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A thesis submitted in partial fulfillment of the requirements for the degree in Master of Engineering Science

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STUDY OF THE HYDRODYNAMICS, MASS TRANSFER AND ENERGY REQUIREMENTS OF A RECTANGULAR AIR-LIFT BIOREACTOR FOR ELECTRICAL POWER GENERATION

(Thesis format: Monograph)

by

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Graduate Program in Chemical and Biochemical Engineering

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Engineering Science

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Abstract

Despite the increasing importance of air-lift reactors, very little published information is available on how the ratio of aerated to non-aerated cross-sectional areas ($Ad/Ar$) of the reactor, and the aerating system affect the oxygen mass transfer, energy efficiency and other performance characteristics. The main goal of this work was to define the optimal operating conditions in terms of oxygen mass transfer, hydrodynamics and energy utilization in a rectangular air-lift reactor for use in a biological fuel cell by identifying its oxygen mass transfer coefficient and liquid circulation behavior. A new empirical model for the dependence of the mass transfer coefficient on the non-aerated to aerated compartment ratio in the air-lift reactor was developed and used for optimization of the operating conditions. We believe that this work may be useful for the design and optimization of biochemical and other processes that require air-lift reactors.

Keywords

Air-lift reactor, volumetric oxygen mass-transfer coefficient, downcomer to riser ratio, hydrodynamic characteristics; energy efficiency
Co-Authorship Statement

Stanimir Drandev was the principal author. The supervisor Dr. Dimitre Karamanev made revisions and recommendations. Based on some portions of results in this thesis, one paper is submitted, and another one is under preparation for submission to peer reviewed journals. The contribution of each author is given below:

1. Study of the hydrodynamics and mass transfer in a rectangular air-lift bioreactor.

Submitted to Chemical Engineering Science

Authors: Stanimir S. Drandev, Kalin I. Penev, Dimitre Karamanev

Experimental work and data analysis were performed by Stanimir Drandev. Kalin Penev contributed to the development of the empirical model of the system. Dimitre Karamanev and Kalin Penev provided consultation regarding experimental work and data analysis. The manuscript was written and revised by Stanimir Drandev and reviewed by Dimitre Karamanev and Kalin Penev.

2. Energy consumption and energy balance in rectangular air-lift reactor for power generation in a microbial fuel cell.

Prepared for publishing in Biotechnology Letters

Authors: Stanimir S. Drandev, Dimitre Karamanev

Experimental work and data analysis were performed by Stanimir Drandev. Dimitre Karamanev provided consultation regarding experimental work and data analysis. The manuscript was written and revised by Stanimir Drandev, and reviewed by Dimitre Karamanev.
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Last but not least, I am grateful to my wife, Emmanuelle, for her trust and support. Her infinite patience and spirit have always encouraged me to go further.
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Preface

Access to clean and renewable energy is one of the greatest challenges facing the humanity. Nature can inspire innovative solutions for sustainable energy systems and technology design, which is subject of the BIONICS. Some renewable energy technologies already imitate processes found in nature. Such a processes of imitation of the models, systems, and elements of nature for the purpose of solving complex human problems is called biomimetics or biomimicry.

One particular example, which demonstrates both approaches is the integration of a ferrous iron oxidizing microorganisms in the presence of an electron acceptor, and a biological fuel cell into a single electricity generation system known as BioGenerator. In this case molecular oxygen is used as a final electron acceptor. In the nature molecular oxygen is mainly biogenic – a by-product of the most common type of photosynthesis, which is a part of natural surroundings of the microorganisms, as long as the microorganisms can never be a closed system. However, when processes from the nature are replicated, oxygen has to be supplied continuously to the system in order to maintain it as close as it is possible to its innate conditions. It is this urge of the research of conditions, necessary to provide the environment closer to the natural that is central to the current work.
Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
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<tbody>
<tr>
<td>$A$</td>
<td>Cross-sectional area ($m^2$)</td>
</tr>
<tr>
<td>$a$</td>
<td>Gas-liquid interfacial area per unit of liquid volume ($m^{-1}$)</td>
</tr>
<tr>
<td>$C$</td>
<td>Concentration ($mg·L^{-1}$)</td>
</tr>
<tr>
<td>$d$</td>
<td>Diameter (mm)</td>
</tr>
<tr>
<td>$E^o$</td>
<td>Standard oxidation-reduction potential</td>
</tr>
<tr>
<td>$F$</td>
<td>Faraday constant ($C·mol^{-1}$)</td>
</tr>
<tr>
<td>$h$</td>
<td>Height (m)</td>
</tr>
<tr>
<td>$I$</td>
<td>Electrical current (A)</td>
</tr>
<tr>
<td>$J^O$</td>
<td>Molar flux of oxygen ($mol·m^{-2}·s^{-1}$)</td>
</tr>
<tr>
<td>$K$</td>
<td>Overall mass transfer coefficient ($m·s^{-1}$)</td>
</tr>
<tr>
<td>$k_{La}$</td>
<td>Volumetric mass transfer coefficient ($s^{-1}$)</td>
</tr>
<tr>
<td>$L$</td>
<td>Length (m)</td>
</tr>
<tr>
<td>$M$</td>
<td>Molar mass ($g·mol^{-1}$)</td>
</tr>
<tr>
<td>$m$</td>
<td>Mass ($g$)</td>
</tr>
<tr>
<td>$N$</td>
<td>All values from a population (–)</td>
</tr>
<tr>
<td>$N_{O2}$</td>
<td>Oxygen mass transfer rate per unit of reactor volume ($mol·m^{-3}·s^{-1}$)</td>
</tr>
<tr>
<td>$n$</td>
<td>Number (–)</td>
</tr>
<tr>
<td>$P$</td>
<td>Power density ($W·m^{-3}$)</td>
</tr>
<tr>
<td>$p$</td>
<td>Pressure (Pa)</td>
</tr>
<tr>
<td>$s$</td>
<td>Standard deviation based on the sample (–)</td>
</tr>
<tr>
<td>$Q$</td>
<td>Total electric charge passed through the substance ($C$)</td>
</tr>
<tr>
<td>$q$</td>
<td>Specific uptake rate of microorganisms ($mol·m^{-3}·s^{-1}$)</td>
</tr>
<tr>
<td>$t$</td>
<td>Time (s)</td>
</tr>
<tr>
<td>$U$</td>
<td>Superficial velocity ($m·s^{-1}$)</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
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<tr>
<td>--------</td>
<td>------------------------------</td>
</tr>
<tr>
<td>( V )</td>
<td>Voltage (V)</td>
</tr>
<tr>
<td>( V_L )</td>
<td>Liquid volume (m³)</td>
</tr>
<tr>
<td>( v )</td>
<td>Velocity (m·s⁻¹)</td>
</tr>
<tr>
<td>( W )</td>
<td>Width (m)</td>
</tr>
<tr>
<td>( x )</td>
<td>Value from a population (−)</td>
</tr>
<tr>
<td>( \bar{x} )</td>
<td>Mean of the sample (−)</td>
</tr>
<tr>
<td>( z )</td>
<td>Valency number (−)</td>
</tr>
<tr>
<td>( \hat{z} )</td>
<td>Distance (m)</td>
</tr>
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**Greek Letters**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \varepsilon )</td>
<td>Gas holdup, (−)</td>
</tr>
<tr>
<td>( \rho )</td>
<td>Density (kg·m⁻³)</td>
</tr>
<tr>
<td>( \tau_r )</td>
<td>Response time of the dissolved oxygen probe (s)</td>
</tr>
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</table>

**Subscripts**

<table>
<thead>
<tr>
<th>Symbol</th>
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<tbody>
<tr>
<td>( c )</td>
<td>Relative to circulation</td>
</tr>
<tr>
<td>( D )</td>
<td>Relative to dispersion</td>
</tr>
<tr>
<td>( d )</td>
<td>Relative to downcomer of reactor</td>
</tr>
<tr>
<td>( EL )</td>
<td>Relative to electricity</td>
</tr>
<tr>
<td>( G )</td>
<td>Relative to gas</td>
</tr>
<tr>
<td>( i )</td>
<td>Relative to integer</td>
</tr>
<tr>
<td>( L )</td>
<td>Relative to liquid</td>
</tr>
<tr>
<td>( M )</td>
<td>Relative to manometer</td>
</tr>
<tr>
<td>( O_2 )</td>
<td>Relative to oxygen</td>
</tr>
<tr>
<td>( o )</td>
<td>Relative to orifices</td>
</tr>
<tr>
<td>( r )</td>
<td>Relative to riser; in the case of ( \tau_r ) it is relative to response</td>
</tr>
<tr>
<td>( t )</td>
<td>Relative to top of reactor</td>
</tr>
<tr>
<td>( X )</td>
<td>Relative to biomass</td>
</tr>
</tbody>
</table>
Superscripts

* Equilibrium value in each phase

Abbreviations

ALR Air-lift reactor
AMD Acid mine drainages
DO Dissolved oxygen
DI Deionized (water)
ESS Energy storage system
FIB Ferrous iron biooxidation
IOM Iron oxidizing microorganisms

OTR Oxygen transfer rate (mol \( O_2 \cdot m^{-3} \cdot s^{-1} \))

OUR Oxygen uptake rate (mol \( O_2 \cdot m^{-3} \cdot s^{-1} \))

PEM Proton exchange membrane

SE Standard error (–)

CI Confidence interval (–)
Chapter 1

1 Introduction

1.1 Motivation

Humanity is on the verge of a profound shift in the way it generates and uses energy. With fossil fuels resources depletion and pollution increase, producers and law makers are looking forward to develop alternative energy technologies that are more environmentally sound and renewable (Bang et al., 2000). Nowadays, worldwide power generation is responsible for more pollution than any other single activity (Dunn, 1997). However according to Farhar (1996), the humanity is beginning to recognize the link between energy use and environmental degradation.

In the last few years a steady growth in the share of renewables for the electricity generation, heat, and fuel production was achieved. In respect to the electricity generation, renewables fall into two major categories: hydropower and new renewables (Renewables 2015 Global Status Report, 2015). The rapid growth of global electricity generation from renewable energy sources at the end of 2014 accounted for 16.6% and 6.2% respectively for hydropower and other renewables (Renewables 2015 Global Status Report, 2015). The other renewable on the other hand can be wind and solar power, bio-power, geothermal power and ocean (tidal) power (Twidell and Weir, 2006; Natural Resources Canada – Government of Canada, 2015). The wind and sun are the most important sources for electricity generation on a global scale due to their unlimited
quantity and environmentally friendly nature. Only in 2014, the power generated from photovoltaic panels and wind turbines rose respectively by 30% and 16%, thus accounting for almost 65% of the worldwide electricity generation from non-hydro renewable sources of energy (Renewables 2015 Global Status Report 2015).

Unfortunately there is a significant drawback of taking advantage from fictitiously unlimited capacity of wind and solar energies for electricity generation. It comes from the fact that, unlike conventional power units, wind and solar power produced varies over time and weather conditions. The power supply from those sources is out-of-control and greatly unpredictable (Ambec and Crampes, 2010). It depends on weather conditions that are hardly forecasted more than five days ahead (Baranes et al., 2014). The intermittency of electricity supplied from windmills and solar photovoltaic panels makes power dispatch even more challenging, because such a power cannot be introduced to the electrical grid without smoothing. For example a high perforation of wind power, caused by the nature of wind uncertainty raises a system instability. The integration of an energy storage system (ESS) is one of the best solutions to assure the stability and power quality of an energy system with facilitating perforation of distributed wind and solar resources (Sahithi and Madhusudhan Rao, 2015). Nowadays, a number of new and promising methods based on old concepts, or completely new ideas have been proposed. Some of the most important energy storage methods available or under development today for renewable-based power plants include supercapacitors and flywheels, pumped hydro, compressed air storage, hydrogen storage or rechargeable and redox flow batteries
(Hadjipaschalis et al., 2009). Of these technologies, the only commercially proven large scale and currently the most cost effective technique in means of storing large amounts of electrical energy on an operating basis is pumped hydro, but unfortunately the capital costs and the presence of appropriate geography are critical drawback factors (Deane et al., 2010). In a mid- to long-term the use of hydrogen as an energy carrier is considered as the most promising method, as the hydrogen systems can provide viable, sustainable options for meeting the world's energy requirements (Elam et al., 2003). The hydrogen-based electricity production includes as a first step conversion of surplus electricity to hydrogen by electrolysis. The next stage is storage of the produced hydrogen as compressed gas or cryogenic liquid in physical storage systems, or solid-state storage systems based on chemical or physical binding of hydrogen to a solid material, which can potentially store more hydrogen per unit volume (Momirlan and Veziroglu, 2005). Yet, the main challenge in hydrogen-based energy production is the conversion of the stored hydrogen back to electricity in a time-controlled manner, cause of the absence of well-established, reliable H₂-to-electricity conversion technology (Karamanev, 2012). A schematic diagram of electricity-hydrogen-electricity conversion is shown at Figure 1.1.
Three alternative routes in wind and solar plants are currently in use to achieve a balance between demand and supply: (1) Methanation of the produced renewable power hydrogen with CO$_2$ and subsequent feed-in of the renewable power methane into the natural gas grid; (2) Direct feed-in of H$_2$ into the natural gas grid with regard to the maximum allowable H$_2$ concentration; (3) Use of hydrogen from renewable power in a dedicated infrastructure for applications which require hydrogen, i.e. fuel-cell-based processes (Schiebahn et al., 2015). Significant drawback of the first two methods are the low efficiency, increased maintenance cost and decreased life of the equipment. Moreover, in some cases burning the NG-H$_2$ mixture in turbines causes higher emissions of pollutants like SO$_2$ and NO$_x$ (Barnes and Levine, 2011; Gahleitner, 2013).
In the third scenario the hydrogen is used as an intermediate fuel. In such a case the fuel cells are widely regarded as a key solution for H₂-to-electricity conversion systems. However, this technology involves significant scientific, technological and socioeconomic barriers to the commercialization of hydrogen and fuel cells as clean energy technologies of the future. The main obstacles associated with fuel cells that must be overcome are the high cost and the short life cycle (Edwards et al., 2008). It comes mainly from the fact that it is almost impossible to run a conventional fuel cell with non- or low-platinum electrocatalyst due to the extremely slow oxygen reduction reaction (Shao, 2013). The solution is to increase significantly the latter process.

The BioGenerator is the first biologically based H₂-to-electricity conversion system. It is a promising alternative of the conventional fuel cells, capable to generate successfully power densities over 1800 W∙m⁻² on a laboratory scale (Karamanev et al. 2013). The BioGenerator is a microbial hydrogen redox flow fuel cell, in the cathode of which the oxygen reduction is replaced with the reduction of ferric ions which are continuously regenerated by aerobic oxidation of special types of chemolithoautotrophic and/or mixotrophic microorganisms such as *Leptospirillum* genus, *Ferroplasma* genus, *Sulfobacillus* genus, *Alicyclobacillus*, and any combination between them (Hojjati et al., 2013). Moreover the electrical generation is coupled with the consumption of carbon dioxide from atmosphere and its transformation to single-cell protein into microbial cells. In such a case the use of any noble metal catalyst in the cathodic reaction is avoided thus overcoming the high price as a main obstacle at the commercialization of the fuel cells
(Neef, 2009). The inimitable design of the BioGenerator makes it suitable for stationary applications for smoothing the output of wind and solar power plants. In the light of the above the BioGenerator seems to offer a sustainable and cost effective solution of the problems associated with the conventional fuel cells. However, the bottleneck in the course of commercialization of this technology is to minimize even further the energy losses of the system. It is unacceptable to generate electricity having high energy losses. The major energy input, consequently losses of energy are due to the regeneration of the oxidant, ferric ions in the bioreactor. Supplying the iron oxidizing microorganisms with substrates, necessary for their normal functioning is performed in a bioreactor, where the oxygen and carbon dioxide are introduced with air in order to secure suitable conditions for proper functioning of the microorganisms. That is how the suitable environment for functioning of the microorganisms is created. Introduction of air to the bioreactor by aeration is indeed the most energy-consuming process of the entire BioGenerator. Therefore optimization of the operating conditions in the bioreactor is necessary in order to minimize the energy requirements of the BioGenerator.

1.2 Objectives

In light of the above findings, the main objectives of this work are:

1. To examine the volumetric liquid-phase oxygen mass-transfer coefficient in a rectangular, split-vessel air-lift reactor (ALR), to be used in the BioGenerator that meets the unique requirements of this system.
2. To study the effects of different gas distributors on the volumetric mass transfer coefficient, considering the net energy input and the subsequent energy produced from the BioGenerator.

3. To study the hydrodynamic characteristics, such as the gas holdup and the liquid circulation time and their effect on the performance characteristics of ALR, respectively the BioGenerator.

1.3 Thesis Outline

Based on the objectives, this thesis is presented in the following chapters as follows:

Chapter 1 is an introduction. It discusses background of the work, and outlines the objectives of the present study.

Chapter 2 introduces the BioGenerator by discussing its fundamentals, constitutive components, and involved reactions, and further describes the fundamentals of bioreactor. Following that, different types of bioreactors are reviewed and appropriate type is chosen. At the end, methods for determination of volumetric oxygen mass-transfer coefficient are briefly assessed.

Chapter 3 describes the materials and methods of fabrication, different measurements and the set up used in the development as well as study of the volumetric oxygen mass-transfer coefficient and other important characteristics of the bioreactor.
Chapter 4 shows the results obtained in this study. It starts with analysing the influence of a stepwise change of non-aerated-to-aerated cross-sectional areas ratio on the volumetric oxygen mass-transfer coefficient, gas holdup, liquid velocity, and mean liquid circulation time. Appropriate approach for determination of the volumetric oxygen mass-transfer coefficient by investigating the effect of mixing in the bioreactor by measuring levels of dissolved oxygen in the transverse to velocity vector planes in the system was considered in that case. In addition, it discusses the effect from decreased liquid level in the system on volumetric oxygen mass-transfer coefficient obtained. Finally, in this chapter the effect of using different aerating devices on the hydrodynamic characteristics and energy performance of BioGenerator are discussed.

Chapter 5 summarizes the conclusions obtained in this study and by providing recommendations, directs the reader towards future research on the development of bioreactor for the purposes of BioGenerator.
Chapter 2

2 Background and Literature Review

2.1 Ferrous Iron Biooxidation – Principles and Applications

As stated in the Introduction, replacing the oxygen at the cathode reaction with ferric ions and their subsequent regeneration by iron oxidizing microorganisms is the main idea behind the BioGenerator. The ferrous iron biooxidation (FIB) agents, known better as iron oxidizing microorganisms (IOMs) comprise a diverse group of prokaryotes. Their natural habitats are sites where iron and sulphide-containing minerals are exposed to the atmospheric influence and moisture, such as abandoned and partially flooded coal or sulphide ore mines, mine tailings (waste from the mining process) unless in extremely arid climate (Johnson and Hallberg, 2003). However, the process was not recognized as microbial until the middle of the 20th century when a small rod-shaped Gram-negative bacterium was discovered in the acid mine drainages (AMD) and linked to the leaching of the sulphide minerals. The microorganism was called Ferrobacillus ferrooxidans, synonymous with Thiobacillus ferrooxidans (Silverman and Lundgren, 1959), and recently reclassified as Acidithiobacillus (At.) ferrooxidans in the year 2000 (Kelly and Wood 2000). Long time after its discovery At. ferrooxidans was widely considered the most important IOM. However, lately attention has been shifted to other IOMs, i.e. the bacteria of genus Leptospirillum (Rawlings et al., 1999) and archaea from the genus Ferroplasma. The reason is that the sulphide minerals undergo slow abiotic oxidation, accompanied by acidification of the site once exposed to the atmospheric moisture and
oxygen. The conditions for growth of chemolithotrophic microorganisms arise with the drop of abiotic chemical oxidation rate when the pH drops below 4-3 (Johnson and Hallberg 2003; Rohwerder et al., 2003). That is, why microorganisms, tolerating lower pH are preferable. They obtain the necessary energy for their growth in the form of electrons from biooxidation of the ferrous iron (Eq. 2.1) and oxidation of various inorganic sulphur compound, such as thiosulfate (Eq. 2.2):

\[ 2Fe^{2+} + 0.5O_2 + 2H^+ \rightarrow 2Fe^{3+} + H_2O \]  
\[ S_2O_3^{2-} + 2O_2 + H_2O \rightarrow 2H^+ + 2SO_4^{2-} \]  

The process was used at the second century BC by Chinese, and a few centuries later by Romans for extraction of dissolved by microorganisms copper from AMDs using chemical reduction of the copper ion with metallic iron (Ehrlich et al., 2001). The process is known as “cementation”, and is still one of the most important biohydrometalurgical¹ methods for extraction of metals from low grade ores. The method can be used successfully for pre-treatment of precious metal ores (Olson et al., 2003), desulphurization of coal and treatment of H₂S gases and AMDs (Jordan et al., 1996;

¹ Biohydrometallurgy is “that branch of biotechnology [which] deals with the study and application of the economic potential of the interactions between the microbial world and the mineral kingdom” (Rossi, 1990).
Nemati et al., 1998). Generally novel potential application of the FIB can be found in the microbial fuel cells (Karamanev et al., 2005). The following section is dedicated to the BioGenerator – an integrated unit, consisting of a fuel cell and a bioreactor for ferrous iron biooxidation.

2.2 Fundamentals of the BioGenerator

2.2.1 Idea

The main idea behind the invention of the BioGenerator was to improve sluggish kinetics associated with the oxygen reduction reaction on the cathode of the most popular proton-exchange membrane (PEM) hydrogen-oxygen fuel cells. Indeed, the BioGenerator uses the capability of microorganisms for sustainable regeneration of oxidants employed at the reduction reaction in fuel cell (Karamanev et al., 2013).

It continuously produces electricity from hydrogen fuel and atmospheric oxygen in a system, consisting of two major units: a fuel cell and a bioreactor. That is, why it is considered the first biologically based system for H2-to-electricity conversion, which has capability to serve as part of the intermediate energy storage in integration of renewable power to electrical grid.

2.2.2 Structure and reactions

Hydrogen fuel enters the anode compartment of the fuel cell of the BioGenerator, where it is electrochemically split into protons and electrons through an electrocatalytic oxidation reaction (Eq. 2.3). Knowing that the electricity is directed flow of electrons,
another reaction that consumes these generated electrons has to be run on the other side of the electrical circuit. The oxidant, ferric ions (Fe\(^{3+}\)) consume these electrons at the cathode and the electromotive force stimulates the anodic reaction to produce more electrons, which increases the electrical current. In other words in the cathode reaction, ferric ions accept electrons on the surface of graphite felt (cathode) and are converted to ferrous ions (Fe\(^{2+}\)) (Eq. 2.4). The formed ferrous ions, are recirculated to the bioreactor with the catholyte (i.e. the solution, which passes through the cathodic compartment), where through a microbial reaction, are oxidized back into ferric ions, thus completing the bioregenerative cycle of the oxidant supply to the fuel cell (Eq. 2.5 and Figure 2.1).

\[
\begin{align*}
H_2(g) &\xrightarrow{\text{Pt cat}} 2H_2O(l) + 2e^- , E^0 = 0 \text{ V vs. SHE} \quad (2.3) \\
2Fe^{3+}_\text{(aq)} + 2e^- &\rightarrow 2Fe^{2+}_\text{(aq)}, E^0 = 0.77 \text{ V vs. SHE} \quad (2.4) \\
2Fe^{2+}_\text{(aq)} + 2H^+_\text{(aq)} + 1/2 O_2(g) &\xrightarrow{\text{IOM}} 2Fe^{3+}_\text{(aq)} + H_2O(l) \quad (2.5)
\end{align*}
\]

The overall reaction of the integrated BioGenerator system results in water formation from oxygen and hydrogen:

\[
H_2(g) + 1/2 O_2(g) \rightarrow 2H_2O(l) \quad (2.6)
\]

where \(E^0\) is the standard oxidation-reduction potential of the reaction, versus the potential of a standard hydrogen electrode (SHE). The real potential is condition dependent.
2.2.3 Bioreactor

According to IUPAC a bioreactor is: “An apparatus used to carry out any kind of bioprocess; examples include fermenter or enzyme reactor.”. In other words any manufactured or engineered device or system that supports a biologically active environment could be named this way. A bioreactor may be a vessel in which a chemical process, which involves organisms or biochemically active substances derived from such organisms is carried out. This process can either be aerobic or anaerobic. In most of the cases these bioreactors are cylindrical, ranging in size from litres to cubic metres. In the case of tissue engineering or biochemical engineering, a bioreactor refers to a device or system meant to grow cells, or tissues in the context of cell culture.
Based on the mode of operation the bioreactors are classified as batch, fed batch or continuous. Organisms growing in bioreactors may be free suspended in liquid medium, or may be attached (immobilized) to the surface of a solid medium. Immobilization can be applied to various types of bioprocesses, including enzymes, cellular organelles, microbial, animal and plant cells (Peinado et al., 2006). It is useful in the cases of continuous modes of operation, since it prevents washing out the microorganisms with the reactor effluent. However, the main limitation of the method is the restricted active surface. Suspension bioreactors can use wider variety of organisms, and can operate at much larger scales than that of immobilized ones. In that case the microorganisms leave the vessel with the effluent flow.

One of the fastest growing type of bioreactors are the air-lift reactors (ALRs). They have been gradually entering the industrial biotechnology and different multiphase chemical processes, because of the improved hydrodynamics and mass transfer performance, comparing to the traditional stirred-tank vessels and bubble columns (Margaritis and Sheppard, 1981; Joshi et al., 1990; Schugerl, 1990; Chang et al., 1994; Fontana et al., 2009). Just like bubble columns they are type of pneumatically agitated reactors (Choi et al., 1996). According to Merchuk (1990) ALRs can be divided in two main types based on their structure: (1) internal loop ALRs, in which pertinent baffles are placed in the reactor, in order to create compartments necessary for circulation, and (2) external loop ALRs, where the circulation pattern is through separate and distinct limbs (Figure 2.2). Further modifications on either type can be performed for purposes of changing direction
of the circulation, extent of gas disengagement from the liquid phase and flow rate of the distinct phases (Margaritis and Sheppard, 1981; Lazarova et al., 1997; Lu et al., 2000). Regardless of the configuration ALRs have four distinct compartments with different flow characteristics, which provide different mass and heat transfer, namely: (1) riser; (2) gas separator; (3) downcomer, and (4) base. Gas is injected at the base of the riser (aerated zone), where it flows mainly upwards, passes through the top of reactor, disengaging the part of the gas and entering the downcomer (non-aerated zone) where it descends to the base. The driving force for the liquid recirculation is the hydrostatic pressure difference between riser and the downcomer, whereas the resisting force is the frictional pressure drop around the flow circuit. However, the main feature that distinguishes an air-lift reactor from a bubble column is the controlled liquid recirculation through a downcomer after partial or total disengagement of the gas at the top of the column, whereas the circulation is induced in the system by permanently injecting gas in the riser, thus creating a net density difference between the riser and downcomer of the reactor. Amongst the advantages that ALRs offer are: simple construction, absence of mechanically moving parts, regular fluid flow, good mass transfer properties, high thermal stability, low energy consumption which determine low building and operation costs (Majeed and Békásy-Molnár, 1995; Couvert et al., 2004; Winterbottom, 2007). Despite of the fact that parameters like geometry, type, architecture of the gas distributor, gas and liquid flow rate can be designed and controlled, another crucial parameters like
interfacial area, gas hold-up or mass transfer coefficient cannot be regulated directly (Vial et al., 2001).

Figure 2.2 Air-lift reactor types

2.2.4 Volumetric oxygen mass transfer coefficient

One of the most important design parameters of ALRs employed in chemical and biochemical applications is gas-liquid oxygen transfer rate (OTR) (Siegel and Merchuk, 1988; Merchuk and Osemberg, 1992; Kilonzo and Margaritis, 2004; Juraščík et al.,
The rate of oxygen transfer from the gas phase to the liquid, the rate at which oxygen is transported into the cells, and the oxygen uptake rate (OUR) by the microorganism for growth, maintenance and production determine the dissolved oxygen concentration in a suspension of aerobic microorganisms. The rate of oxygen consumption by microorganisms in latter processes is high, compared with the solubility of oxygen in the media. That is why any interruption in oxygen supply may affect significantly the process performance, which requires a fairly good estimation of oxygen mass transfer, especially when reactor design improvement and scale-up are considered (García-Ochoa and Gómez, 1998; García-Ochoa et al., 2000; Badino et al., 2001; Çalik et al., 2004; Martin et al., 2004; Puthli et al., 2005; Kocabaş et al., 2006; Liu et al., 2006; Garcia-Ochoa et al. 2010).

The rate of oxygen concentration change in the liquid phase is related to the volumetric mass-transfer coefficient ($k_La$):

$$\frac{dC}{dt} = k_La \cdot (C^* - C) - q_{O_2} \cdot C_X = OTR - OUR$$

where $dC/dt$ is oxygen accumulation rate in the liquid phase, $OTR$ represents the oxygen transfer rate from the gas to the liquid, and $OUR$ is the oxygen uptake rate in the presence of microorganisms; the driving force for the oxygen mass transfer is the difference between $C^*$ and $C$, which are respectively the equilibrium and the available oxygen concentration in the solution; and, $OUR$ can be expressed as the product between the
specific oxygen uptake rate of the microorganisms \( (q_{O_2}) \) and the biomass concentration \( (C_x) \). Several methods, based on chemical, physical or biological principles, have been developed for experimental determination of the oxygen transfer rate in bioreactors (Garcia-Ochoa and Gomez, 2009; Moutafchieva et al., 2013). The first that became adopted were chemical methods, to which belong Sodium sulfite oxidation method (Cooper et al., 1944) and Absorption of CO\(_2\) proposed by Danckwerts and Gillham (1966). However, the most commonly used nowadays methods for oxygen transfer measurement are the physical methods, in particular: Dynamic method (Baird et al., 1993; Nocentini et al., 1993; García-Ochoa and Gómez, 1998; Sanchez et al., 2000; Clarke et al., 2006; Zhang et al., 2006) and Gas phase analysis (Van’t Riet, 1979). Other methods for measuring the volumetric mass transfer coefficient have been also proposed for improvement some aspects of the classical methods, based on chemical (Ortiz-Ochoa et al., 2005; Hill, 2006) or physical principles (Gauthier et al., 1991; Pedersen et al., 1994; Carbajal and Tecante, 2004).

2.3 Summary

Supplying the IOMs with substrate in the bioreactor is a main limiting factor of the entire BioGenerator due to the high amounts of energy necessary to reach the desired aeration rate. Despite numerous studies on hydrodynamic and mass transfer characteristics in different types of ALRs (Chisti et al., 1988; Popovic and Robinson, 1989; Chisti, 1989), very little published information is available on how these parameters are affected with the stepwise change of the downcomer to riser cross-sectional area ratio \( (A_d / A_r) \). For
example, some authors report increasing of the overall gas holdup ($\varepsilon$) and $k_{La}$ with decreasing $A_d/A_r$ (Koide et al., 1983); whereas, others detect the opposite effect (Al-Azzi and Al-Kuffe, 2010; Sanjari et al., 2014). In all previous studies, experiments were performed in concentric draft tube air-lift reactors with limited number of $A_d/A_r$ ratios (maximum of 5), originating from the innate hinders, associated with the cylindrical cross-sectional area. By contrast, ALRs with rectangular cross-section are more versatile, and give better performance characteristics for a given oxygen transfer rate (Merchuk and Gluz, 2002). Moreover big rectangular vessels are usually easier to build than cylindrical reactors (Couvert et al., 1999; Petersen and Margaritis, 2001). However, even less attention has been paid for the change of the $k_{La}$ and hydrodynamic characteristics with stepwise change of $A_d/A_r$ ratio of rectangular ALRs. Some of the works published are from Gourich et al., 2006; Siegel and Merchuk, 1988; Tobajas et al., 1999, where the maximum ratios used were even less (maximum of 3).

In light of the above findings, the aim of this work is to examine the changes of the volumetric liquid-phase mass-transfer coefficient of oxygen in a rectangular, split-vessel ALR with gradually changing of the downcomer to riser cross-sectional area ratio at different aeration flow rates using the dynamic (“gas on, gas off”) method. The effects of different gas distributors on the volumetric mass transfer coefficient, considering the net energy input, and hydrodynamic characteristics, such as the gas holdup and the liquid circulation time were determined.
3 Materials and Methods

In the present study, the following design parameters of the air-lift reactor were held constant: (1) reactor length, width and height; (2) partition board height and distance from the reactor base, i.e. bottom clearance; (3) air distributor position and height from the reactor base for a constant ungassed liquid height; (4) liquid height above the partition board ($h_l$), except for the case when $h_l$ was the examined parameter. The following parameters were varied in the study of the performance characteristics of the air-lift reactor: (1) ratio of the riser to downcomer areas ($A_d/A_r$); (2) liquid circulation path within the air-lift reactor; (3) horizontal position of the dissolved oxygen (DO) probe; (4) type of the gas-distributor and the orifice size of the air jets ($d_o$).

3.1 Reactor

The reactor consisted of a poly(methyl methacrylate) (acrylic glass) column (17 mm wall thickness) with a rectangular cross-section, flat bottom and a total volume of 0.202 m³ (0.300×0.273×2.470 m) (Figure 3.1). Two circular flanges (0.14 m diameter) were situated on the two opposite walls at 0.110 m from the bottom to their central axes for servicing the bottom compartment of the reactor, where the gas distributor was fixed. Through a drilled hole in one of the flanges a flexible tube providing gas for the distributor was inserted.
A partition board made of acrylic glass (0.011×0.273×1.242 m) was fixed in the reactor in order to separate the column into aerated and non-aerated compartments. The support for the partition board was secured by six threaded rods made by 316L grade stainless steel screwed in threaded holes drilled in the board (Figure 3.1 B). Thus, different positions of the partition board with respect to the vertical walls (different \( A_d/A_r \) ratios) were achieved by screwing (unscrewing) the rods in different directions into the partition board. The rods were equipped with rubber bushes at each end for a tight grip to the reactor walls to assure the vertical position of the baffle in the reactor. This way riser-to-downcomer ratios of 0.2 to 5.0 were achieved (Table 3.1). Separate ports were drilled for the dissolved oxygen (DO) probe and two pairs of platinum electrodes (1.20 m apart) in the reactor wall on the downcomer side of the reactor.

All experiments were carried out with deionized (DI) water at room temperature and atmospheric pressure. A static liquid height of 1.44 m, which gives liquid volume of 114.4 L, was chosen for all the experiments except for one, in which it was decreased to 1.39 m (113.6 L) in order to observe the change in \( k_{La} \) with decreasing the liquid headspace to 0.05 m above the partition board.
Figure 3.1 Schematic diagram of the rectangular air-lift reactor, used in the experiment:

(1) column; (2) partition board; (3) gas distributor; (4) manometer; (5) filter; (6) rotameter; (7) valves; (8) DO probe; (9) Pt-electrodes; (10) threated rod

The distance from the bottom of the reactor to the lower end of the partition board (base) was chosen to be 0.1 m, the same as the distance from the top of the partition board to the static liquid height level (Chisti, 1989) for all the experiments, except one in which the headspace was decreased to 0.05 m, as it was taken into account that at the vast majority of air-lift designs the bottom connection zone between the riser and downcomer is very simple and usually not considered to significantly affect the overall reactor behavior (Merchuk et al. 1996). However, the design of this section can influence gas holdup, liquid velocity and if applicable- solid phase flow.
Table 3.1 Gas distributor types and $Ad/Ar$ ratios used at the experiment

<table>
<thead>
<tr>
<th>Test no.</th>
<th>Gas distributor type</th>
<th>Orifice characteristics</th>
<th>$Ad/Ar$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>$A_d/A_r$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Count</td>
<td>diameter /mm</td>
</tr>
<tr>
<td>1 to 7</td>
<td>Perforated tube 5 rows</td>
<td>200</td>
<td>2</td>
</tr>
<tr>
<td>8</td>
<td>Perforated tube 4 rows</td>
<td>160</td>
<td>2</td>
</tr>
<tr>
<td>9</td>
<td>Perforated tube 2 rows</td>
<td>80</td>
<td>2</td>
</tr>
<tr>
<td>10</td>
<td>Perforated tube 1 row</td>
<td>40</td>
<td>2</td>
</tr>
<tr>
<td>11</td>
<td>Perforated tube 2 rows</td>
<td>80</td>
<td>1</td>
</tr>
<tr>
<td>12</td>
<td>Finely perforated rubber tube</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>13</td>
<td>Aeos™ ePTFE Zeus® Industrial Products</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

3.2 Gas Distributors

Several different gas distributors were tested in order to find the optimal ratio between the oxygen mass transfer coefficient $k_{La}$ and the power necessary to overcome the pressure losses in each case. Two were soft porous tubes: (1) finely perforated rubber tube distributor (Marineland Aquarium Products) (Figure 3.2), and (2) Aeos™ ePTFE Extruded Special tube, with internal diameter of 0.511+/-0.039, wall thickness of
0.045+/–0.005, and microporous structure (average area of the pores 6 μm²), made by expanded polytetrafluoroethylene (PTFE) with 0.28g/cm³ density and 90% porosity by Zeus® Industrial Products, Inc. (Orangeburg, USA) (Figure 3.3).

![SEM image of a finely perforated rubber tube distributor (Marineland Aquarium Products)](image)

**Figure 3.2** SEM image of a finely perforated rubber tube distributor (Marineland Aquarium Products)

The five other distributors were made from rigid PTFE tubes with internal diameter of 5/8" and a wall thickness of 1/16". The length of the gas distributors was chosen 230 mm in order to take up as much of the riser length as it is possible, and the external diameter was selected the way it fits at the riser compartment, when minimum Ar was used (see Section 3.1). One row of orifices (2.0 mm diameter, do) with inter-orifice distance of 5.0 mm were drilled at the first one. The number of orifices (no) was 40. The second distributor had two rows orifices with the same geometry and dimensions as the first one, angle of 44° between the rows and no of 80. The third gas distributor had two rows of
orifices with $d_o$ of 1 mm at a distance of 5 mm between them and the same angle of 44° between the rows giving the total number of 80 jets. The last two types of gas distributors used were respectively with four and five rows orifices with $d_o = 2$ mm with 5 mm distance between the orifices and 44° angle between the rows, assuring a total of 160 and 200 gas jets (Figure 3.4). All the parameters for the used gas distributors are shown in Table 3.1.

PTFE was chosen as gas distributors’ material due to its excellent chemical and biofouling resistance. The diameter of the rigid gas distributors, the diameter of the orifices and the distance between them were based on a preliminary study (Pupkevich, 2014).
3.3 Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy (SEM) was the technique used to produce high-resolution images of a surface of the porous materials used as gas distributors in this study. In SEM technique the high-powered indirect microscope produces an image by bombarding a sample with a beam of high-energy electrons. Signals are generated as a result of sample-electrons interactions containing useful information about the microstructure, surface morphology orientation of constitutive materials and chemical compositions of the sample. This information includes surface morphology, chemical composition, orientation of constitutive materials and chemical compositions (Egerton, 2005). Figure 3.5 shows how a scanning electron microscope works.
Figure 3.5 Scheme of an electron scanning microscope (SEM) (based on Schweitzer n.d.)

SEM can be used to obtain meaningful information about the size of the pores and their distribution at the aerating device. In this study, samples were cut in small (0.5 cm$^2$) pieces, and after being coated by gold, were analyzed using a LEO Zeiss1540XB FIB/SEM equipment.

3.4 Dissolved oxygen measurement

The dynamic method based on the dissolved oxygen (DO) measurement was chosen for the determination of the $k_{La}$. As a part of physical methods it employs the response of oxygen probe to concentration changes of the dispersed gas in the medium, under non-stationary conditions. These methods are the most commonly used nowadays for
estimation of oxygen transfer, as they are based on the measurement of dissolved oxygen concentration in the liquid during its absorption or desorption in the solution. The technique is very convenient for analyzing the influence of operational conditions on the volumetric mass transfer coefficient, and is well described in the literature (Baird et al., 1993; Nocentini et al., 1993; Benyahia and Jones, 1997; García-Ochoa and Gómez, 1998; Tobajas and García-Calvo, 2000; Sanchez et al., 2000; Clarke et al., 2006; Zhang et al., 2006). The method consists of continuous measurement of the dissolved oxygen concentration during its absorption or desorption in the aqueous solution after a step change in the concentration in the inlet gas (Garcia-Ochoa and Gomez, 2009). (1) The dynamic technique of desorption includes supplying air in the reactor until the oxygen saturation concentration in the liquid for the certain conditions is reached. At the next stage, nitrogen is introduced downwards into the vessel and the decrease of dissolved oxygen concentration is recorded as a function of time.

(2) The dynamic technique of absorption was used in this study. It incorporates the elimination of oxygen from the liquid phase of the reactor, for example by bubbling nitrogen or by the addition of sodium sulfite, until the oxygen concentration in the solution reaches zero. At the next step, the liquid is put again in contact with air, and the increase of the oxygen concentration is measured in time as shown in Figure 3.6.
Figure 3.6 Schematic diagram, illustrating the change of oxygen concentration in time when applying the dynamic method of absorption.

The experiments in the present work were conducted using DI water in the absence of microorganisms. In such cases, biochemical reactions do not take place and the Oxygen Uptake Rate (OUR) expressed by the last term of Eq. (2.7) is equal to zero, and the oxygen accumulation rate in the liquid phase - $dC/dt$ is represented only by the Oxygen Transfer Rate (OTR):

$$
\frac{dC}{dt} = k_L a \cdot (C^* - C) = OTR
$$

(3.1)

At the start of each measurement, nitrogen gas was bubbled through the liquid until the oxygen concentration decreased to a reasonable minimum, usually 5-10% of saturation oxygen concentration. Then, the liquid was put in contact with air bubbles, and the variation (increase) of the oxygen concentration was measured as a function of time.
Seven geometric configurations (i.e. $A_d/A_r$ ratios) were used: 0.2, 0.33, 0.5, 1.0, 2.0, 3.0 and 5.0, each at five different air flow-rates (1.2, 3.0, 3.9, 4.8 and 6.0 m$^3$/h), giving the total number of 35 sets (Table 3.1, test nos. 1-7). The five air-flow rates correspond to aeration rates of 0.18, 0.44, 0.57, 0.70 and 0.87 VVM (volume air per volume liquid per minute), or expressed as effective superficial gas velocity ($U_G$): 0.004, 0.011, 0.014, 0.017 and 0.021 m/s, calculated on the basis of the total reactor cross-sectional area. DO measurements with the gas distributor consisting of five rows of orifices (see Table 3.1) were performed with the orifices facing upwards and also, by flipping the distributor, with the orifices facing downwards. The experiments with all other perforated tube distributors were performed with the orifices facing downwards for all the latter range of gas flow rates, using $A_d/A_r$ of 2.0 since highest values of $k_{La}$ were obtained for that ratio. The experiments with the porous type gas distributors were performed at the same $A_d/A_r$ ratio of 2.0. The concentration of the dissolved oxygen in the liquid phase was measured by an Orion 3 Star DO Benchtop meter (Thermo Fischer Scientific, Waltham MA, USA) equipped with Orion 081010MD oxygen probe (Figure 3.7). The analog signal was digitalized and registered by Star Plus Navigator® software. The oxygen probe was inserted horizontally at 1.1 m from the bottom of the reactor in the downcomer, giving the response to concentration changes of the dispersed gas in the liquid medium, under non-stationary conditions (see Figure 3.1). For each $A_d/A_r$ ratio, three different horizontal positions of the DO probe, relative to the distance between the reactor wall and the
partition board in the downcomer, were used: at the reactor wall, 1/4 in, and at the midpoint (1/2 in) between the reactor wall and the partition board.

![Orion 3 Star DO Benchtop meter](image)

**Figure 3.7** Orion 3 Star DO Benchtop meter, equipped with Orion 081010MD oxygen probe

The filling solution of the probe was replaced and the probe was calibrated before every set of the experiment.

### 3.5 Determination of $k_{La}$

The oxygen concentration was recorded as a function of time, and Eq. (2.7) was used after integration:

$$\ln(C^* - C) = -k_{La} \cdot t$$  \hfill (3.2)
The change of the DO concentration in the liquid as a function of time was plotted, and the maximum saturation concentration of DO \( (C^*) \) was determined from the graph (see Figure 3.6). The slope of the \( \ln (C^* - C) \) vs. time relationship was used for \( k_{La} \) calculation (Figure 3.8).

**Figure 3.8** Schematic diagram of determination the volumetric oxygen mass transfer coefficient

Moreover, for accurate determination of oxygen concentration values the response time of the electrode, \( \tau_r \) was also considered as it is a critical parameter. The response affects the correct determination of the mass transfer coefficient if the characteristic time for the oxygen transport, \( (1/ k_{La}) \), is of the same order than the response time of the electrode. For the correct estimation of \( k_{La} \), the response time of the electrode (\( \tau_r \)) was determined from the time necessary to reach 63% of the final value measured when exposed to a step change of concentration, by switching it from a solution with zero oxygen concentration
(1g sodium sulfite and 50 µl cobalt nitrate, as a catalyst in 100 ml of water) to 100% oxygen saturated solution (Van’t Riet, 1979). It was found that the characteristic time of the probe was less than 7 s, and therefore $\tau_r << (1/ k_{La})$, in such a case according to Garcia-Ochoa and Gomez (2009) no correction in the response model was needed. However, in order to avoid any errors due to the response time of the electrode the first measurement of the DO was registered 30 s after the start of the gassing. For the same purpose the last 5% of each run was truncated as the error of the difference $C^* - C$ (from which $k_{La}$ was obtained) became very large at values of $C$ very close to $C^*$.

### 3.6 Gas Holdup Measurement

By definition the gas holdup, known also as gas void fraction is the volume fraction of gas-phase in the gas-liquid (or slurry) dispersion. The overall gas holdup ($\varepsilon$) refers to the reactor as a whole:

$$\varepsilon = \frac{V_G}{V_G + V_L} \quad \text{(3.3)}$$

where $V_G$ and $V_L$ are, respectively, the volumes of the gas and liquid (or slurry) in the reactor. In air-lift reactors, the individual riser and downcomer gas holdups, $\varepsilon_r$ and $\varepsilon_d$, respectively, can be identified individually and related to the overall holdup.

An inverted U-tube manometer was used for calculating the gas hold-up in the riser ($\varepsilon_r$) of the air-lift reactor by measuring the pressure difference between two points situated at 1.1 m apart (Figure 3.9).
From there $\varepsilon_r$ was calculated, using that:

$$p_2 - p_1 = \rho_D \cdot g \cdot \delta$$  \hspace{1cm} (3.4)

But,

$$p_1 = \rho_M \cdot g \cdot h_1 + p_M$$  \hspace{1cm} (3.5)

And

$$p_2 = \rho_M \cdot g \cdot h_2 + p_M$$  \hspace{1cm} (3.6)
Therefore,

\[ p_2 - p_1 = \rho_M \cdot g \cdot (h_2 - h_1) \]  \hspace{1cm} (3.7)

But,

\[ \hat{z} + h_1 = h_2 + \Delta h_M \]  \hspace{1cm} (3.8)

Therefore,

\[ h_2 - h_1 = \hat{z} - \Delta h_M \]  \hspace{1cm} (3.9)

The substitution of Eq. 3.9 in Eq. 3.7 leads to

\[ p_2 - p_1 = \rho_M \cdot g \cdot (\hat{z} - \Delta h_M) \]  \hspace{1cm} (3.10)

Equating Eq. 3.4 and Eq. 3.10 after subsequent rearrangement yields

\[ \rho_D = \frac{\rho_M \cdot (\hat{z} - \Delta h_M)}{\hat{z}} \]  \hspace{1cm} (3.11)

But,

\[ \rho_D = \rho_L \cdot (1 - \varepsilon_r) + \rho_G \cdot \varepsilon_r \]  \hspace{1cm} (3.12)

From Eq. 3.11 and Eq. 3.12 and the fact that \( \rho_M = \rho_L \) follows that:

\[ \varepsilon_r = \frac{\rho_L}{\rho_L - \rho_G} \frac{\Delta h_M}{\hat{z}} \]  \hspace{1cm} (3.13)
where, \( p_1 \) and \( p_2 \) were the pressures at points 1 and 2; \( p_M \) was the gauge pressure of the gas used for the manometer (air at atmospheric pressure); \( g \) - the gravity acceleration; \( \rho_M, \rho_D, \rho_L \) and \( \rho_G \) were consecutively the densities of liquid in the manometer, gas-liquid dispersion inside the reactor, liquid and gas used in the experiment; \( \Delta h_M \) was the difference between the two liquid levels in the inverted U-tube manometer, and \( \hat{z} \) was the distance between the two measurement points.

Because of the difficulties in measuring the gas hold-up in the downcomer (\( \varepsilon_d \)), it was calculated using the fact that typically the height of the gas-liquid dispersion, \( h_D \) is equal at the riser and downcomer:

\[
h_{D, \text{riser}} = h_{D, \text{downcomer}} = h_D
\]  

(3.14)

And from the balance equation for the amount of the gas in the reactor:

\[
\text{Total volume of gas in the reactor} = \text{Volume of the gas in the riser} + \text{Volume of the gas in the downcomer}, \text{ or:}
\]

\[
V_D \cdot \varepsilon = V_{D_r} \cdot \varepsilon_r + V_{D_d} \cdot \varepsilon_d
\]  

(3.15)

Which for reactors with the uniform cross-sections of the riser and the downcomer can be written as:

\[
h_D \cdot (A_r + A_d) \cdot \varepsilon = h_D \cdot A_r \cdot \varepsilon_r + h_D \cdot A_d \cdot \varepsilon_d
\]  

(3.16)
Then the riser and downcomer gas hold-ups, $\varepsilon_r$ and $\varepsilon_d$ were related to the overall holdup by:

$$\varepsilon = \frac{A_r \varepsilon_r + A_d \varepsilon_d}{A_r + A_d} \quad (3.17)$$

### 3.7 Liquid Velocity and Mean Circulation Time

The flow rate of liquid in the downcomer was determined by a tracer technique. A pulse of 0.2 L of saturated sodium chloride solution was poured quickly at the top of the riser. The conductivity was followed at downstream locations by two pairs of Pt-electrodes placed 1.2 m vertically apart in the downcomer. Their signals were recorded simultaneously at a frequency of 10 Hz. Multifunction Data Acquisition (DAQ) NI USB-6000; 10 kS/s; 12-bit resolution and NI-DAQMX software (NI SignalExpress 2014) by National Instruments (Austin, Texas, USA) were used for the data acquisition. The Pt-electrodes, were connected in 2 parallel electrical circuits to external power supply, generating 5V DC. In both of the parallel circuits 2.2 kΩ resistors (R1 and R2) were connected in series and the voltage around each of them was registered from the DAQ (Figure 3.10). Pouring the sodium chloride solution in the reactor induced electrochemical reaction of electrolyte dissociation (Eq. 3.18 and Eq. 3.19) between each pair of electrodes, increasing electrical conductivity at each circuit. An increase of the electrical current between positive and negative electrode of the first pair, and after certain time at the second pair of electrodes was registered by measuring the voltage drop around the resistors.
\[ NaCl_{(s)} \rightarrow NaCl_{(aq)} \tag{3.18} \]

\[ NaCl_{(aq)} \rightarrow Na^+_{(aq)} + Cl^-_{(aq)} \tag{3.19} \]

**Figure 3.10** Scheme of the liquid velocity measurement arrangement

From the difference between the first moments of the two conductivity signals, i.e. triggering of the picks (Figure 3.11), and the distance between the electrodes the liquid velocity in the downcomer \( v_{Ld} \) was calculated:

\[ v_{Ld} = \frac{h_{electrode}}{t_{peaks}} \tag{3.20} \]

where \( h \) represents the distance between two couples of electrodes, and \( t \) is the time between two peaks.
Figure 3.11 Typical response of the Pt-electrodes to pulse input of tracer the air-lift reactor. The red curve corresponds to the signal from the first couple of electrodes, whereas the white shows the respond from the second couple.

The superficial liquid velocity in the riser \((U_{lr})\) and the mean circulation time \((t_c)\) in the reactor were calculated using the relationships:

\[
v_{lr} = v_{ld} \frac{A_d(1 - \varepsilon_d)}{A_r(1 - \varepsilon_r)} \]  \hspace{1cm} (3.21)
\[
v_{lr} = \frac{U_{lr}}{1 - \varepsilon_r} \]  \hspace{1cm} (3.22)
\[ t_c = \frac{L_r}{U_{Lr}} + \frac{L_d}{U_{Ld}} \]  

(3.23)

where \( v_{Lr} \) was the liquid velocity in the riser, \( L_r \) and \( L_d \) were respectively the length of the riser and downcomer.

### 3.8 Error Analysis

To estimate the error of the measurements, used in this study statistical analysis based on the line error were performed after each set of experiments for \( k_{La} \) determination. For the experiments, giving the highest statistical error (highest \( U_{gr} \) used) (see Section 3.4), five repetitive determinations of the measured value were performed at \( A_d/A_r \) of 2.0 while keeping the other parameters of the system constant. This way the error of the method was defined. For correct estimation of the gas holdup, \( \epsilon \) the number six measurements—were performed also at each \( U_{gr} \).

The (sample) standard deviation was calculated using:

\[ s = \sqrt{\frac{1}{N-1} \sum_{i=1}^{N} (x_i - \bar{x})^2} \]  

(3.24)

where \( x_1, x_2, \ldots, x_N \) denote all \( N \) values from a population, and \( \bar{x} \) is the mean of the sample.

Then the standard error was determined by:
Finally the approximate confidence intervals for the mean was calculated:

Upper 95% limit = \( \bar{x} + (SE \cdot 1.96) \), and

Lower 95% limit = \( \bar{x} - (SE \cdot 1.96) \)  

\[
SE_{\bar{x}} = \frac{s}{\sqrt{N}} 
\]  

(3.25)
Chapter 4

4 Results and Discussion

4.1 Outlook

The performance of air-lift reactor is highly dependent on its internal configuration, the type of the aerating device used, consecutively the different gas and liquid flow patterns, physical properties of the gas and liquid, and the operational conditions which determine the reactor hydrodynamic characteristics (Figure 4.1).

![Diagram of oxygen transfer rate (OTR) dependence on volumetric mass transfer coefficient and hydrodynamic parameters in bioreactors.](image)

Figure 4.1 Dependence of oxygen transfer rate (OTR) on volumetric mass transfer coefficient and hydrodynamic parameters in bioreactors (based on Garcia-Ochoa and Gomez, 2009)
In the case of a typical aeration process, the oxygen is transferred from a rising gas bubble to bulk liquid. In absence of biomass the oxygen is transferred from the interior of the bubble and gas film, then it moves across the gas–liquid interface diffuses through the relatively stagnant liquid film surrounding the bubble and finally it is transported to the bulk liquid (Figure 4.2). The liquid film resistance \( \frac{1}{k_L} \) around bubbles usually control the overall transfer rate. The simplest and most used theory for gas–liquid mass transfer is the two film model (Whitman, 1923), describing the flux through gas and liquid film as the product of the driving force by the mass transfer coefficient, according to:

\[
J^o = K_G \cdot (p_G - p^*) = K_L \cdot (C^* - C_L)
\]  

and the oxygen mass transfer rate per unit of reactor volume, \( N_{O2} \), is obtained multiplying the overall flux by the gas–liquid interfacial area per unit of liquid volume, \( a \):

\[
N_{O2} = J^o \cdot a = k_La \cdot (C^* - C_L)
\]  

Because it is difficult to measure \( k_L \) and \( a \) separately, usually the product \( k_La \) is measured and this parameter, called volumetric mass transfer coefficient, characterizes the transport from gas to liquid.

As it was mentioned above the oxygen mass transfer is one of the most important design parameters of gas–liquid (–solid) reactors employed for chemical and biochemical applications, as any scarcity of oxygen may affect significantly the process performance. That is why the correct determination of the oxygen mass transfer coefficient plays
crucial role for reactor design and scale up. An ideal reactor should have an efficient mixing giving a maximum transfer rate, at a minimum energy input (Gaddis, 1999; Gogate and Pandit, 1999; Rainer, 1990). This puts even more significance if one consider the BioGenerator, where the main point is electricity generation. Considering this, the maximum energy efficiency of the bioreactor, accounting for the main energy consumption in the system is essential. In other words, in case that the aim of the system is to produce energy; any undue energy losses bring negative effect on the system performance.

**Figure 4.2** Steps and resistances for oxygen transfer from gas bubble to bulk liquid at the absence of living organisms: (1) transfer from the interior of the bubble and gas film; (2) movement across the gas–liquid interface; (3) diffusion through the relatively stagnant liquid film surrounding the bubble; (4) transport through the bulk liquid
In bioreactor, both the oxidant (O\(_2\)) and liquid (H\(_2\)O) are fluids under standard conditions. The solubility of the oxygen in water is only about 8.4 mg/L at 24\(^\circ\) C. This dissolved oxygen has to be maintained at the maximum level in the bioreactor, where it is consumed during the respiration process of the microorganisms. That brings the necessity of more air bubbles with smaller diameter to be produced at the aerating device, giving higher gas-liquid interfacial area (\(a\)), thus increasing the overall volumetric mass transfer coefficient (\(kL\alpha\)). The latter can be achieved using the huge variety of micro-porous materials developed nowadays. This sounds promising when dealing with big batches of products having high final price (i.e. medicine, food industry). However, there is one big difference; this solution may not be viable in the case of BioGenerator where the energy used for aeration has to be minimized. There is a tradeoff between the performance and energy efficiency. In other words, not all the changes targeted to increase the performance, i.e. the rate of oxygen mass transfer, can enhance the cost price of the product, in this case- electrical energy.

Another factor to be considered for system optimization is the capital cost of the BioGenerator system. It comes from the fact that the BioGenerator requires large volumes of the ALR and non-conventional materials for its components (Pupkevich, 2014). Based on the latter, the rectangular shape of the bioreactor is preferable due to the simplicity of its construction. Although it has some disadvantages originating from the presence of eventual dead zones it suits very well on the specifics of the BioGenerator system. Moreover, such a geometry facilitates servicing and maintenance of the reactor.
Nonetheless, the rectangular shape of the bioreactor gives us practically unlimited number of ratios between aerated and non-aerated compartment of the ALR.

Last but not least, using rectangular vessel reveals one big advantage: in general, the concentric draft tube design differs significantly from the rectangular split vessel one. If one assume that the annular section of the draught tube reactor is the downcomer, one can define the “width” of the downcomer as the distance between the external wall and the draught tube, $W_d$ and the “width” of the riser as the diameter of the draught tube, $W_r$, whereas for the rectangular airlift, the widths of the riser and the downcomer are the distances between the partition board and the opposing external walls of the reactor.

Comparing the ratio of width of downcomer to riser, $W_d/W_r$ for a rectangular split-vessel and a concentric draught tube ALRs shows that for rectangular apparatus $A_d/A_r = W_d/W_r$, which is not the case when using concentric draught tubes, where

$$\frac{A_d}{A_r} = \frac{(W_d+W_r)^2}{W_r^2} - 1.$$  

For example, for $A_d/A_r$ of 5, in the rectangular ALR, $W_d/W_r$ is 5:1. However, for the same $A_d/A_r$ ratio, $W_d/W_r$ for a concentric tube airlift is 1.45:1 as it can be seen from Figure 4.3. From that can be concluded that the at the same $A_d/A_r$ ratio rectangular split vessel ALRs provide wider channel for one of the compartments (i.e. downcomer), than the concentric draught tubes ALRs (Figure 4.4), which helps to avoid the wall effects, and as can be seen further in this chapter improves the mass transfer and hydrodynamic limitations coming from narrowing the downcomer.
Figure 4.3 Relationship between cross-sectional area ratio and the width of the liquid flow channels ratio for rectangular split-vessel and concentric draught tube air-lift reactors with the equal reactor cross-sectional areas.

Figure 4.4 Schematic diagram of the concentric draught tube (left-hand side) and rectangular split-vessel ALRs with equal cross-sectional areas at the same $A_d/A_r$ ratio.
The BioGenerator, in particular, experiences difficulties for assuring sufficient aeration in the bioreactor, necessary for the aerobic respiration of the iron oxidizing microorganisms (IOM) at low energy input. Due to the simplicity and versatility of the latter described construction of the ALR used in this study, oxygen mass transfer, hydrodynamic characteristics, and energy requirements of the system can be extensively investigated.

As mentioned earlier, the main factors on which depend the desired performance of the ALR are: (1) the internal configuration of the air-lift; (2) the type and geometry of the aerating device used; and (3) the energy input into the air-lift. Based on the above, in this chapter, the main goal was to enhance the oxygen mass transfer and minimize the energy losses. Therefore, the following steps and experiments were implemented and comprise the content of this chapter:

- The importance of DO probe placement in the depth of the reactor was examined for correct determination of the $k_{La}$ in the ALR and the factors causing different measurement results were investigated to find the most reliable result.
- The results of the different orientation of the apertures of the aerating device was compared, and the higher $k_{La}$ resulting from the both cases: (1) jets running upwards and (2) jets running upwards was determined.
- The effect of variety of $A_d/A_r$ ratios on $k_{La}$ was explored, and based on that best position of the partition board inside the reactor was established.
• Using the results from the above experiments, an empirical model, describing the system behavior at different flow rates was developed giving the relation between $A_d/A_r$ ratio and $k_{La}$ for each case.

• The influence of the decreased liquid headspace above the partition board was estimated.

• Comparison of different types of aerating devices was performed based on the aeration rates achieved; further the pressure drop of each of the aerating devices was measured and compared with the corresponding aeration rate in order to find the best solution for the studied system.

• The dependence of the gas holdup- $\varepsilon$ on $k_{La}$ was studied.

• In order to better understand the hydrodynamic behavior of the system, the obtained results for $k_{La}$ were compared with the liquid circulation times for $A_d/A_r$ ratios used.

4.2 Influence of the DO Probe Position on $k_{La}$ Determination

Considering that the volumetric mass transfer coefficient is a global characteristic of the reactor, its determination should be independent on the position of the DO probe. However, the data presented in Figure 4.5 shows clear dependence of measured $k_{La}$ value on the position of the DO probe relative to the width of the downcomer. The effect can be seen in all cases, but is most obvious at the lower aeration rates used (1.2, 3.0 and 3.9 m$^3$/h). This difference was found to be most prominent for the value of $A_d/A_r$ of 2.0 for
each position of the DO probe, whereas the difference between the results obtained at all the three different positions of the probe was found to diminish at the lower $A_d/A_r$ ratios (left hand side of Figure 4.5). The latter behavior could be explained with the different flow regimes that occurred at the adjacent vertical planes of the downcomer, more distinctly with increasing of the downcomer cross-sectional area. It can be deduced that there is insufficient mixing in the downcomer, particularly near the walls of the reactor, and attention should be paid when comparing $k_{La}$ results for different systems and/or conditions. Assuming that best mixing is achieved in the zones farthest from the walls of the non-aerated compartment, in the following sections we have considered only the $k_{La}$ measured at the center (“1/2 in”) of the downcomer. Thus the better mixing at the areas close to the geometrical center of the non-aerated compartment was defined, comparing to the areas closer to the walls due to different liquid flow formations (e.g. swirls and eddies) away from the center. To estimate the error of the method, six experiments at $Q_G = 6$ m$^3$/h and $A_d/A_r = 2.0$ were performed, giving a standard deviation ($s$) of 11.8%, with a 95%-confidence interval of +/-10.4%.
Figure 4.5 Typical response of the DO probe, inserted at different horizontal positions in the downcomer with the gradually change of the $A_d/A_r$ ratio at 4.8 m$^3$/h (0.017VVM) using an aerating device with 200 orifices, (a) for the orifices facing upwards, (b) for the orifices facing downwards
4.3 Effect of the $A_d/A_r$ Ratio on $k_L a$

The influence of $A_d/A_r$ ratio on the volumetric mass-transfer coefficient was observed with gradual change the proportion of non-aerated to aerated compartment of the reactor. In contrast to previous works reporting a limited number of $A_d/A_r$ ratios (maximum 5) using concentric draught tube ALR (Al-Azzi and Al-Kuffe, 2010; Chisti et al., 1988; Onken and Weiland, 1980), the design of our reactor allowed virtually unlimited number of $A_d/A_r$ ratios giving the complete picture for the effect of that parameter (see Section 4.1). A maximum of nine $A_d/A_r$ ratios were used in this work, spanning between 0.2 and 5.0. Summarized information about change of the $k_L a$ with $A_d/A_r$ ratio for the different values of $U_G$ is given in Figure 4.6. Additional confirmation for the influence of $A_d/A_r$ ratio can be observed at Figure 4.5 and Figure 4.7. It can be seen that systematically higher values of $k_L a$ were obtained at $A_d/A_r$ of 0.5 and 2.0 with a distinct maximum at $A_d/A_r = 2.0$ for all values of $U_G$ used. This finding contradicts the results obtained by Tobajas, Siegel, and Apitz (1999), that the downcomer to riser cross-sectional area ratio exhibits only a slight influence on $k_L a$. However, in the latter study experiments were conducted over a limited range of downcomer to riser cross-sectional area ratios ($A_d/A_r = 0.65$ to 1.0), using concentric draught tube ALR which does not describe completely the behavior of system used.
Figure 4.6 Variations of the oxygen mass-transfer coefficient at the same position of the probe with the change of the non-aerated to aerated surface areas ratio at the different superficial gas velocities in the riser using an aerating device with 200 orifices, (a) for the orifices facing upwards, (b) for the orifices facing downwards.
4.4 Effect of the Orifices Orientation of the Aerating Device on $k_{La}$

In some industrial reactors the orifices of the aerating device are facing downwards in order to avoid filling the aerating device with liquid, which may affect the gas bubble distribution. For that reason we compared the characteristics of the air-lift reactor when the aeration orifices were facing upwards and downwards. Figure 4.5, 4.6 and 4.7 show that in the case of the gas distributor with orifices facing downwards the resulting values for $k_{La}$ were about 13% higher than when the orifices face upwards, for the whole range of the air flow-rates used. The maximum $k_{La}$ obtained was 146 h$^{-1}$, as shown at Figure 4.6-b, for orifices facing downwards at $A_d/A_r = 2$. The higher $k_{La}$, obtained with the aerating device with orifices facing downwards could be explained by better mixing at the dead zones around the bottom corners of the reactor. In this case, the air-jets formed at the aerating device are running downwards, and with increasing $U_G$ the mixing improves. That is why the results for the $k_{La}$ obtained with this type of aerating device with orifices facing downwards were chosen to compare with other types of aerating devices in the following experiments.
Figure 4.7 Variations of the volumetric mass transfer coefficient with changing the superficial gas velocity in the riser at five different overall gas velocities

4.5 Effect of the Liquid Level Above the Partition Board on $k_{La}$

Figure 4.8 shows the $k_{La}$ values obtained when the liquid headspace above the partition board- $h_l$ was lowered by 5 cm when all other parameters of the system were kept constant. It can be clearly seen that $k_{La}$ is lower at the lower $h_l$, whereas the difference between the values rises at the higher $U_{Gr}$ used, and it is almost twice higher at the highest $U_{Gr}$ value, which confirms the results obtained by (Chisti, 1989). Based on the results the liquid height of 10 cm above the partition board was chosen for the rest of the experiments.
Figure 4.8 Comparison between the results for oxygen mass-transfer coefficient obtained at different liquid headspace above the partition board

4.6 Empirical Correlations for $k_L a$

Figure 4.9 shows the results for $k_L a$ as a function of $U_G$ with the stepwise change of $A_d/A_r$ ratio. The equation that describes the behavior of the system for any the $A_d/A_r$ ratio was postulated to be:

$$k_L a = \alpha \cdot U_G^\beta$$  \hspace{1cm} (4.3)

where the coefficient $\alpha$ was determined to be between 2.67 and 7.89 at different $A_d/A_r$ ratios, and the value for $\beta$ was found to be constant at 1.33±0.02. From Figure 4.9 the relation between the apparent coefficient $\alpha$ and $A_d/A_r$ ratio can be obtained. Two main cases appear with changing the geometry of the air-lift reactor: (1) in the case of $A_d/A_r \leq 1$, $\alpha$ appears to be constant at 5.912 with standard error of 12%, whereas at (2) $A_d/A_r > 1$,
\( \alpha \) gradually decreases. There is an apparent discontinuity at \( k_L \alpha \) as a function of \( A_d/A_r \). That discontinuity can be explained with the role of the riser and downcomer in the main mass-transfer process with changing the \( A_d/A_r \) ratio. In the case of \( A_d/A_r \leq 1 \) the residence time of the gas-liquid dispersion in the riser is higher than in the downcomer. In addition, the higher number of the air bubbles in the riser provides higher contact surface between the gas and the liquid phase. That is why the main mixing, and therefore the main mass-transfer process takes place in the riser. In such cases the \( A_d/A_r \) ratio does not have strong impact on \( k_L \alpha \) and the air-lift reactor behaves more as a bubble column (left hand-side of Figure 4.10). In the second case, \( A_d/A_r > 1 \) the higher liquid velocity in the riser implies shorter contact time between the gas bubbles and the liquid, which results in the more significant mass-transfer in the downcomer. Thus, at \( A_d/A_r > 1 \) there is a strong influence of \( A_d/A_r \) ratio on \( k_L \alpha \), which can be seen at the right-hand side of Figure 4.10.

Considering the difference in the two distinct regimes that occur at \( A_d/A_r \leq 1 \) and \( A_d/A_r > 1 \), two relations describe the behavior of the system at every \( A_d/A_r \) ratio. The final model of the system is shown in Eq. (4.4).
Figure 4.9 Variations of the oxygen mass-transfer coefficient with the change of effective superficial gas velocity for the different $A_d/A_r$ ratios

Considering the difference in the two distinct regimes that occur at $A_d/A_r \leq 1$ and $A_d/A_r > 1$, two relations describe the behavior of the system at every $A_d/A_r$ ratio. The final model of the system is shown in Eq. (4.4).

$$k_La = \begin{cases} 
\alpha \cdot U_G^\beta, & \text{for } \frac{A_d}{A_r} \leq 1 \\
\alpha' \cdot U_G^\beta' \cdot \left(\frac{A_d}{A_r}\right)^\gamma, & \text{for } \frac{A_d}{A_r} > 1 
\end{cases}$$

(4.4)

where $\alpha = 5.91 \pm 0.74$, $\beta = 1.35 \pm 0.021$

$\alpha' = 6.15 \pm 1.11$, $\beta' = 1.31 \pm 0.037$, $\gamma = -0.474 \pm 0.098$
The predictions of Eq. (4.4) agreed with the measured data within ±13% standard error, or within ±25% (95% CI) (Figure 4.11). Exclusions can be observed for the higher $k_La$ values at $A_d/A_r$ ratio of 5.0 correlated with the equation which are in the zone with high value of the standard error.

**Figure 4.10** Volumetric mass-transfer coefficient as a function of $Ad/Ar$ ratio for the two main cases occurring for the system
Figure 4.11 Predicted (Eq. (4.4)) vs. measured $k_{La}$ for the different $A_d/A_r$ ratios

4.7 Effect of the Different Gas Distributors on the Energy Consumption

Figure 4.12 compares the $k_{La}$ obtained, using different perforated tube gas distributors (see Table 3.1). The $A_d/A_r$ ratio of 2.0 was used for all the sets of experiments. It can be clearly seen that $k_{La}$ increases with the increasing the number of the orifices with the same $d_o = 2$ mm. Comparison of two identical gas distributors with the same number of the orifices and different orifice diameters was also done. About 16% higher values of $k_{La}$ for the device with $d_o = 1$ mm were obtained, compared with the values using the device with $d_o = 2$ mm, yet the pressure losses for the aerating device with $d_o = 1$ mm were found to increase at the same order of magnitude.
Figure 4.12 Variations of the oxygen mass-transfer coefficient with the changing the number of the orifices of the aerating device

Figure 4.13 shows the relation between the theoretical electric power obtained per unit volume, $P_{EL}$, and the total pressure drop, $P_G$ as functions of effective superficial gas velocity, $U_G$. The power obtained per unit volume of the reactor, $P_{EL}$ was calculated as the theoretical electric power per unit volume $V_L$, which could be achieved at reduction of the oxygen supplied with the aerating air to Hybrid Fe(II)/Fe(III) Redox Flow Fuel Cell System (Hojjati et al., 2013), with reversible cell potential $E_r^0 = 0.788$ V. $P_G$ showed the pressure losses for our system using different aerating devices. Three different aerating devices were used in the experiment. The first one was finely perforated rubber tube, the second one was Aeos™ porous tube and the last one was the teflon tube with 200 orifices (see Section 3.2). The $Ad/Ar$ ratio of 2 was chosen (see Section 4.3). Faraday’s law was used to calculate $P_{EL}$:
\[ m = \frac{Q}{F} \cdot \frac{M}{z} \]  \hspace{1cm} (4.5)

After rearrangement and differentiation with respect to time gives:

\[ \frac{dQ}{dt} = \frac{d}{dt} \left( \frac{m}{M} \cdot F \cdot z \right) = \frac{F \cdot z \cdot dm}{M \cdot dt} \]  \hspace{1cm} (4.6)

Where \( m \) is the mass of the substance liberated at an electrode in grams; \( Q \) is the total electric charge passed through the substance; \( F = 96485 \text{ C mol}^{-1} \) is the Faraday constant; \( M \) is the molar mass of the substance; \( z \) is the valency number of ions of the substance (electrons transferred per ion).

But,

\[ \frac{dQ}{dt} = I \]  \hspace{1cm} (4.7)

And

\[
\begin{cases}
\frac{dm}{dt} = \frac{d}{dt} (C \cdot V_L) = V_L \frac{dC}{dt} \\
\frac{dC}{dt} = k_L a \cdot (C^* - C)
\end{cases}
\]  \hspace{1cm} (4.8)

Or

\[ \frac{dm}{dt} = V_L \cdot k_L a \cdot (C^* - C) \]  \hspace{1cm} (4.9)
Substituting Eq. (4.7) and Eq. (4.9) in Eq. (4.6), and assuming that for time $t_0 = 0$ to $t_1 = t$ the dissolved oxygen concentration in the liquid changes from $C_0 = 0$ to $C = C^*$ gives the relation between the electrical current and the OTR:

$$I = F \cdot \frac{Z}{M} \cdot V_L \cdot k_L a \cdot C^*$$

(4.10)

$$P_{EL} = \frac{I}{V_L} \cdot V$$

(4.11)

The power, necessary to overcome the total pressure drop for the system, $P_G$ was calculated by multiplying the pressure drop at the aerating device, $p_G$ by the air flow-rate, $Q_G$ per unit liquid volume, $V_L$ for the all five air flow-rates used in the experiment.

$$P_G = \frac{p_G \cdot Q_G}{V_L}$$

(4.12)

It was found that the highest $P_{EL}$ was obtained when using the finely perforated rubber tube, about 22% higher than $P_{EL}$ obtained with Aeos tube, and almost 33% higher than $P_{EL}$ obtained with the perforated tube at the same $U_G$. However, the energy losses in this case were 16% higher than theoretically received energy, which is significant in the case of using the air-lift reactor for energy production, where the aim is to minimize the energy input to the system (Pupkevich, 2014). It can be seen also that the Aeos tube showed satisfactory results. In that case $P_G$ was 8% of $P_{EL}$, which is a significant decrease of the energy losses of the system. However the best ratio $P_G/P_{EL}$ was obtained with the perforated teflon tube. As shown the $P_G$ was only 4.5% of $P_{EL}$ at the highest $U_G$ used.
As it is shown in Figure 4.14 the highest values of $k_La$ at a certain $U_G$ were obtained using the perforated rubber tube, whereas the results for $k_La$ for the other two types of aerating devices were quite similar. Despite of that the best $P_G/P_{EL}$ ratio at the highest $k_La$ values was observed using the perforated teflon tube.

More detailed information about energy efficiency of the system, expressed as $P_G/P_{EL}$, using different aerating devices specified for the values of $k_La$ is shown at Figure 4.15. The shape of the curve for the perforated rubber tube can be explained with the elasticity and the structure of the material used (see Figure 3.2). The small crevices at the surface of the material and its bubbly structure do not allow uniform formation of bubbles. In other words, at the lower $U_g$ used air accumulates inside the caverns, which are in the

**Figure 4.13** Variations of the theoretical electric power obtained and pressure loss at the different effective superficial gas velocities used
structure of the material, and at certain moment when the pressure increases enough the bubble is formed at the surface of the tube. At the higher $U_g$ the air inside the tube has enough pressure to keep the crevices of the material open all the time, and as a result the bubbles formed have higher initial size, which causes the observed drop in $k_{La}$. The other two aerating devices showed similar characteristics with better results for $k_{La}$ for Aeos tube. However, the superiority of the rigid perforated tube was obvious. In conclusion, when using the air-lift reactor for energy production the optimal $P_G/P_{EL}$ to $k_{La}$ ratio was given by the perforated tube.

![Graph showing variations of the theoretical electric power received and pressure loss compared to the values of volumetric mass-transfer coefficient obtained](image.png)

**Figure 4.14** Variations of the theoretical electric power received and pressure loss compared to the values of volumetric mass-transfer coefficient obtained
4.8 Effect of the Gas Holdup on $k_La$

Figure 4.16 shows the change of the $k_La$ with the change of the overall gas-holdup ($\epsilon$) for the aerating device with 200 orifices facing upwards at the different $A_d/A_r$ ratios. The rise of $\epsilon$, resulting from the increasing of $U_G$ contributes for higher $k_La$ values. The highest $k_La$ values can be seen again at the ratio of $A_d/A_r$ of 2.0. Six repetitive measurements at each $A_d/A_r$ ratio were performed in order to obtain meaningful statistical information for each experimental point shown, resulting in maximum standard deviation (STD) of 14.1% with a 95% CI (confidence interval) of +/-11.3%. The latter confirms the conclusions, made from Figure 4.5–Figure 4.7. Noticeable effect of the partition board location on gas holdup was observed. This disagrees with the small influence of the area or diameter ratios of downcomer and riser on gas holdup in internal loop airlift reactors in
water, salt solution and other low viscosity media, described by Weiland (1984) and confirmed later by Tobajas et al. (1999).

Figure 4.16 Variations of the volumetric mass-transfer coefficient with the increased overall gas holdup

4.9 Effect of the Mean Circulation Time of the Liquid on $k_{La}$

According to some authors the type of the gas distributor has negligible effect on liquid circulation rate (Onken and Weiland, 1980; Merchuk, 1986) if the cross-section of the riser is uniformly sparged; however Chakravarty et al., 1974 express an opposite opinion. The influence of gas distributor on liquid circulation could appear eventually if either its operating regime or the distributor type contributes in a high degree to the total energy input brought with the kinetic energy of the gas jet into the reactor, which is not usually
the case in air-lift reactors. The perforated aerating device with 200 orifices facing downwards was chosen for this experiment. The effect of the mean liquid circulation time, $t_c$ on the volumetric mass-transfer coefficient for a given downcomer to riser area ratio is shown in Figure 4.17. The different $A_d/A_r$ ratios affected the liquid and gas circulation patterns inside the air-lift reactor, yet also gave different riser and downcomer areas available for flow. As shown in Figure 4.17, the small $A_d/A_r$ ratios resulted in considerably higher $t_c$ and lower $k_{La}$ values, whereas $t_c$ values appeared to be very close to each other for ratios of $A_d/A_r$ from 0.5 to 5.0, giving also closer values for $k_{La}$. It was easy again to recognize the two main mixing regimes, resulting from changing the internal geometry of the air-lift reactor (see Section 4.3). As seen at that section, at the lower dowcomer to riser are ratios the air-lift behaves more as a bubble-column reactor, the flow pattern throughout the downcomer is not well defined and a lot of back mixing occurs in the riser. As a sequence, the values of $U_{GR}$ and $v_{LR}$ are lower at the same air-flow rates, comparing with the cases with higher $A_d/A_r$ ratio, which in combination with the higher back mixing in the riser implies that not all the air-water dispersion circulates throughout the downcomer which results in higher mean liquid circulation times.
Nonetheless there is much less scattering of the mean liquid circulation times at higher $A_d/A_r$ ratios, which demonstrates the stabilizing effect of the downcomer on the liquid circulation patterns. In addition, the values of $t_c$ for the latter case were lower than those obtained for the lower $A_d/A_r$ ratios. Also, comparison of the both main regimes, shows that the higher $A_d/A_r$ ratios contribute for higher $k_{La}$ than the lower ones. It can be seen that for $A_d$ smaller than the area of the bottom clearance, there is a significant resistance in this section. The latter agrees with the conclusions that the impact of the frictional losses in the top and bottom connecting sections between the riser and the downcomer are crucial for flow direction changes (Chisti et al., 1988). This means that the well-designed
internal configuration can improve significantly the mass transfer and hydrodynamic characteristics of the air-lift reactor.
Chapter 5

5 Conclusions and Recommendations

5.1 Conclusions

The position of the DO probe in the depth of the reactor played significant role, and attention should be paid when comparing $k_{La}$ results for different systems and/or conditions.

The two directions of the orifices of a conventional aerating device, showed superiority of the method when its air-jets were directed downwards at constant other conditions. The reason was that the orientation downwards of the air-jets provided additional mixing of the liquid at the dead zones around the bottom of the reactor, thus improving mass transfer and hydrodynamic characteristics of the ALR.

Although porous aerating devices showed enhanced mass transfer characteristics, their energy efficiency was way lower, compared with the perforated ones.

Changing the position of the partition board revealed the ratio between the downcomer to riser areas of 2.0, for which highest values of the volumetric mass transfer coefficient were obtained. The effect of the partition board was to stabilize the liquid circulation pattern as indicated by less variance in the circulation times. Based on that, two distinct flow regimes were examined. The poorly defined liquid circulation patterns resulting at low $A_d/A_r$ ratios led to generally longer circulation times, and lower $k_{La}$ values than those
obtained at higher $A_d/A_r$ ratios. It can be considered that at very low $A_d/A_r$ ratios (when the width of the riser is lower or equal to the height of the base), the liquid circulation rate is insufficient for adequate oxygen mass transfer. Depending on the orifice/pore size and airflow rate used, the pressure drop across the orifices/pores may constitute a significant part to the total pressure drop and must be included if power consumption calculations are made. The power efficiency for oxygen transfer was found to be profoundly influenced by the orifice/pore size, and there was less effect due to varying the number of orifices.

We have characterized the oxygen mass transfer and liquid circulation behavior in a rectangular air-lift reactor and have found the optimal operating conditions in terms of oxygen mass transfer and energy utilization. A new empirical model for the dependence of the mass transfer coefficient on the position of the partition board in the air-lift reactor was developed and used for optimization of the operating conditions. We believe that this work may be useful for the design and optimization of biochemical and other processes that require air-lift reactors.

### 5.2 Recommendations

The bioreactor plays a crucial role in overall performance of BioGenerator. Due to the unique structure and designation of the system, specific aspects of bioreactor performance characteristics have to be improved. That is why, future work could be done
in continuing the current study or develop new elements and approaches to achieve high performance and low energy consumption of the bioreactor used for BioGenerator.

- The ratio of non-aerated to aerated compartment \((A_d/A_r)\) is a crucial parameter that affects the overall performance of bioreactor. Based on the results, presented in this study, more profound research might be conducted in determining the exact position of the partition board inside the ALR. The \(A_d/A_r\) ratio influences mass transfer and hydrodynamic characteristics of the bioreactor. In addition, it affects the liquid circulation time, thus changing the behavior of the whole system. That is why the effect of these parameters in long-term operations can contribute to minimize the overall energy input of ALR by significantly decreasing the volumes of the aerating gas to the reactor.

- The liquid headspace of gas separator compartment and the bottom opening at base of ALR are among the parameters that can influence the performance of the bioreactor for both short-term and long-term operations. Other than controlling the mass transport, these connections play another important role by driving the liquid circulation pattern in the reactor. Not all the parameters that help decrease the input energy at the reactor can have a positive effect on the oxygen mass transfer. As observed in this work, lowering the liquid headspace above the partition board could help decrease the aerating gas volumes but had a negative effect on \(k_{la}\). On the other hand the closer the bottom opening area is to the area
of the downcomer, the worse the circulation times are. Therefore, based on the demand, one should consider exploring the change of the overall ALR performance characteristics with the stepwise change of both gas separator and base compartment parameters. This may be of considerable importance to the oxygen transfer by increasing the gas holdup (residence time) of the gas bubbles, thereby increasing the efficiency of oxygen utilization.

- One of the challenges of studying the oxygen mass transfer for any bioreactor is the optimal ratio between $k_{L,a}$, obtained and the energy, necessary to overcome the pressure at the orifices/pores of the aerating device. This ratio is even more important in the case, when the bioreactor is used for energy production (i.e. BioGenerator), where every aspect of energy loses affects negatively the efficiency of the system. In other words, the smaller bubbles are produced at aerating device, the higher contact surface between the gas and the liquid is achieved. This increases the volumetric oxygen mass transfer coefficient ($k_{L,a}$), but at the same time increases the pressure losses at the aerating device too. That can become very energy consuming. Depending on the orifice/pore size and airflow rate used, the pressure drop across the orifices/pores may constitute a significant part to the total pressure drop and must be included when power consumption calculations are made. The power efficiency for oxygen transfer was found to be profoundly influenced by the orifice/pore size, and there was less effect due to varying the number of orifices. Therefore, an extended study on
different materials use for aerating devices could be considered for further research.

- More work could be done to create detailed fluid-flow model of the present air-lift reactor for study the effect of the changes of the internal geometry on its performance characteristics for the future scale up.

- One can think of replacing the current structure of the ALR with trickling bed reactor. This might bring us at least three advantages. One is eliminating the necessity of recirculating high volumes of liquid, which will decrease the energy input into the reactor. Second is the immobilization of the microorganisms on the surface of the fill, which has some opportunities versus free suspended microorganisms. Last but not the least it can facilitate the maintenance of the bioreactor compared with the case with free suspended culture.
References


Margaritis, A., Sheppard, J.D., 1981. Mixing time and oxygen transfer characteristics of


Appendices

Appendix A: Typical graphs from DO measurements (a), and $k_{La}$ determination (b), obtained for the same $A_d/A_r$ ratio using five different aeration rates.
\[ y = -0.2314x + 2.0996 \quad R^2 = 0.9981 \]

\[ y = -0.6549x + 1.911 \quad R^2 = 0.9996 \]

\[ y = -0.9126x + 1.8398 \quad R^2 = 0.9987 \]

\[ y = -1.1462x + 1.7485 \quad R^2 = 0.9987 \]

\[ y = -1.7645x + 1.5659 \quad R^2 = 0.9971 \]
Appendix B: Sample excel sheet used for calculation the error of the method of $k_{L,a}$ determination

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**Appendix C**: Sample excel sheet used for calculation the error of the method of gas holdup, $\varepsilon$ determination

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Curriculum Vitae

Name: Stanimir S. Drandev

Post-secondary Education and Degrees:
- The University of Western Ontario, London, Ontario, Canada
  - 2013-2015 M.E.Sc
  - University “Prof. D-r Asen Zlatarov”
  - Burgas, Bulgaria
  - 1995-2000 M.E.Sc

Honours and Awards:
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  - 1996-1998

Related Work Experience:
- Teaching Assistant
  - The University of Western Ontario
  - 2014-2015
  - Multiple Engineering Positions
  - LUKOIL Neftochim Burgas Ltd.
  - 2001-2010

Publications: