at a fixed flow rate and solvent properties. (b) Scaling for variation of the A_{in} as Ka $A_{in} \sim 1/Ka^{1/2}$ shows interfacial area decreases with increased Ka value. Inset of (b) shows the variation of the normalized developed interfacial area per unit length (APL) with Ka .
- Figure 8:** (a) Scaling for effects of the inertia achieved by varying solvent flow rates on the interfacial area shows a relation $A_{in} \sim Re^{2/5} / Ka^{1/2}$ for $\theta=60^\circ$. Solvents do not have same Reynolds number at a fixed flow rate. (b) Variation of A_{in} with Ka for different inclination angles

shows A_{in} decreases with increasing θ values at $Q=2\times 10^{-6}$ m³/sec. Inset shows scaling for A_{in} with θ as $A_{in} \sim 1/(\sin\theta)^p Ka^{1/2}$.

Figure 9: Temporal evolution of the normalized wetted area (A_{wn}) for $Ka = 15$ at $Q=1.05\times 10^{-5}$ m³/sec at different γ values delineates two regimes for wetting speed of solvents. The normalized wetted time $t_w^* = t_w / (\mu_l^3 / \sigma_l^2 \rho_l)$ increases with increasing contact angle. Inset shows the scaling of t_w^* with γ as $t_w^* \sim 1/\cos^{1/2} \gamma$.

Figure 10: (a) Shape of the interface ($f=0.50$) for different contact angles at $Ka=15$, $\theta=60^\circ$ and $Q=2\times 10^{-6}$ m³/sec. (b) Variation of the normalized interfacial and wetted areas with contact angles shows the decreased areas with increasing contact angle for same case.

Figure 11: (a) Variation of renormalized interfacial area (A_{in}/A_{70}) with γ shows two regimes for variation of interfacial area depending on Ka value. Inset shows variation of the A_{in} with γ at $Q= 2\times 10^{-6}$ m³/sec for $\theta=60^\circ$ and Ka values. (b) Scaling of A_{in} with γ for both regimes shows that highly viscous solvent is more sensitive to the change in contact angle.

Figure 12: (a) Variation of the A_{in} with Ka for different γ values at $Q=2\times 10^{-6}$ m³/sec and $\theta=60^\circ$. (b) Normalizing the interfacial area by contact angle, Reynolds number and inclination angle results in merger of all curves into single one with Ka . It confirms a scaling relation as $A_{in} \sim Re^{2/5} / Ka^{1/2} (1 - \cos\gamma)^m \sin\theta^p$.

Figure-1

Figure 1

Figure-2

Figure 2

Figure-3

Figure 3

Figure-4

Figure 4

Figure-5

Figure 5

Figure-6

Figure 6

Figure-7

Figure 7

Figure-8

Figure 8

Figure-9

Figure 9

Figure-10

Figure 10

Figure-11

Figure 11

Figure-12

Figure 12

Table 1: Physical properties of the solvents at 25°C and 1atm

Solvent	μ_l (mPa/s)	ρ_l (Kg/m ³)	σ (mN/m)	Ka
Water	0.89	997.0	72.80	3969
20%MEA	1.18	996 [43]	57.8 [44]	2173
30% MEA	2.52	988 [43]	55.0 [44]	750
26.73% AMP [46]	2.70	995.8	43.01	534
40% MEA	3.71	979 [43]	54.80 [44]	450
0.073xMPZ [48]	5.56	1005.3	54.42	258
48.8% MDEA	9.25	1016.6	47.56	117
0.10x MPZ[48]	10.75	1000.9	47.25	93
0.51x MPZ [48]	13.36	946.41	34.37	50
0.41x MPZ [48]	23.48	962.20	35.89	25
0.31x MPZ [48]	36.42	981.31	38.40	15
$Ka = \sigma_l \left(\rho_l / \mu_l^4 g \right)^{1/3}$ %: Percentage by weight, x: mole fraction				