Contents lists available at ScienceDirect

Chemical Engineering Research and Design

journal homepage: www.elsevier.com/locate/cherd

Direct spatiotemporally resolved fluorescence investigations of gas absorption and desorption in liquid film flows

Viktoria Kapoustina[a,*], *Jesse Ross-Jones*[a], *Michael Hitschler*[b], *Matthias Rädle*[a], *Jens-Uwe Repke*[c]

[a] *Institute for Process Control and Innovative Energy Conversion, Mannheim University of Applied Sciences, Mannheim, Germany*
[b] *hte GmbH, Heidelberg, Germany*
[c] *Institute of Thermal, Environmental and Natural Products Process Engineering, Freiberg University of Mining and Technology, Freiberg, Germany*

ARTICLE INFO

Article history:
Received 17 October 2014
Received in revised form 13 March 2015
Accepted 25 March 2015
Available online 1 April 2015

Keywords:
Planar Laser Induced Fluorescence
Diffusion
Mass transfer
Liquid film flow
Absorption
Desorption

ABSTRACT

An optical measuring technique, combining Planar Laser Induced Fluorescence (PLIF) with the effect of fluorescence quenching, is used for the local concentration analysis of a gas absorbed and desorbed in a thin liquid film flow. The absorption and desorption process is visualized by using oxygen in a mixture of water, ethanol and glycerol. Fluorescence is strongly reduced by the presence of molecular oxygen as a result of dynamic quenching. The resulting decrease in intensity is detected and interpreted through image processing. The image analysis provides a spatiotemporal value of fluorescence intensity and therefore enables the direct characterization of local transport phenomena in the liquid film flow. In this way, the impact of a single pyramidal microstructure on mass transfer into the film flow is examined. The results are compared to liquid film flow over a smooth surface. The measuring methodology is validated through diffusion experiments.

1. Introduction

The characterization of mass transfer and transport phenomena in liquid film flows is crucial in multi-phase unit operations, such as distillation and absorption processes in packed towers. Here, the liquid phase often occurs as a film ($d \approx 0.1$–1 mm) on a textured surface. However, experimental methods for the direct measurement of local transfer parameters in the liquid film are still limited, since measurements inside thin liquid films are complex. These measurements, however, are needed for the optimal design of the process equipment (texture on the packing surface in distillation or absorption towers) and for the development of novel methodologies to predict mass transfer parameters.

Various efforts have been made to investigate liquid film flow over smooth surfaces (e.g. Oron et al., 1997; Roberts and Chang, 2000; Xu et al., 2008a). Some studies have also been made to investigate film flow over roughened surfaces (Davies and Warner, 1969) and over wavy substrates (Trifonov, 1998; Wang, 1981; Zhao and Cerro, 1992).

However, for high separation performance with low pressure drop, the well-defined surfaces of structured packing is state of the art in distillation and absorption processes. Although structured packing is known to enhance mass

* *Corresponding author at*: John-Deere-Straße 81a, 68163 Mannheim, Germany. Tel.: +49 621 292 6503.
E-mail address: v.kapoustina@hs-mannheim.de (V. Kapoustina).
http://dx.doi.org/10.1016/j.cherd.2015.03.024

Nomenclature

A	absorption
c	speed of light ($m\,s^{-1}$)
c_{dye}	dye concentration ($mg\,L^{-1}$)
c_Q	quencher concentration ($mg\,L^{-1}$)
D	diffusion coefficient ($mm^2\,s^{-1}$)
d	film thickness (mm)
f	frequency (s^{-1})
h	Planck's constant
I_0	light intensity in absence of a quencher
I_Q	light intensity in presence of a quencher
K_{SV}	Stern–Volmer constant ($L\,mg^{-1}$)
k	parameter
l	distance (cm)
m	slope
P_{opt}	power (optical) (mW)
$\dot{V}_g$	flow rate gas ($cm^3\,h^{-1}$)
$\dot{V}_l$	flow rate liquid ($cm^3\,h^{-1}$)
x	horizontal spatial coordinate (mm)
y	vertical spatial coordinate (mm)
y_{front}	vertical position of diffusion front (mm)

Greek letters

ε	molar extinction coefficient ($L\,mol^{-1}\,cm^{-1}$)
η	dynamic viscosity (mPa s)
λ	wavelength (nm)
ρ	density ($kg\,m^{-3}$)

transfer, only a few studies have examined film flow over structured packing. Kohrt et al. (2011) measured the integral mass transfer in order to analyse the impact of different packing material textures to liquid-side controlled mass transfer. They found that mass transfer is intensified up to 80% by using a textured surface instead of a smooth surface on the inclined plate. Basic studies on the influence of structured surfaces on mass transfer have been made by Kohrt et al. (2011), Shetty and Cerro (1997, 1998) and Valluri et al. (2005).

Bühlmann (1987) showed that microstructured packing further enhances mass transport as compared to non-textured packing. Repke et al. (2011) conducted basic studies on film flow over microstructured packing. They found microstructured surfaces had a significant impact on the fluid dynamics of the film flow as well as on mass transfer. The results indicate that more factors than just the increased phase boundary interface, stabilization of the film and improved wetting are responsible for the enhanced mass transfer.

In order to deepen the understanding of local mass transfer characteristics, a spatiotemporally resolved non-invasive observation technique is required that does not disturb the liquid film flow and the transport process of interest.

Laser Doppler Anemometry (LDA) and Particle Image Velocimetry (PIV) are well-established technologies that are applied to investigate the velocity field inside a moving liquid, including liquid film flow on textured surfaces and downwards annular geometries (Dietze et al., 2009; Dietze and Kneer, 2011; Paschke et al., 2008; Xu et al., 2008b; Zadrazil and Markides, 2014). General information about these techniques is provided by Durst et al. (1976) (LDA) and Adrian and Westerweel (2011) (PIV). A general survey of flow visualization is given by Freymuth (1993), Merzkirch (1987) and Yang (1989).

(Planar) Laser Induced Fluorescence (PLIF) can be used for film thickness and velocity measurements (Farias et al., 2012; Lel et al., 2005), as well as for concentration field measurements in liquids (Alekseenko et al., 2013; Arratia and Muzzio, 2004; Bouche et al., 2013; Charogiannis and Beyrau, 2013). Mathie et al. (2013) presented a combined measurement of film thickness and free-surface temperature, marking the liquid with a temperature-dependant dye.

The combination of fluorescence intensity measurements with the effect of fluorescence quenching for gas concentration measurements in liquids was first introduced by Vaughan and Weber (1970). This method enables quantitative measurements in two-phase (gas–liquid) systems. Many authors have adapted and refined the method to address different issues.

Roy and Duke (2004) measured transfer rates across oxygen–water bubble interfaces. Gas exchange at a free water–atmosphere interface has been investigated by Münsterer and Jähne (1998) and by Woodrow and Duke (2001). Schagen and Modigell (2005) measured gas concentration inside a film flow over a smooth surface, using a photometric detection system. The measuring system described requires a simultaneous measurement, over the entire film flow, of the local film thickness for concentration analysis.

So far, no experimental methods were found, where an optical measuring technique was used to investigate film flow over single microstructures with respect to mass transfer analysis. In this study, we therefore introduce the PLIF method in combination with fluorescence quenching as a means of demonstrating the impact of a single microstructure on the gas transfer into a liquid film flow, and compare this result to the film flow over a smooth surface. The microstructure, used in this first study, is a single pyramid, which can be regarded as a simplified surface structure that will be expanded to a textured surface in the following step. In a more complex form, these microstructures could be used in technical evaporators, condensers or column packages.

2. Materials and methods

2.1. Substance system

The Ruthenium complex $Ru(dpp)_3Cl_2$ (*Tris-(4,7-diphenyl-1,10-phenanthroline)-ruthen-ium dichloride*, Sigma–Aldrich), an orange powder with a molecular weight of 1169 $kg\,kmol^{-1}$, is used as fluorescence dye ($\lambda_{fluoro,max}$ = 612 nm). A mixture of ethanol (96 vol.% p.a., VWR), purified water and glycerol (97 vol.% p.a., VWR) is used as solvent. The solvent's composition was chosen in order to generate a refractive index of 1.41, which matches that of the surface structures used in flow experiments. The characteristics of the solvent are summarized in Table 1. The dye's concentration in the solvent is 5 $mg\,L^{-1}$. Molecular oxygen (Linde Gas) is used to quench the fluorescence.

Table 1 – Characteristics of the indicator solution studied.

Ethanol (wt.%)	Water (wt.%)	Glycerol (wt.%)	$\eta_{25\,°C}$ (mPa s)	$\rho_{25\,°C}$ ($kg\,m^{-3}$)
30	20	50	9.4	1053