

Transfert de masse dans les écoulements gaz-liquide horizontaux intermittents et application aux photobioréacteurs

Pierre Valiorgue

► To cite this version:

Pierre Valiorgue. Transfert de masse dans les écoulements gaz-liquide horizontaux intermittents et application aux photobioréacteurs. Mécanique des fluides [physics.class-ph]. Université Claude Bernard - Lyon I, 2012. Français. NNT: 2012LYO10266 . tel-01127607

HAL Id: tel-01127607 https://theses.hal.science/tel-01127607

Submitted on 7 Mar 2015 $\,$

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers. L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés. N ° d'ordre 2012-ISAL-266-2012

Année 2012

THÈSE

Mass transfer in intermittent horizontal gas-liquid flow and application to photobioreactors

Présentée devant l'Université Claude Bernard Lyon 1

> pour obtenir le GRADE de DOCTEUR

École doctorale : Mécanique, Énergétique, Génie Civil, Acoustique

> Spécialité : MÉCANIQUE des FLUIDES

par

Pierre VALIORGUE Ingénieur

Thèse soutenue le 3 décembre 2012 devant la Commission d'examen

Jury

MARC BUFFAT Abdelkader MOJTABI Anthony ROBINSON Arnaud MULLER FEUGA Hamda Ben Hadid Mahmoud El Hajem Professeur Professeur Assistant Professor Docteur, HDR Professeur Maître de Conférences Président Rapporteur Rapporteur Examinateur Directeur de thèse Co-directeur de thèse

LMFA - UMR CNRS 5509 - Université Claude Bernard Lyon 1 43, boulevard du 11 Novembre 1918, 69622 Villeurbanne cedex (FRANCE)

UNIVERSITÉ CLAUDE BERNARD - LYON 1

Président de l'Université Vice-président du Conseil d'Administration Vice-président du Conseil des Études et de la Vie Universitaire Vice-président du Conseil Scientifique Secrétaire Général M. le Professeur François-Noël GILLY M. le Professeur Hamda BEN HADID

M. le Professeur Philippe LALLE M. le Professeur Germain GILLET M. Alain HELLEU

LES DIRECTEURS DES COMPOSANTES SANTÉ

Faculté de Médecine Lyon Est -
Claude Bernard
Faculté de Médecine et de Maïeutique
Lyon Sud - Charles Mérieux
UFR d'Odontologie
Institut des Sciences Pharmaceutiques
et Biologiques
Institut des Sciences et Techniques
de la Réadaptation
Département de formation et Centre
de Recherche en Biologie Humaine

M. le Professeur J. ETIENNE

Mr K. M'BAREK M. le Professeur D. BOURGEOIS

Mme la Professeure C. VINCIGUERRA

M. le Professeur Y. MATILLON

M. le Professeur P. FARGE

LES DIRECTEURS DES COMPOSANTES ET DEPARTEMENTS DE SCIENCES ET TECHNOLOGIE

Faculté des Sciences et Technologies **Département Biologie** Département Chimie Biochimie **Département GEP Département Informatique Département Mathématiques Département Mécanique Département Physique** Département Sciences de la Terre **UFR Sciences et Techniques des Activités Physiques et Sportives Observatoire de Lyon Polytech Lyon** Institut Universitaire de Technologie de Lyon 1 Institut Universitaire de Formation des Maîtres Institut de Science Financière et d'Assurances

M. F. De MARCHI M. le Professeur F. FLEURY Mme le Professeur H. PARROT M. N. SIAUVE M. le Professeur S. AKKOUCHE M. le Professeur A. GOLDMAN M. le Professeur H. BEN HADID Mme S. FLECK Mme la Professeure I. DANIEL

M. C. COLLIGNON M. B. GUIDERDONI M. P. FOURNIER M. C. VITON M. A. MOUGNIOTTE Mme la Professeure V. MAUME-DESCHAMPS

Acknowledgements

Les travaux présentés dans ce mémoire ont été réalisés au Laboratoire de Mécanique des Fluides et d'Acoustique (LMFA) de Lyon dirigé par Monsieur Michel LANCE. Je souhaiterais adresser mes sincères remerciements à mes deux directeurs de thèse : Monsieur Hamda BEN HADID, Professeur à l'Université Claude Bernard de Lyon, et Monsieur Mahmoud EL HA-JEM, maître de conférences à l'Institut National des Sciences Appliquées (INSA) de Lyon, qui ont encadré cette thèse. Je tiens également à remercier les dirigeants de l'entreprise Microphyt, Monsieur Arnaud MULLER-FEUGA et Monsieur Michel LEMAR avec qui le sujet de thèse a été élaboré. Leur soutien financier qui a permis la réalisation de la partie expérimentale de cette thèse.

Je remercie les rapporteurs de cette thèse, Monsieur Abdelkader MOJTABI, Professeur à l'Université de Toulouse et Monsieur Anthony ROBINSON, Assistant Professor au Trinity College de Dublin, pour l'intérêt qu'ils ont porté à mon travail et pour leurs remarques pertinentes qui ont permis d'approfondir et d'enrichir les problématiques abordées. Merci également aux autres membres du jury qui ont accepté de juger ce travail : Monsieur MULLER-FEUGA, H.D.R. et directeur de Microphyt, et Monsieur Marc BUFFAT, Professeur à l'Université Claude Bernard de Lyon.

Ma reconnaissance s'adresse également :

à toute l'équipe du LMFA pour leur aide sur le plan scientifique, ou tout simplement pour la sympathie qu'ils m'ont témoignée, et en particulier à Jean-Yves CHAMPAGNE, Serge SIMOENS, Valéry BOTTON, Gilbert TRAVIN, Maryline GALINDO et à Cédric MARMOUNIER,

à mes collègues et en particulier à Nicolas SOUZY, Bongo DJIMAKO et Rhamona SADANI pour leur aide et la bonne ambiance au travail,

à mes amis pour leurs facultés naturelles à me sortir la tête du guidon,

à ma famille et à Sophie.

Abstract

Résumé long

L'utilisation des microalgues a connu une recrudescence récente dans de nombreux domaines cruciaux pour l'humanité - en particulier la santé, la nourriture, l'énergie et l'environnement. Sécuriser un approvisionnement fiable de ces micro-organismes est devenu un enjeu industriel. Pour assurer le succès des cultures de microalgues photoautotrophes fragiles et/ou à croissance lente dans des photobioréacteurs tubulaires fermés (PBR), quatre conditions doivent être respectées tout en opérant sous asepsie : assurer la transmission optimale de la lumière, des conditions de température contrôlées, un mélange hydrodynamique et le transfert de masse de l'oxygène et dioxyde de carbone.

Le photobioréacteur tubulaire étudié, développé par Microphyt pour cultiver des microalgues fragiles et/ou à croissance lente, a été présenté. Les conditions hydrodynamiques dans le photobioréacteur ont été présentées du point de vue la phycologie et de la mécanique des fluides. L'influence du transfert de masse sur le changement d'échelle du photobioréacteur, la productivité et la bioconversion du CO_2 a été soulignée justifiant ainsi l'intérêt applicatif d'une étude sur la modélisation du transfert de masse gaz-liquide dans des photobioréacteurs horizontaux.

Dans les trois premiers chapitres de cette thèse, un modèle unidimensionnel de transfert de masse dans l'écoulement gaz-liquide du photobioréacteur sera développé. Dans le **premier chapitre**, le transfert de masse entre une bulle de gaz allongée sous un écoulement turbulent de liquide dans un conduit a été étudié expérimentalement. Il est démontré à partir des mesures expérimentales de transfert de masse, que l'interface d'une bulle immobilisée allongée peut être considérée comme un plan pour ce qui concerne le transfert de masse. Les données mesurées du coefficient de transfert de masse k_L , estimé à l'aide de cette simplification, correspondent à une corrélation établie par Lamourelle (1972) donnée pour un écoulement turbulent de liquide s'écoulant le long d'une colonne dont l'expression est : Sh_L = $1.76 \times 10^{-5} \times \text{Re}^{1.506} \times \text{Sc}^{0.5}$. Dans cette expression, le nombre de Reynolds Re est défini sur le diamètre hydraulique, Sc correspond au nombre de Schmidt et Sh_L au nombre de Sherwood.

Pour différentes applications, il est suggéré que les résultats obtenus pour la géométrie étudiée pourraient être utilisés dans des systèmes où le transfert de masse doit être contrôlé. Une formule pour le transfert de masse utilisant l'hypothèse d'une interface plane est proposée pour la prédiction du temps de contact nécessaire pour réaliser un objectif de dissolution.

Dans le **deuxième chapitre**, on trouvera une étude de la modélisation de la forme de l'interface des écoulements intermittents. La prédiction de la surface d'échange est cruciale pour la précision du modèle de transfert de masse développé dans le chapitre précédent. Pour les écoulements de type "slugs", quelques modèles de prédiction de la hauteur du film liquide le long de la bulle sont disponibles dans la littérature. Ces modèles qui utilisent la notion de cellule unitaire nécessitent une prédiction de la vitesse du nez de la bulle dont la prédiction reste approximative. Il est montré que lorsque la taille des bulles devient suffisamment longue, ces modèles prédisent des hauteurs de bulles qui tendent vers la hauteur de liquide prédite pour un écoulement stratifié.

Les modèles sont ensuite comparés aux données expérimentales pour des débits proches de ceux rencontrés dans les photobioréacteurs de Microphyt. L'adaptation du dispositif expérimental utilisé dans le Chapitre 1 à l'observation d'un écoulement gaz-liquide co-courant ainsi que le

traitement des données utilisées pour reconstruire l'interface sont décrits. Les mesures ont ensuite été comparées aux modèles de cellule unitaire et pour un écoulement stratifié. Il a été conclu qu'un meilleur modèle pour le nez de la bulle permettrait d'améliorer la prédiction du modèle unitaire. Pour les débits observés, le modèle de cellule unitaire n'améliore pas de façon significative la prédiction donnée par Taitel (1976) pour un écoulement stratifié.

L'efficacité de la bioconversion du CO_2 dans la biomasse lors de la production a été rarement documentée, et une part importante du gaz introduit dans les systèmes de production de microalgues est soupçonnée d'être libérée dans l'atmosphère. Un modèle permettant de prédire l'efficacité de la bioconversion du CO_2 d'un photobioréacteur est développé dans le **troisième chapitre**. L'efficacité de la dissolution et les effets du gaz de balayage ont été modélisés en utilisant une théorie classique des écoulements diphasiques de Taitel (1976) combinée au modèle de dissolution précédemment développé.

Lors d'une culture continue de microalgues dont la concentration était maintenue constante, la biomasse récoltée et la masse injectée de CO_2 dans le réacteur ont été relevées. Les efficacités de dissolution et de bioconversion ont été évaluées pour un gaz injecté contenant 10% de CO_2 et des conditions de cultures qui n'étaient pas optimisées (la concentration en CO_2 dans le gaz utilisé correspond à celle dans les gaz rejetés par une cimenterie). Une approche analytique basée sur un bilan de masse a été utilisée afin de déterminer la part de CO_2 entraînée par le gaz de balayage (air). Grâce à ces mesures et au modèle proposé, les effets sur l'efficacité de bioconversion du dioxyde de carbone de paramètres tels que le temps de production, la concentration en CO_2 dans le gaz injecté, les débits et la longueur du photobioréacteur ont également été évalués et discutés.

Les deux derniers chapitres visent à simuler numériquement le transfert de masse gazliquide et à le valider. Dans le **quatrième chapitre**, une amélioration du traitement des données issues de mesures PLIF est présentée et appliquée à une bulle montante librement dans un liquide au repos.

L'originalité de la mesure réside dans la correction de l'erreur introduite par la variation de l'atténuation du plan laser traversant le liquide lors de l'étalonnage avec le pH. Ces essais serviront de cas-test pour la validation de la simulation numérique.

Dans le dernier chapitre, une simulation numérique du transfert de masse à travers une interface gaz-liquide est développée sous COMSOL. Un terme de pénalité est ajouté à la méthode numérique de level-set proposée par COMSOL pour améliorer la conservation de la masse. L'écoulement prédit par cette méthode a été partiellement validé avec un test sur la vitesse de montée de bulles pour des bulles de diamètre inférieur à trois centimètres. Une implémentation du suivi du champ de concentration du gaz diffusant à travers l'interface est ensuite présentée. Enfin, la prise en compte du changement de volume est ajoutée au modèle. Elle a été comparée aux mesures reportées dans le premier chapitre sur le cas de la bulle allongée.

Résumé court (< 1700 caractères)

Sécuriser un approvisionnement fiable de micro-algues est récemment devenu un enjeu industriel. Pour assurer la croissance de micro-algues dans des photobioréacteurs clos, un transfert de masse optimum de l'oxygène et du dioxyde de carbone doit être assuré. Dans cette thèse, une étude du transfert de masse gaz-liquide dans les conduites horizontales a été menée. Dans les trois premiers chapitres, un modèle unidimensionnel de transfert de masse dans le photobioréacteur a été développé. Tout d'abord, le transfert de masse entre une bulle de gaz allongée et un écoulement liquide turbulent a été étudié expérimentalement. En considérant l'interface comme étant plane, les coefficients de transfert de masse mesurés sont proches d'une corrélation de Lamourelle (1972). Le modèle de Taitel pour les écoulements stratifiés a été comparé à des modèles plus complets pour la prédiction de l'interface des bulles allongées. Une approche analytique basée sur un bilan de masse et utilisant les modèles testés a ensuite été développée et adaptée à un photobioréacteur afin de prédire l'efficacité de la conversion du CO₂ en biomasse en fonction des paramètres d'exploitation. Les deux derniers chapitres visent à développer une simulation numérique du transfert de masse gaz-liquide. Une mesure de la concentration en CO₂ dans le sillage d'une bulle de gaz ascendante a été effectuée à l'aide d'une méthode améliorée de traitement des données de Fluorescence Induite par Plan Laser (FIPL). Enfin, une simulation numérique a été réalisée sous COMSOL.

MOTS CLEFS : transfert de masse, bulle allongée, bioconversion du CO₂, écoulement gazliquide, photobioréacteur, microalgue, FIPL.

SHORT ABSTRACT (< 1700 CHARACTERS)

Securing a reliable supply of microalgae has recently become an industrial stake. To ensure successful growing of microalgae in enclosed, tubular photobioreactor systems as in Microphyt, an optimum mass transfer of oxygen and carbon dioxide should be secured. In this thesis an investigation of the gas-liquid mass transfer in horizontal pipes has been conducted. In the first three chapters, a one dimensional mass transfer model in horizontal gas-liquid flows will be developed and applied to horizontal photobioreactors. Firstly, a study of mass transfer between an elongated gas bubble under a turbulent liquid flow immobilized in a duct has shown that under the hypothesis considering the interface as a flat plane estimated, the measured mass transfer coefficients appear to be well fitted by a correlation from Lamourelle (1972). The interface prediction for stratified flows have been compared to more complete unit-cell models for intermittent flow interface and found to be a good first estimate. The photobioreactor's conversion efficiency of CO₂ into biomass as a function of operating parameters is investigated using an analytical approach to complete the mass balance and classical two-phase flow approach from Taitel (1976). The last two chapters aim at developing a numerical simulation of gas-liquid mass transfer. A measurement of CO₂ wake structures behind free rising bubbles have realised using an improved data treatment method for Planar laser-induced fluorescence (PLIF) and pH sensitivity of fluorescein sodium. Finally, an implementation of the experimental measurements under COMSOL has been realised.

KEYWORDS : mass transfer, elongated bubble, CO₂ bioconversion, gas-liquid flow, photobioreactor, microalgae, PLIF, calibration.

Table of Contents

Та	ble of	Contents	9
Li	st of H	ligures	13
Li	st of T	Fables	17
In	trodu	ction	19
	Gas-	liquid flow in horizontal pipes	21
		Flow regimes	22
		Taitel's flow regime map prediction	23
	Gas-	liquid mass transfer in a horizontal photobioreactor	27
		Mass transfer and photobioreactor's design	27
		Hydrodynamic Culture conditions in horizontal photobioreactors	28
		Mass transfer models for bioreactors	30
	Refe	rences	32
1	Elon	gated gas bubble dissolution under a turbulent liquid flow	33
	1.1		36
	1.2	Experimental rig	37
	1.3	Data treatment procedure	38
	1.4		40
		1.4.1 Decay of the bubble length	40
		1.4.2 Error on the mass transfer coefficient	42
	1.5	Results and discussion	43
	1.6	Conclusion	45
	Refe	rences	46
2	Gas.	liquid intermittent flow interface	47
-	2.1	Introduction	50
	2.2	The implemented unit cell model	52
	2.2	2.2.1 Bubble nose	52
		2.2.2 Bubble hody	52
		2.2.3 Back of the bubble	53
	2.3	The stratified flow hypothesis	53
	2.4	Experimental test loop	54
		2.4.1 Data acquisition	54
		1	

	2.5	Data Treatment	57
		2.5.1 Edge detection and interface reconstruction	57
		2.5.2 Uncertainty	61
	2.6	Results	62
	2.7	Conclusion	64
	Refe	erences	65
•	Б		
3	Exp	erimental assessment and modeling of CO_2 mass transfer in a horizontal co- cept gas-liquid photobioreactor	67
	3 1	Introduction	70
	3.2	Mass transfer modeling	70
	5.2	3.2.1 Conservation of mass	70
		3.2.1 Conservation of mass $\dots \dots $	72
		3.2.2 Model for n _{edisor}	73
	33	Measurements of Mass Transfer Efficiencies	74
	5.5	3.3.1 Measurement of n_{disc}	74
		3.3.2 Measurement of n _{CO}	74
		3.3.2 Evaluation of $n_{total and}$	75
	34	Results and discussion	76
	5.1	3.4.1 Dissolution model	76
		3.4.2 Influence of dissolution and stripping on the photobioreactor's MTE	, 0
		and optimum length	78
	3.5	Conclusion	79
	Refe	erences	80
4	Con	centration measurement in the wake of a free rising bubble using planar laser	,
	indu	iced fluorescence (PLIF) with a calibration taking into account for fluorescence	83
			85
	$\frac{1}{4}$	Experimental setup	86
	4.2 4.3	Data treatment	92
	т.Э	4.3.1 Beer-Lambert law for non-optically thin systems	92
		4.3.2 Extinction coefficient variation calibration	93
	44	Application to free rising hubble wake	95
	4.5	Conclusion	97
	Refe	erences	98
_			/ 0
5	T.T.		101
•	Nun	nerical simulation of gas-liquid mass transfer	101
C	Nun 5.1	nerical simulation of gas-liquid mass transfer Introduction Numerical simulation of mass transfer through a maying interface	101 103
C	Nun 5.1 5.2	nerical simulation of gas-liquid mass transfer Introduction Numerical simulation of mass transfer through a moving interface Implementation and validation	101 103 104
C	Nun 5.1 5.2 5.3	nerical simulation of gas-liquid mass transfer Introduction Numerical simulation of mass transfer through a moving interface Implementation and validation 5.3.1 Level set implementation	101 103 104 105
C	Nun 5.1 5.2 5.3	nerical simulation of gas-liquid mass transfer Introduction Numerical simulation of mass transfer through a moving interface Implementation and validation 5.3.1 Level-set implementation 5.3.2 Implementation of the scalar diffusion through the interface	101 103 104 105 105
C	Nun 5.1 5.2 5.3	Introduction Introduction Numerical simulation of mass transfer through a moving interface Introduction Implementation and validation Implementation 5.3.1 Level-set implementation 5.3.2 Implementation of the scalar diffusion through the interface Simulation of the elongated hubble dissolution	101 103 104 105 105 108
	Nun 5.1 5.2 5.3 5.4	nerical simulation of gas-liquid mass transfer Introduction Numerical simulation of mass transfer through a moving interface Implementation and validation 5.3.1 Level-set implementation 5.3.2 Implementation of the scalar diffusion through the interface Simulation of the elongated bubble dissolution Conclusion	101 103 104 105 105 108 110 112
	Nun 5.1 5.2 5.3 5.4 5.5 Refe	nerical simulation of gas-liquid mass transfer Introduction Numerical simulation of mass transfer through a moving interface Implementation and validation 5.3.1 Level-set implementation 5.3.2 Implementation of the scalar diffusion through the interface Simulation of the elongated bubble dissolution	101 103 104 105 105 108 110 113 115

Conclusion	117
Appendix A : Head Loss	119
Appendix B : Calculus of kla from measurements	123
Appendix C : Mass transfer simulations using Elmer	125
Appendix D : Mass transfer simulations using a source term in Fluent	127

List of Figures

1	Sketch of the six observable flow regimes for two-phase flow in a horizontal pipe as described in [1]	
2	Summary of the notations used in this chapter are defined to be congruent to Taitel [1].	24
3	Relationship of equation (3.8) relating X, Y and the dimensionless liquid height for turbulent friction coefficients.	25
4	Taitel flow pattern map example with limits plotted for gas-liquid flow in a horizontal test duct of circular cross section with an inner diameter of 80mm.	26
5	The pair of photobioreactors under their East-West oriented greenhouse. South is to the left of the image [9].	28
6	Hydrodynamic events observed in the photobioreactors as depicted in [9] from the phycological point of view.	29
7	Schematic of the boundary layers on both sides of a gas-liquid interface	30
1.1	Sketch of the experimental test loop. Gravity driven water from the upper tank flows through a settling chamber and in the duct where the bubble dissolution is observed. Then water goes through rotameters and is brought back to the upper	
	tank	38
1.2 1.3	Picture of the experimental test loop corresponding to figure (1.1) Side view (a) and top view (b) of the immobilised bubble localised at 2.9 meters from the inlet of the test duct and undergoing a water flow over a Reynolds	39
1.4	Ln $\left(\frac{L(t)}{L_0}\right)$ is plotted for three Reynolds Numbers values. The exponential evolution of $L(t)$ supports the flat interface approximation. The slope of the fitted	40
1.5	least square line is proportional to the mass transfer coefficient. \ldots \ldots \ldots Experimental dissolution data for air and CO ₂ into water are correlated as a	41
	tion from Lamourelle [15].	44
2.1	Sketch of an intermittent flow showing the aperiodic behaviour of the flow and the shape of the bubbles. The bubbles have different lengths and speed, they can be divided into three parts : the head, the body and the end of the bubble.	50
2.2	Unit cell sketch as described in Mazza [10] with modeling parameters for the bubble height such as velocity, geometrical parameters and forces in the mass conservation and momentum equilibrium.	52

2.3	Sketch of the adapted experimental test rig. The square duct used in the first chapter has been replaced with a circular cross section pipe (2). A gas injection with controlled mass flow rate have been inserted at the inlet of the pipe (1) and gas-liquid separation column has been added at the outlet of the pipe (3)	55
2.4	Top view of the acrylic glass (PMMA) pipes in which the gas-liquid flow have been observed. The 13 meters long pipe have a circular cross-section of 80 mm diameter.	55
2.5	Side view of the adapted experimental set up described in figure (2.3) and (2.4).	56
2.6	Sketch of the data acquisition set-up capturing images of the intermittent flow. The test tube is lit by lamp which orientation has been chosen such that reflec- tions of light on the duct toward the camera are minimal.	57
2.7	Images of the intermittent flow captured with the Dalsa Falcon 1.4M100 HG CMOS camera and treated for interface detection using Scilab's canny edge detection feature. The edge detection has been first applied to an average background image (a) in order to detect the pipe position and define a mask. Examples of detection for the nose, body and end of the bubble are shown respectively in pictures (b,c,d and e).	58
2.8	Validation of the routine finding the displacement between two frames of the same bubble nose. Frame (b) taken at a small time interval (1/f with f the acquisition frequency) after frame (a) is displaced and correlated to frame (a). The displacement giving the maximum correlation coefficient is taken as the displacement of the bubble front between the two frames and tested in frame (c) where frame (b) have been added to frame (a).	59
2.9	Reconstructed elongated bubble interface (a) and train of bubbles (b) from mul- tiple frames taken with a high speed camera at 100Hz.	60
2.10	Elongated bubble interface profile averaged over twenty bubbles for water flow- ing at a rate of 4000 liters per hour and air at a rate of 30 liters per minute	63
3.1	Diagram of the carbon dioxide punctual dissolution phase (a) and continuous air stripping phase (b).	71
3.2	Summary of the notations used in this chapter are defined to be congruent to Taitel [1].	72
3.3	Cell density and absorbance evolution with time and details for the measure- ment period. Absorbance give an idea of the size of the cells and therefore the density of biomass.	75
3.4	Dissolution MTE, η_{diss} , as a function of the photobioreactor's length and injected gas concentration as predicted by the one-dimensional model presented in section 3.2.2	76
3.5	The ratio $\frac{k_L(Re) \times S_i}{Q_G}$ is a function of Q_L and Q_G . Flow rates maximising this ratio are the optimum flow rates for dissolution.	77
3.6	Measurements and extrapolation of the evolution of $\eta_{CO_2convertedtobiomass}$, η_{diss} and $\eta_{stripped}$ as a function of the photobioreactor's length, L_{tubes} , for carbon dioxide concentration in the injected gas up to 10% and non-optimised flow rates.	78

4.1	Schematic view of the Planar Laser Induced Fluorescence experimental set-up used for CO_2 concentration measurements in the wake of a free rising CO_2 bubble dissolving into an aqueous solution of fluorescein illuminated by an	
	argon laser plane.	87
4.2	Picture of the experimental setup described in figure 4.1.	87
4.3	Fluorescence trapping and photobleaching test using linearity assessment of the Beer-Lambert law of attenuation for the Argon ion laser/sodium-fluorescein system as a function of concentration [14; 13]	88
4.4	Specification of the influence of surfactants in the medium comparing experi- mentally measured rising bubble velocities with data from the literature (Clift,	20
4.5	A correlation of CO ₂ concentration as a function of pH in the tank using a Metler Toledo CO ₂ InPro 5000 probe and pH equilibrium with atmosphere to complete the PLIF measuring range : $[CO_2](\frac{mg}{l}) = 2411390 \times exp(-pH/0.216642)$	89 22) 90
4.6	Time evolution of CO ₂ concentration from the reaction kinetic differential equations system (4.1) solved for the source term F_{CO_2}/δ and the influence of the source term on the CO ₂ concentration.	91
4.7	Schematic view of the camera observation area and of the Region Of Interest in which the CO_2 concentration have been measured.	93
4.8	Standard deviation of the non-corrected extinction coefficient ε measurements, for a given pH during calibration. As the amplitude of the extinction increases with the length travelled by the laser beam, the dispersion of the measured extinction coefficient diminishes with the distance between two pixel columns	
4.9	used for its determination	94
4.10	$\frac{n_0}{T}$ without correction for extinction coefficient variations	95 96
5.1	Visual (a) and quantitative (b) comparison of mass conservation using COM- SOL's level-set simulation for a two centimetres diameter rising bubble with and without the penalty term. In b), the ratio of the bubble's section area over its initial section area V/V_0 is plotted with and without the introduced penalty term : $\beta \delta(\phi) (1 - (\int_{\Omega} H(\phi) d\Omega) / Vol^*)$ with $\beta = 10$.	106
5.2	Rising velocity evolution with time of a gas bubble in quiescent water simulated using COMSOL's level-set with the introduced penalty correction for different diameters on the same mesh.	107
5.3	Final rising velocity as a function of the bubble diameter.	108
5.4	Level-set simulation of a dissolving rising bubble using COMSOL	109

5.5	Concentration profils along the middle vertical line of the domain from the
	simulation presented in figure 5.4
5.6	Simulation of the dissolving elongated bubble investigated in Chapter 1 using
	COMSOL and the presented mass conservation penalty term. The hypothesis
	of a constant height bubble while dissolving has not been well simulated 112
5.7	$ln(\frac{L(t)}{L_0})$ is plotted for a Reynolds number Re = 24540. The exponential evolu-
	tion of the interface length $L(t)$ that was supporting the flat interface approxi-
	mation used in Chapter 1 for the measurements of mass transfer coefficients is
	not very perfectly reproduced in the numerical simulation. The order of mag-
	nitude of the slope could be reproduced. The difference may be attributed to
	the fact that in the simulation the bubble height was not as constant as in the
	experiment
6.8	Measured and calculated frictional pressure drop of water and air as a function
	of flow quality - from [4]
6.9	Comparison of the measured pressure drop with correlations from the literature
	of Müller-Steinhagen [4], Lockhart [5] and Friedel [6]. The measuring condi-
	tions were close from microphyt's operating conditions i.e. for liquid flow rates
	varying from 1000 L/hr to 6000 L/hr and a fixed gas flow rate of 11 N.L/min. $% \lambda = 1000$. $\lambda = 1000$ L/hr and a fixed gas flow rate of 11 N.L/min. $\lambda = 1000$ L/hr and a fixed gas flow rate of 11 N.L/min. $\lambda = 1000$ L/hr and a fixed gas flow rate of 11 N.L/min. $\lambda = 1000$ L/hr and a fixed gas flow rate of 11 N.L/min. $\lambda = 1000$ L/hr and a fixed gas flow rate of 11 N.L/min. $\lambda = 1000$ L/hr and a fixed gas flow rate of 11 N.L/min. $\lambda = 1000$ L/hr and a fixed gas flow rate of 11 N.L/min. $\lambda = 1000$ L/hr and a fixed gas flow rate of 11 N.L/min. $\lambda = 1000$ L/hr and a fixed gas flow rate of 11 N.L/min. $\lambda = 1000$ L/hr and a fixed gas flow rate of 11 N.L/min. $\lambda = 1000$ L/hr and a fixed gas flow rate of 11 N.L/min. $\lambda = 1000$ L/hr and a fixed gas flow rate of 11 N.L/min. $\lambda = 1000$ L/hr and 10 L/hr and 1
8.10	Level-Set simulation of a dissolving rising bubble using Elmer multiphysics 126
9.11	Volume Of Fluid simulation of a dissolving rising bubble using the flow mod-
	eling simulation software ANSYS Fluent. A User Defined Function has been
	used in order to define a source term located at the bubble interface for the
	simulation of the mass transfer between the bubble and the liquid

List of Tables

1.4	Summary of the presented mass transfer theories.	36
1.6	Measurements numerical values	43
2.4	Summary of different models using the concept of unit cell	51

Introduction

Multiphase flows are involved in a large number of industry processes and natural environment phenomenons. More specifically, gas-liquid flows are frequently reported in scientific publications related to nuclear, petroleum, and numerous processing industries. Those publications are reflecting the current need for understanding of the gas-liquid flow behaviour in such systems despite the considerable amount of research performed on this subject. Common problematic issues are concerned with drilling and transportation in the petroleum industry or loss-of-coolant accident in the nuclear industry. In the chemical industry, applications are often related to mass transfer in reactors.

This work has been realised in the framework of a project that aimed to develop an horizontal photobioreactor producing microalgae. It is also concerned with gas-liquid mass transfer which is one of the essential functions of a photobioreactor. The oxygen and carbon dioxide concentrations in the culture broth that will ensure successful growing conditions for microalgae are achieved by co-current circulation of gas and liquid in the photobioreactor. Improving both design and operation of the photobioreactor for both production and optimum use of carbon dioxide necessitates a better understanding of the mass transfer in horizontal gas-liquid flows.

In the two first chapters of this thesis, a one dimensional mass transfer model in horizontal gas-liquid flows will be developed and applied to horizontal photobioreactors. In a first chapter, a study of mass transfer from an immobilised elongated bubble will be presented. In the second chapter, models for the interface area prediction for horizontal gas-liquid flows will be emphasised. The photobioreactor's conversion efficiency of CO_2 into biomass as a function of operating parameters will be investigated in the third chapter.

The two last chapters aim at developing a numerical simulation of gas-liquid mass transfer. In the third chapter, an improved PLIF data treatment technique will be presented and applied to a free rising bubble in order to produce comparative data for the numerical simulation. In the last chapter, numerical simulations of the free rising bubble test case and of the elongated bubble dissolution are presented.

Contents

Gas-liquid flow in horizontal pipes	21
Flow regimes	22
Taitel's flow regime map prediction	23
Gas-liquid mass transfer in a horizontal photobioreactor	27
Mass transfer and photobioreactor's design	27
Hydrodynamic Culture conditions in horizontal photobioreactors	28
Mass transfer models for bioreactors	30
References	32

Nomenclature

Greek symbols

α	Slope of the duct, []
ν	Kinematic viscosity, $\left[\frac{m^2}{s}\right]$
ρ	Mass density, $\left[\frac{kg}{m^3}\right]$
σ	Surface tension, $\left[\frac{N}{m}\right]$

 τ Shear stress, [*Pa*]

Latin symbols

Α	Section area of the pipe, $[m^2]$
A_G	Section area occupied by the gas phase, $[m^2]$
A_L	Section area occupied by the liquid phase, $[m^2]$
a	, [m]
С	Molar concentration, $\left[\frac{mol}{m^3}\right]$
D	Diameter of the pipe, $[m]$
F	Dimensionless parameter, []
8	Gravity, $\left[\frac{m}{s^2}\right]$
h_L	Liquid height for stratified flow, $[m]$
Κ	Dimensionless parameter, []
k	Mass transfer coefficient, $\left[\frac{m}{s}\right]$
Р	Pressure, [Pa]
S	Perimeter, [m]
Т	Dimensionless parameter, []
и	Velocity in the x direction, $\left[\frac{m}{s}\right]$
X	Lockhart and Martinelli dimensionless parameter, []
X	Coordinate in the downstream direction, $[m]$.

Subscripts and superscripts

~	Dimensionless variable,
G	Gas,
i	Interface,
L	Liquid phase,
S	For a monophasic flow,
W	Wall

Gas-liquid flow in horizontal pipes

Multiphase flow in pipes has often been simplified to two-phase flow in the literature. A common example is in the petroleum industry when water, oil and gas phases are considered as two-phase flow with water and oil being viewed as the liquid phase, even though three-phase flow studies have been reported recently for example in [1] for stratified three-phase flow.

Flow regimes

Early research on two-phase flow in horizontal pipes has identified five or six flow regimes based on the interface distribution. They are depicted in figure 1 and defined in [2] as following :



FIGURE 1: Sketch of the six observable flow regimes for two-phase flow in a horizontal pipe as described in [1].

- 1. Stratified smooth flow : "In this case the liquid flows at the bottom of the pipe with gas at the top, and the interface between them is smooth",
- 2. Stratified wavy flow : "The liquid and gas are separated as above, but the interface is wavy",
- 3. Elongated bubble flow in Taitel's article is divided into two subcategories, plug and slug flow. Plug flow is defined as : "Elongated gas bubbles located adjacent to the top part of the tube move downstream. They are separated by sections of continuous liquid". And slug flow is defined as : "Liquid slugs separated by gas pockets move violently downstream. The slug may be aerated with distributed small bubbles at higher gas flow rates. The distinction between elongated bubbles flow and slug slow is not well defined. Basically, both have the same general appearance, and the differences between them are based on the degree of agitation of the flow and the height of the liquid film in between slugs",
- 4. Annular flow : "Annular flow takes place at high gas flow rates. The gas flows in the center of the pipe while the liquid flows as an annular. Because of gravity the film is

thicker at the bottom than at the top of the pipe. Annular flow can be visualized as developing from slug flow when the aeration in the slug becomes sufficiently high to form a continuous gas phase.

5. Dispersed bubble flow : "For high liquid flow rates, the gas is dispersed in the form of small bubbles within a continuous liquid phase. Normally, the bubble density at the top will be somewhat higher than at the bottom of the pipe".

These flow regimes are often reported in the literature as flow regime maps describing the observed flow regime as a function of two parameters such as the liquid and gas velocities. The different flow regimes defined in [2] have been identified visually explaining why their definition is still approximative and the variations between the different flow regime maps reported in the literature. It is possible to find in the literature more systematic ways of defining flow regimes as in [4] where they are defined using probability theory (Continuous Hidden Markov Model). Such methods allow for boundary thickness between flow regimes to be estimated.

Taitel's flow regime map prediction

Theoretical models predicting the flow regime maps can be found in the literature. Taitel's model [1] allows determining the transitions between flow regimes for horizontal gas-liquid flows as a function of :

- the liquid and gas phase velocity,
- gravity,
- the liquid and gas kinematic viscosity,
- the liquid and gas mass density,
- the pipe diameter.

Stratified flow liquid height prediction

It is shown in Taitel [1] using a momentum balance on each phase that the dimensionless liquid height \tilde{h}_L equilibrium for stratified flow can find by solving the following equation :

$$X^{2}[(\tilde{u}_{L}\tilde{D}_{L})^{-n}\tilde{u}_{L}^{2}\frac{\tilde{S}_{L}}{\tilde{A}_{L}}] - [(\tilde{u}_{G}\tilde{D}_{G})^{-m}\tilde{u}_{G}^{2}(\frac{\tilde{S}_{G}}{\tilde{A}_{G}} + \frac{\tilde{S}_{i}}{\tilde{A}_{L}} + \frac{\tilde{S}_{i}}{\tilde{A}_{G}})] - 4Y = 0$$

$$\tag{1}$$

where *X* is the dimensionless Lockhart and Martinelli parameter. The other geometrical parameters are described in figure 2. They can all be expressed as a function of the dimensionless liquid height.

$$\tilde{A}_L = 0.25 [\pi - \cos^{-1}(2\tilde{h}_L - 1) + (2\tilde{h}_L - 1)\sqrt{1 - (2\tilde{h}_L - 1)^2}]$$
⁽²⁾

$$\tilde{A}_G = 0.25[\cos^{-1}(2\tilde{h}_L - 1) - (2\tilde{h}_L - 1)\sqrt{1 - (2\tilde{h}_L - 1)^2]}$$
(3)

$$\tilde{S}_L = \pi - \cos^{-1}(2\tilde{h}_L - 1) \tag{4}$$

$$\tilde{S}_G = \cos^{-1}(2\tilde{h}_L - 1) \tag{5}$$



FIGURE 2: Summary of the notations used in this chapter are defined to be congruent to Taitel [1].

$$\tilde{S}_i = \sqrt{1 - (2\tilde{h}_L - 1)^2}$$
(6)

$$\tilde{u}_L = \frac{\tilde{A}}{\tilde{A}_L} \tag{7}$$

$$\tilde{u}_G = \frac{\tilde{A}}{\tilde{A}_G} \tag{8}$$

The dimensionless parameter, Y, takes into account the slope of the pipe. The relationship from equation (3.8) between X, Y, and the dimensionless liquid height is plotted in figure 3.

For an horizontal pipe, Y is zero and the dimensionless liquid height can be found knowing the dimensionless Lockhart and Martinelli parameters which is a function of the liquid and gas phase velocities.

Flow pattern transition boundary prediction

Transitions between flow regimes have been plotted as an example of Taitel's map in figure 4. Equations for flow pattern transitions are given in dimensionless form in Dukler [16].

Stratified flow to Elongated bubble flow limit

The transition between intermittent flow and annular flow is given by $\frac{h_L}{D} = 0.5$ or $X_B \simeq 1.6$. The limit is obtained by solving equation (9).

$$X = \frac{\left| \left(\frac{dP}{dx}\right)_L^S \right|}{\left| \left(\frac{dP}{dx}\right)_G^S \right|} = X_B \simeq 1.6 \tag{9}$$

Stratified wavy flow to Elongated bubble flow limit

The transition between the intermittent flow and stratified is given by the Kelvin-Helmholtz stability criteria for wave formation. It is the solution of equation $F = F_A$ where :



FIGURE 3: Relationship of equation (3.8) relating *X*, *Y* and the dimensionless liquid height for turbulent friction coefficients.

$$F = \sqrt{\frac{\rho_G}{\rho_L - \rho_G}} \frac{U_G^S}{\sqrt{D \times g \times \cos(\alpha)}} \text{, and}$$
(10)

$$F_A = \frac{1 - \tilde{h}_L}{\tilde{u}_G} \sqrt{\frac{\tilde{A}_G}{d\tilde{A}_G/d\tilde{h}_L}}.$$
(11)

Stratified smooth flow to Stratified wavy flow limit

Waves developing above this limit are due to the gas phase velocity. Those waves grow slowly compared to the Kelvin-Helmholtz waves and will develop if effects of pressure and



FIGURE 4: Taitel flow pattern map example with limits plotted for gas-liquid flow in a horizontal test duct of circular cross section with an inner diameter of 80mm.

shearing on the wave are stronger than viscous dissipation in the wave. The limit is given by $K = K_C$.

$$K = F \sqrt{\frac{DU_L^S}{\nu_L}} = F \sqrt{Re_L^S}$$
(12)

$$K_C = \frac{20}{\tilde{u}_G \sqrt{\tilde{u}_L}} \tag{13}$$

Elongated bubble flow to dispersed bubble flow limit The last limit is given by the equation $T = T_D$, where :

$$T = \sqrt{\frac{(\frac{dP}{dx})_L^S}{(\rho_L - \rho_G) \times g \times cos(\alpha)}}, \text{ and}$$
(14)

$$T_D = 2 \frac{\tilde{D}_L^{0.1}}{\tilde{U}_L^{0.4}} \sqrt{\frac{2\tilde{A}_G}{\tilde{S}_i}}$$
(15)

Gas-liquid mass transfer in a horizontal photobioreactor

The utilization of microalgae in fields such as health, food, energy and environment have significantly increased in the last years and specialized industries offering to secure a reliable supply of these essential microorganisms have subsequently developed. At present, the global production of microalgal monocultures is mainly limited to a handful of species including extremophiles (e.g. Arthrospira sp., Dunaliella sp.) and fast growers (e.g. Chlorella sp., Scenedesmus sp., Nannochloropsis sp.). Due to their natural resistance to predators and competitors, these species can be produced in open systems such as ponds, tanks, and bubble columns. However, most species constituting the bulk of microalgal biodiversity are difficult to cultivate because of slow growth rates or cell wall fragility. Slow growing species must be cultivated in closed systems in order to ensure their dominance, while the cultivation of delicate species requires special precautions in order to avoid forces which could stress the cells, especially shear, centrifugal forces and surface tension. To ensure successful slow growing and/or fragile microalgae photoautotrophic cultures in enclosed tubular photobioreactor (photobioreactor) systems, four conditions must be met whilst operating under asepsis : ensure optimum light transmission, thermo-controlled conditions, hydrodynamic mixing and mass transfer of oxygen and carbon dioxide.

Mass transfer and photobioreactor's design

Mass transfer is necessary for carbon dioxide to reach the cells to provide them with carbon, while photosynthetic oxygen needs to be removed to prevent oxygen saturation conditions from inhibiting the photosynthetic reaction (Ogawa et al. in [5]). These cross processes, carbon dioxide introduction and oxygen removal, occur at the gas-liquid interface. Mass transfer and more particularly oxygen removal efficiency is critical as it determines the size of the mass transfer device, the pump and the piping, and hence limits the kinds of species suitable for cultivation within a given reactor configuration. With respect to this key problem, several steps marked the evolution of the horizontal tubular photobioreactors since this design appeared in the late 70s (e.g. in Jüttner [6]; Pirt [7]).

Generally, an intimate contact is created for gas exchange by bubbling in a gas lift or by a waterfall in a special tower placed on the loop circuit. Typically, movement and mass transfer took place devices in which the culture passed every 10 minutes in order to limit the dissolved oxygen concentration at peak sunlight. Due to the limitations caused by pumping and to the size of the mass transfer tower, the possibility of scaling up such design is poor and production

is limited to the most resistant species, which are often easily cultivated in open ponds. Near horizontal manifold type photobioreactors were investigated by Tredici and co-workers. Low shear stress and reduced fouling were also observed but the scale-up capacity was limited by mass transfer reduction in designs over 40 meters in length.

The investigated photobioreactor described by A. Muller-Feuga in [8], is a two-phase flow reactor and the whole length of the piping between inlet and outlet is the site of mass transfer between the co-current circulating gas and liquid. Air was injected continuously for oxygen stripping and an automat compared the culture pH with set values for controlling the injection of CO_2 .

The photobioreactor developed by Microphyt was designed for slow growing and/or fragile microalgae. It has been successfully operated to supply the dermo-beauty care industry with active biomass of three delicate species of microalgae, including the Chlorophyte Neochloris oleoabundans and the Rhodophyte Porphyridium cruentum. Even if the device has proved satisfactory for microalgae production, the influence of the mass transfer on the scale up of the process, productivity and bioconversion of CO_2 remained unclear and therefore there improvement difficult to predict. This observation is the origin of the need for understanding of mass transfer in the device.

Hydrodynamic Culture conditions in horizontal photobioreactors



FIGURE 5: The pair of photobioreactors under their East-West oriented greenhouse. South is to the left of the image [9].

The photobioreactor consists of a 1,200 m serpentine glass piping circuit, with a 76 mm inside diameter and 4.5 mm wall thickness, folded horizontally in 24 straight runs with a vertical



FIGURE 6: Hydrodynamic events observed in the photobioreactors as depicted in [9] from the phycological point of view.

height of 3 m and a width of 0.3 m, forming a 50 m long tubular fence illustrated in figure (5).

The culture loop was closed by stainless steel piping, creating a segment of the photobioreactor for liquid and gas exchange with the outside environment. Gas and liquids were injected at the lowermost point of the piping, just downstream of the positive displacement pump. A liquid volume reduction to $4,700 \pm 300$ l resulted from the injection of gas at the above mentioned flow rate. The outlet for gas and liquid was located at the uppermost point of the piping. The photobioreactor investigated here shares the concept of co-circulation of gas and liquid in near horizontal flows with some other designs as the Biocoil system (Tredici in [10]), for example.

From a phycological point of view, reported in [9], the observed hydrodynamic events following each other at least every 5 seconds including waves described in figure (6), promote mixing and therefore renewal of microalgae exposed to light. The flow conditions of the photobioreactor proved satisfactory as neither harmful speed variation nor small bubble generation were observed. The liquid broth containing microalgal suspensions was considered as one homogeneous liquid phase.

Regarding flow patterns from fluid mechanics theory for horizontal pipes in figure 1, the observed hydrodynamic events would be classified as intermittent flow. The flow pattern map for two phase flow in horizontal pipes predicted by Taitel [1] has been plotted in figure (5) for an inner pipe diameter of 80 millimeters and an air-water system as an approximation for the photobioreactor's conditions. For the range of the averaged velocities of the phases in the pho-



FIGURE 7: Schematic of the boundary layers on both sides of a gas-liquid interface.

tobioreactor, Taitel's map would also predict an intermittent flow. It should be noted that the operated pump outflow rate variations are important in rectilinear sections of the photobioreactor that are close from the pump. These variations would further increase the instabilities responsible for the transition between stratified and intermittent flow.

Mass transfer models for bioreactors

As depicted in figure (7), the dissolving gas first undergoes diffusion across a stagnate gas film, then absorption, next stagnate liquid layer and finally diffusion and convection. The third step through the stagnate liquid layer is the rate-limiting step explaining why the mass transfer coefficient through the liquid layer is considered as a good approximation of the overall mass transfer coefficient in correlations found in the literature. The molecular mass gas flux ϕ through the interface is then written :

$$\phi = k_L \times (C_{sat} - C) = k_L (\frac{p}{H} - C), \qquad (16)$$

where k_L is the liquid side mass transfer coefficient, C is the local molar concentration in the bulk of the fluid, and C_{sat} is the saturation concentration which is evaluated using the Henry constant H and the duct operating pressure p.

In order to take into account the interfacial area, the volumetric mass transfer coefficient k_{la} is usually evaluated. The k_{la} is the product of the liquid side mass transfer coefficient with the

specific interfacial area per unit volume a ([m2/m3]). Empirical correlations of this volumetric mass transfer coefficient are then reported as a function of system parameters such as liquid physical properties (surface tension, viscosity), global systems operating parameters such as power input per volume or superficial gas velocity in bubble columns.

Overall k_{la} measurements for the photobioreactor consider a constant specific interfacial area per unit volume, *a*, and a constant driving concentration gradient along the photobioreactor. However, the aim is to dissolve most of the injected carbon dioxide and both quantities will vary along the photobioreactor. Moreover, k_{la} coefficients determination are not sufficient to describe the conversion efficiency of CO₂ to biomass of a photobioreactor. Indeed, the influence of contact time is not evaluated even though this parameter is crucial for mass transfer, especially for horizontal photobioreactors.

These observations highlight the need for a different approach for mass transfer prediction in horizontal gas-liquid flows. In the three first chapters of this thesis, a one dimensional prediction of mass transfer in horizontal gas-liquid flows will be developed and applied to horizontal photobioreactors. In a first chapter, a study of mass transfer from an immobilised elongated bubble will be presented. In the second chapter, models for the interface area prediction for intermittent horizontal gas-liquid flows will be emphasised. The photobioreactor's conversion efficiency of CO_2 into biomass as a function of operating parameters will be investigated in the third chapter.

The two last chapters aim at developing a two-dimensional numerical simulation of gasliquid mass transfer. In the third chapter, an improved PLIF data treatment method will be presented and applied to a free rising bubble in order to produce comparative data for the numerical simulation. In the last chapter, numerical simulations of the free rising bubble test case and of the elongated bubble dissolution are presented.

References

- [1] Y. Taitel, D. Barnea, J. Brill, Stratified three phase flow in pipes, International Journal of Multiphase Flow 21 (1) (1995) 53–60.
- [2] Y. Taitel, N. Lee, A. E. Dukler, Transient gas-liquid flow in horizontal pipes : Modeling the flow pattern transitions, AIChE Journal 24 (5) (1978) 920–934.
- [3] Y. Taitel, A. E. Dukler, A model for predicting flow regime transitions in horizontal and near horizontal gas-liquid flow, AIChE Journal 22 (1) (1976) 47–55.
- [4] A. Mahvash, A. Ross, Two-phase flow pattern identification using continuous hidden markov model, International Journal of Multiphase Flow 34 (3) (2008) 303–311.
- [5] T. Ogawa, T. Fujii, S. Aiba, Effect of oxygen on the growth (yield) of chlorella vulgaris, Archives of Microbiology 127 (1) (1980) 25–31.
- [6] F. Jüttner, Thirty liter tower-type pilot plant for the mass cultivation of light-and motionsensitive planktonic algae, Biotechnology and Bioengineering 19 (11) (1977) 1679–1687.
- [7] S. Pirt, Y. Lee, M. Walach, M. Pirt, H. Balyuzi, M. Bazin, A tubular bioreactor for photosynthetic production of biomass from carbon dioxide : design and performance, Journal of Chemical Technology and Biotechnology. Biotechnology 33 (1) (1983) 35–58.
- [8] A. Muller-Feuga, Photosynthetic reactor for cultivating microorganisms, and method for cultivating microorganisms.
- [9] A. Muller-Feuga, M. Lemar, E. Vermel, R. Pradelles, L. Rimbaud, P. Valiorgue, Appraisal of a horizontal two-phase flow photobioreactor for industrial production of delicate microalgae species, Journal of Applied Phycology 24 (3) (2012) 1–7.
- [10] M. Tredici, Mass production of microalgae : photobioreactors, Handbook of microalgal culture (2004) 178–214.

Chapter 1

Elongated gas bubble dissolution under a turbulent liquid flow

In order to develop a one dimensional mass transfer model of the gas-liquid flow in the horizontal tubular photobioreactor, mass transfer between an elongated homogeneous gas bubble under a turbulent liquid flow in a duct has been investigated experimentally. It is demonstrated from experimental mass transfer measurements, that the interface of an immobilised elongated bubble can be approximated as a flat plane. Measured mass transfer experimental data, estimated using this simplification, appear to be well fitted by $Sh_L = 1.76 \times 10^{-5} \times Re^{1.506} \times Sc^{0.5}$, a correlation from Lamourelle [15], given for a turbulent liquid flow in wetted-wall columns. A formula drawn from this hypothesis is proposed for mass transfer prediction in photobioreactors. For different applications, it is suggested that the results obtained for the studied geometry could be used to build mass transfer feedback control systems.

Contents

1.1	Introduction		
1.2	Experimental rig		
1.3	Data treatment procedure		
1.4	Data acquisition		
	1.4.1 Decay of the bubble length		
	1.4.2 Error on the mass transfer coefficient		
1.5	Results and discussion 43		
1.6	Conclusion		
Refe	erences		

Nomenclature

Greek symbols

α	Slope of the interpolated bubble length data,	$ln(\frac{L}{L_0})(t)$
2		0

δ

ν

Film thickness, [m]Kinematic viscosity, $[\frac{m^2}{s}]$ Molecular gas flux, $[\frac{mol}{s \times m^2}]$ ø

Latin symbols

С	Molar concentration, $\left[\frac{mol}{m^3}\right]$
D	Diffusion constant, $\left[\frac{m^2}{s}\right]$
D_h	Hydraulic diameter of the duct, $[m]$
Н	Henry's constant, $\left[\frac{Pa.m^3}{mol}\right]$
h	Bubble height, [m]
h_{eq}	Equivalent bubble height, $[m]$
k	Mass transfer coefficient, $\left[\frac{m}{s}\right]$
L	Bubble length, [m]
N_A^*	Molar flux, $\left[\frac{mol}{m^2s}\right]$
n	Molar quantity, [mol]
р	Pressure, [Pa]
$p_{\rm CO_2,atm}$	Partial pressure of CO_2 in the air at atmospheric pressure
R	Ideal gas constant, $\left[\frac{J}{mol.K}\right]_{-}$
Re	Reynolds number, $Re = \frac{U \cdot D_h}{v}$
S	Mass transfer exchange area, $[m^2]$
Sc	Schmidt number, $Sc = \frac{v}{D}$
Sh	Sherwood number, $Sh = \frac{k_L \cdot D_h}{D}$
Т	Temperature, [K]
t	Time, $[s]$
U	Mean liquid velocity over the duct section area, $\left[\frac{m}{s}\right]$
V	Bubble volume, $[m^3]$
W	Bubble width and pipe width, $[m]$
X	Molar fraction of the injected gas

Subscripts and superscripts

0	Initial value
atm	Atmospheric
contact	Final value, at the end of the photobioreactor
L	Liquid
sat	Saturation
1.1 Introduction

This chapter deals with mass transfer between a homogeneous elongated gas bubble and a turbulent liquid flow in which it is set, as represented in figure 1.3. As explained in the introduction, on one hand CO_2 injection improves culture productivity in closed photobioreactors, and is used for pH regulation [2; 3]. On the other hand, the accumulation of oxygen in long horizontal tubular photobioreactors inhibits photosynthesis [4]. A lower concentration of oxygen is obtained by air stripping. As a consequence, gas exchange of CO_2 and O_2 takes place simultaneously within photobioreactors and in both directions between the co-current gas and liquid phases. In the first step of the technological development of the photobioreactors, waste gases are removed through a degasser and released to the atmosphere. A one dimensional model of mass transfer within the photobioreactor is then of interest in order to improve the use by the culture of the injected CO_2 .

A simplified configuration is investigated in this chapter considering only CO₂ mass transfer into water from an immobilised elongated gas bubble. To our knowledge, there is no mass transfer data for such a configuration reported in the literature even though gas transfer across free water surfaces is a long standing research subject. Several two-phase flow mass transfer models can be found in the literature, a non-exhaustive list of those relevant to our study are summarised in table 1.4. Among those models, Lewis and Whitman film theory [5], introduced gas and liquid film with their respective coefficients. Higbie's penetration theory [6] relates the mass transfer coefficient to the diffusion constant and to the time of exposure. Later, Danckwerts [7] developed the surface renewable theory allowing for the turbulence to be taken into account. A model for turbulent concentration fluctuations, based on an empirical correlation for falling-films, is developed in Lamourelle [15]. In this model, the turbulent motion of the film is accounted for by introducing a turbulent diffusion coefficient which is the sum of the diffusion constant and the turbulent eddy diffusivity. This later is taken as a function of transverse position within the film and the flow parameters. Grossman and Heath [8] noted that in falling-film mass absorption, three turbulent eddy diffusivity profiles are usually used to model turbulence : in the vicinity of the wall [9], in the core region [10] and near the interface [15].

Theory		Expression
Film theory	[5]	$k_L = \frac{D}{\delta_L}$
Penetration theory	[6]	$k = 2 imes \sqrt{rac{D}{\pi \cdot t_e}}$
Surface renewal theory	[7]	$k_w = \sqrt{D \times r}$
Lamourelle	[8]	$Sh_L = 1.76 \times 10^{-5} \times Re^{1.506} \times Sc^{0.5}$

TABLE 1.4: Summary of the presented mass transfer theories.

It can be noticed that, in Lamourelle [15], the assumption of a smooth interface is used regardless of the actual roughness or wave induced turbulence. Moreover, all of the presented models are for high Schmidt numbers and predict that the mass transfer coefficient varies with the square root of the diffusion coefficient. As noted by Grossman [11], the velocity and concentration fluctuations are the most important mechanisms for turbulent mass transfer problems, but they are also the less accurately predictable quantities.

Another model taking those fluctuations into account is the surface divergence model. However, the parameters of both models cannot be measured close enough to a moving surface due to the lack of existing adequate experimental techniques (Jähne and H. Haußetaecker [12]). Therefore, an experimental correlation predicting the mass transfer remains the best suited to start designing a process.

This chapter is structured in four sections, starting with the description of the experimental test facility. Then, the data treatment procedure to determine the mass transfer coefficient is detailed. Following that, the experimental data acquisition is explained along with an error analysis. Results are presented and discussed in the last section.

1.2 Experimental rig

The experimental rig, depicted in figure 1.1, allows observing mass dissolution from a gas bubble immobilised in a square section test duct. The test duct of six meters length has a square section $(0.08 \times 0.08 \text{ m}^2)$ and is entirely made of Plexiglas. It is situated 4.7 meters below the upper tank free surface level. The hydrodynamic facility produces a gravity driven liquid flow that circulates between two constant level tanks. The tested flow rates, measured by rotameters, correspond to a liquid phase Reynolds number varying in the range of 6926 to 43282. This range includes the operating conditions encountered in the industrial photobioreactor developed by Microphyt SAS (industrial partner) where the average liquid Reynolds number is Re =22000. Here, the Reynolds number is defined as $Re = U_L D_h/v_L$ where U_L and v_L are the velocity and kinematic viscosity of the liquid phase. D_h is the hydraulic diameter defined as $4 \times (w \times (w - h))/(3 \times w - 2 \times h)$.

Mass transfer from a gas bubble immobilised upstream of an obstacle (figure 1.3) is observed. The obstacle used to immobilise the gas is a prism made of Plexiglas fixed at 2.9 meters from the inlet of the test section. It occupies the whole channel width w = 80 mm and has a length l = 15 mm. Its height h = 10 mm, equivalent to $\frac{1}{8}$ of the duct height is chosen to avoid gas entrainment for Reynolds number up to 43282 (measurement values are given in 1.6). For higher regimes, the gas bubble can be partially or completely entrained.

The bubble gas is injected using a syringe through a valve (see figure 1.3) and is either 99.7 % pure CO₂ or air. The liquid is tap water which is in contact with air at atmospheric pressure, p_{atm} , which was measured using a barometer and was recorded along with temperature for each run. Following Henry's law, the saturation concentration increases with pressure enabling the air bubble to be dissolved into the water. The data treatment procedure to determine the dissolution coefficient is developed in the following section.





1.3 Data treatment procedure

As noted by Boettcher [17], the molecular gas flux ϕ through a gas-liquid interface can be expressed as a function of the local molar concentration *C* and the molar concentration at saturation *C*_{sat} by the following relation :

$$\phi = k_L \times (C_{sat} - C) = k_L (\frac{p}{H} - C), \qquad (1.1)$$

where k_L is the liquid side mass transfer coefficient. C_{sat} is the saturation concentration at the duct operating pressure p and C is taken as the atmospheric saturation concentration. Both pressure, p, and concentration, C, are considered as constant during the measurements. The following relation can express the molecular loss rate :

$$\frac{dn}{dt} = -S \times \phi, \tag{1.2}$$

where S describes the mass exchange area. The negative sign corresponds to a decreasing molar quantity n in the gas bubble. This quantity can be expressed by the ideal gas law as :



FIGURE 1.2: Picture of the experimental test loop corresponding to figure (1.1).

$$n = \frac{p \times V}{R \times T} = \frac{p}{R \times T} L(t) \times h \times w.$$
(1.3)

During the experiment, the width w remains constant since the gas bubble occupies the whole duct width. This assumption is correct almost until the full disappearance of the gas bubble. In equation (1.2), the surface S is considered flat and approximated to a rectangle of length L(t) and width w. The length to height ratio of the gas bubble is in the order of 100 at the beginning of the experiment and is kept greater than 15.

The combination of equations (1.1), (1.2) and (1.3) yields :



FIGURE 1.3: Side view (a) and top view (b) of the immobilised bubble localised at 2.9 meters from the inlet of the test duct and undergoing a water flow over a Reynolds number range of 6500 to 38000.

$$\frac{dL(t)}{dt} = -k_L(Re) \times (C_{sat} - C) \frac{R \times T}{p \times h} \times L(t).$$
(1.4)

For each experiment, the term in front of L(t) on the right-hand side of equation (1.4) is considered as a constant. Then, the time evolution of the bubble length L(t) can be expressed by the following exponential law equation :

$$\frac{L(t)}{L_0} = e^{-k_L(Re) \times (C_{sat} - C) \times \frac{R \times T}{p \times h} \times t} = e^{-\alpha \times t}.$$
(1.5)

Each experimental run consists of measuring the parameters of equation (1.5) at fixed Reynolds number in order to obtain k_L . The measuring method and accuracy are explained in the following section.

1.4 Data acquisition

1.4.1 Decay of the bubble length

Considering that the width and the height of the bubble remain constant over the experiment, the mass transfer coefficient is linked to the bubble length evolution with time as ex-



FIGURE 1.4: $Ln(\frac{L(t)}{L_0})$ is plotted for three Reynolds Numbers values. The exponential evolution of L(t) supports the flat interface approximation. The slope of the fitted least square line is proportional to the mass transfer coefficient.

pressed in equation (1.5). The measurement of the bubble length and time have been obtained out of pictures taken at a rate of two per second with a Nikon D80 camera (3872×2592 pixels) with a 14 mm lens. Two hundred pictures per bubble were acquired. The time, *t*, at which they are taken is recorded within the stored metadata of the output JPEG file leading to an accuracy of half a second. For the length measurements, a ruler was settled in the measurement plane giving an accuracy of 0.5 mm.

In figure 1.4.1, $ln(L/L_0)$ is plotted as a function of time for different Reynolds number

values, in the case of CO₂ gas bubbles. As it can be seen on the figure, the experimental data is distributed around a straight line. The slope of the curves, α , has been obtained fitting the data with the least square method. The standard deviation of $ln(L/L_0)/t$ from α is found to be less than 5%. Therefore, for a fixed Reynolds number, α can be considered as a constant. Using equation (1.5), the mass transfer coefficient k_L can be determined :

$$k_L(Re) = \frac{\alpha(Re)}{(C_{sat} - C)} \frac{p \times h}{R \times T}.$$
(1.6)

The absolute value of the measured slopes increases with the Reynolds number and so does the mass transfer coefficient, as predicted by equation (1.6).

1.4.2 Error on the mass transfer coefficient

The expression for the relative error on the mass transfer coefficient k_L is given by the following equation :

$$\frac{\Delta k_L}{k_L} = \frac{\Delta \alpha}{\alpha} - \frac{\Delta T}{T} + \frac{\Delta p}{p} + \frac{\Delta h}{h} - \frac{\Delta (C_{sat} - C)}{(C_{sat} - C)}.$$
(1.7)

The relative error on the interpolated exponential decay rate α , is taken as the standard deviation of the data as determined earlier, i.e. around 5%. For each experiment with air, the temperature *T* is a well known quantity but may vary within 5 degrees during the day so the quantity $\frac{\Delta T}{T}$ is estimated to be 1.75%. The relative error for the pressure $\frac{\Delta p}{p}$ is about 0.7% since the atmospheric pressure is measured and the height of the water column is maintained within 10 cm in the upper tank.

The determination of the bubble height *h* has received particular care. Its average over the bubble length is evaluated by injecting a known volume V_{atm} of air at atmospheric pressure and temperature. It should be noted that *h* remains almost constant over the experiment. Thus, measuring the initial bubble length L_0 is enough to determine the value of *h* as written in equation (1.8).

$$h = \frac{V_0}{L_0 \times w} = \frac{p_{atm} \times V_{atm}}{L_0 \times w \times p_0}.$$
(1.8)

From equation (1.8), the quantity $\frac{\Delta h}{h}$ can be evaluated as shown here after.

$$\frac{\Delta h}{h} = \frac{\Delta p}{p} + \frac{\Delta V_{atm}}{V_{atm}} - \frac{\Delta L_0}{L_0} - \frac{\Delta w}{w} = 0.007 + 3/60 - 5/500 - 0 = 4.7\%.$$
(1.9)

The last term in equation (1.7) is the relative error induced by $\Delta(C_{sat} - C)$. C_{sat} and C are evaluated as following :

$$C_{sat} = \frac{p}{H} = \frac{p_{atm} + 0.47}{29.41} \times 44 \approx 2.2 \frac{g}{l}$$
(1.10)

$$C = \frac{p_{\text{CO}_2,atm}}{H} = \frac{p_{atm} \times 0.036}{29.41} \times 44 \approx 0.05 \ \frac{g}{l}.$$
 (1.11)

The value $H = 29.41 \frac{l.atm}{mol}$ has been taken from [14]. The maximum deviation of C from the atmospheric saturation concentration can be evaluated. Even though the liquid

Gas	Re	h (mm)	<i>k</i> _L (m/s)	Sh	$\Delta(Sh)$
	6926	4.5	$5.21 imes 10^{-6}$	201	9
Air	13853	4.5	$1.17 imes 10^{-5}$	450	21
$D_{Air} = 2.08 \times 10^{-9}$	20942	5.4	$2.45 imes 10^{-5}$	943	43
m^2/s	28194	6.5	4.32×10^{-5}	1663	76
	35874	8.5	5.77×10^{-5}	2222	101
CO	24540	5.9	$2.94 imes 10^{-5}$	1232	99
$D_{2} = 1.01 \times 10^{-9}$	28194	6.5	$4.90 imes 10^{-5}$	2051	164
$D_{\rm CO_2} = 1.91 \times 10$	35874	8.5	6.63×10^{-5}	2779	222
m / S	43282	9.1	8.30×10^{-5}	3478	278

TABLE 1.6: Measurements numerical values.

phase is not renewed during the experiment, each dissolved bubble adds 2 g of CO₂ to the 1400 liters of the experimental rig. Thus, ten dissolved bubbles induce a relative error for $\Delta[\Delta(C_{sat} - C)]/[\Delta(C_{sat} - C)]$ of 0.7%.

The sum of these errors leads to a 8% relative error for the mass transfer coefficient.

1.5 Results and discussion

As demonstrated, α is independent of the bubble length. Corollary, from equation (1.6), the mass transfer coefficient is also considered as a constant for a fixed Reynolds number. Mass transfer coefficients are presented in their dimensionless form using the Sherwood number $Sh = \frac{k_L \cdot D_h}{D}$ and plotted as a function of the Schmidt number, $Sc = \frac{v}{D}$, and the Reynolds number. The values for the diffusion coefficient, D, for pure gas are those reported in [15]. For air, the diffusion coefficient is obtained using a weighted geometric average as suggested by Vignes [16]. Lamourelle, in [15], proposed the following empirical relation for wetted-wall columns : $Sh_L = 1.76 \times 10^{-5} \times Re^{1.506} \times Sc^{0.5}$. This configuration involves a turbulent liquid flow and a flat interface. In spite of the fact that Lamourelle's data were obtained for lower flow regimes, namely 1300 < Re < 8300, and in a different geometry, the measured experimental data appear to be well fitted by this correlation, as shown in figure 1.5.

Both results from figure 1.4.1 and figure 1.5 show that the hypothesis of a flat exchange interface is justified for elongated gas bubble dissolution under a turbulent flow. Using this hypothesis, applied to horizontal tubular photobioreactors, the accepted molar fraction X of injected CO₂ that will be released to the atmosphere is expressed in equation (1.12),

$$\frac{n_{\text{released}}}{n_0} = e^{-\alpha \times t_{\text{contact}}} < X.$$
(1.12)

with n_{released} being the molar quantity contained in the bubble reaching the end of the photobioreactor after a contact time t_{contact} . Replacing α and rearranging in equation 1.12, with h_{eq} being the equivalent bubble height defined as the ratio of the gas bubble cross section over the exchange interface width w, equation (1.13) is obtained.



FIGURE 1.5: Experimental dissolution data for air and CO_2 into water are correlated as a function of the Schmidt and the Reynolds number and compared to a correlation from Lamourelle [15].

$$t_{\text{contact}} > \frac{-ln(X) \times p \times h_{eq}}{R \times T \times k_L(Re) \times (C_{sat} - C)}.$$
(1.13)

Lamourelle's correlation should be used with care to estimate k_L when applied to photobioreactors since the flow regime, co-current, is different.

Considering equation (1.2), a linear relationship relates the molecular transfer rate and the bubble length for the immobilised elongated bubble geometry. The molecular gas flux can be

estimated with Lamourelle's correlation. Using those results, one could build feedback control system where the molecular transfer rate, $\frac{dn}{dt}$, is tuned with a gas injection controlled by the bubble length.

1.6 Conclusion

This chapter investigated mass transfer between a homogeneous immobilised elongated gas bubble and a turbulent liquid flow in which it was set. For the particular studied geometry, mass transfer measurements have been found to be well correlated by Lamourelle's correlation proposed for wetted-wall columns. The hypothesis of a flat exchange interface is shown to be appropriate for elongated gas bubbles dissolving into a turbulent flow. Applied to horizontal tubular photobioreactors, a relationship for mass transfer can be obtained for a predicted bubble height. In the following chapter, models for the interface area prediction and equivalent bubble height of intermittent horizontal gas-liquid flows will be emphasised.

References

- [1] A. P. Lamourelle, O. C. Sandall, Gas absorption into a turbulent liquid, Chemical Engineering Science 27 (5) (1972) 1035–1043.
- [2] F. Rubio, F. Fernández, J. Pérez, F. Camacho, E. Grima, Prediction of dissolved oxygen and carbon dioxide concentration profiles in tubular photobioreactors for microalgal culture, Biotechnology and bioengineering 62 (1) (1999) 71–86.
- [3] E. M. Grima, F. Fernández, F. G. Camacho, Y. Chisti, Photobioreactors : light regime, mass transfer, and scaleup, Journal of Biotechnology 70 (1-3) (1999) 231–247.
- [4] E. Molina, J. Fernández, F. Acién, Y. Chisti, Tubular photobioreactor design for algal cultures, Journal of Biotechnology 92 (2) (2001) 113–131.
- [5] W. K. Lewis, W. G. Whitman, Principles of gas absorption., Industrial & Engineering Chemistry 16 (12) (1924) 1215–1220.
- [6] R. Higbie, The rate of absorption of a pure gas into a still liquid during short periods of exposure, Trans. Am. Inst. Chem. Eng 31 (365-389) (1935) 13.
- [7] P. V. Danckwerts, Significance of liquid-film coefficient in gas absorber, Ind. and Eng. Chemistry 43 (6) (1951) 1460–1466.
- [8] G. Grossman, M. T. Heath, Simultaneous heat and mass transfer in absorption of gases in turbulent liquid films, International Journal of Heat and Mass Transfer 27 (12) (1984) 2365–2376.
- [9] E. R. Van Driest, On turbulent flow near a wall, AIAA Journal Special supplement : Centennial of powered flight 23 (11) (1956) 1007–1011.
- [10] H. Reichardt, Vollständige darstellung der turbulenten geschwindigkeitsverteilung in glatten leitungen, Z. angew. Math. Mech. (1951) 208–219.
- [11] G. Grossman, Heat and mass transfer in film absorption, in : Handbook of Heat and Mass Transfer, Gulf Publishing, Houston, TX, 1986, p. 211–257 Chap. 6.
- [12] B. Jähne, H. Haußecker, Air-water gas exchange, Annual Review of Fluid Mechanics 30 (1) (1998) 443.
- [13] E. Boettcher, J. Fineberg, D. P. Lathrop, Turbulence and wave breaking effects on airwater gas exchange, Physical Review Letters 85 (9) (2000) 2030–2033.
- [14] R. Sander, Compilation of Henry's law constants for inorganic and organic species of potential importance in environmental chemistry, Max-Planck Institute of Chemistry, Air Chemistry Department, 1999.
- [15] CRC handbook of chemistry and physics, 2009–2010, 90th ed., Journal of the American Chemical Society 131 (35).
- [16] A. Vignes, IEC Fund 5 (1966) 189–199.

Chapter 2

Gas-liquid intermittent flow interface

Gas-liquid slug interface prediction is crucial to the accurate determination of mass transfer in such flows. Few models predicting the liquid film height along the bubble based on the unit cell model are available in the literature as well as for the bubble nose and for the end of the bubble. However, the prediction of the bubble nose velocity necessary for those models remains approximate. The implemented models are described. One of their common characteristics is that the bubble height predicted by the elongated bubble models at the end of sufficiently long bubbles tends to the liquid height predicted for stratified flow.

The implemented models are compared to experimental data for flow rates close to those encountered in Microphyt's photobioreactor. The adaptation for co-current gas-liquid flow from the experimental rig used in chapter 1 is described along with the data treatment used to estimate the liquid height under the bubble.

The implemented unit cell model has been compared to the stratified flow prediction and to the measurements. It has been concluded that a better nose model would improve the prediction. It is difficult to make a conclusion concerning the liquid height at the end of the bubble because of the influence of the return bend two meters downstream from the measuring point. The unit cell model have not improved significantly the stratified flow prediction for the observed flow.

Contents

2.1	Introduction	
2.2	The implemented unit cell model	
	2.2.1 Bubble nose	
	2.2.2 Bubble body	
	2.2.3 Back of the bubble	
2.3	The stratified flow hypothesis	
2.4	Experimental test loop	
	2.4.1 Data acquisition	
2.5	Data Treatment 57	
	2.5.1 Edge detection and interface reconstruction	
	2.5.2 Uncertainty	
2.6	Results	
2.7	Conclusion	
Refe	erences	

Nomenclature

Greek symbols

α	Void Fraction, []
λ	Angle giving the position of the interface in the pipe cross section,
ν	Cell's frequency, $[Hz]$
ρ	Density, $\left[\frac{kg}{m^3}\right]$
τ	Shear stress, $\left[\frac{N}{m^2}\right]$
θ	Pipe angle of inclination, []
ξ	Position of the center of inertia,

Latin symbols

A	Cross section area, $[m^2]$
C_0	Constant characterizing the liquid plug velocity, []
C_{∞}	Constant characterizing the slip velocity between the two phases, []
D	Inner diameter of the pipe, $[m]$
f	Friction factor, []
8	Acceleration of gravity, $[m^2]$
G	Center of gravity,
h	Height, $[m]$
j	Superficial velocity, $\left[\frac{m}{s}\right]$
L_G	Bubble length, $[m]$
Р	Pressure, [Pa]
Q	Volumetric flow rate, $\left(\frac{m^3}{s}\right)$,
S	Geometric length in the section of the pipe, $[m]$
U_M	Velocity of the mixture, $\left[\frac{m}{s}\right]$
U_t	Velocity of the bubble nose, $\left[\frac{m}{s}\right]$
и	Absolute velocity of the phase, $\left[\frac{m}{s}\right]$
V_G	Bubble volume, $[m^3]$
V	Relative velocity of the phase, $\left[\frac{m}{s}\right]$
X	Position relative to the nose of the bubble, $[m]$

Subscripts and superscripts

G	Gaseous phase,
i	Interface between the two phases,
*	T + + + + + +

- *L* Liquid phase,
- *Lf* Liquid phase in the film under the bubble,
- *Ls* Liquid phase in the liquid plug.

2.1 Introduction

As described in the introduction chapter, an intermittent flow is encountered in Microphyt's photobioreactor. In chapter 3, mass transfer has been modeled as a function of the interface area which can be expressed as a function of the bubble height considering that the interface is horizontal for each cross section of the pipe. In order to get a first prediction of the equivalent bubble height in the photobioreactor, a simplification assuming a stratified flow was used. In order to assess this hypothesis and improve the prediction of the equivalent bubble height and therefore of the dissolution model, the elongated bubble profile prediction have to be investigated.



FIGURE 2.1: Sketch of an intermittent flow showing the aperiodic behaviour of the flow and the shape of the bubbles. The bubbles have different lengths and speed, they can be divided into three parts : the head, the body and the end of the bubble.

As illustrated in figure (2.1), elongated bubbles can be divided in three regions [1] :

Head of the bubble :

Near the nose of the bubble the velocity is three dimensional and the bubble height varies rapidly with the longitudinal position.

Body of the bubble :

In the body region, variations of the bubble height as a function of longitudinal position are weak.

End of the bubble :

At the rear of the bubble, an Hydraulic jump characterized by its staircase shape may be followed by a tail of decreasing height. Conditions for the appearance of the tail depending on the mixture Froude number are discussed in [1]. If no tail is observed, the elongated bubble flow is named "plug flow".

Due to the varying lengths of those three regions, the considered flow is unsteady and nondeterministic. A first simplification considering the bubbles as "unit cells" has been proposed by Wallis in [2]. In this approximation, the intermittent flow is considered as a set of bubbles of identical length following each other turning the flow into a steady periodic flow. This hypothesis has been used by Dukler [3] who proposed a first global model for the bubble. This model has been completed later by Nicholson [4], Kokal [5], Taitel [6], Andreussi [7] and Cook [8]. Those models which are summarised in table 2.4, can only be applied to the body of the bubble and are not able to predict the shape of the nose or the end of the bubble. A model describing the shape of the bubble over its entire length have been presented in Netto [1]. It is comprised of four submodels corresponding to the four parts of the bubble, namely the nose, the body, the hydraulic jump and the tail of the bubble.

Authors	Descripton
Dukler, 1975 [3]	Only model not taking into account the slip velocity, not accurate
	for higher pressure because of the hypothesis of a negligible shear
	stress at the gas interface.
Nicholson, 1978 [4]	Close to Dukler but taking into account for the slipping velocity
	(still not accurate for higher pressure conditions).
Kokal, 1989 [5]	Takes into account the interface, gas phase neglected.
Taitel, 1990 [6]	Gas phase taken into account.
Fabre, 1992 [9]	Based on statistic unit cells.
Andreussi, 1993 [7]	Only one taking into account dispersed bubbles in the liquid film.
Cook, 2001 [8]	Gravity effects on the gas phase neglected.
Netto, 1999 [1]	Inertia of the gas phase neglected. Model for the entire length of
	the bubble.

TABLE 2.4: Summary of different models using the concept of unit cell

Models presented in table (2.4) necessitate complementary equations in order to estimate the velocity of the bubble nose U_t as well as friction factors f_i , f_G and f_{Lf} . A summary of complementary equations in the literature have been presented in [10] along with a comparison of the different models for air-water bubbles of 400 diameters using the same complementary equations. The main conclusions of this study are the following :

- for close to atmospheric pressure conditions, differences between the models are attributed to the complementary equations. It seems that the approximations made by the different models are valid for those conditions since Dukler and Hubbard's model [3] give results very close to the more complete Taitel and Barnea's model [6] showing that liquid inertia was well taken into account.
- for higher pressure conditions, the hypothesis of a negligible shear stress at the gaseous interface in the models of Dukler and Nicholson is no longer valid.

In Mazza [10], a complete model has been derived from mass conservation and momentum balance equations and compared to experimental data. Good agreement has been found between the profile prediction with reality using the measured nose velocity. An attempt using complementary equations for the nose velocity U_t resulted in overestimated liquid height.

Other models have been developed looking at the unsteady nature of the intermittent flow. Those models do not follow the evolution of each bubble but bring other information such as the growth and coalescence of bubbles or the distribution of the bubble lengths which are not described by the unit cells model but necessary to estimate the length of the interface, for example which is widely distributed around its average value as noted by Fabre in [9]. It has been shown in Cook [11; 12] that for plugs with a minimal length of ten diameters, velocities of the front and rear of the plug were equal and that the plug length was fixed. Once all of the liquid plugs have reached their minimal length, the coalescence is finished and the bubble velocity is constant for every bubble.

In the following chapter, the implemented unit cell model predicting the liquid height along the bubble will be described. Following this, the approximation used in chapter 2 while predicting the liquid height in the conversion to biomass model will be explained. Thirdly, the adapted experimental test loop used to validate the liquid height prediction theory will be presented and a comparison between theoretical predictions and experimental measurements will be developed in the last section.

2.2 The implemented unit cell model

As described in Netto [1], models can be found in the literature for the four parts of the bubble as distinguished in the unit cell model.

2.2.1 Bubble nose

The bubble nose has a three dimensional shape. However, considering the relatively small length of this part of the bubble compared to the length of the bubble, most authors have used a simple two dimensional model for the void fraction proposed by Benjamin in [13] and reported in equation (2.1).

$$\alpha_{Lf} = 1 - 0.775 \frac{x}{D} + 0.354 \left(\frac{x}{D}\right)^2 \text{ for } \frac{x}{D} < 1$$
(2.1)

2.2.2 Bubble body

Bubble body models are based on mass and momentum conservation equations [1]. Variables necessary to write these mass conservation and momentum balances at the interface, such as velocities, geometrical parameters and forces, have been reported in figure 2.2.



FIGURE 2.2: Unit cell sketch as described in Mazza [10] with modeling parameters for the bubble height such as velocity, geometrical parameters and forces in the mass conservation and momentum equilibrium.

Equation (2.2) predicting the liquid height as a function of the bubble length has been derived in Mazza [10] from mass conservation and momentum equilibrium equations. The equation is valid as long as the one-dimensional separated phases momentum equations is valid and the gas-liquid interface is considered to have a single curvature along the pipe axis while at the pipe cross section it is plane. As a consequence, this equation applies to flows without small bubbles or interfacial momentum and with negligible surface tension and small liquid height variations with the bubble length.

$$\frac{dh_{Lf}}{dx} = \frac{\frac{S_{Lf}}{A}\tau_{Lf} - \frac{\alpha_{Lf}}{\alpha_G}\frac{S_G}{A}\tau_G - \alpha_{Lf}(\frac{1}{\alpha_{Lf}} + \frac{1}{\alpha_G})\frac{S_i}{A}\tau_i}{\alpha_{Lf}((\rho_{Lf} - \rho_G)g - (\frac{\rho_{Lf}}{\alpha_{Lf}}v_{Lf}^2 + \frac{\rho_G}{\alpha_G}v_G^2)\frac{d\alpha_{Lf}}{dh_{Lf}})}$$
(2.2)

In equation (2.2), the derivative of the liquid height with respect to the bubble length is expressed as a function of the gravitational constant g, of the geometry of the flow (S_{Lf} , S_G , S_i , A, α_{Lf} , α_G , α_{Lf}) also represented in figure (3.2), of the fluids properties such as the density ρ_{Lf} , ρ_G , of the relative velocities of the gas and liquid phase in the bubble nose inertial frame, v_G et v_{Lf} , and of the shear stresses τ_{Lf} , τ_G , τ_i (that can be expressed as a function of friction factors and velocities).

The expression in equation (2.2) takes into account the shear stresses on each phase, the effects of gravity and of the inertia of both phases. Models presented in table (2.4) can be compared to equations (2.2) since they either neglect parts of this equation or replace it with their velocity expressions.

Netto in [1] neglects the inertia term of the gaseous phase and takes into account the gravity effects on this phase. Netto's model expressing the derivative with respect to the length of the bubble of the ratio of the liquid cross-section area to the pipe cross-section area α_{Lf} is expressed in equation (2.3).

$$\frac{d\alpha_{Lf}}{dx} = \frac{\frac{S_{Lf}}{A}\tau_{Lf} - \frac{\alpha_{Lf}}{\alpha_G}\frac{S_G}{A}\tau_G - \alpha_{Lf}(\frac{1}{\alpha_{Lf}} + \frac{1}{\alpha_G})\frac{S_i}{A}\tau_i}{\alpha_{Lf}(\rho_{Lf} - \rho_G)gD\frac{\pi}{4sin(\lambda/2)} - \rho_{Lf}v_{Lf}^2}$$
(2.3)

2.2.3 Back of the bubble

Models for the hydraulic jump intensity at the back of the bubble can found in the literature. In Wallis [2], assuming a constant pressure in the gas phase, a model has been developed that can be used to determine the liquid area ratio at the end of the hydraulic jump, knowing the liquid area ratio at the end of the bubble body. The interface in the hydraulic jump is considered to be linear. The main parameter determining the liquid area fraction at the end of the bubble body is a Froude number based on the relative velocity. If the obtained value for the liquid area ratio is greater than unity, there will be no tail at the back of the bubble. When a tail exists, the liquid height at the end of the bubble is considered to be constant.

2.3 The stratified flow hypothesis

In chapter 2, while predicting the liquid height in the conversion to biomass model, the flow pattern has been approximated as a stratified flow. In order to determinate the physical meaning of this approximation, the liquid height predicted by the unit cell body model have been expressed for a long bubble body.

When the length of the bubble becomes sufficiently large, the liquid height tends to a constant value. As a consequence, variations of the liquid height with the distance from the nose, $\frac{dh_{Lf}}{dx}$, tends to zero when the distance becomes large. Applied to the model of Mazza [10] given in equation (2.2), equation (2.4) is obtained for horizontal flow.

$$\frac{dh_{Lf}}{dx} = 0 \Leftrightarrow \frac{S_{Lf}}{A} \tau_{Lf} - \frac{\alpha_{Lf}}{\alpha_G} \frac{S_G}{A} \tau_G - \alpha_{Lf} (\frac{1}{\alpha_{Lf}} + \frac{1}{\alpha_G}) \frac{S_i}{A} \tau_i = 0$$
(2.4)

Multiplying equation (2.4) by $\frac{-1}{\alpha_{L_f}}$, equation (2.5) is obtained which corresponds to the equation formulated in Taitel [1] for stratified flow. It can also be expressed as a dimensionless equation as in equation (2.6) where X is the Lockhart and Martinelli parameter.

$$\frac{S_G}{A_G}\tau_G - \frac{S_{Lf}}{A_{Lf}}\tau_{Lf} + S_i\tau_i(\frac{1}{A_{Lf}} + \frac{1}{A_G}) = 0$$
(2.5)

$$X^{2}[(\tilde{u}_{L}\tilde{D}_{L})^{-n} \tilde{u}_{L}^{2} \frac{\tilde{S}_{L}}{\tilde{A}_{L}}] - [(\tilde{u}_{G} \tilde{D}_{G})^{-m} \tilde{u}_{G}^{2} (\frac{\tilde{S}_{G}}{\tilde{A}_{G}} + \frac{\tilde{S}_{i}}{\tilde{A}_{L}} + \frac{\tilde{S}_{i}}{\tilde{A}_{G}})] = 0$$
(2.6)

As a consequence the stratified flow approximation predicts a liquid height corresponding to one predicted by the unit cell body model at the end of a sufficiently long bubble. The approximation will then be valid if the liquid plugs' length is negligible compared to the liquid slugs' length and if the liquid slugs and sufficiently long. In order to test if those hypothesis are valid in Microphyt's configuration experimental measurements of liquid height have been performed using the experimental test loop presented in the following section.

2.4 Experimental test loop

The experimental test loop presented in chapter 1 has been adapted as shown in figure (2.3). Air is injected through a Brooks mass flow controller device into a 80 millimeters acrylic glass (PMMA) duct. Observations of the flow pattern have been taken at 6 meters from the injection point in an 8 meters straight section of the pipe. A 180° return bend was used for an investigation of the flow in a similar configuration as Microphyt's photobioreactor ¹. The flow goes through a separation column and air is released to the atmosphere through a gas-liquid separator while water goes back to the lower tank through rotameters, a Proline Promag 50 flow meter and a hydraulic valves system allowing for water flow rate to be adjusted.

2.4.1 Data acquisition

Shadowgraph measurements have been used in order to evaluate the interface exchange area through the bubble height. Those measurements are well suited for later in situ measurements on photobioreactors since it is not intrusive and takes advantages of both the transparency of the pipe and the opacity of the culture broth.

^{1.} A pressure drop study has been reported in Appendix A



FIGURE 2.3: Sketch of the adapted experimental test rig. The square duct used in the first chapter has been replaced with a circular cross section pipe (2). A gas injection with controlled mass flow rate have been inserted at the inlet of the pipe (1) and gas-liquid separation column has been added at the outlet of the pipe (3).



FIGURE 2.4: Top view of the acrylic glass (PMMA) pipes in which the gas-liquid flow have been observed. The 13 meters long pipe have a circular cross-section of 80 mm diameter.

A camera recording the flow was located six meters downstream from the air injection point as illustrated in figure (2.6). Tap water has been coloured with rhodamine and a white screen has been placed behind the pipe. A lamp pointing at the screen has been placed such that reflections of light on the duct toward the camera are minimal. A Dalsa Falcon 1.4M100 HG



FIGURE 2.5: Side view of the adapted experimental set up described in figure (2.3) and (2.4).



FIGURE 2.6: Sketch of the data acquisition set-up capturing images of the intermittent flow. The test tube is lit by lamp which orientation has been chosen such that reflections of light on the duct toward the camera are minimal.

CMOS camera facing the test tube has been positioned at the same height as the test section. A ruler was placed on top of the tube before each experiment in order to determine the scale. An example of captured images is given in figure (2.7) for the nose, the body and the end of the bubble.

2.5 Data Treatment

2.5.1 Edge detection and interface reconstruction

A canny edge detection feature from Scilab has been used for interface detection on images of the intermittent flow captured with the camera and reconstruction of the interface. Results of the applied image treatment are shown in figure (2.7). A mask used to select the part of the picture corresponding to the pipe has been defined using the edge detection on an average background image in figure (2.7 - a). Examples of detection for the nose, body and end of the bubble are shown respectively in the pictures of figure (2.7 - b, c, d and e).

As said in the introduction of this chapter and shown in Cook [11; 12], for bubbles longer

a) Average background image



b) Bubble nose



c) Wavy interface behind bubble nose



- e) Bubble end

d) Bubble body



FIGURE 2.7: Images of the intermittent flow captured with the Dalsa Falcon 1.4M100 HG CMOS camera and treated for interface detection using Scilab's canny edge detection feature. The edge detection has been first applied to an average background image (a) in order to detect the pipe position and define a mask. Examples of detection for the nose, body and end of the bubble are shown respectively in pictures (b,c,d and e).



c) validation of the maximum correlation test to find the displacement

FIGURE 2.8: Validation of the routine finding the displacement between two frames of the same bubble nose. Frame (b) taken at a small time interval (1/f with f the acquisition frequency) after frame (a) is displaced and correlated to frame (a). The displacement giving the maximum correlation coefficient is taken as the displacement of the bubble front between the two frames and tested in frame (c) where frame (b) have been added to frame (a).



FIGURE 2.9: Reconstructed elongated bubble interface (a) and train of bubbles (b) from multiple frames taken with a high speed camera at 100Hz.

than ten diameters, velocities of the front and rear of the plug were equal and that the plug length was fixed. The velocity of the front of the bubble has been estimated measuring the magnitude of the displacement of the front of the bubble between two frames. The validation of this method is shown in figure (2.8). Using the determined velocity and the hypothesis that the velocity of the slug is uniform along its length, the bubble's profile can be reconstructed as shown in figure (2.9). An average bubble profile can then be obtained as shown in figure (2.10) for a series of bubbles. The average bubble and plug's length can then be estimated for the considered conditions enabling validation of the uniform velocity hypothesis.

2.5.2 Uncertainty

On each image, the distance in pixels between the top of the duct and the position of the detected interface is measured and then scaled to millimeters as expressed in equation (2.7). The position of the duct has been determined from average background images.

$$h_G = (h_{topoftheduct} - h_{interface}) \frac{L_{G,mm}}{L_{G,pix}}$$
(2.7)

The profile of the elongated bubble height is then reconstructed as done in figure (2.9) using the velocity of the bubble nose measured as done previously on the images averaging the overlapping parts of the bubble.

Uncertainty on interface height measurements can be established from equation (2.7) and is given by equation (2.8).

$$\Delta h_G = (\Delta h_{topoftheduct} + \Delta h_{interface}) \frac{L_{G,mm}}{L_{G,pix}} + (h_{topoftheduct} - h_{interface}) \frac{L_{G,mm}}{L_{G,pix}^2} \Delta L_{G,pix}$$
(2.8)

Uncertainty on the reading of the ruler used for the determination of the scale is considered as negligible compared to the error due to the pixels. Relative incertitude on one measurement of the bubble height is calculated by visually estimating the width of the interface and of the top of the duct.

Applied to a liquid flow rate of $Q_L = 4000 \ l.h^{-1}$ and a gas flow rate of $Q_G = 30 \ l.min^{-1}$, incertitudes have been estimated as follows :

$-h_{topoftheduct} = 230 \ pix;$	$\Delta h_{topoftheduct} = 2pix;$
$-h_{interface} = 185 \ pix;$	$\Delta h_{interface} = 5 pix;$
$- L_{G,mm} = 180 mm;$	$\Delta L_{G,mm} \ll 1 pix;$
$- L_{G,pix} = 400 \ pix;$	$\Delta L_{G,pix} = 2pix;$

Resulting in the following incertitude and relative incertitude on the bubble height of equations (2.9) and (2.10).

$$\Delta h_G = (2+5)\frac{180}{400} + (230-185)\frac{180}{400^2} \times 2 = 2.8 \ mm \tag{2.9}$$

$$\frac{\Delta h_G}{h_G} = \frac{2.8}{20.25} = 14\% \tag{2.10}$$

2.6 Results

The bubble liquid height profile predicted by unit cell theory of Netto, Fabre and Paresson [1] (FFP model), the equivalent liquid height for stratified gas-liquid flows and measurements of the liquid height profile of the elongated bubble have been plotted together on figure (2.10) so that they can be compared.

A few conclusions can be drawn from figure (2.10). First of all, as shown in section 2.3, the unit cell model converges toward the stratified flow liquid height equilibrium, regardless of the nose conditions. It can be noted that the nose profile defined in subsection 2.2.1 does not depend on flow rates. It has an important influence on the bubble body prediction. For the tested flow rates, it does not fit our data as shown in figure (2.10). The unit cell model without bubble nose over predicts the length of the bubble nose.

The unit cell model with bubble nose relates two values : the liquid height at the end of the bubble nose and the equilibrium liquid height at the end of the bubble. If those two values are well predicted, the unit cell model can be a good fit to the bubble interface profile. For the flow rates considered, the unit cell model does not improve the prediction over the simple stratified flow prediction. However, it should be noted that the return bend two meters downstream of the measuring point may also influence the bubble profile measurements.

Error bars on the measurements have been added as described in the previous section. The measured bubble profile is higher than the stratified flow liquid height. It has been estimated that the equivalent bubble height i.e. the bubble liquid height profile weighted by the interface area is 5.5% larger than the one predicted by the stratified flow. For the considered range of liquid height this approximation corresponds to an error of 7.3% on the interface area and therefore on the molecular transfer rate.



FIGURE 2.10: Elongated bubble interface profile averaged over twenty bubbles for water flowing at a rate of 4000 liters per hour and air at a rate of 30 liters per minute.

2.7 Conclusion

A comparison of the different unit cell models describing the bubble interface profile have been presented along with models for the nose and the tail of the bubble. The different hypothesis used the unit cell models have been highlighted.

It has been noted that the different models limit when the bubble's length becomes sufficiently large tends toward the liquid height predicted for stratified flow.

The experimental rig used to test the elongated bubble models have been described along with the image treatment necessary to reconstruct the interface liquid height profile.

The implemented unit cell model has finally been compared to the stratified flow prediction and to the measurements. It has been concluded that a better nose model would improve the prediction. It is difficult to conclude concerning the accuracy of the prediction of the liquid height at the end of the bubble because of the influence of the return bend two meters downstream from the measuring point. For the particular application concerned in this study, unit cell models have not improved significantly the stratified flow prediction. The stratified flow prediction will then be used to predict the equivalent bubble height of intermittent flow in following chapter for the investigation of horizontal photobioreactor's conversion efficiency of CO_2 into biomass as a function of operating parameters.

References

- J. F. Netto, J. Fabre, L. Peresson, Shape of long bubbles in horizontal slug flow, International Journal of Multiphase Flow 25 (6-7) (1999) 1129 – 1160.
- [2] G. B. Wallis, One-Dimensional Two-Phase Flow, 1969.
- [3] A. E. Dukler, M. G. Hubbard, A model for gas-liquid slug flow in horizontal and near horizontal tubes, Industrial & Engineering Chemistry Fundamentals 14 (4) (1975) 337– 347.
- [4] M. K. Nicholson, K. Aziz, G. A. Gregory, Intermittent two phase flow in horizontal pipes : Predictive models, The Canadian Journal of Chemical Engineering 56 (6) (1978) 653–663.
- [5] S. Kokal, J. Stanislav, An experimental study of two-phase flow in slightly inclined pipes-II. liquid holdup and pressure drop, Chemical Engineering Science 44 (3) (1989) 681 – 693.
- [6] Y. Taitel, D. Barnea, Two-phase slug flow, Adv. Heat transfer 20.
- [7] P. Andreussi, K. Bendiksen, O. Nydal, Void distribution in slug flow, International Journal of Multiphase Flow 19 (5) (1993) 817 828.
- [8] M. Cook, M. Behnia, Bubble motion during inclined intermittent flow, International Journal of Heat and Fluid Flow 22 (5) (2001) 543–551.
- [9] J. Fabre, A. Line, Modeling of two-phase slug flow, Annual Review of Fluid Mechanics 24 (1) (1992) 21–46.
- [10] R. Mazza, E. Rosa, C. Yoshizawa, Analyses of liquid film models applied to horizontal and near horizontal gas-liquid slug flows, Chemical Engineering Science 65 (12) (2010) 3876–3892.
- [11] M. Cook, M. Behnia, Pressure drop calculation and modelling of inclined intermittent gas-liquid flow, Chemical Engineering Science 55 (20) (2000) 4699–4708.
- [12] M. Cook, M. Behnia, Slug length prediction in near horizontal gas-liquid intermittent flow, Chemical Engineering Science 55 (11) (2000) 2009–2018.
- [13] T. B. Benjamin, Gravity currents and related phenomena, Journal of Fluid Mechanics 31 (1968) 209–248.
- [14] Y. Taitel, A. E. Dukler, A model for predicting flow regime transitions in horizontal and near horizontal gas-liquid flow, AIChE Journal 22 (1) (1976) 47–55.

Chapter 3

Experimental assessment and modeling of CO₂ mass transfer in a horizontal co-current gas-liquid photobioreactor

Microalgae cultures have been recently regarded as a means to bioremediate industrial CO_2 . However, the CO_2 conversion to biomass efficiency of CO_2 into biomass has been seldom documented, and a significant part of the gas introduced in microalgae production systems is suspected of being released in the atmosphere. In this second chapter, the CO₂ conversion to biomass efficiency of an industrial horizontal tubular photobioreactor will be modelled. Dissolution efficiency and effects of stripping gas have been modelled using a classical two-phase flow approach [1] combined with the dissolution model developed and presented in Chapter 1 and in [2]. During a continuous culture run at a steady microalgae concentration, harvested biomass and injected CO₂ mass in the reactor were monitored. CO_2 dissolution and CO_2 conversion to biomass efficiencies were evaluated for injected CO₂ concentrations of 10% (waste gas) and non-optimised conditions. An analytical approach to complete the mass balance was used in order to determine the part of stripped CO₂. Through these measurements and the proposed model, the effects of production time, injected CO₂ concentration, flow rates and photobioreactor's length on the carbon dioxide fixation efficiency were also assessed and discussed.

Contents

3.1	Introduction		70
3.2	Mass t	transfer modeling	70
	3.2.1	Conservation of mass	70
	3.2.2	Model for η_{diss}	72
	3.2.3	Model for $\eta_{stripped}$	73
3.3	Measu	rements of Mass Transfer Efficiencies	74
	3.3.1	Measurement of η_{diss}	74
	3.3.2	Measurement of $\eta_{CO_2 converted tobiomass}$	74
	3.3.3	Evaluation of $\eta_{stripped}$	75
3.4	Result	ts and discussion	76
	3.4.1	Dissolution model	76
	3.4.2	Influence of dissolution and stripping on the photobioreactor's MTE and	
		optimum length	78
3.5	Conclu	usion	79
Refe	erences		80

Nomenclature

Greek symbols

η	Mass Transfer Efficiency (MTE),
ν	Kinematic viscosity, $\left[\frac{m^2}{s}\right]$
Φ	Pipe diameter, [<i>m</i>]
Φ_h	Hydraulic diameter of the duct, $[m]$
φ	Molecular gas flux, $\left[\frac{mol}{s \times m^2}\right]$
ρ	Density, $\left[\frac{kg}{m^3}\right]$

Latin symbols

Α	Section area, $[m^2]$
С	Constant in the friction factor correlation
С	Carbon dioxide molar concentration, $\left[\frac{mol}{m^3}\right]$
D	Diffusion constant, $\left[\frac{m^2}{s}\right]$
8	Gravity, $\left[\frac{m}{s^2}\right]$
h	Height, $[m]$
k	Mass transfer coefficient, $\left[\frac{m}{s}\right]$,
k_{La}	Volumetric mass transfer coefficient, $\left[\frac{1}{s}\right]$,
Μ	Molar mass, $\left[\frac{kg}{mol}\right]$
т	Carbon dioxide mass, $[kg]$
р	Pressure, [Pa]
R	Ideal gas constant, $\left[\frac{J}{mol,K}\right]$
Re	Reynolds number, $Re = \frac{U \cdot \Phi_h}{v}$
S	Perimeter, [m]
Sc	Schmidt number, $Sc = \frac{v}{D}$
Sh	Sherwood number, $Sh = \frac{k_L \cdot \Phi_h}{D}$
Т	Temperature, $[K]$
t	Time, $[s]$
U	Mean velocity over the duct section area, $\left[\frac{m}{s}\right]$
V	Exponent in equation (3.8) , see Taitel in $\begin{bmatrix} 1 \end{bmatrix}$
W	Exponent in equation (3.8), see Taitel in [1]
x	Coordinate in the downstream direction along the duct, $[m]$
X	Lockhart and Martinelli parameter.

Subscripts and superscripts

CO ₂ convertedtobi	<i>comass</i> CO ₂ contained in the output dry microalgae,
diss	CO ₂ dissolved,
eq	Equivalent height,
G	Gas,
i	Interface,
injected	CO ₂ injected into the photobioreactor,

L	Liquid,
undiss	CO ₂ undissolved and directly rejected to the atmosphere,
prod	Production of the microalgae mass harvested,
residual	CO_2 dissolved in the liquid and remaining dissolved,
S	Superficial, for single fluid flow,
sat	Saturation,
stripped	CO_2 driven to the atmosphere by the stripping air,
~	Dimensionless variable.

3.1 Introduction

This chapter deals with the experimental assessment and modeling of CO_2 conversion to biomass in Microphyt's windy wavy and wiped photobioreactor converting CO_2 into valueadded microalgae. Mass transfer modeling of such biotechnological processes is a first step toward understanding the coupled physics-biology in the photobioreactor and the optimisation of the process. It may help increase the CO_2 conversion to biomass efficiency of industrial waste gas containing 10% to 20% of CO_2 [3; 4; 5].

Few mass transfer models and measurements applied to photobioreactors can be found in the literature published during the two last decades. As highlighted in [9; 10], the information on CO_2 conversion to biomass efficiency pertains to the unique values of air- CO_2 mixture employed and of CO_2 concentration in the algal suspension [10]. Very little data concerning the produced biomass and the injected mass of CO_2 are available in the literature as can be found in [10]. Those performance measurements are functions of injected gas concentration but also of flow regimes through mass transfer coefficients and contact time between gas and liquid. Therefore, mass transfer efficiencies (MTE) should be measured for operating injected gas conditions i.e. flue gas concentration concerning our application as done in [10], for an outdoor cultivation of *Chlorella spirulina*.

Concerning mass transfer models, most frequently overall mass transfer coefficients or volumetric mass transfer coefficients are correlated to process parameters [11; 12; 13; 14]. To our knowledge, there is no mass transfer model in the literature relating the carbon dioxide mass injected to the biomass produced in photobioreactors.

This chapter is structured in three sections. In the first section, a model for horizontal photobioreactor's CO₂ MTE as a function of k_{La} , contact time and process parameters is proposed. Experimental measurements method will then be explained and finally, results will be presented and discussed in the last section.

3.2 Mass transfer modeling

3.2.1 Conservation of mass

As depicted on figure (3.1, a), the carbon dioxide mass injected in the photobioreactor, $m_{injected}$, is partially dissolved into the liquid phase (m_{diss}) and the remaining part is directly rejected to the atmosphere, as written in equation (3.1). The continuously injected air represented in figure (3.1, b) is also driving a mass ($m_{stripped}$) of carbon dioxide dissolved into the



FIGURE 3.1: Diagram of the carbon dioxide punctual dissolution phase (a) and continuous air stripping phase (b).

liquid to the atmosphere. The carbon dioxide dissolved in the liquid phase will either be transformed into biomass ($m_{CO_2 converted tobiomass}$) or remain in dissolved form in the liquid ($m_{residual}$), as described by the mass balance written in equation (3.2).

$$m_{injected} = m_{undiss} + m_{diss} \tag{3.1}$$

$$m_{diss} = m_{stripped} + m_{residual} + m_{CO_2 converted to biomass}$$
(3.2)

Dividing equation (3.2) by the carbon dioxide mass injected, equation (3.3) concerning the photobioreactor's MTE is obtained. The photobioreactor's CO₂ conversion to biomass MTE, $\eta_{CO_2 converted tobiomass}$, is defined as the ratio of the carbon dioxide mass contained in the output microalgae dry mass ($m_{CO_2 converted tobiomass}$) over the carbon dioxide mass injected ($m_{injected}$). Similarly, η_{diss} , $\eta_{stripped}$ and $\eta_{residual}$ are defined as the ratios of respectively m_{diss} , $m_{stripped}$ and $m_{residual}$ over $m_{injected}$.

$$\eta_{CO_2 converted to biomass} = \eta_{diss} - \eta_{stripped} - \eta_{residual}$$
(3.3)

In the next sections, dissolution and stripping phases are modelled as functions of process parameters .


FIGURE 3.2: Summary of the notations used in this chapter are defined to be congruent to Taitel [1].

3.2.2 Model for η_{diss}

As depicted in [9; 7], the flow regime in the photobioreactor is mainly made of long slugs that are more or less wavy. From chapter one [2], a model for dissolution efficiency (η_{diss}) of an elongated gas bubble into a turbulent flow has been developed and is expressed in equation (3.4).

$$\eta_{diss} = 1 - e^{-k_L(Re) \times (C_{sat} - C) \times \frac{R \times T}{p \times h_G} \times t}$$
(3.4)

In this model, the interface was considered as a flat plane and the equivalent bubble height h_G , is defined as the ratio of the cross section area occupied by the gas, A_G , over the interfacial contact width S_i , see figure (3.2).

The contact time *t* between the bubble and the liquid is estimated from the gas section area A_G , the photobioreactor's total length L_{tubes} and the gas flow rate Q_G , as expressed in equation (3.5). Replacing h_G and contact time into equation (3.4), leads to the expression of η_{diss} as a function of operating parameters in equation (3.6).

$$t = \frac{A_G \times L_{tubes}}{Q_G} \tag{3.5}$$

$$\eta_{diss} = 1 - e^{-k_L(Re) \times (C_{sat} - C) \times \frac{R \times T}{p} \times \frac{S_i}{\mathcal{Q}_G} \times L_{tubes}}$$
(3.6)

Estimations of the mass transfer coefficient and of the equivalent bubble height are required in order to evaluate η_{diss} from equation 3.6. The mass transfer coefficient k_L , has been evaluated using a correlation of the Sherwood number $Sh = \frac{k_L \cdot \Phi_h}{D}$, the Schmidt number, $Sc = \frac{v}{D}$, and the Reynolds number, $Re = \frac{U \cdot \Phi_h}{v}$, proposed in Lamourelle [15] and expressed in equation (3.7) which has been tested successfully for an immobilised elongated bubble in [2].

$$Sh_L = 1.76 \times 10^{-5} \times Re^{1.506} \times Sc^{0.5}$$
 (3.7)

Concerning the equivalent bubble height, h_G , it has been estimated by solving the momentum balance equation (3.8) for horizontal stratified flow. In this dimensionless equation, X is the Lockhart and Martinelli's parameter defined in equation (3.9). The other dimensionless parameters in equation (3.8), including \tilde{S}_i , are explicitly defined in [16] as a function of the dimensionless liquid height, \tilde{h}_L .

$$X^{2}\left[\left(\tilde{U}_{L}\tilde{\Phi}_{L}\right)^{-\nu}\tilde{U}_{L}^{2}\frac{\tilde{S}_{L}}{\tilde{A}_{L}}\right] - \left[\left(\tilde{U}_{G}\tilde{\Phi}_{G}\right)^{-w}\tilde{U}_{G}^{2}\left(\frac{\tilde{S}_{G}}{\tilde{A}_{G}} + \frac{\tilde{S}_{i}}{\tilde{A}_{L}} + \frac{\tilde{S}_{i}}{\tilde{A}_{G}}\right)\right] = 0$$
(3.8)

$$X^{2} = \frac{\left| \left(\frac{dp}{dx}\right)_{S,L} \right|}{\left| \left(\frac{dp}{dx}\right)_{S,G} \right|} = \frac{\frac{4c_{L}}{\Phi} \left(\frac{U_{S,L}\Phi}{v_{L}}\right)^{-v} \frac{\rho_{L}(U_{S,L})^{2}}{2}}{\frac{4c_{G}}{\Phi} \left(\frac{U_{S,G}\Phi}{v_{G}}\right)^{-w} \frac{\rho_{G}(U_{S,G})^{2}}{2}}$$
(3.9)

A relationship between liquid flow rate, gas flow rate and liquid height can be expressed replacing equation (3.9) into equation (3.8). The obtained equation is solved for \tilde{h}_L using dichotomy knowing the injected gas and liquid flow rates and therefore velocities for the guessed liquid height.

From those quantities, a Scilab algorithm calculates the mass transfer coefficient predicted by Lamourelle's correlation, equation (3.7), and the MTE, with equation (3.6), for each rectilinear section of the photobioreactor.

3.2.3 Model for $\eta_{stripped}$

Stripping air is injected continuously therefore the interface is along the entire length of the photobioreactor. The interface for the gas-liquid flow is approximated to $S_i \times L_{tubes}$. The interface width S_i is considered as a constant along the photobioreactor's length since the mass transferred is small compared to the mass injected.

As noted by Boettcher in [17], the molecular gas flux through a gas-liquid interface can be expressed as a function of the local molar concentration C and the molar concentration at saturation of the stripping gas $C_{sat stripped}$ by equation (3.10).

$$\frac{dn_{stripped}}{dt} = -(S_i \times L_{tubes}) \times \phi = -k_L \times (S_i \times L_{tubes}) \times (C_{sat \ stripped} - C)$$
(3.10)

Integrating equation (3.10) with respect to time, the stripping MTE can be expressed as in equation (3.11).

$$\eta_{stripped} = -k_L \times (S_i \times L_{tubes}) \times (C_{sat \ stripped} - C) \times M_{CO2} \times \frac{t_{prod}}{m_{injected}}$$
(3.11)

In equation (3.11), the coupled effects of cell density, light, momentum or temperature influencing the culture growth are affecting the stripping phase and therefore the CO₂ conversion to biomass process. They are implicitly taken into account through t_{prod} , the production time. In order to evaluate mass transfer efficiencies, mass transfer measurements on an industrial photobioreactor have been realised and their acquisition is described in the following section.

3.3 Measurements of Mass Transfer Efficiencies

During data acquisitions, the microalgae specie cultivated in the photobioreactor is chlorophyte *Neochloris oleoabundans*. The aim of the measurements on the photobioreactor is to determine the orders of magnitudes for dissolution, stripping and photobioreactor's MTEs for non-optimised conditions.

3.3.1 Measurement of η_{diss}

A Gastec CO₂ dosage kit has been used for the measurements. These kits are given for carbon dioxide concentrations from 0.5 to 20 % of the volume. During data acquisition, injection flow rates of air and CO₂ have been set with an injected gas containing up to 10% of CO₂. Measurements of CO₂ concentration at the injection point and the exit of the photobioreactor show a dissolution MTE, η_{diss} , of 72%. The coefficient of variation of 5% given for this probe is considered as the relative error for each measurement. The relative error on η_{diss} is then of 10%.

3.3.2 Measurement of $\eta_{CO_2 converted tobiomass}$

From its definition, $\eta_{CO_2 converted tobiomass}$ evaluation requires the measurement of the harvested microalgae's dry mass and of the consumed mass of CO₂ to produce it, considering that $\eta_{residual}$ is considered to be negligible. The residual mass of dissolved CO₂ in the culture broth photobioreactor has been measured with a metler toledo inPro 5000 and is evaluated to be less than 20 mg/L.

During the photobioreactor's development phase, food grade carbon dioxide gas bottles of 37.4 kg were used to feed microalgae. The injected mass of CO_2 have been estimated from the gas bottles' weight.

From June 16th to July 7th, 18.54 kilograms of dry biomass were harvested. It should be noted that, from the photosynthesis' stoichiometry for *Neochloris oleoabundans* given in [18], 1.88 grams of CO_2 are CO_2 converted to biomass when 1 gram of dry microalgae is produced. This coefficient is then applied in order to find the equivalent gas mass of CO_2 contained into the produced mass of microalgae.

As can be seen in figure (3.3), microalgae concentration evolution with time is very stable against harvesting disruptions over the 22 days harvesting period. The final cell density was measured around 1.6×10^8 cells per millilitre, higher than the starting cell density around 1×10^8 cells per millilitre. Given that on average 1.7 g of dry biomass were harvested from a litre of culture broth for an average cell density of 1.3×10^8 cells per millilitre, the equivalent of 3.69 kg dry biomass have been produced without being harvested. Using Pruvost [18], 34.85 kg of CO₂ were converted into the harvested dry biomass which has been produced using 105.4 kg of CO₂ gas. The minimum biomass conversion efficiency is then estimated to 33% considering only the carbon fraction in the harvested biomass. Considering that 3.69 kg of dry biomass that

have been estimated to remain in the photobioreactor without being harvested, the maximum biomass conversion efficiency is estimated to 40%.



FIGURE 3.3: Cell density and absorbance evolution with time and details for the measurement period. Absorbance give an idea of the size of the cells and therefore the density of biomass.

3.3.3 Evaluation of $\eta_{stripped}$

 $\eta_{stripped}$ is evaluated from equation (3.3). The error is the sum of errors on η_{diss} and $\eta_{CO_2convertedtobiomass}$. For the considered culture conditions, orders of magnitude of $\eta_{stripped}$ and $\eta_{CO_2convertedtobiomass}$ are similar. Considering that from equation (3.11), $\eta_{stripped}$ is proportional to production time, t_{prod} , if the time of production is reduced, the photobioreactor's MTE will increase by the same proportion. As a consequence, research efforts on optimum light, momentum and heat conditions for microalgae's growth rate will have a strong impact on the global photobioreactor's CO₂ conversion to biomass efficiency.

3.4 Results and discussion

3.4.1 Dissolution model



FIGURE 3.4: Dissolution MTE, η_{diss} , as a function of the photobioreactor's length and injected gas concentration as predicted by the one-dimensional model presented in section 3.2.2.

The dissolution model presented in section 3.2.2 is plotted against the dissolution measurement on figure (3.4). Each mark on the figure represents a linear section of the photobioreactor, where the liquid height, CO_2 concentration, pressure and mass flow rates are considered as constants. For the considered conditions, carbon dioxide is dissolved regularly along the photobioreactor. Dissolution measurements on the photobioreactor and model are showing a good agreement. The order of magnitude of the influence of the injected gas carbon dioxide concentration can also be evaluated from figure (3.4).



FIGURE 3.5: The ratio $\frac{k_L(Re) \times S_i}{Q_G}$ is a function of Q_L and Q_G . Flow rates maximising this ratio are the optimum flow rates for dissolution.

Another result from the dissolution model concerns optimum flow conditions for dissolution. As expressed in equation (3.6), for a fixed photobioreactor's length, dissolution is improved when the ratio $\frac{k_L(Re) \times S_i}{Q_G}$ is as large as possible. This ratio is a function of three variables Q_G , Q_L and h_L that are related by the momentum balance equation (3.8). For industrial parameters $5 < Q_G \left[\frac{N \cdot l}{min}\right] < 100$ and $20 < Q_L \left[\frac{l}{min}\right] < 450$, \tilde{h}_L and S_i can be considered as constants since the standard deviations are evaluated as respectively 6% and 8.5% of the averaged values, for the considered flow rates. As a consequence, effects of Q_L and Q_G on $\frac{k_L(Re) \times S_i}{Q_G}$ are decoupled. Practically, as can be seen on figure (3.5) for the range of considered flow rates, dissolution will be improved by increasing the liquid flow rate and therefore turbulence and by decreasing the gas flow rates and thus enhancing contact time, as long as the flow rates are compatible with culture conditions.



FIGURE 3.6: Measurements and extrapolation of the evolution of $\eta_{CO_2convertedtobiomass}$, η_{diss} and $\eta_{stripped}$ as a function of the photobioreactor's length, L_{tubes} , for carbon dioxide concentration in the injected gas up to 10% and non-optimised flow rates.

3.4.2 Influence of dissolution and stripping on the photobioreactor's MTE and optimum length

Combining equations (3.3), (3.6) and (3.11), an expression of $\eta_{CO_2 converted tobiomass}$ as a function of the photobioreactor's length, L_{tube} , is obtained. In order to assess the interest of scaling, it is possible to derive an semi-empirical relation for the optimum length of the photobioreactor considering an equivalent constant concentration gradient along the photobioreactor as expressed in equation (3.12).

$$L_{opti} = \frac{L_{tube}}{1 - \eta_{diss}(L_{tube})} \times ln\left(\frac{\eta_{diss}(L_{tube}) - \eta_{CO_2convertedtobiomass}(L_{tube})}{ln\left(\frac{1}{1 - \eta_{diss}(L_{tube})}\right)}\right)$$
(3.12)

For the considered conditions, the optimum length and relative influence of dissolution and stripping on scaling for the photobioreactor's MTE are plotted in figure (3.6). It appears that the photobioreactor's length is close to the optimum length for carbon dioxide CO_2 conversion to biomass efficiency.

3.5 Conclusion

A model for the CO_2 conversion to biomass process, based on a mass balance have been presented. The influence of dissolution and stripping are taken into account and they have been measured on an industrial photobioreactor alongside with CO_2 conversion to biomass efficiency. Numerical applications of a dissolution model for elongated bubbles, adapted for two phase flow, emphasised the influence of the injected CO_2 concentration and flow rates on the dissolution efficiency. The stripping model highlighted the relationship between production time due to culture conditions and CO_2 conversion to biomass efficiency. Substituting the measurements into the model, the influence of scaling of the photobioreactor on the CO_2 conversion to biomass efficiency have been assessed. Research on microalgae growth rate with oxygen would help improving the CO_2 conversion to biomass efficiency of photobioreactors through the stripping phase and the predictions of this one dimensional model. The two last chapters aim at developing higher dimensional numerical simulations of gas-liquid mass transfer. In order to produce comparative data for such numerical simulations, concentration measurements behind a free rising gas bubble dissolving into water have been realised using Planar Laser Induced Fluorescence and reported in the following chapter.

References

- [1] Y. Taitel, A. E. Dukler, A model for predicting flow regime transitions in horizontal and near horizontal gas-liquid flow, AIChE Journal 22 (1) (1976) 47–55.
- [2] P. Valiorgue, M. Hajem, A. Vassilev, V. Botton, H. Hadid, Elongated gas bubble dissolution under a turbulent liquid flow, Chemical Engineering and Processing : Process Intensification (2011).
- [3] L. Cheng, L. Zhang, H. Chen, C. Gao, Carbon dioxide removal from air by microalgae cultured in a membrane-photobioreactor, Separation and Purification Technology 50 (3) (2006) 324–329.
- [4] D. Ayhan, Biodiesel from oilgae, biofixation of carbon dioxide by microalgae : A solution to pollution problems, Applied Energy 88 (10) (2011) 3541–3547.
- [5] K. G. Zeiler, D. A. Heacox, S. T. Toon, K. L. Kadam, L. M. Brown, The use of microalgae for assimilation and utilization of carbon dioxide from fossil fuel-fired power plant flue gas, Energy Conversion and Management 36 (6-9) 707–712.
- [6] R. K. Mandalam, B. Palsson, Elemental balancing of biomass and medium composition enhances growth capacity in high-densityChlorella vulgaris cultures, Biotechnology and Bioengineering 59 (5) (1998) 605–611.
- [7] A. Muller-Feuga, M. Lemar, E. Vermel, R. Pradelles, L. Rimbaud, P. Valiorgue, M. El Hajem, J. Champagne, Design and assessment of an industrial windy, wavy and wiped tubular photobioreactor, in : 4th congress of International Society for Applied Phycology, Halifax, Canada, 2011.
- [8] T. Ogawa, T. Fujii, S. Aiba, Effect of oxygen on the growth (yield) of chlorella vulgaris, Archives of Microbiology 127 (1) (1980) 25–31.
- [9] T. M. Sobczuk, F. G. Camacho, F. C. Rubio, F. G. A. FernÃindez, E. M. Grima, Carbon dioxide uptake efficiency by outdoor microalgal cultures in tubular airlift photobioreactors, Biotechnology and Bioengineering 67 (4) (2000) 465–475.
- [10] J. Doucha, F. Straka, K. Lívanský, Utilization of flue gas for cultivation of microalgae chlorella sp.) in an outdoor open thin-layer photobioreactor, Journal of Applied Phycology 17 (5) (2005) 403–12.
- [11] D. Baquerisse, Modelling of a continuous pilot photobioreactor for microalgae production, Journal of Biotechnology 70 (1-3) (1999) 335–342.
- [12] K. Loubiere, J. Pruvost, F. Aloui, J. Legrand, Investigations in an external-loop airlift photobioreactor with annular light chambers and swirling flow, Chemical Engineering Research and Design 89 (2) (2011) 164–171.

- [13] R. Reyna-Velarde, E. Cristiani-Urbina, D. J. Hernández-Melchor, F. Thalasso, R. O. Cañizares-Villanueva, Hydrodynamic and mass transfer characterization of a flat-panel airlift photobioreactor with high light path, Chemical Engineering and Processing : Process Intensification 49 (1) (2010) 97–103.
- [14] L. Fan, Y. Zhang, L. Zhang, H. Chen, Evaluation of a membrane-sparged helical tubular photobioreactor for carbon dioxide biofixation by chlorella vulgaris, Journal of Membrane Science 325 (1) (2008) 336–345.
- [15] A. P. Lamourelle, O. C. Sandall, Gas absorption into a turbulent liquid, Chemical Engineering Science 27 (5) (1972) 1035–1043.
- [16] A. E. Dukler, Y. Taitel, Flow pattern transitions in gas-liquid systems : measurement and modeling 2 (1-4) (1986) 1–94.
- [17] E. Boettcher, J. Fineberg, D. Lathrop, Turbulence and wave breaking effects on air-water gas exchange, Physical Review Letters 85 (9) (2000) 2030–2033.
- [18] J. Pruvost, G. Van Vooren, G. Cogne, J. Legrand, Investigation of biomass and lipids production with neochloris oleoabundans in photobioreactor, Bioresource Technology 100 (23) (2009) 5988–5995.

Chapter 4

Concentration measurement in the wake of a free rising bubble using planar laser induced fluorescence (PLIF) with a calibration taking into account for fluorescence extinction variations

In order to produce comparative data for numerical simulations of gas-liquid mass transfer, concentration have been measured in the wake of a dissolving free rising bubble. Such measurements have been realised using a Planar Laser-Induced Fluorescence (PLIF) data treatment taking into account variations of the fluorescence extinction due to pH during the calibration step has been developed. It is shown that the proposed method needs to be implemented when a product of extinction coefficient variations, length travelled by the laser and fluorescence concentration becomes large such as in large tank experiments. The influence of extinction coefficient variations has been evaluated for a CO_2 concentration measurement test case in the wake of a free rising bubble.

Contents

4.1	Introduction			
4.2	Experimental setup			
4.3	Data treatment 92			
	4.3.1 Beer-Lambert law for non-optically thin systems			
	4.3.2 Extinction coefficient variation calibration			
4.4	Application to free rising bubble wake			
4.5	Conclusion			
Refe	erences			

Nomenclature

Greek symbols

δ	Diffusive length scale, $[m]$
8	Molar extinction coefficient, $\left[\frac{L}{mol m}\right]$
ф	Quantum yield of the fluorescence, []

Latin symbols

A	Fraction of the available light collected, []
С	Carbon dioxide molar concentration, $\left[\frac{mol}{m^3}\right]$
С	Fluorescein molar concentration, $\left[\frac{mol}{m^3}\right]^m$
F_{CO_2}	Molecular gas flux $F_{CO_2} = K_{LCO_2} \times (C_{sat} - C_{CO_2(aq)}), [\frac{mol}{s m^2}]$
h	Length of the vertical sides of the Region Of Interest (ROI), $[m]$
I_0	Initial light intensity, [U.A.]
Ie	Laser excitation intensity, [U.A.]
I_f	Fluoresced intensity, [U.A.]
<i>k</i> _{dehyd}	Dehydration rate of H ₂ CO ₃ , $\left[\frac{1}{s}\right]$
k _{hyd}	Hydration rate of CO ₂ (aq), $\left[\frac{1}{s}\right]$
L_d	Length between the diverging lens and the camera field of view, $[m]$
L _{fluo}	Distance traversed by the laser beam in the fluorescent fluid to reach the
0	considered element of the ROI, $[m]$
L_s	Length of the sampling volume along the incident beams, $[m]$
L_w	Width of the camera field of view, $[m]$
r	Coordinate in the downstream direction along a beam of light, $[m]$

Subscripts

k	Pixel column position along the laser beam,
l	Pixel column position along the laser beam,
pH	Value of the parameter for a given pH,
ref	Value of the parameter for a reference pH before measurements.

4.1 Introduction

This study is concerned with experimental measurements of CO_2 concentration fields using Planar Laser Induced Fluorescence (PLIF). A CO_2 concentration measurement in the wake of a free rising bubble have been performed. Such a measurement could be useful as a validation for numerical simulations of interfacial mass transfer. These simulations are often applied as a test case to free rising bubbles. Simulated mass transfer coefficient are then measured and compared with others local and mean Sherwood numbers [3; 12; 4; 1].

In Crimaldi [3], an extensive review of studies using PLIF is presented, reporting various calibration methods and attenuation treatments. Regarding calibration of mass transfer PLIF systems, a first approach found in the literature consists in assuming a linear relationship be-

tween re-emitted light intensity and concentration using two known reference points on the image such as in Jirka [11; 12]. Another procedure calibrating quantum yield variations of fluorescence is used by many other authors. Variations of emission intensities are attributed to the concentration of a quencher inhibiting fluorescence as predicted by the Stern-Volmer relationship. In most studies [17; 5; 1], the linear relationship between the ratio of intensity to reference pH intensity and quencher concentration is obtained from averaged images. However, for large tank experiments, the Stern-Volmer type of calibration should be applied locally because of the light absorption. Therefore, in a large tank experiment reported by Variano in [9], each pixel was calibrated individually from its time averaged intensity. The obtained pixel intensities were then normalised dividing by their reference pH pixel intensity.

Concerning attenuation of fluorescence with distance, most corrections in the literature are based on the Beer-Lambert law which describes attenuation with an exponential decay along a laser beam [20]. The Optically Thin (OT) criteria is used to caracterise systems with a low absorbance of the laser by the fluorophore. In Melton [16], a PLIF experiment has been carried out under optically thin conditions and variations of fluorescence intensity with distance were approximated by a linear function even though deviations were observed. This OT criteria is also evaluated in Roudet [17] and Walker [20] and used as a justification for neglecting attenuation. Attenuation can also be estimated using an exponential fit as in Sarathi [18]. In Jirka [11], effects of attenuation as a function of length are corrected by fitting an exponential curve through the measured intensities in order to obtain flat-fielded images. An analytical expression is given in Crimaldi [3] for non collimated laser sheets.

The calibration step can be affected by pH when it is used as a quencher since variations of the extinction coefficient as a function of the pH may be important as reported in [15; 20]. Those variations are even more important while calibrating non-optically thin systems. However, in the literature and as said explicitly in [18], attenuation is taken into account separately from calibration, similarly to a post-processing step and there is no information concerning the effects of pH on attenuation during the calibration.

This chapter is structured in three sections, starting with the description of the experimental test facility. Then a PLIF calibration procedure taking into account extinction coefficient variations is explained. The presented data treatment method is applied to concentration measurements in the wake of a free rising bubble and discussed in the last section.

4.2 Experimental setup

The 99.7% pure CO₂ gas bubble rises in the middle of a transparent tank having a squared section of side dimensions of 270mm. The tank is filled with 45 liters of demineralised water containing $5 \times 10^{-7} \pm 0.1\%$ mol/l of dissolved fluorescein-sodium. The Planar Laser Induced Fluorescence experimental set-up described in figure (4.1) uses an argon laser mounted with a 488 nm bandpass filter in the fluorescein's excitation spectra and a cylindrical lens to obtain a sheet of light of 1 mm thickness. A camera connected to a computer captures fluorescence fluctuations due to pH variations in the laser sheet. Those variations result from the reaction of water with the dissolved CO₂ in the bubble wake.



FIGURE 4.1: Schematic view of the Planar Laser Induced Fluorescence experimental set-up used for CO₂ concentration measurements in the wake of a free rising CO₂ bubble dissolving into an aqueous solution of fluorescein illuminated by an argon laser plane.



FIGURE 4.2: Picture of the experimental setup described in figure 4.1.

The reference pH at which experiments started was around 7, in a region where fluoresceinsodium is highly sensitive to pH changes [19]. The concentration of the fluorescent dye has been chosen such that the maximum of the greyscale was used.



FIGURE 4.3: Fluorescence trapping and photobleaching test using linearity assessment of the Beer-Lambert law of attenuation for the Argon ion laser/sodium-fluorescein system as a function of concentration [14; 13].

A Linearity test of fluorescence signal versus dye concentration was performed as shown in figure (4.3). From Karasso [13; 14], it implies that no fluorescence trapping nor photobleaching was observed. It should be noted that fluorescence is a diffuse process so emission is independent of the direction and therefore independent of the position of the camera [14; 20]. Regarding temperature dependence, a variation of 0.3% per degree Kelvin at pH > 9 has been reported in Walker [20]. A variation of two degrees Kelvin has been observed during the experiment.

Images of rising bubbles in a laser sheet are recorded using a Dalsa Falcon 1.4M100 HG CMOS camera with vertical binning leading to a resolution of 480×688 with a scale of 0.1

mm per pixel vertically and 0.2 mm per pixel horizontally. About 25 frames were acquired for a single rising bubble at a frequency of 100 frames per second and with an exposure time of 1 ms. Images were acquired under a very low external parasite light since the greyscale level of the camera was null when there was no fluorescein in the water tank. The received light intensity was too low for a 488 nm band-stop filter to be placed between the camera and the laser sheet.



FIGURE 4.4: Specification of the influence of surfactants in the medium comparing experimentally measured rising bubble velocities with data from the literature (Clift, [19]) for contaminated and pure water.

Influence of surfactants on the motion and mass transfer from bubbles were discussed in Clift [19]. The main effect is to reduce the mobility of all or part of the interface resulting in different rise velocities. This velocity difference have been used to specify the medium in the water tank in Stöhr [19]. Experimental velocity measurements have been compared to data reported in Clift [19] as shown in figure (4.4). Velocities have been measured 300 mm above the bubble injection nozzle where terminal rising velocity has been reached [7]. Rising velocities

have been found to be close to the pure water conditions.



FIGURE 4.5: A correlation of CO₂ concentration as a function of pH in the tank using a Metler Toledo CO₂ InPro 5000 probe and pH equilibrium with atmosphere to complete the PLIF measuring range : $[CO_2](\frac{mg}{T}) = 2411390 \times exp(-pH/0.2166422)$

A correlation relating CO_2 concentration as a function of pH in the medium is presented in figure (4.5). CO_2 concentrations have been measured with a Metler Toledo CO_2 InPro 5000 probe that has a 10% measuring error above its detection limit of 14.7 mg/L. It has been checked that the exponential behaviour of the correlation was valid for CO_2 concentration in the medium in equilibrium with the atmosphere and therefore for the whole PLIF measuring range.

The velocity of the CO_2 reaction with water needs to be discussed. As written in Gibbons [10] about CO_2 reaction kinetics with water : "although the acid-base equilibrium is essentially instantaneous, the dehydration rate of H_2CO_3 is relatively slow" implying that the time to reach equilibrium for H_2CO_3 and pH may not be short enough to track CO_2 concentration variations(cited in Asher [1]). The H_2CO_3/CO_2 reaction kinetic has been modelled with the

coupled differential equations system (4.1) where k_{dehyd} is the dehydration rate of H₂CO₃ and k_{hyd} is the hydration rate of CO₂. The system has been solved analytically with Maple in [1] with source term F_{CO_2}/δ (where F_{CO_2} is the molecular gas flux and δ is a diffusive length scale of CO₂) considered as a constant and applied during a given time called here exposure time.



$$\begin{cases} \frac{d [CO_2]}{d t} = \frac{F_{CO_2}}{\delta} + k_{dehyd} [H_2 CO_3] - k_{hyd} [CO_2] \\ \frac{d [H_2 CO_3]}{d t} = k_{hyd} [CO_2] - k_{dehyd} [H_2 CO_3] \end{cases}$$
(4.1)

FIGURE 4.6: Time evolution of CO₂ concentration from the reaction kinetic differential equations system (4.1) solved for the source term F_{CO_2}/δ and the influence of the source term on the CO₂ concentration.

In order to determine the time for the reaction to reach equilibrium, the same system has been solved using the same reaction rates values as in [1]. However, the initial condition of CO₂ spot has been changed in order to have realistic contact with bubble : the source term F_{CO_2}/δ has been modelled as a function of time as a shifted cosinus of maximum F_{CO_2}/δ and semiperiod the exposure time necessary to reach the maximum CO₂ concentration in the wake of the bubble determined from figure (4.10). It is shown on figure (4.6) that for the used continuous source term, $[CO_2]_t - [CO_2]_{t=0}$ is very close from the integral of the source term $\int_0^{t_e} \frac{F_{CO_2}(t)}{\delta} dt$ meaning that for the initial concentrations used the evolution of concentrations is mainly related to the evolution of the source term. Therefore the time to reach equilibrium is very close from the exposure time. The presented analysis seems to indicate that the reaction has been fully completed between two frames.

4.3 Data treatment

4.3.1 Beer-Lambert law for non-optically thin systems

From Walker [20], considering that no saturation occurred for all present measurements, considering that attenuation can be neglected along the receiving sampling volume length, the fluorescence intensity at the detector can be described by the Beer-Lambert equation (4.2).

$$I_f = I_0 A \phi \varepsilon L_s c \exp(-\int_{L_{fluo}} \varepsilon c dr)$$
(4.2)

 I_0 stands for the initial light intensity, A is the fraction of the available light intensity collected, ϕ is the quantum yield of the fluorescence, ε is the molar extinction coefficient, L_s is the length of the sampling volume along the incident beams, c the fluorescein concentration, L_{fluo} is the distance travelled by the laser beam in the fluorescent fluid and r is the coordinate in the direction along a beam of light (figure (4.7)).

Dividing each pixel intensity by a reference intensity measured at a reference pH and considering that c, A, L_s and I_0 are constant, the following equation (4.3) is obtained :

$$\frac{I_f}{I_{f,ref}} = \frac{\phi \,\varepsilon \, exp(-\int_{L_{fluo}} \varepsilon \,c \,dr)}{\phi_{ref} \,\varepsilon_{ref} \, exp(-\int_{L_{fluo}} \varepsilon_{ref} \,c \,dr)} = \frac{\phi \,\varepsilon}{\phi_{ref} \,\varepsilon_{ref}} exp\left(c \int_{L_{pH \neq pH_{ref}}} (\varepsilon_{ref} - \varepsilon) dr\right)$$
(4.3)

Considering that the length over which the reaction is observed $(L_{pH\neq pH_{ref}})$ is small, the following relationship, expressed in equation (4.4), is obtained for the intensity variation as a function of pH for each pixel.

$$\frac{I_{f,pix}}{I_{f,ref,pix}} \approx \frac{\phi \,\varepsilon}{\phi_{ref} \,\varepsilon_{ref}} \tag{4.4}$$

Therefore $(\phi \varepsilon)/(\phi_{ref}\varepsilon_{ref})$ needs to be calibrated as a function of pH. Experimentally, background images are acquired for different pH values for a fixed concentration of fluorescein and divided by the same reference as previously.

$$\frac{I_{f,pH,pix}}{I_{f,ref,pix}} = \frac{\phi_{pH}\varepsilon_{pH}}{\phi_{ref}\varepsilon_{ref}}exp\left(c\int_{L_{fluo}}(\varepsilon_{ref}-\varepsilon)dr\right)$$
(4.5)

From equation (4.5), if $L_{fluo}c(\varepsilon_{ref} - \varepsilon)$ is not negligible, molar extinction coefficient variations have to be taken into account during the calibration of $(\phi\varepsilon)/(\phi_{ref}\varepsilon_{ref})$ as a function of pH for each pixel. A method for molar extinction coefficient determination from background images at known and fixed concentration is presented in the following section.



FIGURE 4.7: Schematic view of the camera observation area and of the Region Of Interest in which the CO₂ concentration have been measured.

4.3.2 Extinction coefficient variation calibration

Extinction coefficient measurements as a function of pH have been carried out from homogeneous background images acquired for uniform concentrations of CO_2 in the fluid after mixing. Within the Region Of Interest which has been approximated to a laser beam, ratios of intensities at different positions along the laser beam can be expressed using equation (4.2). If the intensity at one position along the laser beam was taken as a pixel column of the region of interest, the ratio of intensities received by two pixel columns can be written as follows :



FIGURE 4.8: Standard deviation of the non-corrected extinction coefficient ε measurements, for a given pH during calibration. As the amplitude of the extinction increases with the length travelled by the laser beam, the dispersion of the measured extinction coefficient diminishes with the distance between two pixel columns used for its determination.

$$\frac{I_{f,k}}{I_{f,l}} = exp(-\varepsilon c L_{k,l}) \tag{4.6}$$

with k and l being the index position of pixel columns.

The decreasing intensity due to the diverging lens has to be corrected during the extinction coefficient variations calibration as a function of pH. Assuming no fluorescent dye and a constant thickness of the laser sheet, considering light flow conservation, the ratio of received light per unit area of two pixel columns k and l can be determined geometrically :

$$\frac{I_k}{I_l} = \frac{h_k}{h_l} = \frac{L_d + L_w}{L_d} \tag{4.7}$$

where I_k and I_l are the light intensity received by the pixels of two pixel columns k and l belonging to the region of interest and of respective height h_k and h_l . L_w is the width of the camera observation area, and L_d is the distance between this area and the diverging lens, as

shown in figure (4.7).

This contribution has been taken into account in equation (4.8). As it is a constant for any pair of pixel column, it has no influence on the extinction coefficient variations $\Delta \varepsilon$ as a function of pH.

$$\varepsilon = -\frac{ln \frac{l_{f,k}}{l_{f,l}}}{cL_{k,l}} - \frac{ln(1 + \frac{L_w}{L_d})}{cL_{k,l}}$$
(4.8)

The influence of the length between two columns for the determination of the non-corrected ε is shown in figure (4.8).

4.4 Application to free rising bubble wake



FIGURE 4.9: Example for the middle column of the image of extinction coefficient variations effects on the calibration of $\frac{\phi_0 \varepsilon_0}{\phi \varepsilon}$. The correction is compared to the so called Stern-Volmer relationship corresponding to the calibration of intensities $\frac{I_0}{I}$ without correction for extinction coefficient variations.



FIGURE 4.10: Example of application of the calibration on rising bubble images in raw A resulting in the transformed CO₂ concentration images in raw B. Subtracting the background, CO₂ concentration increase map and profiles are presented in raw C. A map along with profiles of the relative difference with an uncorrected calibration are presented in raw D.

The influence of molar extinction coefficient variations on pixel intensity calibration expressed in equation (4.5) as a function of pH are shown in figure (4.9) for concentration measurement of CO_2 in the wake of a free rising gas bubble.

As attenuation is decreasing with decreasing pH [15], non-corrected background images would result in overestimated calibrated pixel intensities as a function of pH. It can be noted that the linear relationship predicted by the non-corrected Stern-Volmer relationship is only valid for a given range of pH as illustrated in figure (4.9).

Using corrected correlations relating pixel intensities to pH, the acquired images are firstly transformed to pH levels and then to CO_2 concentrations levels using the correlation depicted in figure (4.5). Acquired images and CO_2 processed images are presented in figure (4.10, A and B). Black areas appear to the left of the bubble when it shadows the laser light. Concentration variations are presented in figure (4.10, C) subtracting the background image. Concentration variation profiles of horizontal and vertical sections are also plotted. In figure (4.10, D) a comparison is done between two calibrations taking or not taking into account extinction coefficient variation.

As can be seen in the comparison figure, the two calibrations differ most where extinction coefficient variations are the larger that is to say in the bubble wake. The particular measurement application exhibits relative differences of concentration to 125% in the bubble wake for the higher CO₂ concentrations.

4.5 Conclusion

A PLIF data treatment method taking into account extinction coefficient variations with pH during calibration has been presented. An application to a CO₂ concentration measurement in the wake of a free rising bubble has shown the error that may be induced if extinction coefficient variations with pH during calibration are not taken into account. The criteria $L_{fluo}c(\varepsilon_{ref} - \varepsilon)$ has been proposed in order to determine whether the method should be used. The data treatment method allows for the technique to be used for a wider range of parameters as for example higher fluorescein concentrations and larger distances in the liquid for large tank experiments. The obtained measurements can be used as a comparative test case for the gas-liquid mass transfer numerical simulations that will be presented in the following chapter.

References

- [1] Asher, W., Litchendorf, T. : Visualizing near-surface concentration fluctuations using laser-induced fluorescence. Experiments in Fluids **46**(2), 243–253 (2009)
- [2] Clift, R., Grace, J., Weber, M., Clift, R. : Bubbles, drops, and particles, vol. 3. Academic press New York (1978)
- [3] Crimaldi, J. : Planar laser induced fluorescence in aqueous flows. Experiments in fluids 44(6), 851–863 (2008)
- [4] Dani, A. : Transfert de masse entre une bulle et un liquide : simulations numériques directes et fluorescence induite par nappe laser. Phd thesis, Institut National des Sciences Appliquées (INSA) de Toulouse (2007)
- [5] Dani, A. : Transfert de masse entre une bulle et un liquide : simulations numériques directes et fluorescence induite par nappe laser (2007)
- [6] Deshpande, K., Zimmerman, W. : Simulation of interfacial mass transfer by droplet dynamics using the level set method. Chemical Engineering Science **61**, 6486–6498 (2006)
- [7] Fdhila, R., Duineveld, P. : The effect of surfactant on the rise of a spherical bubble at high reynolds and peclet numbers. Physics of Fluids **8**, 310 (1996)
- [8] Figueroa-Espinoza, B., Legendre, D. : Mass or heat transfer from spheroidal gas bubbles rising through a stationary liquid. Chemical Engineering Science 65(23), 6296–6309 (2010)
- [9] Garbe, C., Handler, R., Jähne, B. : Transport at the air-sea interface : measurements, models and parametrizations. Springer Verlag (2007)
- [10] Gibbons, B., Edsall, J., et al. : Rate of hydration of carbon dioxide and dehydration of carbonic acid at 25 degrees. The Journal of biological chemistry 238, 3502 (1963)
- [11] Jirka, G. : Application of LIF to investigate gas transfer near the air-water interface in a grid-stirred tank. Experiments in Fluids **37**(3), 341–349 (2004)
- [12] Jirka, G., Herlina, H., Niepelt, A. : Gas transfer at the air-water interface : experiments with different turbulence forcing mechanisms. Experiments in Fluids 49(1), 319–327 (2010)
- [13] Karasso, P., Mungal, M. : Scalar mixing and reaction in plane liquid shear layers. Journal of Fluid Mechanics 323, 23–64 (1996)
- [14] Karasso, P., Mungal, M. : PLIF measurements in aqueous flows using the nd : YAG laser. Experiments in fluids 23(5), 382–387 (1997)
- [15] Lindqvist, L. : A flash photolysis of fluorescein. Arkiv for Kemi Band 16(nr 8), 60 (1960)
- [16] Melton, L., Lipp, C. : Criteria for quantitative PLIF experiments using high-power lasers. Experiments in fluids 35(4), 310–316 (2003)

- [17] Roudet, M. : Hydrodynamique et transfert de masse autour d'une bulle confinée entre deux plaques. Ph.D. thesis (2008)
- [18] Sarathi, P., Gurka, R., Kopp, G., Sullivan, P. : A calibration scheme for quantitative concentration measurements using simultaneous PIV and PLIF. Experiments in Fluids 52(1), 247 (2012)
- [19] Stöhr, M., Schanze, J., Khalili, A. : Visualization of gas-liquid mass transfer and wake structure of rising bubbles using pH-sensitive PLIF. Experiments in Fluids 47, 135–143 (2009)
- [20] Walker, D. : A fluorescence technique for measurement of concentration in mixing liquids. Journal of Physics E : Scientific Instruments **20**, 217 (1987)
- [21] Wylock, C., Larcy, A., Colinet, P., Cartage, T., Haut, B. : Direct numerical simulation of bubble-liquid mass transfer coupled with chemical reactions : Influence of bubble shape and interface contamination. Colloids and Surfaces A : Physicochemical and Engineering Aspects (2011)

Chapter 5

Numerical simulation of gas-liquid mass transfer

A numerical simulation of mass transfer in gas-liquid flows has been developed. The interface has been tracked using a modified level-set method with a penalty term that has been shown to improve mass conservation. The method has been partly validated with a test on rising bubble velocities for bubble diameters less than 3 centimeters. A simulation of scalar concentration in the bubble wake using a source at the gas-liquid interface in a diffusion-convection equation has been presented. Volume variations due to mass transfer have been taken into account using an additional equation quantifying mass loss and allowing for the volume to vary through the mass conservation penalty term. Applied to the elongated bubble test case, the bubble length exponential decay rate with time appears to be of the order of magnitude of the one measured in the experiment.

Contents

5.1	Introduction		
5.2	Numerical simulation of mass transfer through a moving interface 104		
5.3	3 Implementation and validation		
	5.3.1 Level-set implementation		
	5.3.2 Implementation of the scalar diffusion through the interface 108		
5.4	Simulation of the elongated bubble dissolution		
5.5	Conclusion		
Refe	erences		

Nomenclature

Greek symbols

β	Penalty factor in the level-set method,
δ	Dirac function in the level-set method,
ε	Half thickness of the interface or an arbitrary chosen small number,
ϵ_{ls}	Constant in Comsol's level-set method,
γ	Constant in Comsol's level-set method,
ν	Kinematic viscosity, $\left[\frac{m^2}{s}\right]$,

Latin symbols

d	Rising bubble diameter, [m],
D	Diffusion constant, $\left[\frac{m^2}{s}\right]$,
Н	Heaviside function in the level-set method,
k	Mass transfer coefficient, $\left[\frac{m}{s}\right]$,
Pe	Peclet Number, $\frac{d.U}{D}$,
Re	Reynolds number, $Re = \frac{U \cdot d}{v}$,
Sc	Schmidt number, $Sc = \frac{v}{D}$,
Sh	Sherwood number, $Sh = \frac{k_L \cdot d}{D}$,
U	Mean velocity, $\left[\frac{m}{s}\right]$,
V	Bubble "volume" i.e. section area for 2D simulations, $[m^2]$
Vol^*	Theoretical or initial volume of the bubble (or section area in 2D), $[m^2]$

Subscripts and superscripts

0	Initial state,
L	Liquid,

5.1 Introduction

Simulations of gas-liquid mass transfer are at their early stage of their development and it has been decided that the implemented numerical method should be first validated against test cases. Mass transfer measurements presented in chapter 1 and chapter 4 for the dissolution of an elongated bubble and of a rising bubble can be used as test cases. The rising bubble test case is a quite popular application test case in the literature related to numerical simulations of gas-liquid mass transfer [1; 2; 3; 4; 5; 6; 7; 8; 9; 10; 11; 12].

In recent studies, fundamental work has been undertaken considering at bubbles represented by solid wall interfaces. In [2] and [3], studies concerning the effects of contamination of the interface on the flow field and local Sherwood numbers have been reported.

For simulations convecting the interface, the work in recent publications concentrates on the implementation of mass transfer through the interface. Most common convecting interface approaches are qualified as one-fluid approaches, meaning that a single set of governing equations is used to describe the fluid motion in both fluids. Among them, four original methods : VOF, Level-Set, Phase-Field and Constrained Interpolated Propagation method. They mainly differ on how a marker function is advected (and how surface tension is found) [13]. They do not require any modification of the flow solver near the interface except allowing for variable density and viscosity and are based on three general assumptions which are the continuum hypothesis, the hypothesis of sharp interfaces and the neglect of intermolecular forces [13].

In the VOF method of Hirt and Nichols (1981), a marker function is advected and to prevent numerical diffusion the marker does not start to flow into a new cell until the current cell is full [13].

In the Level-Set method introduced by Osher and Sethian (1988) [14], the interface is identified with the zero contour of a continuous level-set function. The main difference with the VOF method is that the regularity of the interface has increased [13].

In the Constrained Interpolated Propagation (CIP) method introduced by Takewaki et al. (1985), the transition from one fluid to another is described by a cubic polynomial, advecting both the marker function and its derivative [13].

In the Phase-Field method, the smoothed region between the different fluids is described in a thermodynamically consistent way. However actual implementations simulate artificially thick interfaces for numerical reasons [13] and it is not clear whether this method has any advantages over the level set method for example which also has a thick interface for different reasons.

The thickness of the interface varies from one cell in VOF methods to a few cells in front-Tracking methods such as Level-Set, but once the marker function has been found, the specific scheme for the interface advection is essentially irrelevant for the rest of the computations [13].

In order to improve the hypothesis of sharp interfaces, the so called "sharp interface methods"have been developed. Among them, the Immersed-Interface method of Lee and LeVeque (2003), explicitly incorporates the jump across the interface into the finite difference equations but is limited to fluids with the same viscosity. The "ghost fluid" method introduced by Fedkiw et al. (1999) the level-set function is modified : numerical approximations to derivatives near the interface are found using fictitious values (from extrapolation or otherwise) are assigned to grid points from the other side of the interface [13].

In the following section, the orders of magnitude of the mesh in gas-liquid mass transfer systems are discussed along with the implementation strategy. An interface tracking implementation in COMSOL and its comparison with experimental rising bubble velocity is then described. Next, the simulation of the passive scalar field induced by the mass transfer is applied to the rising bubble dissolution. Finally, volume evolution with mass transfer is implemented and compared with the elongated bubble dissolution model.

5.2 Numerical simulation of mass transfer through a moving interface

Numerical methods for the simulation of mass transfer through a moving interface have to be adapted to the relevant dimensionless parameters and particularly the two most important for the considered application : the Schmidt number and the Reynolds number.

Let us consider the Schmidt number which physically relates the relative thickness of the hydrodynamic layer and mass-transfer boundary layer. The practical situations concerned typi-

cally have Schmidt numbers of the order of a thousand meaning that the mass transfer boundary layer and therefore the concentration gradient that have to be simulated are a thousand times smaller than the hydrodynamic layer. The mass transfer boundary layer thickness is evaluated in [15] as being of the order of $O(d \times Pe)$ where d is the bubble diameter and Pe is the Peclet number. Applied to the rising bubble, the mass transfer boundary layer is then of the order of $5 \times 10^{-4} \times d$ or one hundredth of a millimetre. According to the experience in the laboratory, a minimum of five nodes within the boundary layer are necessary. The distance between two nodes should then be of two micrometers within the boundary layer for a direct numerical simulation of the mass transfer to be possible. The example of a direct simulation of mass transfer using the open source simulation software Elmer presented in Annexe C is not correct since the grid size does allow for the driving concentration gradient to be accurate.

The grid size would be even bigger for the elongated bubble test case considering the length of the interface. As it is too computationally expensive to use direct numerical simulation for mass transfer for the tested cases, an experimental mass transfer model has to be introduced into the numerical simulation. A standard way to do this is by adding a source term to the diffusion-convection equation of a passive scalar. In Annexe D, An example of this implementation using Fluent and the Volume Of Fluid function us given. A source term at the interface can be added based on the Volume Of Fluid function as shown.

Concerning Reynolds numbers between 7,000 and 40,000 and of 5,000 respectively for both the elongated bubble from Chapter 1 and the rising bubble from Chapter 4, the liquid flow is considered as turbulent since they are above the critical Reynolds Number. As it is also too computationally expensive to resolve all the scales of turbulence for the velocity field down to the Kolmogorov scale, and even more for concentration field, down to the Batchelor scale, turbulent fluctuations of the velocity and concentration equations will have to be modeled as well.

The numerical method implemented in COMSOL 4.2a will be described in the following section and confronted to the rising bubble validation test-case.

5.3 Implementation and validation

The level set method have been shown to be appropriate for elongated bubbles flows as shown by Lakehal in [13] using Ascomp software TransAT. It has been said previously that the Level-Set method was introduced by Osher and Sethian (1988) [14], however the first application of the method to fluid interface tracking were on two-dimensional rising bubbles and fall of droplets are attributed to Sussman et al. (1994) [16] and Chang et al. (1996) [17]. The two-phase flow with mass transfer simulation presented here will be confronted to the test case investigated in Chapter 4 of the rising bubble with mass transfer.

5.3.1 Level-set implementation

A modified version of COMSOL's level-set has been used in this study. In the level-set method, the different fluid regions are identified by a smooth marker function (called ϕ here), which is positive in one fluid and negative in the other [13]. The boundary between the fluids is identified by an isoline of the marker function. The level-set function moves with the fluid



FIGURE 5.1: Visual (a) and quantitative (b) comparison of mass conservation using COM-SOL's level-set simulation for a two centimetres diameter rising bubble with and without the penalty term. In b), the ratio of the bubble's section area over its initial section area V/V_0 is plotted with and without the introduced penalty term : $\beta\delta(\phi) (1 - (\int_{\Omega} H(\phi) d\Omega)/Vol^*)$ with $\beta = 10$.

according to the convection equation (5.1) where γ and ε_{ls} are two constant of COMSOL's method, *t* is the time and \vec{u} is the velocity field calculated from the Navier-Stokes and mass conservation equations.

Both the rising bubble and the elongated bubble test cases exhibit Reynolds Numbers that are clearly above their respective critical Reynolds Number. Unfornately, no turbulence model was available with the implemented level set method in COMSOL's 4.2a version which has been used for the presented simulations.

$$\frac{\partial \phi}{\partial t} + \overrightarrow{u} \cdot \nabla \phi = \gamma \cdot \nabla \cdot \left(\varepsilon_{ls} \cdot \nabla \phi - \phi \cdot (1 - \phi) \frac{\nabla \phi}{\|\nabla \phi\|} \right)$$
(5.1)



FIGURE 5.2: Rising velocity evolution with time of a gas bubble in quiescent water simulated using COMSOL's level-set with the introduced penalty correction for different diameters on the same mesh.

From the signed marker function, a Heaviside function $H(\phi)$ can be defined as written in equation 5.2 where the function is zero in the liquid phase and one in the gas phase. A smooth transition between the two phases is added using ε which is the half thickness of the interface or an arbitrary chosen small number. It is possible to build a dirac delta function δ at the interface the same way or from the gradient of the Heaviside.

$$H(\phi) = \begin{cases} 0, & \phi < -\varepsilon \\ \frac{1}{2} + \frac{\phi}{2\varepsilon} + \frac{1}{2\pi} sin\left(\frac{\pi\phi}{\varepsilon}\right), & -\varepsilon \leqslant \phi \leqslant \varepsilon \\ 1, & \phi > \varepsilon \end{cases}$$
(5.2)

A method developed in El Otmani [18] that improves mass conservation have been implemented. In this method a penalty term, $\beta\delta(\phi) (1 - (\int_{\Omega} H(\phi)d\Omega)/Vol^*)$, is added to the level-set convection equation. In this term, β is the penalty factor, Vol^* the theoretical or initial volume, and δ the dirac function. If the value of the penalty factor is large, the accuracy of the mass conservation is very high but resolution time is increased [18]. The accuracy of the method and the influence of coefficient β have been discussed in [18].


FIGURE 5.3: Final rising velocity as a function of the bubble diameter.

The contribution to mass conservation of the penalty term is presented in figure 5.1 on a two centimeters diameter rising bubble test-case.

As a validation test-case for the interface convection, single rising bubbles have been simulated for different diameters. Their velocity stabilizes at their final rising velocity as shown in figure 5.2. Final rising bubble velocities have been plotted as a function of bubble diameter in figure 5.3 and compared to experimental data from Clift [19] for pure water. Rising velocities have only been partially validated for bubble diameters less than 3 cm. The surface tension coefficient had to be increased for bubbles diameters larger than 1 cm in order to avoid bubble break up. For those bubble diameters, the implementation of a scalar diffusion through the interface is described.

5.3.2 Implementation of the scalar diffusion through the interface

The aim of the simulation is to determinate whether it is possible to numerically predict the concentration away from the interface using a simple mass transfer coefficient. Results for a simulation with a source term uniformly distributed along the interface proportional to the mass transfer coefficient are displayed in figure (5.4). The proportionality term in the source term has been tuned so that the concentration in the wake of the bubble corresponds to the one



FIGURE 5.4: Level-set simulation of a dissolving rising bubble using COMSOL.

measured in Chapter 4. However, the amplitude has not been derived from mass transfer correlation from the literature. Concentration profils along the middle vertical line of the domain from the simulation presented in figure 5.4.



FIGURE 5.5: Concentration profils along the middle vertical line of the domain from the simulation presented in figure 5.4.

5.4 Simulation of the elongated bubble dissolution

For the simulation of the bubble volume decrease in the elongated gas bubble dissolution test case, the introduced penalty term have been used. The theoretical volume of the bubble, Vol^* , have been varied accordingly to the empirical correlation presented in Chapter one.

Using equation (1.1) and equation (5.4) from Chapter one, the total molecular loss rate through the interface could be calculated using the following equation :

$$\frac{dn}{dt} = -S \times k_L \times (C_{sat} - C), \tag{5.3}$$

where *n* is the molar quantity, *C* is the local molar concentration and C_{sat} the molar concentration at saturation. k_L is the liquid side mass transfer coefficient and *S* describes the mass exchange area or length for 2D simulations.

The new theoretical volume of the bubble could then be calculated using the perfect gas equation as shown in the next equation :

$$\frac{n_0}{V_0} = \frac{n_0 - \int_0^T n(t)dt}{Vol^*},$$
(5.4)

where 0 and T denote respectively the initial and calculation step times.

 $ln(\frac{L(t)}{L_0})$ is plotted for a Reynolds number Re = 24540. The exponential evolution of the interface length L(t) that was supporting the flat interface approximation used in Chapter 1 for the measurements of mass transfer coefficients is not very well reproduced in the numerical simulation. The slope of the fitted least square line interpolating the data for a length larger than 25 centimeters has been measured. It been evaluated for gas bubble length to height ratios larger than 15 as done in Chapter 1. Longer bubbles could not be simulated because they were carried away.

For simulation time reasons, k_L in the simulation have been taken as a hundred times the experimental mass transfer coefficient. Considering that the slope of the interpolated bubble length data is proportional to the mass transfer coefficient for elongated bubble dissolution as shown in Chapter one, measured and simulated slopes of the exponential bubble length decay can be compared in figure 5.7. The difference between the two slope coefficients could be explained by the fact that the bubble height decreases during the numerical simulation which differs from experimental observation.







FIGURE 5.7: $ln(\frac{L(t)}{L_0})$ is plotted for a Reynolds number Re = 24540. The exponential evolution of the interface length L(t) that was supporting the flat interface approximation used in Chapter 1 for the measurements of mass transfer coefficients is not very perfectly reproduced in the numerical simulation. The order of magnitude of the slope could be reproduced. The difference may be attributed to the fact that in the simulation the bubble height was not as constant as in the experiment.

5.5 Conclusion

In this last chapter, a numerical simulation of mass transfer in gas-liquid flows has been developed. The interface has been tracked using a modified level-set method with a penalty term that has been shown to improve mass conservation. A validation test on rising bubble velocities have been partly for bubble diameters inferior to 3 centimeters. A simulation of scalar concentration in the bubble wake using a source at the gas-liquid interface in a diffusion-convection equation has been presented. Volume variations due to mass transfer have been taken

into account using an additional equation quantifying mass loss and allowing the adjustment of the volume through the mass conservation penalty term. Applied to the elongated bubble test case, the bubble length evolution with time in the simulation is of the order of magnitude of the one measured in the experiment. The difference may be attributed to the fact that in the simulation the bubble height was not as constant as in the experiment.

References

- [1] K. Deshpande, W. Zimmerman, Simulation of interfacial mass transfer by droplet dynamics using the level set method, Chemical Engineering Science 61 (2006) 6486–6498.
- [2] A. Dani, A. Cockx, P. Guiraud, Direct numerical simulation of mass transfer from spherical bubbles : the effect of interface contamination at low reynolds numbers, International Journal of Chemical Reactor Engineering 4 (4) (2006) 2.
- [3] B. Figueroa-Espinoza, D. Legendre, Mass or heat transfer from spheroidal gas bubbles rising through a stationary liquid, Chemical Engineering Science 65 (2010) 6296–6309.
- [4] A. Ganguli, E. Kenig, A CFD-based approach to the interfacial mass transfer at free gasliquid interfaces, Chemical Engineering Science 66 (14) (2011) 3301–3308.
- [5] J. Khinast, A. Koynov, T. Leib, Reactive mass transfer at gas-liquid interfaces : impact of micro-scale fluid dynamics on yield and selectivity of liquid-phase cyclohexane oxidation, Chemical engineering science 58 (17) (2003) 3961–3971.
- [6] A. Koynov, J. Khinast, G. Tryggvason, Mass transfer and chemical reactions in bubble swarms with dynamic interfaces, AIChE journal 51 (10) (2005) 2786–2800.
- [7] H. Oka, K. Ishii, Numerical analysis of Two-Phase flow with mass transfer by a level set method., Theor Appl Mech Jpn 51 (2002) 353–362.
- [8] S. S. Ponoth, J. McLaughlin, Numerical simulation of mass transfer for bubbles in water, Chemical Engineering Science 55 (2000) 1237–1255.
- [9] C. Zhu, T. Fu, X. Gao, Y. Ma, Numerical simulation of concentration field on liquid side around bubble during rising and coalescing process in Non-Newtonian fluid, Chinese Journal of Chemical Engineering 19 (2011) 799–807.
- [10] C. Yang, Z. Mao, Numerical simulation of interphase mass transfer with the level set approach, Chemical Engineering Science 60 (2005) 2643–2660.
- [11] J. Wang, P. Lu, Z. Wang, C. Yang, Z. Mao, Numerical simulation of unsteady mass transfer by the level set method, Chemical Engineering Science 63 (2008) 3141–3151.
- [12] C. Wylock, A. Larcy, P. Colinet, T. Cartage, B. Haut, Direct numerical simulation of bubble-liquid mass transfer coupled with chemical reactions : Influence of bubble shape and interface contamination, Colloids and Surfaces A : Physicochemical and Engineering Aspects 381 (2011) 130–138.
- [13] G. Tryggvason, D. Lakehal, S. Banerjee, S. Zaleski, ETH IET LKE course 2012, part IIB : computational Multi-Fluid dynamics.
- [14] S. Osher, J. A. Sethian, Fronts propagating with curvature-dependent speed : algorithms based on Hamilton-Jacobi formulations, Journal of computational physics 79 (1) (1988) 12–49.

- [15] B. Aboulhasanzadeh, S. Thomas, M. Taeibi-Rahni, G. Tryggvason, Multiscale computations of mass transfer from buoyant bubbles, Chemical Engineering Science 75 (2012) 456–467.
- [16] M. Sussman, P. Smereka, S. Osher, A level set approach for computing solutions to incompressible two-phase flow, Ph.D. thesis, UCLA (1994).
- [17] Y. C. Chang, T. Y. Hou, B. Merriman, S. Osher, A level set formulation of eulerian interface capturing methods for incompressible fluid flows, Journal of Computational Physics 124 (2) (1996) 449–464.
- [18] R. El Otmani, M. Zinet, M. Boutaous, H. Benhadid, Numerical simulation and thermal analysis of the filling stage in the injection molding process : Role of the mold-polymer interface, Journal of Applied Polymer Science 121 (3) (2011) 1579–1592.
- [19] R. Clift, J. Grace, M. Weber, R. Clift, Bubbles, drops, and particles, Vol. 3, Academic press New York, 1978.

Conclusion

Gaz-liquid mass transfer in horizontal photobioreactors have been investigated in this thesis. The first three chapters of this thesis deal with the development of a one dimensional mass transfer model in those photobioreactors.

The first chapter deals with mass transfer between an homogeneous immobilised elongated gas bubble and a turbulent liquid flow in which it is set. For the particular studied geometry, mass transfer measurements have been found to be well fitted by Lamourelle's correlation proposed for wetted-wall columns. The hypothesis of a flat exchange interface is shown to be appropriate for elongated gas bubbles dissolving into a turbulent flow. Applied to horizontal tubular photobioreactors, a relationship allowing for mass transfer to be evaluated as a function of design and operating parameters is obtained. For different applications, the immobilised elongated gas bubble geometry could be of interest for the design of a mass transfer feedback control system.

In the second chapter, a review of unit cell models describing the bubble interface profile have been presented. A comparison of the hypothesis highlighted the differences between unit cell models. Unit cell models predicting the body of the bubble can be completed with models for the body and the tail of the bubble in order to describe the entire length of the bubble. When the bubble's length becomes sufficiently large, unit cells models tend toward the value predicted for stratified flows. An experimental rig have been adapted in order to observe horizontal elongated bubble flow and reconstruct the averaged bubble profile. Unit cell models have then been confronted to the acquired data and compared to the stratified flow prediction. It has been concluded that a better nose model would improve unit cell model predictions. For the observed flow, unit cell models do not improved significantly the bubble profile prediction compared to the stratified flow prediction.

In the third chapter, the developed model has then been adapted to the photobioreactor in order to predict the bioconversion efficiency of the process. The relative influence of dissolution and stripping have been evaluated using a mass balance. They have been measured on Microphyt's photobioreactors alongside with bioconversion efficiency. Numerical applications of a dissolution model for elongated bubbles, adapted for two phase flow, emphasised the influence of the injected CO_2 concentration and flow rates on the dissolution efficiency. The stripping model highlighted the relationship between production time due to culture conditions and bioconversion efficiency. Substituting the measurements into the model, the influence of scaling of the photobioreactor on the bioconversion efficiency have been assessed. Research on microalgae growth rate with oxygen would help improving the bioconversion efficiency of photobioreactors through the stripping phase.

The two last chapters aim at developing a numerical simulation of gas-liquid mass transfer. In the fourth chapter, a Planar Laser Induced Fluorescence (PLIF) data treatment method taking into account for extinction coefficient variations with concentration during calibration has been presented. An application of the technique to CO_2 concentration field measurements in the wake of free rising bubbles have produced comparative data for the numerical simulation developed in the last Chapter. It has also shown that important errors may be induced if extinction coefficient variations with concentration during calibration are not taken into account. The data treatment method allows for the technique to be used for a wider range of parameters for example increasing the fluorescence concentration or observing at larger distances in the bulk of the liquid.

In the last chapter, a numerical simulation of mass transfer in gas-liquid flows has been developed. The interface has been tracked using a modified level-set method with a penalty term that has been shown to improve mass conservation. A validation test on rising bubble velocities have been partly for bubble diameters inferior to 3 centimeters. A simulation of scalar concentration in the bubble wake using a source at the gas-liquid interface in a diffusion-convection equation has been presented. Volume variations due to mass transfer have been taken into account using an additional equation quantifying mass loss and allowing the adjustment of the volume through the mass conservation penalty term. Applied to the elongated bubble test case, the bubble length evolution with time in the simulation is of the order of magnitude of the one measured in the experiment. The difference may be attributed to the fact that in the simulation the bubble height was not as constant as in the experiment.

Appendix A : Head Loss

The measured friction factor of the PMMA test loop has been found to be well correlated by the Blasius equation defining the lower boundary of the friction factor for turbulent flow through smooth pipes. Similar head loss measurements are expected for the glass pipes of the photobioreactor since they are smoother than PMMA.

It has been reported in [1], that a 16 meters length pipe was necessary for the observation of fully developed slug flow. As a consequence, the empirical measurements on the test loop can only be viewed as an evaluation of the order of magnitude of the pressure drop.

From two-phase pressure drop theory as reviewed in [2], three components contribute to the total head loss :

- the static pressure drop,
- the momentum pressure drop,
- and the frictional pressure drop.

For a horizontal tube, there is no change in static head, so the static pressure drop is null. The momentum pressure drop is calculated from the difference between the inlet and outlet vapor qualities and corresponds here to the effect of the dissolution on the pressure drop. The frictional pressure can then be obtained here by subtracting the momentum pressure drop from the measured total pressure. On the test loop air will be used and therefore only the frictional pressure drop will be considered.

A number of models describing the frictional pressure have been reported in the literature [3]. The three most accurate reported in [3] are correlations from Lockhart and Martinelli, Friedel and Müller-Steinhagen.

The general trend for frictional pressure drop has been described in [4] and figure (6.8). The frictional pressure drop increases with increasing flow quality (\dot{x}), passes through a maximum for $\dot{x} = 0.85$, and then falls to the frictional pressure drop for single-phase gas flow for $\dot{x} = 1$.

The friction pressure drop correlation presented in [4] considers a linear increase of the pressure drop with increasing quality for $\dot{x} < 0.7$.

In order to get an idea of the order of magnitude of the pressure in microphyt's photobioreactor, measurements have been realised for flow rates close from microphyt's operating conditions and compared to correlations found in the literature. The order of magnitude of the measured pressure drop would not increase significantly the energy consumed by the pump. From the tested correlations, it has been found that the Muller-Steinhagen [4] was giving the best prediction for the pressure drop at the tested flow rates and the diameter of the pipe, as shown in figure (6.9). Considering the important literature on the subject and the lack of practical interest for the particular application, investigations have been discontinued.



FIGURE 6.8: Measured and calculated frictional pressure drop of water and air as a function of flow quality - from [4].

References

- [1] P. Lin, T. Hanratty, Effect of pipe diameter on flow patterns for air-water flow in horizontal pipes, International Journal of Multiphase Flow 13 (4) (1987) 549–563.
- [2] J. Thome, Engineering data book iii, Wolverine Tube Inc (2004) Chapiter 13.
- [3] R. Revellin, J. R. Thome, Experimental two-phase fluid flow in microchannels, Ph.D. thesis, EPFL, Lausanne (2005).
- [4] H. Müller-Steinhagen, K. Heck, A simple friction pressure drop correlation for two-phase flow in pipes, Chemical Engineering and Processing : Process Intensification 20 (6) (1986) 297–308.
- [5] R. W. Lockhart, R. C. Martinelli, Proposed correlation of data for isothermal two-phase, two-component flow in pipes, Chem. Eng. Prog 45 (1) (1949) 39–48.
- [6] L. Friedel, Improved friction pressure drop correlations for horizontal and vertical twophase pipe flow, in : European two-phase flow group meeting, Paper E, Vol. 2, 1979.



FIGURE 6.9: Comparison of the measured pressure drop with correlations from the literature of Müller-Steinhagen [4], Lockhart [5] and Friedel [6]. The measuring conditions were close from microphyt's operating conditions i.e. for liquid flow rates varying from 1000 L/hr to 6000 L/hr and a fixed gas flow rate of 11 N.L/min.

Appendix B : Calculus of kla from measurements

In Chapter 2, the dissolution efficiency is expressed (3.4) as :

$$\eta_{diss} = 1 - e^{-k_L(Re) \times (C_{sat} - C) \times \frac{R \times T}{p \times h_G} \times t}$$
(7.5)

It is common in bioengineering to evaluate mass transfer through kla coefficients.

$$\eta_{diss} = 1 - e^{-kla(Re) \times (C_{sat} - C) \times \frac{R \times T}{p} \times t}$$
(7.6)

Applied to the photobioreactor, the kla coefficient can be evaluated measuring the dissolution coefficient and the contact time of the bubble with the liquid. In Chapter 2, the dissolution efficiency have been evaluated to be $72\% \pm 10\%$.

In the model presented in Chapter 2, the contact time has been evaluated from the average velocity corresponding to the flow rate through the equivalent gas section area for stratified flow. This model for the contact time allowed the parameter study presented in section 3.4 on the length of the photobioreactor and the operated flow rates. In order to have better estimate of the kla, a direct measurement of the contact time is realised.

$$kla(Re) = \frac{-ln(1 - \eta_{diss}) \times p}{R \times T \times (C_{sat} - C) \times t}$$
(7.7)

It should be noted that the kla is not necessary the best tool to evaluate mass transfer efficiency for microphyt's photobioreactor. Indeed, horizontal photobioreactors'length are much less limited than other reactors, therefore the contact time can be very large and comparing kla coefficients does not take into account for this particularity which have a large impact on the CO_2 bioconversion as shown in section 7.7. This explains why a comparison of different types of photobioreactors should only be done using the final CO_2 bioconversion efficiencies.

Appendix C : Mass transfer simulations using Elmer

In Elmer, both a level-set solver and an advection-diffusion solver are available. A summary of their implementation based on Elmer's model manual is given in the following sections. Obtained simulations are displayed in the last section.

Level-set implemention in Elmer

The level-set have been decomposed into four steps as described in Elmer's model manual :

1. Advection : the level set function, which is defined by a marker function ϕ so that at the interface $\phi = 0$, inside the fluid of interest $\phi > 0$ and elsewhere $\phi < 0$, is updated by solving the equation :

$$\frac{\partial \phi}{\partial t} + \vec{u} \cdot \nabla \phi = a \tag{8.8}$$

where \vec{u} is the convection field and *a* is the normal flux on the interface.

- 2. Reinitialization : the level set function is modified such that the absolute value of function equals the shortest distance to the zero level-set.
- 3. Volume conservation : A correction is added to the level-set function if the new volume, V, calculated with an integral has changed with respect to the initial volume V_0 . (A is the perimeter of the bubble).

$$d\phi = \frac{V_0 - V}{A}.\tag{8.9}$$

4. Surface tension : the surface tension force is smeared out to a volume force within a narrow band from the interface.

Advection-diffusion implemention in Elmer

The Advection-diffusion solver describes the transport of a chemical species by convection and diffusion. It is possible to add sources or sinks to the model. The advection-diffusion equation used reads :

$$\frac{\partial C_i}{\partial t} + (\nabla \cdot \vec{v})C_i + (\vec{v} \cdot \nabla)C_i = \nabla \cdot (D_i \nabla C_i) + S_i.$$
(8.10)

where \vec{v} is the advection velocity, D_i the diffusion coefficient and S_i is a source, sink or a reaction term. The diffusion coefficient have been specified at the interface using volume species sources S_i and the level set variable.

The velocity of the advecting fluid, \vec{v} , in the example shown below is calculated by the Navier-Stokes equation. Given volume species sources S_i have been prescribed at the interface using the level-set.

However, the estimated amount of work required to set-up the variable replacement giving one equation for diffusion as described in Chapter 5 led us to change of software.

Results



FIGURE 8.10: Level-Set simulation of a dissolving rising bubble using Elmer multiphysics.

Appendix D : Mass transfer simulations using a source term in Fluent

Using the flow modeling simulation software ANSYS Fluent, it is possible to define a source term in a passive scalar field. As a preliminary study, the dissolving rising bubble test case has been implemented in Fluent using the Volume Of Fluid (VOF) model for interface tracking. This VOF function has then been used in order to set a source term at the interface using a User Defined Function which is written hereafter. The obtained concentration fields are given in figure (9.11).

User Defined Function code :

1.12e-04 1.06e-04 1.01e-04 9.52e-05 8.96e-05 8.96e-05 7.84e-05 7.84e-05 7.28e-05 6.72e-05 6.16e-05 5.04e-05 9.32e-05 9.32e-05 9.22e-05 9.32e-05 9.32e-05 9.22e-05 9.32e-05 9.32e-05 9.22e-05 1.12e-05 1.12e-05 1.12e-05 5.60e-06 -2.09e-18 Contours of Scalar-0 (mbture)	(Time=2.0000e-02)	6
452e-04 428e-04 428e-04 3.84e-04 3.84e-04 3.82e-04 3.38e-04 2.71e-04 2.71e-04 2.26e-04 2.26e-04 2.26e-04 1.58e-04 1.58e-04 1.58e-04 1.36e-04 1.36e-04 1.36e-04 1.36e-05 6.78e-05 2.26e-	× →→ (Time=2.0000e-01)	
5.54e-04 5.26e-04 4.38e-04 4.38e-04 4.38e-04 4.38e-04 3.88e-04 3.88e-04 3.88e-04 3.05e-04 2.49e-04 2.22e-04 1.94e-04 1.36e-05 5.54e-05 5.54e-05 2.77e-05 0.000e+00 Contours of Scalar-0 (mixture)	(Time=4.0000e-01)	
1e-02 1e-04 1e-06 1e-08 1e-10 1e-12 1e-14 1e-16 1e-18 88000 88500 89000	98500 90000 90500 9100	<u>~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~</u>

FIGURE 9.11: Volume Of Fluid simulation of a dissolving rising bubble using the flow modeling simulation software ANSYS Fluent. A User Defined Function has been used in order to define a source term located at the bubble interface for the simulation of the mass transfer between the bubble and the liquid.

<u>FOLIO ADMINISTRATIF</u> <u>THÈSE SOUTENUE DEVANT I'UNIVERSITÉ CLAUDE BERNARD LYON 1</u>

NOM : VALIORGUE	DATE de SOUTENANCE : 3 Décembre 2012			
Prénoms : Pierre, Gérald				
TITRE : Transfert de masse dans les écoulements gaz-liquide horizontaux intermittents et application aux photo- bioréacteurs Mass transfer in intermittent horizontal gas-liquid flow and application to photobioreactors				
NATURE : Doctorat	Numéro d'ordre : 2012-ISAL-266-2012			
École doctorale : MEGA				
Spécialité : Mécanique des Fluides				
Cote B.I.U Lyon : T 50/210/19 / et bis	CLASSE :			

Abstract général :

Sécuriser un approvisionnement fiable de micro-algues est récemment devenue un enjeu industriel. Pour assurer la croissance de micro-algues dans des photobioréacteurs clos, un transfert de masse optimum de l'oxygène et du dioxyde de carbone doivent être assurés. Dans cette thèse, une étude du transfert de masse gaz-liquide dans les conduites horizontales a été menée. Dans les trois premiers chapitres, un modèle unidimensionnel de transfert de masse dans le photobioréacteur a été développé. Tout d'abord, le transfert de masse entre une bulle de gaz allongée et un écoulement liquide turbulent a été étudié expérimentalement. En considérant l'interface comme étant plane, les coefficients de transfert de masse mesurés sont proches d'une corrélation de Lamourelle (1972). Le modèle de Taitel pour les écoulements stratifiés a été comparé à des modèles plus complets pour la prédiction de l'interface des bulles allongées. Une approche analytique basée sur un bilan de masse et utilisant les modèles testés a ensuite été développée et adaptée à un photobioréacteur afin de prédire l'efficacité de la conversion du CO_2 en biomasse en fonction des paramètres d'exploitation. Les deux derniers chapitres visent à développer une simulation numérique du transfert de masse gaz-liquide. Une mesure de la concentration en CO_2 dans le sillage d'une bulle de gaz ascendante a été effectuée à l'aide une méthode améliorée de traitement des données de Fluorescence Induite par Plan Laser (FIPL). Enfin, une simulation numérique de ces mesures a été réalisée sous COMSOL.

MOTS-CLÉS : mass transfer, CO2 biofixation, gas-liquid, photobioreactor, microalgae, PLIF

Laboratoire(s) de recherche : Laboratoire de Mécanique des Fluides et d'Acoustique UMR CNRS 5509 - Université Claude Bernard Lyon 1, INSA de Lyon, École Centrale de Lyon 43, boulevard du 11 Novembre 1918, 69622 Villeurbanne Cedex FRANCE

Directeur de thèse : Monsieur le Professeur Hamda Ben Hadid

Co-directeur de thèse : Monsieur le Docteur Mahmoud El Hajem

Président du jury : Marc BUFFAT

MARC BUFFAT	Professeur	Président
Abdelkader MOJTABI	Professeur	Rapporteur
ANTHONY ROBINSON	Assistant Professor	Rapporteur
ARNAUD MULLER FEUGA	Docteur, HDR	Examinateur
HAMDA BEN HADID	Professeur	Directeur de thèse
Mahmoud El Hajem	Maître de Conférences	Co-directeur de thèse