# Water-immiscible solvents for the biological treatment of waste gases

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Proefschrift
ter verkrijging van de graad van doctor
op gezag van de rector magnificus
van de Landbouwuniversiteit Wageningen,
dr. C.M. Karssen,
in het openbaar te verdedigen
op woensdag 11 juni 1997
des namiddags te 16:00 uur in de Aula

ISBN 90 5485 802

ISBN 90-5485-685-8

# Acknowledgements

Finally I have the opportunity to thank so many people whose help, cooperation and good will were indispensible for the accomplishment of this thesis. I will start by expressing my sincere gratitude to Hans Tramper my promoter, for giving me the opportunity to work at the department and to put at my service all the means to perform a good work. His experience, creativity and concern were a constant throughout these years. I also would like to thank my co-promoter Rik Beeftink for his guidance specially during the last years of my work. His critical-eye and broad knowledge were much appreciated particularly during correction of the manuscripts and modeling work. I always enjoyed his implicit sense of humour.

A lot of the research in this thesis is the result of the effort of several students and visiting researchers. I am grateful to Esther Hurkmans, Willem Oortwijn, Sebastiaan Sewalt, Jan-Jaap Wesselink, Maria Turtoi, Hugo de Wit, Martijn Wiertz, Floor Boon and Hans Brandsma. Without your cooperation and dedication it would have been impossible to write this thesis.

I am also indebted to Wim Beverloo for his assistance in "attacking" complicated mathematical problems, to Henk van Sonsbeek for the moral support and interest he has always shown, to Fred van der End and Ido Wolters for their inventivity and readiness to help in technical issues, to Sybe Hartmans from the department of Industrial Microbiology for his kind assistance whenever requested and for providing me with the bacteria.

I also would like to thank my colleagues at the department and particularly those who passed through room 615 for their cheerfulness and for creating

a relaxed atmosphere.

The great creativity and the willingness to help of the staff of the technical services at Biotechnion, namely of the "werkplaats", electronics office, photographic services and store were always much appreciated.

My special thanks are to the good friends I made during my stay in the Netherlands for the joyful times and continuous understanding, support and friendship. A lot of words are not necessary... Lucilla, "cara sorellina", for you specially, there are no words to express what our friendship means to me.

I thank Junta Nacional de Investigação Científica e Tecnológica and later the Agricultural University of Wageningen and the Proceskunde department for the financial support.

I want to thank my parents, sister and brothers for their care and support and for making me remember that there is a blue sky and sea waiting for me.

Ad, all I could say would be too little for what you have been to me during all these years. I dedicate this thesis to you.

# Propositions

1. In the biological waste gas purification, larger removal efficiencies can be obtained by using a solvent as intermediate phase if the gaseous contaminant dissolves better in the solvent than in the water and if the system features large gas/solvent and solvent/water interfacial areas and transfer coefficients.
   This dissertation, chapter 7.

2. In biological waste-gas-treatment systems using an intermediate solvent, the mass transfer between gas and water is given by the product of the gas/water driving force and an overall gas/water mass transfer coefficient, which is a function of exchange areas, mass transfer coefficients and partition coefficients between the three different phases.
   This dissertation, chapter 5.

3. The enhancement of the overall volumetric oxygen transfer coefficient upon addition of dodecene in the aqueous medium found by Rols et al. is overestimated, since it is calculated based on the aqueous phase volume rather than the total reactor volume, the latter being a constant.
   Rols, J.L., Condoret, J.S., Fonade C., Goma, G. (1990). Mechanism of enhanced oxygen transfer in fermentation using emulsified oxygen-vectors. Biotechnol. Bioeng. 35: 427-435.

4. The relatively large number of scientific results in the field of biological waste-gas treatment that is published in the German language does not contribute to a widespread knowledge on the subject.

5. Doubting is a step in the process of learning.

6. Living in direct contact with nature helps man understand common occurrences inherent to life.

7. The popularity of the Dutch people abroad is shown by the many expressions in English including the word "Dutch, like: to go Dutch, to beat the Dutch, double Dutch, etc.

7. Love for others and self-love are indistinguishable.

9. The increasing substitution of human labour by machines will hopefully on the long term give man more time to get to know himself as well as his closest.

10. The most appreciated Dutch meal is an Indonesian rice table.

11. The best way to improve the quality of the environment is not by looking for high-tech cleaning solutions but by choosing increasingly more self-sustainable practices.

Propositions belonging to the thesis " Water-immiscible solvents for the biological treatment of waste gases" of Maria Teresa Cesário.

Wageningen, 11th June 1997

"O conhecimento científico progride por eliminação de erros e não por acréscimo de verdades"

Karl Popper

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# Short introduction

In the biological treatment of waste gases, the contaminants are first transferred from the gas to the water phase and, subsequently, converted by micro-organisms. If the compound to be removed is poorly water-soluble, the elimination efficiency is often limited by the mass transfer rate between the gas and the water. A way to reduce this transport limitation is by contacting the gas directly with an intermediate water-immiscible solvent in which these pollutants are better soluble.

The aim of the study described in this thesis was to gain insight about the potential of an intermediate solvent to enhance the mass-transfer rate of hydrophobic compounds from the gas to the water phase.

The first chapter gives an overview of the recent developments found in literature concerning new bioreactor types for a better removal of poorly water-soluble pollutants from waste gases. In this chapter both new systems or slightly modified versions of existing biotechniques are described and discussed with emphasis on mass transfer considerations rather than microbial aspects.

Chapter 2 is an introductory theoretical study which aimed at understanding at which conditions the use of an intermediate solvent in the waste gas treatment is advantageous compared to systems without solvent. In

this study, three solvent-containing systems were compared to bioreactor configurations featuring direct gas/water transfer.

Based on the analysis carried out in chapter 2, a bioreactor configuration was chosen to study the influence of the amount of solvent and of the partition coefficients gas/water and gas/solvent on the mass-transfer rate enhancement. This was carried out in a stirred-tank reactor by sparging gas containing the model contaminant through a solvent-in-water dispersion. The results are given in chapter 3. The effect of the solvent on the gas-to-water transfer was tested in an empirical manner during steady-state experiments in the presence of micro-organisms. This was done by measuring the change of the outlet gaseous concentration or of the linear cell growth rate at increasing solvent hold-ups.

A new technique was developed for the measurement of the gas/water mass transfer in the presence of solvent and in the absence of cells. Removal of the pollutant was achieved not by biological conversion but by passing a continuous flow of compound-free water or gas through the reactor. This way the effect of the cells or their products on the mass transfer coefficient gas/water was avoided. This technique is described in chapter 4.

To predict theoretically at which solvent hold-ups and for which gaseous compounds a relevant intensification of the gas/water mass-transfer enhancement can be expected, a steady-state mathematical model was set-up. This model was validated by carrying out experiments in a particular system configuration. This was done with two model compounds with different solubilities in water, and at different solvent volume fractions. The mass transfer between gas and water was measured in the absence of microbial conversion by using the technique described in the previous chapter. The model set-up and validation are described in chapter 5.

In chapter 6 the influence of the cells on the enhancement of the overall

gas/water mass-transfer coefficient upon solvent addition is addressed. Aiming at this steady-state experiments in the presence and absence of cells were carried out and the enhancement of the overall gas/water mass transfer coefficient at different solvent hold-ups compared.

Stirred-tank reactors were chosen initially as a model system to study the influence of the solvent amount and of the partition coefficients gas/water and gas/solvent on the mass transfer enhancement. These reactors are however not appropriate for waste gas treatment due to hydrodynamic constraints at large gas flows and to a poor fractional removal of the compound caused by an ideally mixing of the gas and the liquid. Larger elimination efficiencies are best achieved in a bioreactor where both the gas and the liquid move in counter-current and plug flow. Chapter 7 describes the use of a two-compartment system featuring transfer of the pollutant from the gas to the solvent in a packed absorber and a stirred-tank reactor for solvent/water transfer and subsequent biological degradation. The solvent is recycled between the absorber and the stirred-tank. The performance of this system was compared with the performance of an identical system without solvent, i.e. with the aqueous phase circulating between the absorber and bioreactor.

# Chapter 1

# Biological treatment of off-gases containing hydrophobic pollutants


## Summary

Conventional biological techniques are not effective in the treatment of off-gases containing poorly water-soluble pollutants. This is particularly valid at concentrations above 0.5 g/m$^3$. To alleviate this problem, the intermediate water layer between the gas and the microorganims must be reduced or the specific gas/water exchange area augmented.

This paper gives an overview of recent developments in the biological treatment of waste gases containing hydrophobic pollutants. These new systems either consist of improved versions of existing biotechniques or of bioreactor configurations that are entirely new in the field of biological waste-gas treatment. Examples of the first group are the bioreactors to which activated carbon or water-immiscible solvents are added, the biofilter with fungi and the combination of a photoreactor with a biofilter, while the mist-foam and the membrane bioreactors belong to the second category. All the systems are described and discussed with emphasis on mass transfer rather than on microbiological aspects.



This chapter has been submitted for publication by the authors M.T. Cesário, J. Tramper and H.H. Beeftink

## Introduction

As a result of man's growing consciousness on environmental issues, a greater demand for the quality of his surroundings is observed. This reality has stimulated the formulation of severe regulations on the maximally allowable concentrations of chemicals discharged to the atmosphere[3,4]. Concerning air pollution control, a strict reduction in the emission of toxic, carcinogenic or odourous compounds is required.

To reduce the discharge of chemicals to the atmosphere, either the treatment of the off-gases produced at the facility, or the implementation of new technologies that decrease the total amount of waste produced are possible. The latter is preferable since it eliminates the need for emission-control equipment. However, this option is sometimes expensive or not feasible and the application of exhaust-gas treatment techniques is often a solution.

Various physico-chemical or biological techniques are available to treat waste gases containing volatile organic compounds (VOCs), particulate matter, or inorganic compounds such as HCl, $NH_3$, HF, $NO_x$ and $SO_x$. Physico-chemical methods include thermal and catalytic incineration, filtration, carbon adsorption, liquid absorption, condensation and electrostatic precipitation. Biological techniques are applicable if the compound to be removed is biodegradable, i.e. when aerobic microorganisms can use this compound as the carbon/energy source[32].

The choice between one of these methods is often determined by the nature of the contaminant (Table 1), its concentration in the waste-gas stream, the desired removal efficiency, and the gas flow rate. Physico-chemical methods are generally applied for the treatment of waste gases containing pollutant concentrations higher than 1-5 $g/m^3$, while for lower pollutant concentrations, the most economical alternatives are adsorption on

activated carbon and biological oxidation[25,41]. Physical methods present the advantage of allowing recovery of the compound, while during chemical or biological oxidation, consumption of the contaminant occurs. Recovery methods are generally applicable for waste gases containing one or a limited number of compounds, while more complex mixtures are most economically incinerated. Good reviews on physical and physico-chemical treatment techniques are found in literature as McInnes *et al.* (1990)[28] and Ottengraf (1986)[32].

Table 1. Off-gas treatment techniques (adapted from McInnes *et al.* 1990)

| | organic compounds | inorganic compounds | particulate matter | $NO_x$ and $SO_x$ |
|---|---|---|---|---|
| Incineration | x | | | |
| Adsorption | x | | | |
| Absorption | x | | | |
| Condensation | x | | | |
| Filtration | | | x | |
| Electrostatic | | | x | |
| Wet scrubbing | | x | x | x |
| Chemical reduction | | | | x |
| Biological degradation | x | x | | x |

## Biological treatment techniques

Biological gas-treatment processes have been introduced in the twenties for the removal of odourous compounds ($H_2S$) from waste gases produced in waste-water treatment plants[26]. This was done in simple beds of soil through which the air was blown. Adsorption of the contaminant and subsequent

degradation by the soil microflora took place in the biobed. Nowadays, the use of biological methods has been extended to the treatment of air contaminated with a broader range of compounds and more sophisticated microbiology and bioreactor technology is applied. Considerable progress has been made in the field of degradation of xenobiotics (recalcitrant compounds with unnatural chemical structures), specially of chlorinated compounds. Biological processes have also been proposed for the oxidation of some volatile inorganic compounds like nitrogen oxide from stack gases, hydrogen sulphide from fuel gases and $NH_3$ from animal breeding plants.

For the biological removal of pollutants from waste gases several types of bioreactors have been used. Excellent reviews with detailed descriptions of each biological technique and its practical applications are found in literature[30,32,41]. Andrews and Noah (1995)[2] present the model equations for the design of different types of bioreactors for waste gas treatment: the biofilter, the trickle-bed bioreactor, the bubble column and the tricke-bed/biofilm reactor. According to these authors, the optimum operating point should be close to the on-set of the mass transfer limitation. Below this point, i.e. in the biological-conversion-rate limited regime, the size of the reactor can be reduced by increasing the amount of biomass in the system, while above this point, i.e. in the mass-transfer-rate limited regime, clogging of the bioreactor might happen due to excess of non-viable biomass .

In the present paper, an overview of the conventional biological treatment techniques is given and their drawbacks in the treatment of poorly water-soluble pollutants discussed briefly. New reactor configurations and adjustments brought on some of the conventional systems to improve the rate of transport of these compounds between the gas and the microorganisms are presented and examined.

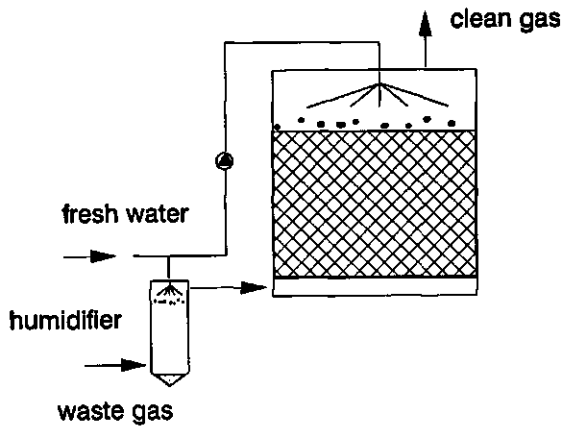


Figure 1. Biofilter

***Biofilter***

The oldest and simplest type of gas-treatment bioreactors is the biofilter. A biofilter consists of a packed bed of support particles through which the gas is blown (Fig. 1). The microorganisms grow on the packing material and degrade the contaminants in the waste-gas. The packing material is a very important process variable in view of the pressure drop over the reactor and of the specific surface area for mass transfer. The most widely used packing materials consist of a mixture of an active fraction like compost or peat and an inert or partially active fraction as polystyrene, lava particles or wood bark. The compost and peat provide a great amount of microorganisms as well as some nutrients for their growth. The coarse fraction contributes to a more loose structure of the packed-bed, preventing therefore high pressure drops in the filter. The specific gas/biofilm surface area in the biofilter[32] ranges from 300 to 1000 $m^2/m^3$. Another important process variable is the humidity in the packing as it very strongly affects biological activity.

Usually, the gas is pre-saturated with water. However, due to an increase of temperature caused by microbial activity, evaporation of water from the packed-bed takes place. For this reason, additional water is sprayed intermittently over the packing material. For optimal operation, the water content in the biofilter should be 40-70% (weight basis)[32]. Besides humidity, the supply of additional inorganic nutrients and the pH are difficult to control. Prior addition of $Ca(OH)_2$ to the packing or periodical washing and drainage can be used to control the pH. This is necessary due to the accumulation of acids like HCl during the degradation of chlorinated compounds. Nutrient limitation can also influence the overall performance of the biofilter. High removal efficiencies can not be maintained since the inorganic nutrients in the compost become exhausted.

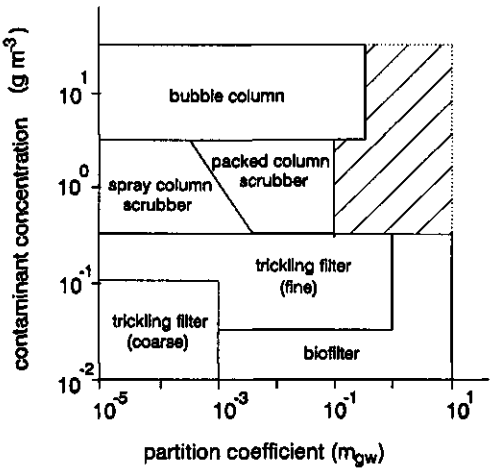


Figure 2. Application range of the conventional biotechniques (adapted from Kok 1992).[25] The shaded section indicates the range for which expansion of the application area of the biological techniques is needed.

Due to the difficult control of humidity and pH and the limited amount of inorganic nutrients in the packing, the biofilter is specially effective for the treatment of waste gases with a relatively low concentration of pollutants. Concentrations of target compounds are usually in the hundreds[25] of $mg/m^3$ (Fig. 2) and the maximum elimination capacity of a conventional compost filter[31] is in the range $1\times10^{-3}$- $5\times10^{-3}$ g carbon/($m^3$reactor.s).

The relatively large exchange area gas/biofilm and the absence of a continuous flow of water through the packing makes the biofilter an attractive bioreactor for the removal of poorly water-soluble pollutants.

### *Trickling filter*

Trickling filters, also called trickle-bed reactors, have been applied for decades in the waste-water treatment. Only recent application of these bioreactors has been proposed for waste-gas purification[13,18,23,24]. The trickling filter consists of a column filled with synthetic packing material on which a biofilm develops (Fig. 3).

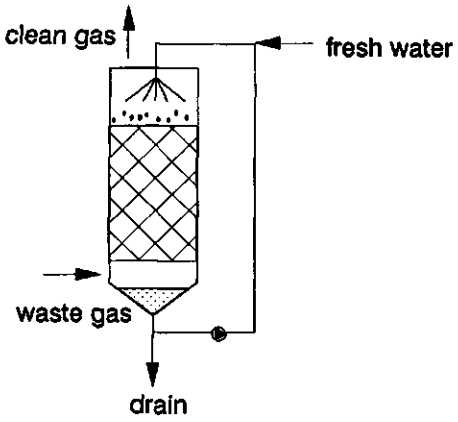


Figure 3. Trickling filter

Water containing the nutrients necessary for microbial growth is continuously sprayed on the top of the packing and recirculated. This water trickles down in a thin film and wets the biofilm. The gas can flow either co- or counter-currently with respect to the water flow. In this type of bioreactor, the pH can be easily controlled and nutrients can be supplied. The trickle-bed reactor has therefore been successfully applied in the removal of chlorinated compounds as dichloromethane which produces HCl during degradation[13,18] and N,N-dimethylacetamide (DMAc) producing ammonia as by-product[44].

In this type of bioreactor, excessive biomass formation may be a problem. For high organic loads and depending on the nature of the compound to be removed[45], a decrease of the elimination efficiency over a long period can be observed due to clogging[23,42,47]. In order to prevent this, Weber and co-authors[45] studied the application of regular NaOH-washes to remove excess biomass. This way the amount of biomass which was formed, equalled the amount removed by the NaOH-wash and high contaminant removal rates were obtained for a long period of time. Another approach to prevent clogging consists in limiting the amount of inorganic nutrients. Using a trickle-bed reactor with a bacterial culture, Weber *et al.* (1994)[47], controlled the amount of biomass formed during degradation of toluene by limiting the amount of nitrogen in the bioreactor. As a consequence a lower degradative activity was observed. When instead of bacteria a fungal culture was used, higher degradation rates were found, which were less influenced by the nitrogen limitation. Over a period of 250 days with an average toluene loading rate of 0.021 g toluene/($m^3$.s), a removal rate of 0.01 g toluene/($m^3$.s) was obtained which is higher than in other reactor systems. A biofilter removes in average circa 0.0055 g/($m^3$.s) of aromatics[41].

Trickling filters have a lower specific surface area (100-300 $m^2/m^3$) than the biofilters[32]. For this reason and because of a thin water film covering the biofilm, this bioreactor is less effective in the removal of poorly water-

soluble pollutants compared to biofilters (Fig. 2). However, because absorption and degradation occur in the same compartment, the mass transfer is enhanced due to an immediate consumption of the compound being transferred. This results in a better removal of poorly water-soluble compounds in relation to bioscrubbers (see below).

***Bioscrubber***

A bioscrubber consists of two compartments: a compartment where mass transfer between the gas and the liquid takes place (scrubber) and a compartment for regeneration of the liquid, usually a stirred-tank reactor (Fig. 4).

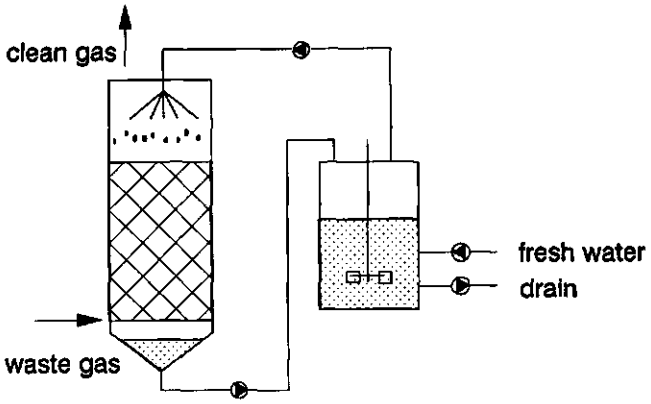


Figure 4. Bioscrubber

The scrubber compartment may be a packed bed similar to a trickling filter, but other designs have been proposed such as a spray column where the liquid is sprayed in very fine droplets. In the regeneration tank, the

contaminant is oxidized by microorganisms suspended in the water phase. The microbial suspension is continuously recirculated over the two units. Because reaction takes place in a separate unit, a better control of the reaction conditions (T, pH, ionic strength) and addition of a carbon/energy source for denitrifying or co-metabolic processes[19] is possible. Moreover, this system also allows an extra supply of oxygen to meet the requirements in the regeneration tank. For these reasons, bioscrubbers can be used for higher pollutant concentrations (inlet concentration > 0.5 g/m$^3$air) compared to trickling filters or biofilters[25] (Fig. 2). The biomass concentration in the tank should not exceed 5-8 g/l (dry weight) to prevent the risk of obstruction in the scrubber[32] and therefore, withdrawal of surplus biomass may be necessary.

A drawback of the bioscrubber compared to the biofilters is a lower specific gas/liquid surface area (= 100-300 m$^2$/m$^3$). Therefore, this system is specially applicable for the removal of well water-soluble contaminants, i.e. with a partition coefficient ($m_{gw}$) < 0.01, where $m_{gw}$ is the ratio between the concentrations in the gas phase (g/m$^3$) and in the aqueous phase (g/m$^3$) at equilibrium. For moderately water-soluble compounds, $0.01 < m_{gw} < 0.1$, high spray columns and large water flows are needed[25].

### *Bubble column*

Another type of gas/liquid contacting device for the treatment of waste gases is the bubble column. In this device, the gas moves in plug flow and is dispersed in the liquid phase which can be considered ideally mixed (Fig. 5). Since the liquid is well mixed, the fractional removal in a bubble column is lower compared to the packed or spray column, where both gas and liquid are in plug flow. Moreover, the specific exchange area gas/liquid of the bubble column ($a$= 100 m$^2$/m$^3$) is generally lower than the one of the packed

column ($a$= 100-300 $m^2/m^3$). For these reasons, the bubble column is less suitable for the elimination of relatively dilute and hydrophobic components since larger reactor volumes are necessary. When more concentrated and very well water-soluble compounds are to be removed (Fig. 2), the complete mixing of the liquid in the bubble column is, however, an advantage compared to the aforementioned bioreactors where humidity control (biofilter), clogging of the packed bed (trickling-filter) or obstruction in the scrubber (bioscrubber) may become a problem. Mixing of the liquid is also advantageous particularly with compounds which may be inhibitory at their equilibrium concentrations (e.g. compounds like $H_2S$, $SO_2$ and $NH_3$ that dissociate upon contact with water).

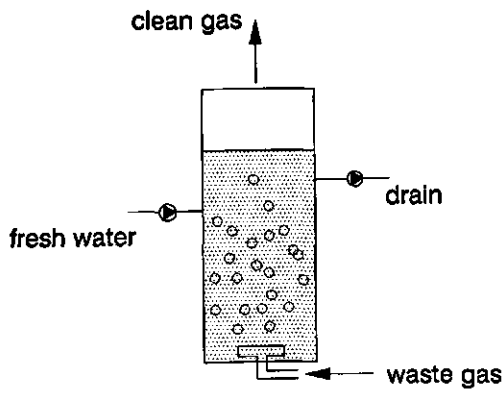


Figure 5. Bubble column

**Short evaluation of the conventional techniques**

Of all the biological conventional techniques, the biofilter is the most effective for the removal of poorly water-soluble contaminants due to its

large specific area for mass transfer gas/biofilm and the absence of a continuous flow of water. This type of bioreactor is, however, not applicable for the removal of chlorinated hydrocarbons due to acidification of the biobed, and for the treatment of gases with high pollutant concentrations because humidification of the packing and availability of inorganic nutrients may become a problem. Fig. 2 shows that an efficient technique for the removal of hydrophobic pollutants ($m_{gw} > 0.1$) at concentrations above 0.5 g/m$^3$ is not available. In order to accomplish large gas/water (or gas/biofilm) mass transfer rates, bioreactors with low water contents or featuring large gas/water (or gas/biofilm) exchange areas are required. In the following, new bioreactor configurations are described which aim at an efficient removal of these compounds without the limitations of a biofilter. Some of the bioreactors described feature a discrete liquid phase which enable control of the reaction conditions (pH, nutrient concentration) allowing therefore the treatment of large organic loads.

## Bioreactors for the removal of hydrophobic gaseous pollutants

New bioreactor configurations aiming at an efficient removal of hydrophobic compounds at concentrations larger than 0.5 g/m$^3$ are described and the operating conditions and experimental results found for each equipment summarized in Table 2.

### *Bioreactors with activated carbon*

#### *Dry-biobed bioreactor*

An improved removal of ethene ($m_{gw}^{20°C} = 7.6$) was accomplished in a

trickling-filter packed with granular, activated-carbon by reducing the wetting of the biobed[11,12]. This packing material was inoculated with a pure culture of *Mycobacterium parafortuitum* E3 and addition of inorganic nutrients was accomplished by occasional sprinkling of the biobed. When pre-humidification of the gas entering the biobed was omitted and thus the wetting of the biobed was reduced, the ethene removal efficiency increased from circa 42 % to about 89.4% (Table 2). This doubling of the removal efficiency was explained as a decrease of the mass transfer resistance in the stationary water layer covering the biofilm. Under decreased wetting, the biological activity is supported by the water retained in the inner pore structure of the granules of activated carbon.

At low water contents ( <40 %- 45 %), the ethene removal was not limited by the transfer rate through the water layer but rather by the degradation capacity of the biofilm. This was found when by increasing the ethene inlet concentration from 127 mg/m$^3$ to 816 mg/m$^3$, upon which the removal rate increased only by a factor 1.3. Optimization of the system should therefore focus on a constant control of the moisture in the dry-biobed.

*Bioscrubber with activated carbon*

The use of activated carbon in a bioscrubber has been proposed by Kok (1992)[25]. The author expected to improve the mass-transfer rate of hydrophobic compounds and to buffer fluctuations in the supply of contaminants by adding activated carbon to the system. The microorganisms would be attached to the suspended particles of activated carbon. Large elimination efficiencies of contaminants with a partition coefficient $m_{gw} > 0.01$ at concentrations in the range 0.5- 5 g/m$^3$ were foreseen.
The use of activated carbon in order to buffer fluctuating concentrations in

the waste-gas stream and achieve a constant contaminant supply has also been studied by Weber et al (1995)[46] in biofilters. These authors observed that mixing the activated carbon with compost in the biofilter did not result in a better buffering while placing a filter of activated carbon upstream the biofilter resulted in a better overall performance of the system. This difference is due to the presence of water in the biofilter. The water in the biofilter diminished the buffer capacity of the activated carbon since the contaminant has first to diffuse through a water film to reach the activated carbon surface.

Therefore, based on the results obtained by Weber *et al.* (1995)[46] we do not expect an enhancement of the removal rate of hydrophobic compounds in the system proposed by Kok (1992)[25] due to the water film covering the activated carbon particles in the bioscrubber. Until now, we have not found results on the performance of this system in the literature.

***Biofilter with fungi***

The use of fungi in biofilters is very interesting for the removal of hydrophobic pollutants since these microorganisms are tolerant for low water activities. The mass transfer rate of these compounds can therefore be improved due to a reduced water layer around the biofilm.

Cox and co-workers[9,10] used biofilters inoculated with fungi on perlite and polyuretane foam. A complete removal of styrene ($m_{gw}$= 0.13) at concentrations in the inlet gas up to 800 mg/m$^3$ were observed when using growing fungi (Table 2). This corresponds to an elimination capacity of circa 0.02 g/(m$^3$.s) which is very high compared to the elimination obtained in a conventional compost biofilter (0.0055 g/m$^3$.s of aromatics[41]). A constant and high microbial activity was observed at 85% humidity in the influent gas and incidental humidification of the bed.

Table 2. Experimental conditions and results with the different bioreactors for hydrophobic pollutant removal. The gas residence time is calculated based on the total volume of the system. In the case of the membrane bioreactors, the total volume is the sum of volume of the membrane module and of the bioreactor with mineral medium.

| system | pollutant | inlet concent. ($mg/m^3$) | gas flow ($m^3/s$); gas vel.(m/s) | liquid flow ($m^3/s$);liq. vel.(m/s) | gas residence time (s) | volumetric removal rate ($g/m^3.s$) | removal efficiency (%) |
|---|---|---|---|---|---|---|---|
| dry biobed[11] | ethene | 127 | $2.5\times10^{-5}$ ($m^3/s$) | - | 43 | 0.0029 | 84.9 |
| | ($m_{gw}$= 7.6) | 816 | | - | 43 | 0.0038 | 30 |
| biofilter with | styrene | 800[10] | $1.2\times10^{-5}$ ($m^3/s$) | - | 38 | 0.02 | 100 |
| fungi[10,27] | ($m_{gw}$= 0.13) | 1245[27] | $1.6\times10^{-2}$ (m/s) | - | ? | ? | 99.9 |
| flat-sheet | propene | 3900 | ? | $2.1\times10^{-4}$ (m/s) | ? | 0.01 | ? |
| memb.[36] | ($m_{gw}$= 10) | | | | | | |
| hollow-fibre | propene | 4000 | $4.6\times10^{-6}$ ($m^3/s$) | 0.9 (m/s) | > 34 | 0.019 | 20 |
| memb.[35] | ($m_{gw}$= 10) | 4000 | $4.6\times10^{-6}$ ($m^3/s$) | 0.034 (m/s) | > 34 | 0.015 | 15.8 |
| | | 4000 | $4.2\times10^{-7}$($m^3/s$) | 0.034 (m/s) | > 368 | 0.04 | 80 |
| dense silicone | DCE | 650 | $1.3\times10^{-5}$ ($m^3/s$) | $1.6\times10^{-5}$($m^3/s$) | 300 | 0.0035 | 91 |
| memb.[15] | ($m_{gw}$= 0.047) | | | | | | |
| two-liquid- | toluene | 800 | 2.7 ($m^3/s$) | 0.014 ($m^3/s$) | ? | ? | 95 |
| phase system[39] | ($m_{gw}$= 0.25) | | | | | | |

Besides a high tolerance to low water activities, the aerial hyphae of fungi form a very high surface area that is in direct contact with the polluted air flowing through the filter. The pollutants are therefore in direct contact with the microorganism without an intermediate aqueous phase. This is specially advantageous for the elimination of hydrophobic contaminants. Majcherczyk *et al.* (1990)[27] proposed the use of a biofilter with white-rot fungi growing on straw to remove a wide range of hydrophobic and hydrophilic pollutants. The white-rot fungi grow as aerial hyphae and when growing on straw, secrete oxidative enzymes that degrade a broad range of aromatics[27]. Due to the very large biologically active surface and the broad substrate specificity, the biofilter inoculated with this type of fungus can be used to treat polluted air containing a variety of contaminants. A removal efficiency of 95-100 % (Table 2) from a gas stream containing compounds as styrene (inlet gas concentration = 1.2 $g/m^3$), lignosulphonate vapour, $H_2S$ and ammonia was observed, when the biofilter was operated for a few days.

***Mist-foam bioreactor***

Thalasso *et al.* (1991)[40] developed the mist-foam bioreactor, a new type of bioreactor where the polluted gas is mixed with the nutrient aqueous solution in an atomising nozzle generating a very fine mist. This mist passes subsequently through a filter bed consisting of synthetic foam (polyuretane) where the microorganisms are attached. In the mist-foam bioreactor the small size of the water droplets produced during atomization generates extremely large gas/liquid exchange areas estimated as $6\times10^4$ - $2\times10^5$ $m^2/m^3$. For this reason the droplets become saturated with the gaseous compound immediatly after atomization of the liquid. The mist-foam bioreactor permits a precise and independent control of the gas and liquid flows and a good versatility because of a wide variety of carrier foams and injector types.

A good distribution of the micro-droplets over the filter-bed, a complete substrate degradation and a stable operation of the bioreactor was observed. Although the reactor was not tested for its capacity to remove hydrophobic pollutants, we expect a good performance of this system due to the large gas/water exchange areas.

*Combined photochemical and biological treatment*

A partial photochemical oxidation of hydrophobic pollutants as a pretreatment step for biological purification, can improve the solubility in water as well as the biodegradability of these compounds resulting in better volumetric elimination efficiencies[16]. This combined method was tested with styrene. Gas containing styrene was passed through a photoreactor using UV-radiation. This resulted in its partial degradation and the generation of oxidation products like benzaldehyde and 1-phenylethanol among others. These compounds are better soluble in water (partition coefficients, $m_{gw}$, circa 100 times lower) and better biodegradable. When feeding gas containing 500 mg/m$^3$ of styrene to a photoreactor and a biofilter in series, a complete removal of styrene and other organic compounds produced in the first step was observed. The authors are planning to test this combined system with other compounds in the future.

*Membrane bioreactors*

The mass-transfer resistance of hydrophobic pollutants from the gas to the biofilm is strongly reduced when the intermediate water boundary layer is almost completely absent. This was observed with a dry biobed of granular activated carbon[11,12] and with a biofilter with fungi[9,10,27]. Another way to achieve this is by using a membrane bioreactor. This type of bioreactors is

advantageous for the removal of hydrophobic compounds when the mass-transfer resistance of the membrane is negligible or very low.

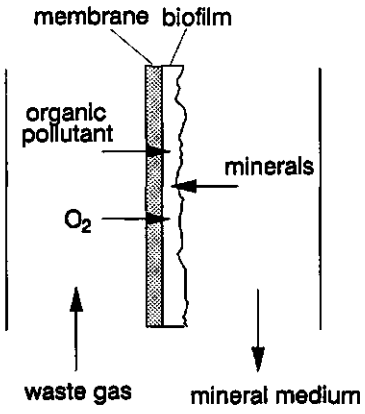


Figure 6. Schematic view of a membrane bioreactor

In this type of bioreactor a membrane separates the gas and the biofilm formed on the other side (Fig. 6). The waste gas flows along one side and the contaminants diffuse through the membrane to the wet biofilm on the other side. The microorganisms are supplied with organic carbon and oxygen from the gas and with minerals from the liquid phase. Since the gas and the biophase are separated (in two compartments) it is possible to control the reaction conditions via the circulating water as in the trickling filter or bioscrubber.

Different types of membranes have been proposed for the removal of poorly water-soluble compounds, namely dense silicone membranes[14,15] and porous hydrophobic membranes.[5,17,20,34,35,36] Dense membranes have a higher mass-transfer resistance than microporous hydrophobic membranes because the contaminants have to dissolve in the membrane material and diffuse

through it, whereas in the porous membranes diffusion is through the air-filled pores of the membrane. The overall gas/water-mass transfer coefficient through the membrane is a function of its thickness, of the gas/water partition coefficient ($m_{gw}$) and of the gas and liquid flows[34]. Reij *et al.* (1997)[34] estimated the mass-transfer coefficient of hydrophobic microporous membranes and dense silicone membranes with a thickness of 100 $\mu$m and similar operating conditions. The overall mass-transfer coefficient is larger in the case of microporous membranes than with silicone membranes for well, moderately and poorly water-soluble compounds.

*Hydrophobic microporous membranes*

Hartmans *et al.* (1992)[17] tested different kinds of hydrophobic membrane materials and selected a polypropylene membrane as no biomass could grow through it and high mass-transfer rates could be obtained. A flat-sheet polypropylene membrane bioreactor was tested for its efficiency to eliminate propene ($m_{gw}^{30°C} = 10$) from synthetic waste gas[36]. From measurements in the absence of microbial activity it was concluded that for the removal of propene, the mass-transfer resistance was totally in the liquid phase, the membrane resistance being negligible.

This membrane bioreactor operated steadily for 20 days at a propene inlet concentration of 3.9 g/m$^3$. The propene flux into the biofilm was $4.2 \times 10^{-5}$ g/(m$^2$membrane. s). The flux through the membrane is given by:

$$F = k_l A \left(\frac{C_g}{m_{gw}} - C_w\right) \quad (1)$$

with $F$, the flux through the membrane (g/s); $k_l$, the overall mass transfer coefficient based on liquid phase concentrations (m/s); $A$, the membrane

surface area ($m^2$); $C_g$ and $C_w$, the concentration in the gas and liquid phases, respectively, ($g/m^3$) and $m_{gw}$, the partition coefficient between the gas and the water, (($g/m^3$gas)/($g/m^3$water)).

Flux and volumetric removal rate are related through the specific area of the membrane ($m^2/m^3$), which is for the flat-sheet membrane 250 ($m^2/m^3$).

Based on these results a hollow-fibre module containing microporous membrane material was evaluated as bioreactor for waste-gas treatment[35]. The propene flux ($g/m^2$membrane. s) in the hollow-fibre was similar to the flat-sheet membrane, however, since the hollow-fibre modules have a larger interface area gas/water (= 637 $m^2/m^3$), higher volumetric removal rates were found. The experimental results obtained with the flat-sheet and the hollow-fibre membranes are given in Table 2. The hollow-fibre membrane was tested with different gas flow rates. Larger removal efficiencies were found for lower gas flow rates; 20 % and 80 % at $4.6\times10^{-6}$ $m^3/s$ and $4.2\times10^{-7}$ $m^3/s$, respectively.

The long-term operational stability of such a bioreactor was studied. Propene elimination was monitored for 170 days, however, from day 65 onwards the removal rate gradually decreased. This decrease is due to clogging of the fibres with biomass. Although clogging of the fibres was prevented by using a higher liquid velocity, the performance of this bioreactor still decreased in time. This was explained by a poor diffusion of nutrients from the liquid to the active part of the biofilm close to the membrane.

*Dense silicone membranes*

Another type of membranes, the dense silicone rubber membranes, have been used to remove moderately and poorly water-soluble contaminants from waste gases. These are selective membranes allowing the transfer of a

particular group of contaminants from the gas to the liquid phase. If on the one hand this type of membranes are seen as advantageous because they retain compounds that could otherwise inhibit biodegradation (e.g. acid vapours), on the other hand the mass-transfer resistance is larger since the contaminant has to dissolve first in the membrane material and diffuse throught it before it reaches the aqueous phase. Fisher *et al.* (1992)[14] used dimethylsilicone rubber membranes to remove aromatic compounds from waste gases. This membrane bioreactor was able to eliminate styrene at a rate of 0.013 g/($m^3$reactor. s). These membranes were shown to remove satisfactorily hydrophobic compounds while hydrophilic compounds like methanol were barely eliminated.

Freitas dos Santos *et al.* (1995)[15] used silicone-rubber membranes to remove dichloroethane from a gaseous waste stream. Dichloroethane (DCE) is a moderately water-soluble compound ($m_{gw}$= 0.047). The membrane module was a spirally wound silicone rubber module with a gas/liquid specific surface area of 1250 $m^2/m^3$. The aqueous medium was recycled on the shell side of the module while the gas passed through the membrane envelope. During experiments in the absence of biological degradation, the mass transfer coefficient in the liquid film was shown to be limiting for the overall mass transfer rate, similarly to the microporous membranes.

The silicone membrane module was tested at a gas flow rate of $1.3\times10^{-5}$ $m^3/s$ and an average DCE concentration of 0.65 $g/m^3$. At these conditions a maximum removal efficiency of 91 % was obtained (Table 2). Due to the formation of a biofilm the DCE flux through the membrane decreased 50 %. The module was however never completely blocked during eleven days of operation.

From Table 2 it is observed that the volumetric removal rate obtained with the dense silicone membranes is lower than with the microporous membranes. Since the specific exchange area is larger for the silicone

membranes, the lower removal rate is due to a lower flux through the membrane. A good comparison between both membranes based on the experimental results is not possible since they were tested with different compounds and at different operating conditions. However, lower removal rates are expected with dense silicone membranes since these membranes have a higher mass-transfer resistance compared to microporous hydrophobic membranes[34].

The authors[15] compared the performance of the silicone membrane bioreactor and of an air-lift bioreactor for the same gas flow rate and similar reactor volumes. Although the presence of a membrane adds extra resistance to mass transfer, the volumetric DCE removal rate is about 3.5 times greater using the membrane reactor than with the air-lift bioreactor. This is due to the much larger specific surface area of the membrane module (1250 $m^{-1}$) compared to the specific surface area in the air lift which was estimated[15] at 210 $m^{-1}$. Another factor favouring the membrane bioreactor is the biofilm attached to the membrane which provides a higher biomass concentration at the interface gas/liquid compared to what is found in an air-lift bioreactor. The mass-transfer rate under these conditions can be improved by a faster degradation rate in the film adjacent to the membrane depending on the relative contributions of diffusion and reaction rate.

For both the porous hydrophobic and the dense silicone membrane bioreactors, and in agreement with the authors[15,34], the problems dealing with clogging and the instable biofilm performance must be solved before this type of bioreactor will be prefered over dry biobeds[11,12] or biofilters in the removal of poorly water-soluble compounds.

Moreover, the probably higher costs of a membrane module is a factor that must be also taken into consideration when choosing between this type of bioreactor and a conventional one.

*Two-liquid-phase systems*

Another way to reduce the gas/water transfer resistance of hydrophobic pollutants is to use an absorbing liquid in which these compounds have a higher solubility.

Water-immiscible solvents have been used to improve the oxygen transfer rate in oxygen-limited aerobic fermentations.[21,22,29,37,38] To be used as absorbent in the waste-gas treatment the solvent must meet the following conditions:

. low vapour pressure,
. immiscible with water
. high affinity for the compound to be removed
. not biodegradable
. not toxic for the biocatalyst
. odourless
. favourable price

The use of a water-immiscible organic solvent to aid in the removal of hydrophobic pollutants from waste gases was first reported by Schippert (1989)[39] and was tested in a bioscrubber. The solvent was added to the suspended activated sludge in the range of 10-40 % (v/v) and the mixture was sprayed over a scrubber compartment. In a cascade of stirred-tank reactors, the compounds were subsequently transferred from the solvent to the water due to their low concentration in the aqueous phase caused by biological degradation. Toluene ($m_{gw}^{25°C} = 0.27$)[1] and styrene ($m_{gw}^{25°C} = 0.1$)[1] were the model pollutants used. Three solvents were recommended, namely di-n-octylphtalate, di-n-nonylphtalate and polydimethylsiloxane.
Larger removal efficiencies were found with higher solvent volume fractions in the liquid. The toluene removal efficiency changed from approximately

3 % in the absence of solvent to circa 95 % at a solvent volume fraction of 40 % (v/v). Furthermore it was observed that the elimination efficiency is independent on the inlet gas concentration as long as the biodegradation capacity in the regeneration tanks is large enough.

Poppe and Schippert (1992)[33] tested this new technique for the removal of a mixture of hydrophilic and hydrophobic compounds in the waste gas by a two-stage bioscrubber. The first stage was a conventional bioscrubber while the second contained an organic solvent. In the first bioscrubber mainly hydrophilic contaminants as acetone, ethylacetate and butylacetate were removed while the hydrophobic compounds as toluene, ethylbenzene and xylene remained in the gas. These compounds were eliminated in the second stage.

By applying a solvent, the transfer of the contaminants from the gas to the liquid (be it a dispersion or the pure solvent) can be considerably improved. However, since the degradation occurs in the aqueous phase, the efficiency of the process is very much dependent on the prompt exchange of the compound between the solvent and the water, i.e. on the solvent/water mass transfer rate. The steady-state model developed by Shippert (1989)[39] assumes that the solvent/water dispersion is an homogeneous liquid, i.e. the mass transfer between these two phases is very fast. This model does not give an insight into the mechanisms for mass transfer between the gas and the water in the presence of the solvent. It does therefore not predict the influence of parameters such as the gas/solvent, gas/water and solvent/water exchange areas, mass transfer coefficients and partition coefficients on the contaminant removal efficiency. The influence of these quantities on the volumetric removal rate of pollutant was studied by Cesário *et al.* (1995)[6]. This was initially done by comparing the performance of three solvent-containing systems with systems featuring direct gas/water transfer. Three compounds with different partition coefficients gas/water were considered, namely:

hexane ($m_{gw}$= 71), dichloromethane ($m_{gw}$= 0.1) and acetone ($m_{gw}$= 0.0016). Because this theoretical study aimed at characterising the different systems in terms of mass transfer, the biological conversion was assumed not to be rate-limiting. From that study it was concluded that the use of organic solvents is advantageous only if the specific exchange area solvent/water is large enough to compensate the additional transport resistance introduced by the solvent.

Due to the large solvent/water exchange area in a stirred-tank reactor the authors have chosen this type of bioreactor to carry out further studies. This was done in one-compartment system with the gas and the two-liquids well mixed. Although this is not the ideal reactor configuration for the treatment of waste gases, because of the poor fractional removal of the pollutant from the gas, and due to hydrodynamic constraints, this bioreactor was used as a model system[7,8] due to its simplicity. In a preliminary approach[7] to study the influence of the partition coefficient gas/water ($m_{gw}$) and of the solvent hold-up on the gas/liquid mass transfer rate, the dispersion was considered as an homogeneous liquid, similarly to Schippert (1989)[39]. The model compounds were toluene ($m_{gw}$= 0.21) and oxygen ($m_{gw}$= 32.7) and the solvent was FC40, a perfluorocarbon[43]. At identical hydrodynamic conditions and gas residence times, an increase of the elimination efficiency was found for both compounds at increasing solvent volume fractions. In Fig. 7, the elimination efficiency enhancement given as the the ratio between the removal efficiency in the presence and absence of solvent, is depicted for toluene and oxygen. It is observed that the enhancement was more pronounced for oxygen; i.e. the compound with the lower solubility in water. The elimination efficiency increased of a factor 1.1 for toluene using a dispersion containing 10 % (v/v) FC40, while the oxygen removal was enhanced by a factor 2 at the same solvent volume fraction.

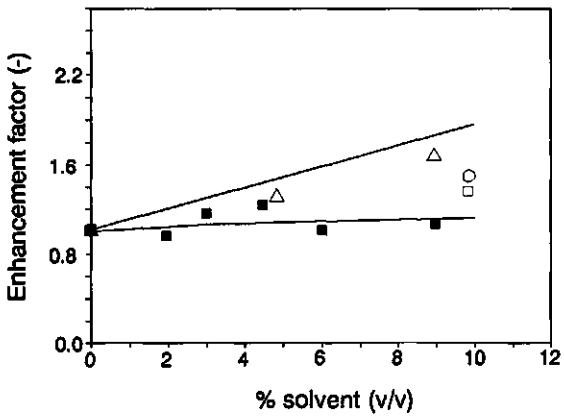


Figure 7. Enhancement of the elimination efficiency for toluene and oxygen at different solvent volume fractions. The points and the lines represent the experimental and the theoretically calculated values, respectively[7]. (■), toluene; (○, □, △), oxygen .

The enhancement of the toluene removal upon solvent addition is very low because the elimination efficiency found without solvent (0 % solvent) was already very high; i.e. circa 92 %. This high value is explained by the relatively low value of the partition coefficient gas/water ($m_{gw}$) but also by the large volumetric mass transfer coefficient ($k_la = 1.7 \times 10^{-2}$ $s^{-1}$) in a STR and the large gas residence time used during the experiments (= 145 s). Addition of a better solvent (lower $m_{gs}$) would not result in an improved elimination rate[7]. These results can not be compared with the ones obtained by Schippert (1989)[39] who found a 24 times higher toluene removal efficiency upon addition of 10 % solvent in a bioscrubber. The elimination efficiency found in the absence of solvent was, however, of 3 % since a different type of equipment and different gas residence times were used.

In a later study[8], Cesário and co-authors developed a steady-state mathematical model for predicting the influence of the solvent hold-up, and of the partition coefficient gas/water ($m_{gw}$) on the gas-to-water mass transfer coefficient. This model was set-up by assuming a possible path for gas/water transfer in the presence of the solvent and thus the influence of the solvent/water, gas/solvent and gas/water exchange areas on the transfer rate could be predicted. Steady-state experiments were carried out to validate the model. The model pollutants were toluene and oxygen. Like in the experiments mentioned above[7], the enhancement found for oxygen was larger than the one found for toluene.

## Short evaluation of the new biotechniques for removal of hydrophobic gaseous pollutants

A summary of the results found with the different biotechniques for hydrophobic pollutant removal is presented in Table 2. A comparison between the systems in terms of removal efficiency is not possible because each system was tested with a different compound and consequently a different value of partition coefficient gas/water. Some of the systems like the hollow-fibre membrane and the dry-biobed were tested with compounds with similar partition coefficients namely propene ($m_{gw}^{30°C}$= 10) and ethene ($m_{gw}^{20°C}$= 7.6), however, these reactors can not be compared because the gas residence time is not known for both of them. The same is valid in the case of the two-liquid-phase system and the biofilter inoculated with fungi, tested with toluene ($m_{gw}^{25°C}$= 0.25) and styrene ($m_{gw}^{25°C}$= 0.13), respectively.
For some techniques like the biofilter with fungi and the microporous membranes, better volumetric removal rates (g/m$^3$.s) are reported compared to conventional compost biofilters (1-5 $\times 10^{-3}$ g C/m$^3$.s)[31].

## Concluding remarks

Biological techniques are efficient and cost-effective means for the treatment of waste gases containing a wide variety of inorganic and organic compounds. Due to the high affinity of the biocatalysts for the substrate, these techniques have been shown to be specially applicable for concentration ranges below 5-10 $g/m^3$. During the last years much effort has been put in developing new micro-organisms or microbial consortia able to degrade a larger number of compounds. An evidence is the increasing number of xenobiotics degraded biologically and the degradation of chlorinated solvents by co-metabolic pathways. Considerable progress has also been made in the bioreactor design in order to expand the application of the different conventional biotechniques to the treatment of larger gas flows, higher pollutant concentrations and the removal of hydrophobic contaminants. A confirmation of the latter are all the recent developments discussed in this paper. Most of these techniques, however, are still in their infancy. Future research will have to focus on improvement of the operational stability for long periods of time and on scaling-up.

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# Chapter 2

## Feasibility of using water-immiscible organic solvents in biological waste-gas treatment


### Summary

In order to conclude about the feasibility of using water-immiscible organic solvents in biological waste-gas treatment, a theoretical study was done in which different types of organic-solvent-containing systems are compared with systems where the pollutant is transferred directly to the water phase. For each system the total equipment volume needed to remove 99% of a pollutant from a waste-gas stream is calculated. Three different pollutants with a different solubility in water are considered: Hexane ($m_{gw}$= 71), dichloromethane ($m_{gw}$= 0.1) and acetone ($m_{gw}$= 0.0016), with $m_{gw}$ the partition coefficient (kg/m$^3$ gas / kg/m$^3$ water) of the pollutant between the gas and the water phase.

From the results it is concluded that the use of organic solvents is only advantageous in case the specific area for mass transfer between solvent and water is large enough to compensate for the additional transport resistance introduced by the solvent, and secondly if the solvent shows a sufficiently high affinity for the pollutants.



This chapter has been published in Bioprocess Engineering 1995, 12, 55-63 by the authors M.T. Cesário, H.H. Beeftink and J. Tramper

## Introduction

### *General*

Industrial waste-gas treatment has become an important topic in the last decades. The concern about atmospheric discharge of industrial waste gases has increased in recent years to such an extent that more severe legislation at this point was unavoidable. This control on the emission of toxic or obnoxious compounds caused an increased effort towards the development of efficient, simple and cheap techniques for waste-gas purification.

Since the early sixties, the biological removal of volatile organic pollutants from waste gases turned out to be an attractive alternative to physico-chemical methods. Biocatalysts have a high substrate affinity, therefore the use of biological treatment techniques can be efficiently applied to low concentration ranges ($<5$ g/m$^3$)[8]. Moreover, the pollutants are converted to harmless oxidation products (e.g. $CO_2+H_2O$), while the process can be carried out at low pressure and temperature. In comparison to other techniques, biological treatment is relatively cheap[11].

The number of contaminants that can be removed by biological treatment is still increasing. Until recently, many organic compounds present in industrial exhaust gases were considered not to be biodegradable (xenobiotics), e.g. chlorinated hydrocarbons (vinyl and methylene chloride), amides, toluene and xylenes. Over the last few years, however, several new bacterial strains have been isolated that degrade these xenobiotics to such an extent that biological treatment became feasible[12].

Systems for biological gas treatment use either attached bacteria (biofilters and trickling filters) or suspended bacteria (bioscrubbers)[12]. In biofilters and trickling filters, the gas passes through a filter bed to which bacteria are attached. The water-soluble compounds are transferred to the water phase from which they diffuse into the biolayer. While in the trickling filter the

water is continuously recycled over the filter bed, it is stationary in the biofilter and only added to compensate for evaporation losses.

In biofilters and trickling filters, pollutant transfer and degradation take place in the same compartment. In bioscrubbers, these processes occur in separate units: a scrubber for gas/water pollutant transfer and an aerated stirred-tank bioreactor containing freely suspended microorganisms where contaminant bioconversion takes place.

Systems with direct gas/water transfer are not effective for the removal of pollutants that dissolve poorly in water ($m_{gw} > 0.1$), especially if these are present at low concentrations. From the three techniques mentioned above, the biofilter is most effective due to the large specific area for mass transfer ($a_{biofilter}$ = 300-1000 $m^{-1}$; $a_{trickling\text{-}filter}$ = 100-300 $m^{-1}$; $a_{bioscrubber} \approx 250$ $m^{-1}$)[3]. A major drawback of biofilters, however is the difficulty to maintain a sufficiently high water level in the carrier material at high gas loads and degradation rates. Another disadvantage of the biofilter is the poor pH control. For this last reason a biofilter can not be used to remove chlorinated hydrocarbons as acid metabolites are produced.

Because the conventional biological techniques are not suitable, a new efficient system for the treatment of large gas flows containing low concentrations of poorly water-soluble pollutants is needed. When low concentrations of such pollutants are to be removed from exhaust gases, the use of an apolar, water-immiscible, organic solvent with a high affinity for the pollutants is of particular interest.

### *Water-immiscible organic solvents in biocatalysis*

In the last few years[9,15] much attention has been paid to biocatalysis in organic media as a possible method to increase the overall volumetric productivity in bioreactors.

Water-immiscible organic solvents with a favourable partition coefficient

have been used in case of toxic or inhibitory substrates or products. Addition of an organic solvent reduces the concentration of the toxic compound in the water phase and higher reactor productivities can be achieved. Besides avoiding toxicity, organic solvents have also been used in order to increase the overall solubility of poorly water-soluble substrates or products. A typical example is the supply of oxygen to the aqueous media, which is the rate-limiting step in many aerobic bioprocesses. Several authors[6,7,14] report an enhancement of the oxygen-transfer rate to the aqueous phase upon addition of an organic solvent with a high affinity for oxygen.

Most studies applying an organic solvent, however, are rather qualitative and an increase of the overall reactor productivity by adding a solvent to the system is often not shown (the productivity is mostly given per $m^3$ aqueous phase). In this paper, the feasibility of using an organic solvent as an intermediary phase for the removal of poorly water-soluble pollutants from waste gases is studied. A quantitative approach is used in order to compare the overall volumetric removal rate of a system containing an organic solvent to a system where no solvent is used. To this end, three different types of organic-solvent-containing systems are compared to two systems where direct gas/water transfer takes place. For each, the total equipment volume required to achieve a removal efficiency of 99% is calculated. Three compounds showing different solubilities in water, i.e. hexane ($m_{gw}$= 71), dichloromethane ($m_{gw}$= 0.1) and acetone ($m_{gw}$= 0.0016), are considered in this study. The organic solvent chosen is dodecene. This study merely aims at characterising the different systems in terms of mass transfer. It is therefore assumed that all substrate transferred to the water phase is immediately consumed or in other words, the biological conversion was not considered to be rate limiting.

## Description of the studied systems

Two systems featuring direct gas/water transfer and bioconversion in one compartment, i.e. an air-lift loop reactor (ALR)[4,22] and a packed absorber, are compared to three two-compartment systems that use an intermediate organic vector. The latter consist of a packed absorber for transfer of the pollutant from the gas to the solvent phase and a bioreactor for transfer of the component from the solvent to the aqueous phase with subsequent conversion. Three bioreactor configurations are considered:

a) Liquid-impelled loop reactor (LLR)[16],
b) packed-bed reactor[3], and
c) mixer-settler[18].

The equipment volume is calculated according to the following scheme:

1) Calculation of the partial mass-transfer coefficients from literature correlations,
2) calculation of the overall mass-transfer coefficient,
3) estimation of the specific area for mass transfer, and
4) determination of the equipment volume from mass balances.

### *Air-lift loop reactor (ALR)*

The ALR is a gas/liquid contacting device that features a liquid continuous phase and a gaseous dispersed phase. Transfer of the contaminant from the gas to the liquid phase containing the microorganisms takes place in the reactor riser compartment (Fig. 1). This reactor shows hydrodynamic constraints at high gas flows due to flooding. The maximum superficial gas velocity is therefore about 0.1 m/s[1].

The ALR volume is determined for steady-state operation using eq. 1 which is derived from a mass balance for the pollutant in the gas phase, while considering the gas and the liquid phase to be in plug- flow and ideally

mixed, respectively:

$$V_{ALR} = \frac{m_{gw}\, Q_g}{K_w\, a_{riser}} \frac{V_{ALR}}{V_{riser}} \ln \frac{\frac{C_{gin}}{m_{gw}} - C_w}{\frac{C_{gout}}{m_{gw}} - C_w} \qquad (1)$$

In this study it has been assumed that all the substrate transferred to the water phase is immediately consumed ($C_w = 0$). Eq. 1 can therefore be simplified. For the ratio $V_{ALR}/V_{riser}$ the typical value of 1.25 is taken[22].

$K_w$ is the overall gas/water mass-transfer coefficient which is estimated from partial mass transfer coefficients according to:

$$\frac{1}{K_w} = \frac{1}{k_w} + \frac{1}{m_{gw}\, k_g} \qquad (2)$$

It is assumed that the gas bubbles have an average diameter of about 6 mm and a circulating interface according to Van't Riet and Tramper[21]. The partial liquid-phase mass-transfer coefficient can thus be calculated from the penetration theory[17]:

$$k_w = 2 \sqrt{\frac{4\, D_w\, v_{bs}}{\pi\, d_p}} \qquad (3)$$

The partial gas-phase mass-transfer coefficient for these bubbles is given by the correlation of Kronig and Brink[17]:

$$\frac{k_g\, d_p}{D_g} = 17.9 \qquad (4)$$

The specific area for mass transfer $a_{riser}$ in eq. 1 is given by eq. 5:

$$a_{riser} = \frac{6\,\epsilon}{d_p} \tag{5}$$

For the gas hold-up ($\epsilon$) in the riser the typical value of 0.1[22] is used.

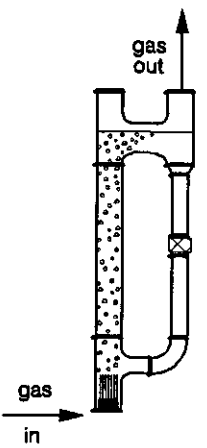


Figure 1. Air-lift loop reactor (ALR)

***Packed absorber***

Packed absorbers are vertical towers that are filled with packing material. The liquid containing the microorganisms is distributed over the packing and flows down its surface. The gas flows upward in counter-current with the falling liquid film. Transfer of the pollutant from the gas to the liquid phase takes place at the surface of this liquid film covering the packing material and is followed by biological degradation (Fig. 2). The liquid is collected at the bottom of the tower and recycled.

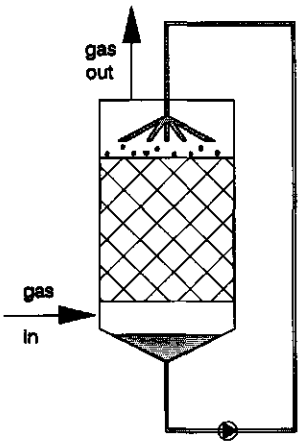


Figure 2. Packed absorber (PA)

The packed-absorber volume is determined from mass balances for the pollutant in the gas and the liquid phases. Assuming that both phases flow counter-current and in plug flow, the packed absorber volume can be determined for steady-state operation by combining both mass balances. The result is given in eq. 6:

$$V_{packed\ absorber} = \frac{\ln\left(\dfrac{\dfrac{C_{gout}}{m_{gw}} - C_{win}}{\dfrac{C_{gin}}{m_{gw}} - C_{wout}}\right)}{K_w\, a\left(\dfrac{1}{Q_w} - \dfrac{1}{m_{gw}\, Q_g}\right)} \qquad (6)$$

The concentration in the outlet liquid ($C_{w,out}$) is calculated from the overall mass balance:

$$Q_g\ (C_{gin} - C_{gout}) = Q_w\ (C_{wout} - C_{win}) \tag{7}$$

Assuming the pollutant concentration in the inlet liquid to be zero ($C_{w,in}=0$) eqs. 6 and 7 can be simplified and combined to:

$$V_{packed\ absorber} = \frac{m_{gw}\ Q_g\ \ln\left(\frac{C_{gin}}{C_{gout}}\left(1 - \frac{1}{\Lambda}\right) + \frac{1}{\Lambda}\right)}{K_w\ a\ \left(1 - \frac{1}{\Lambda}\right)} \tag{8}$$

with: $\Lambda = Q_w/(m_{gw}Q_g)$

$\Lambda$ is the absorption factor; its value ranges from 1.25 to 2 [17]. In this study a value of 1.5 is used.

Because it is assumed that the pollutant transferred from the gas to the aqueous phase is immediately degraded, the outlet liquid concentration is zero ($C_{w,out}=0$). In this case eq. 6 is simplified and $Q_w$ is calculated from $\Lambda = 1.5$.

In order to calculate the packed-absorber volume, the overall mass-transfer coefficient ($K_w$) and the specific area ($a$) for gas/liquid mass transfer must be known. The value of these parameters depends on the type of packing material. The packing material chosen in this study is ceramic Raschig rings with a nominal diameter of 19 mm. The bed porosity and other packing characteristics are given by Treybal[17].

The overall mass-transfer coefficient $K_w$ is determined from eq. 2 if the partial mass-transfer coefficients of the gas (eq. 9) and the liquid phase (eq. 10) are known. The partial mass transfer coefficients are calculated with the correlations of Onda et al[10]:

$$\frac{k_g}{a_p D_g} = 5.23 \left(\frac{\rho_g v_{g,s}}{a_p \mu_g}\right)^{0.7} Sc_g^{0.33} (a_p d_p)^{-2} \quad (9)$$

$$k_w \left(\frac{\rho_w}{\mu_w g}\right)^{0.33} = 0.0051 \left(\frac{\rho_w v_{w,s}}{a_p \mu_w}\right)^{0.667} Sc_w^{-0.5} (a_p d_p)^{0.4} \quad (10)$$

When the tower working conditions approach the "loading point"[13] the specific area for mass transfer is identical to the specific area of the packing material. The loading point is defined as the point where the gas and the liquid start impeding one another. For slightly higher velocities flooding will occur.

***Packed absorber/Liquid-impelled loop reactor (LLR)***

In the combination packed absorber/LLR, removal of the compound from the gas phase and biological conversion occur in two separate compartments (Fig. 3). The gas contacts with an intermediate solvent in a packed column. The solvent containing the pollutant is recycled through the liquid-impelled loop reactor (LLR)[16], which contains the aqueous cell suspension as continuous phase. In this reactor, transfer of the pollutant from the dispersed solvent to the water phase with subsequent biological degradation occurs.

*Packed absorber*

The volume of the packed absorber is calculated using eq. 8 but instead of $m_{gw}$ the partition coefficient of the pollutant between the gas and the solvent ($m_{gs}$) is used. Both partial and overall mass-transfer coefficients ($k_g$, $k_s$ and $K_s$, respectively) are determined in analogy with eqs. 9, 10 and 2, respectively.

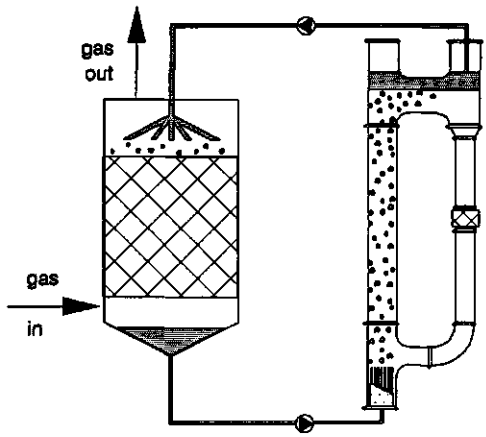


Figure 3. Packed absorber/Liquid-impelled loop reactor

*Liquid-impelled loop reactor (LLR)*

The volume of the LLR is calculated from the mass balance for the pollutant in the solvent phase. Assuming plug-flow for the solvent and an ideally mixed aqueous phase, the LLR volume for steady state operation is given by:

$$V_{LLR} = \frac{m_{sw}\, Q_s}{K_w\, a}\, \frac{V_{LLR}}{V_{riser}}\, \ln\left( \frac{\frac{C_{sin}}{m_{sw}} - C_w}{\frac{C_{sout}}{m_{sw}} - C_w} \right) \qquad (11)$$

The ratio $V_{LLR}/V_{riser} = 1.25$ is taken from Van Sonsbeek[19].

The overall mass-transfer coefficient $K_w$ is calculated in analogy to eq.(2).

The solvent droplets in a LLR have an average diameter of 3 mm[20] and a rigid interface according to the Levich criterion[5]. The partial mass-transfer coefficients on the solvent ($k_s$) and on the water side ($k_w$) can therefore be calculated with eqs. 12 and 13, respectively.

The partial mass-transfer coefficient on the solvent side for rigid droplets[18] is obtained from:

$$Sh_s = \frac{k_s\, d_p}{D_s} = 6.5 \qquad (12)$$

The partial mass-transfer coefficient on the water side is given by Brian and Hales[2]:

$$Sh_w = \frac{k_w\, d_p}{D_w} = (4 + 1.21\ Re_w^{2/3}\ Sc_w^{2/3})^{1/2} \qquad (13)$$

The specific area *a* for solvent/water mass transfer was determined by means of eq. 5 assuming that the solvent hold-up is approximately 5 % of the reactor volume[19].

***Packed absorber/ Packed-bed reactor***

The combination packed absorber/ packed-bed reactor is also a two-compartment system. The transfer of the pollutant from the gas to the organic phase takes place in a packed absorber and the solvent is recycled to a packed-bed reactor containing immobilized cells (Fig. 4). The cells are immobilized in gel beads (of 1.5 mm diameter), that occupy 30 % of the total reactor volume. Another 35% of the reactor is occupied by glass beads to reduce axial dispersion and to attain a high liquid/solid contacting efficiency[3]. Transfer of the pollutant from the solvent to the stagnant water layer around the gel beads, diffusion into the beads and subsequent biological conversion will take place. The water-immiscible organic liquid is recycled between the absorber and the reactor.

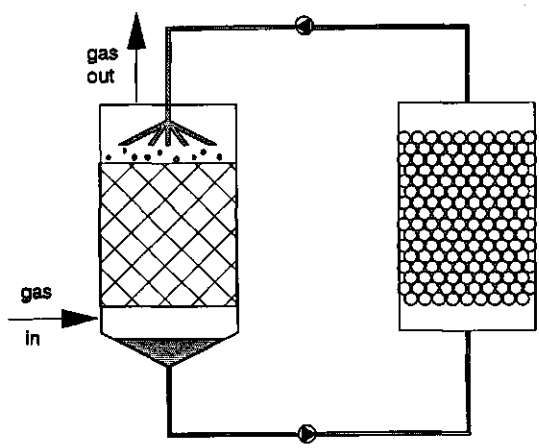


Figure 4. Packed absorber/Packed-bed reactor

The volume of the packed absorber is determined with equation (8). The required volume of the packed-bed reactor is calculated from the mass balance for the pollutant in the solvent phase, assuming a plug-flow solvent phase and no convection in the stagnant water layer around the gel beads. Considering that there is no partitioning of the compound between the water film and the alginate beads, the volume of the packed bed for steady-state operation is given by eq. 14:

$$V_{packed\ bed} = \frac{m_{sw}\, Q_s}{K_w\, a} \ln \left( \frac{\frac{C_{sin}}{m_{sw}} - C_w}{\frac{C_{sout}}{m_{sw}} - C_w} \right) \qquad (14)$$

The overall mass-transfer coefficient $K_w$ can be calculated with eq. 2 provided the partial mass-tranfer coefficients are known. The mass-transfer coefficient in the water side can be calculated from diffusivity and film

geometry (eq. 15). Because the water-film thickness ($\delta_w$) is difficult to determine, a conservative estimate of 0.1 mm was used in the calculations:

$$k_w = \frac{D_w}{\delta_w} \tag{15}$$

The partial mass-transfer coefficient on the solvent side was calculated from[3]:

$$\phi \left(\frac{k_s}{v_{s,s}}\right) Sc^{2/3} = \frac{0.765}{Re^{0.82}} + \frac{0.365}{Re^{0.386}} \tag{16}$$

The specific mass-transfer area is calculated from eq. 5 with the hold-up and the particle size of the gel beads.

***Packed absorber / Mixer-settler***

In this system transfer of the pollutant to the solvent takes place in a packed absorber. The solvent is then transferred to a stirred-tank reactor (mixer), which contains the aqueous medium with the cells (Fig. 5). In this reactor the two liquid phases are intensively mixed and transfer of the pollutant from the solvent to the water phase with subsequent degradation of the pollutant occurs. Both phases are then separated by gravity in the settler and recycled to either the absorber or the mixer.

The volume of the packed absorber is determined with equation (8).

*Mixer*

The required volume of the mixer is calculated from the mass balance for the pollutant in the solvent. The solvent and water phases are assumed to be ideally mixed. The volume of the mixer is given by:

$$V_{mixer} = \frac{Q_s\,(C_{sin} - C_{sout})}{K_w\,a\,(\frac{C_{sout}}{m_{sw}} - C_w)} \tag{17}$$

The overall mass-transfer coefficient ($K_w$) is calculated from eq. (2) provided the partial mass-transfer coefficients are known. The partial solvent mass-transfer coefficient ($k_s$) is determined for rigid solvent droplets by means of eq. 12 and $k_w$ is calculated from[23]:

$$\frac{k_w\,d_p}{D_w} = 2 + 0.47\,[\frac{d_p^{4/3}\,P^{1/3}\,\rho_w}{\mu_w}]^{0.62}\,[d/T]^{0.17}\,Sc_w^{0.36} \tag{18}$$

The solvent-droplet diameter is a function of the power input per unit mass of fluid, given by[23]:

$$P = 1.0\,g^{5/4}\,(\frac{\sigma}{\rho_w})^{1/4}\,(\frac{\Delta\rho}{\rho_w})^{5/4} \tag{19}$$

At this power input the droplet size is equal to:

$$d_p = 0.025\,P^{-0.4}\,(\frac{\sigma}{\rho_w})^{3/5}\,(1 + 2.5\,\epsilon) \tag{20}$$

The solvent-droplet diameter given by eq. 20 is the one obtained for a long residence time so that an equilibrium droplet diameter is reached. Because this is not generally the case, the droplet diameter must be corrected for the real residence time ($\tau$)[23]:

$$\frac{d_p}{d_{p(v)}} = 1 - e^{-0.002 \frac{V_{mixer}}{Q_o + Q_w}} \qquad (21)$$

In order to calculate the specific area $a$ in analogy to eq. 5, the solvent hold-up in the reactor was chosen to be 60% of the total reactor volume. The maximum possible hold-up[13,18] of dispersed phase in the mixer is 0.6-0.8; beyond these values phase inversion may occur.

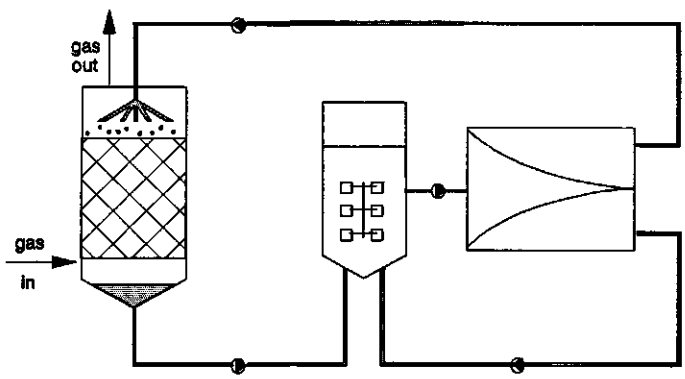


Figure 5. Packed absorber/Mixer-settler

*Settler*

Separation of the dispersion leaving the mixer takes place by means of gravity in a settler. The dispersion can enter the settler at the level of the interface between the two bulk liquids but there is preference to enter it a little below this interface in case the dispersed phase is the lighter one. The solvent droplets first rise to the interface and then coalesce. In general, the coalescence time is larger than the rise time to the interface. Therefore a

layer of solvent droplets below the interface of the two bulk liquids - the coalescence layer - will exist. Because the droplet coalescence is rate-limiting for the separation, it determines the dimensions of the settler.

The coalescence time is calculated from[23]:

$$t_{coalescence} = 3.1\ 10^4\ \frac{\sigma^{0.24}\ \mu_s}{(g\ \Delta\rho)^{1.24}\ d_p^{1.48}} \qquad (22)$$

The bottom area of the settler is given by[23]:

$$A = 40\ \frac{Q_s}{\epsilon}\ (\frac{t_{coalescence}}{H_c})^{1/3} \qquad (23)$$

$H_c$ is the height of the coalescence layer which is assumed to be 0.2 m. The total height of the settler is taken as $7H_c$[23].

## Results and discussion

On basis of the presented correlations, the required volume needed to obtain a 99% reduction of the pollutant concentration in the gas phase is calculated for each of the systems described. Because this study merely aims at characterising the different systems in terms of mass transfer, biological conversion is assumed not to be rate limiting. This makes it possible to simplify the mass-balance equations by considering the pollutant concentration in the water phase to be zero ($C_w$=0). In addition, a 99% reduction of the pollutant concentration in the solvent phase is assumed for the design of the bioreactor. As the pollutant concentration in the solvent entering the packed absorber ($C_{s,in}$) is thus negligible compared to the concentration in the effluent ($C_{s,out}$), the overall mass balance for the packed absorber (eq. 7) can be simplified by considering $C_{s,in}$=0.

In this study three compounds with a different solubility in water are chosen: Hexane, dichoromethane and acetone. Acetone dissolves well in water ($m_{gw}$= 0.001) and therefore the use of an organic solvent was not considered for this pollutant. It is only used as a reference in order to compare the volumes needed to remove a well water-soluble compound with the volumes required to remove moderately or poorly water-soluble compounds (dichloromethane and hexane).

Dodecene is chosen as solvent because both hexane and dichloromethane have a favourable partition coefficient in the system air/dodecene. Values for $m_{gs}$ of 0.012 and 0.006 were experimentally determined for hexane and dichloromethane, respectively.

The partial and overall mass-transfer coefficients and the specific areas obtained in each type of bioreactor are calculated using the correlations given previously. The results are summarized in Table 1.

The overall mass-transfer coefficients for dichloromethane and hexane have the same order of magnitude. The values calculated for acetone are one order of magnitude lower ($K_w \approx 10^{-5}$) compared to those of dichloromethane and hexane ($K_w \approx 10^{-4}$). This is due to the low value of the partition coefficient of acetone in the system gas/water (eq. 2). The specific area for mass transfer from the solvent to the aqueous phase is different for each bioreactor. While in the LLR a value of 100 $m^2/m^3$ is obtained, in the packed-bed reactor and in the mixer this parameter reaches values of 1200 and 15000 $m^2/m^3$, respectively.

The total volume required for 99% removal of acetone, dichloromethane and hexane from a gas flow of 0.8 $m^3/s$ is shown in Fig. 6.

Table 1. Partial and overall mass-transfer coefficients and specific areas calculated for each of the systems described.

| System | parameters | Contaminant | | | Eq. nr |
|---|---|---|---|---|---|
| | | hexane $m_{gw}$= 71 $m_{gs}$= 0.012 | dichloromethane $m_{gw}$= 0.1 $m_{gs}$= 0.006 | acetone $m_{gw}$= 0.001 | |
| ALR | $k_g$ (m/s) | 2.3E-2 | 3.0E-2 | 3.4E-2 | (4) |
| | $k_w$ (m/s) | 2.3E-4 | 2.4E-4 | 2.7E-4 | (3) |
| | $K_w$ (m/s) | 2.3E-4 | 2.2E-4 | 3.0E-5 | (2) |
| | $a$ ($m^{-1}$) | 100 | 100 | 100 | (5) |
| Packed | $k_g$ (m/s) | - | 1.8E-3 | 8E-2 | (9) |
| absorber | $k_w$ (m/s) | - | 4E-4 | 8E-5 | (10) |
| with water | $K_w$ (m/s) | - | 3E-4 | 4E-5 | (2) |
| | $a$ ($m^{-1}$) | - | 250 | 250 | - |
| Packed | $k_g$ (m/s) | 1E-2 | 8E-3 | - | (9) |
| absorber | $k_s$ (m/s) | 1E-4 | 9E-5 | - | (10) |
| with | $K_s$ (m/s) | 5.4E-5 | 3.2E-5 | - | (2) |
| solvent | $a$ ($m^{-1}$) | 250 | 250 | - | - |
| LLR | $k_s$ (m/s) | 1.7E-6 | 1.7E-6 | - | (12) |
| | $k_w$ (m/s) | 2.9E-5 | 3.9E-5 | - | (13) |
| | $K_w$ (m/s) | 2.9E-5 | 1.6E-5 | - | (2) |
| | $a$ ($m^{-1}$) | 100 | 100 | - | (5) |
| Packed- | $k_s$ (m/s) | 3.6E-4 | 1E-3 | - | (16) |
| bed | $k_w$ (m/s) | 1.6E-5 | 1.6E-5 | - | (15) |
| reactor | $K_w$ (m/s) | 1.6E-5 | 1.6E-5 | - | (2) |
| | $a$ ($m^{-1}$) | 1200 | 1200 | - | (5) |
| Mixer | $k_s$ (m/s) | 1.2E-4 | 2.3E-5 | - | (12) |
| | $k_w$ (m/s) | 2.2E-4 | 1.6E-4 | - | (18) |
| | $K_w$ (m/s) | 2.1E-4 | 9E-5 | - | (2) |
| | $a$ ($m^{-1}$) | 15000 | 15000 | - | (5) |

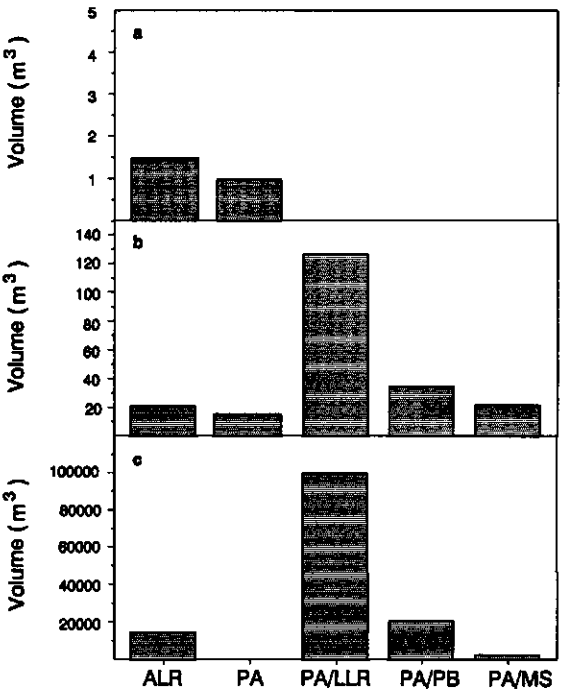


Figure 6. Volume of the different systems for the removal of 99% of pollutant from a gas flow of 0.8 $m^3/s$. a. Acetone; b. Dichloromethane; c. Hexane; ALR. Air-lift loop reactor; PA. Packed absorber; LLR. Liquid-impelled reactor; PB. Packed-bed reactor; MS. Mixer-settler

The removal of acetone is more efficiently accomplished in a packed absorber than in an ALR. This is due to a larger specific area for mass transfer in the packed absorber ($a_{packing}$= 250 $m^{-1}$) compared to the ALR ($a$= 100 $m^{-1}$). Furthermore, the packed absorber is advantageous because it can be used for large gas flows. The maximum allowed superficial gas velocity in a packed absorber (1 m/s)[11] is about one order of magnitude larger than in an ALR (0.1 m/s)[1].

For the removal of dichloromethane the volume of systems with and without solvent is calculated. Similar to the case of acetone, dichloromethane is more efficiently removed in a packed absorber with water ($V_{packed\ absorber}$=15 $m^3$) than in a ALR ($V_{ALR}$=20 $m^3$) because of the larger specific area for mass transfer available in the first bioreactor type.

The volume needed for the removal of dichloromethane is one order of magnitude larger than the volume needed to remove acetone. This is due to the lower solubility of dichloromethane in water.

The total volume of the systems using an organic solvent depends on the type of bioreactor used. The volume of the packed absorber with solvent is 7.5 $m^3$ and equal for each of the three configurations described. For the combination packed absorber/ LLR a total volume of 130 $m^3$ is needed while the packed absorber/packed-bed reactor and packed absorber/mixer-settler require a volume of 35 and 22 $m^3$, respectively. These differences in volume result from the different specific areas for mass transfer available in the three bioreactors. The packed absorber/LLR does not bring any advantage compared to the systems using only water. This is due to the small specific area for mass transfer available in the LLR ($a$= 100$m^{-1}$). The volumes of the packed absorber/packed-bed reactor and packed absorber/mixer-settler have the same order of magnitude as the systems where no solvent is used. As will be shown later on, this may be influenced by using a solvent with a different affinity for the pollutant.

Also for hexane the required volume of the systems with and without solvent is calculated. For the removal of hexane, however, the volume of the packed absorber with water was not determined. The amount of water needed to remove 99% of hexane is extremely large due to its poor solubility. For reasons of flooding the use of a packing is then not possible. The ALR volume needed to remove hexane is approximately 15000 $m^3$ which is about three and four orders of magnitude larger than the volumes for

dichloromethane and acetone, respectively. The total volume of the systems using an organic solvent is again dependent on the type of bioreactor used. The volume of the packed absorber with solvent is equal to 6.5 $m^3$. For the packed absorber/LLR a volume of 100000 $m^3$ is needed, while the combinations packed absorber/packed-bed reactor and packed absorber/mixer-settler require volumes of 21000 $m^3$ and 2700 $m^3$, respectively. The packed absorber/LLR does not bring any advantage compared to the system using only water. The use of an intermediate organic solvent can be advantageous in packed absorber/mixer-settler, however, because the specific area for mass transfer between the two liquid phases in the mixer is sufficiently large.

For dichloromethane, in contrast to what was found for hexane, none of the organic-solvent- containing systems is clearly advantageous compared to the system only using water. This is caused by the fact that dichloromethane is only 16 times more soluble in dodecene than in water, while for hexane this factor is about 6000.

The effect of another solvent (with a different affinity for the compound to be removed) on the packed absorber/mixer-settler volume has been calculated using hexane as pollutant. The required volume of the organic-solvent-containing system is compared with the volume of an ALR. In Fig. 7 the ratio between the volume of these two systems is shown as a function of $m_{gs}$. The total volume of the packed absorber/mixer-settler decreases with a decrease in partition coefficient. If the compound dissolves about 100 times better in the solvent than in water ($m_{gw}$= 71), the total volume of the system containing the organic solvent is about 3 times smaller than the volume of the absorber with water. A lower $m_{gs}$ value results in a decreased packed absorber and settler volume. In contrast, the mixer volume hardly changes with $m_{gs}$ (values not shown).

It is thus shown that the use of an intermediate organic solvent can be

advantageous depending on the affinity of the pollutant to the solvent.

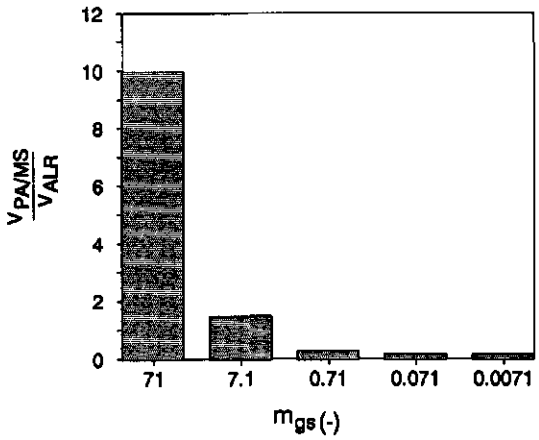


Figure 7. Influence of the $m_{gs}$ value for hexane on the ratio between the volume of the Packed absorber/Mixer-settler (PA/MS) and the volume of the Air-lift loop reactor (ALR)

## Conclusions

When an intermediate solvent phase is used, an extra resistance is added to the system. From this study it is shown that nevertheless a solvent phase can be advantageously used for the removal of poorly water-soluble compounds. Two requirements however, are essential. Firstly a high affinity of the solvent for the pollutant is needed, and secondly a system featuring sufficiently large specific areas for gas/solvent mass transfer in the absorber and solvent/water mass transfer in the bioreactor has to be used.

## List of symbols

| | | |
|---|---|---|
| $a$ | specific area for mass transfer | [$m^{-1}$] |
| $a_p$ | packing material specific area | [$m^{-1}$] |
| $C$ | pollutant concentration | [$kg.m^{-3}$] |
| $D$ | pollutant diffusivity | [$m^2.s^{-1}$] |
| $d$ | stirrer diameter | [m] |
| $d_p$ | bubble, droplet or packing material diameter | [m] |
| $g$ | acceleration of the gravity | [$m.s^{-2}$] |
| $Gr$ | Grashof number : $gd_p^3\Delta\rho(\rho/\mu)^2/\rho$ | [dimensionless] |
| $H$ | height | [m] |
| $K$ | overall mass-transfer coefficient | [$m.s^{-1}$] |
| $k$ | partial mass-transfer coefficient | [$m.s^{-1}$] |
| $m_{gw}$ | partition coefficient of the pollutant in the system gas/water | [$kg/m^3$ gas / $kg/m^3$ water] |
| $m_{gs}$ | partition coefficient of the pollutant in the system gas/solvent | [$kg/m^3$ gas / $kg/m^3$ solvent] |
| $m_{sw}$ | partition coefficient of the pollutant in the system solvent/water: $m_{gw}/m_{gs}$ | [$kg/m^3$ solvent / $kg/m^3$ water] |
| $P$ | power input per unit mass of fluid | [$W.kg^{-1}$] |
| $Q$ | flow | [$m^3.s^{-1}$] |
| $Re$ | Reynolds number: $\rho v d_p/\mu$ | [dimensionless] |
| $Sc$ | Schmidt number: $\mu/\rho D$ | [dimensionless] |
| $Sh$ | Sherwood number: $kd_p/D$ | [dimensionless] |
| $T$ | tank diameter | [m] |
| $t$ | time | [s] |
| $v_{bs}$ | bubble rising velocity | [$m.s^{-1}$] |
| $v_s$ | superficial velocity | [$m.s^{-1}$] |
| $V$ | volume | [$m^3$] |

| | | |
|---|---|---|
| $\phi$ | void fraction | [dimensionless] |
| $\epsilon$ | hold-up | [dimensionless] |
| $\rho$ | density | [$kg.m^{-3}$] |
| $\mu$ | dynamic viscosity | [$kg.m^{-1}s^{-1}$] |
| $\delta$ | film thickness | [m] |
| $\sigma$ | interfacial tension | [$kg.s^{-2}$] |
| $\Delta\rho$ | density difference | [$kg.m^{-3}$] |
| $\tau$ | residence time | [s] |

**Subscripts:**

| | |
|---|---|
| *c* | coalescence layer |
| *in* | to the equipment |
| *out* | from the equipment |
| *g* | gas phase |
| *s* | solvent phase |
| *w* | water phase |

## Acknowledgements

This work was supported by a grant from the Junta Nacional de Investigação Científica e Tecnológica, Lisbon, Portugal. The authors wish to thank W.A. Beverloo for his comments on the manuscript and for the valuable discussions.

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# Chapter 3

## Enhancement of gas-liquid mass transfer rate of apolar pollutants in the biological waste-gas treatment by a dispersed organic solvent


### Summary

Dispersed water-immiscible solvents are known to enhance oxygen transfer rates in oxygen-limited aerobic fermentations. Here, this technique is applied to improve the mass transfer rate of poorly water-soluble gaseous pollutants during the biological treatment of waste gases. In a stirred-tank reactor, the enhancement of mass transfer rates was studied as a function of the pollutant solubility in water. The solvent used was FC40 (up to 10 % v/v) and the model pollutants were toluene and oxygen (moderately and poorly water-soluble, respectively).

The overall volumetric mass transfer coefficient from the gas to the bulk liquid ($k_l a_{gl}$), was measured in transient state, in the absence of microorganisms, and it was found to be essentially constant with the solvent volume fractions tested for both toluene and oxygen. With the values of $k_l a_{gl}$ and of the partition coefficient gas/liquid ($m_{gl}$), the enhancement of the mass transfer rate by solvent addition could be predicted theoretically. A good agreement between the theoretical evaluation and the experimental results from steady-state experiments in the presence of biological consumption was



This chapter has been accepted for publication in Enzyme and Microbial Technology by the authors M.T. Cesário, W.A. Beverloo, J. Tramper and H.H. Beeftink

found. An enhancement of the mass transfer rate of a factor up to 1.1 was found for toluene using a dispersion containing 10 % (v/v) FC40, while the oxygen transfer rate increased by a factor 2 at the same solvent volume fraction. It was further demonstrated theoretically that in solvent-in-water dispersions using solvents with a positive spreading coefficient, the addition of a solvent has hardly any influence on the enhancement of the transfer rate of moderately water-soluble compounds whilst it can have a substantial effect on the enhancement of very poorly water-soluble ones.

## Introduction

The mass transfer rate of apolar gaseous substrates to an aqueous phase is the rate-limiting step in many biological processes, due to the low solubility of these compounds in water. Examples of mass-transfer-limited processes are the removal of apolar gaseous pollutants in the biological treatment of waste gases[3,4,6,19] and the oxygen supply in aerobic fermentations[7,8,9,27]. One possible way to improve the rate of transport towards the water phase is by dispersion in the aqueous medium of a water-immiscible organic solvent in which these apolar compounds are preferentially soluble[13,14,17,23,24]. The most studied example is the enhancement of the oxygen transfer rate in oxygen-transfer-limited fermentations by dispersing a second liquid phase in the culture broth. Examples of these liquids include hydrocarbons[2,11,15,22,23,25,28] and perfluorocarbons[13,14,17,23]. Although the overall oxygen solubility in the dispersion can be raised considerably by addition of an organic solvent to the culture medium, the efficiency of the process is very much dependent on the prompt exchange of the oxygen between the dispersed phase and the aqueous medium and therefore on the solvent/water mass transfer rate, the latter being directly proportional to the interfacial area between the two liquids[3,23].

To our knowledge, organic solvents as mass transfer enhancers have been mostly used to improve the oxygen supply in aerobic fermentations. Recently, the use of perfluorocarbons to enhance the removal of carbon dioxide from the culture broth during an anaerobic fermentation has been mentioned[16,18].

The purpose of the work described in the present paper was to study the effect of a dispersed solvent on the mass transfer rate of compounds with different solubilities in water, aiming at application in the biological waste gas treatment. The mass transfer rate as a function of the solubility of the compound in the solvent was also studied.

Overall volumetric mass transfer coefficients for exchange between the gas and the dispersion, $k_l a_{gl}$, were measured in transient state for dispersions containing various solvent volume fractions by monitoring the compound concentration either in the outlet gas phase or in the liquid phase. With the $k_l a_{gl}$ and the gas/liquid partition coefficients values ($m_{gl}$) determined experimentally, the potential mass transfer rate enhancement was estimated theoretically from a steady-state mass balance. Pseudo steady-state experiments in the presence of a biological reaction were done to confirm the potential enhancements predicted theoretically.

The two model compounds chosen for studying the mass transfer rate enhancement as a function of the compound's solubility in water were toluene and oxygen; the partition coefficient in the system gas/water being 0.21 and 32.7 (mol/m$^3$gas)/(mol/m$^3$water), respectively. The water-immiscible organic solvent used was FC40, a perfluorocarbon. Both toluene and oxygen dissolve better in FC40 than in water and have partition coefficients between gas and solvent of 0.012 and 2.8 (mol/m$^3$gas)/(mol/m$^3$solvent), respectively. Besides showing a better affinity for toluene and oxygen, FC40 was further chosen because of its non-biodegradability, non-toxicity for the cells and low vapour pressure.

During transient state measurements, the oxygen concentration in the liquid phase was measured in time to derive air/liquid overall mass transfer coefficients ($k_l a_{gl}$). Continuous monitoring of the liquid phase concentration is difficult for compounds other than oxygen. Frequent sampling and analysis is an alternative. Another possibility is measuring the change of the outlet gas phase concentration in time. However, this technique is not applicable for poorly-water soluble compounds since accurate $k_l a$'s are difficult to derive. With these compounds, the outlet concentration changes strongly in the first seconds, after the step change is imposed, to a value very close to the inlet gaseous concentration. The rapid initial change and the small difference between the inlet and the outlet gas concentrations are very difficult to follow accurately. For these reasons monitoring of the gas phase concentration is only accurate for moderately poor water-soluble compounds. This was thus the technique chosen to measure the overall volumetric mass transfer coefficients for toluene.

## Theory

### *Transient state mass transfer experiments: measurement of the overall volumetric gas/liquid mass transfer coefficient* $(k_l a)_{gl}$

The overall volumetric mass transfer coefficients to dispersions containing different FC40 volume fractions ($k_l a_{gl}$) were assessed in transient state by solving the mass balances for the compound over the gas and the liquid phase, eqs. 1 and 2, respectively. The gas and the liquid were assumed to be well mixed and the dispersion was considered as a single homogeneous phase which is equivalent to assuming that there is equilibrium between the two liquids. The validity of this assumption will be discussed later.

$$V_g \frac{dC_{gout}}{dt} = F_g (C_{gin} - C_{gout}) - k_l a_{gl} \left(\frac{C_{gout}}{m_{gl}} - C_l\right) V_l \quad (1)$$

$$\frac{dC_l}{dt} = k_l a_{gl} \left(\frac{C_{gout}}{m_{gl}} - C_l\right) \quad (2)$$

with $F_g$ the gas flow rate ($m^3$gas/s), $C_{gin}$ the inlet concentration in the gas phase (mol/$m^3$gas), $C_{gout}$ the concentration in the gas phase leaving the liquid and entering the reactor headspace (mol/$m^3$gas), $C_l$ the mean concentration in the dispersion (mol/$m^3$liquid), $k_l a_{gl}$ the overall volumetric mass transfer coefficient based on overall liquid phase concentrations and on the total liquid phase volume ($s^{-1}$), $m_{gl}$ the partition coefficient of the compound between the gas and the liquid (mol/$m^3$gas)/ (mol/$m^3$liquid), $V_l$ ($m^3$liquid) and $V_g$ ($m^3$gas) the liquid and the gas volume, respectively, and $t$ the time (s).
$C_l$ and $m_{gl}$ are given respectively by:

$$C_l = f_s C_s + f_w C_w \quad (3)$$

and

$$\frac{1}{m_{gl}} = \frac{f_s}{m_{gs}} + \frac{f_w}{m_{gw}} \quad (4)$$

where $C_s$ and $C_w$ are the concentration in the solvent and in the water phase (mol/$m^3$), $f_s$ and $f_w$ are the solvent and the water volume fractions ($m^3$/$m^3$total liquid), and $m_{gs}$ and $m_{gw}$ are the partition coefficients in the system gas/solvent (mol/$m^3$gas)/(mol/$m^3$solvent) and gas/water (mol/$m^3$gas)/ (mol/$m^3$water), respectively. Eq. 4 is derived in appendix 1.

When $k_l a$ values are derived from transient gas concentrations, it is important to take into account the mixing effect of the gas phase in the reactor headspace. This effect is significant during the first seconds of the

measurement and becomes increasingly important the larger the headspace volume and the smaller the gas flow rate are:

$$V_{hs} \frac{dC_{ghs,out}}{dt} = F_g \, (C_{gout} - C_{ghs,out}) \tag{5}$$

with $C_{ghs,out}$ the concentration in the gas phase leaving the reactor (mol/m$^3$gas) and $V_{hs}$ the reactor headspace volume (m$^3$gas).

The mass transfer from the reactor headspace across the surface of the liquid was not taken into account since it is considered to be negligible ($a_{gl} \approx$ 5 m$^2$/m$^3$liquid) compared to the transport from the gas bubbles in the emulsion ($a_{gl} \approx 50$ m$^2$/m$^3$liquid).

The overall gas/liquid transfer coefficient for toluene was calculated by solving numerically the set of equations (1-5) for a range of $k_l a_{gl}$ values. The value giving the best fit of the experimental data ($C_{ghs,out}$) was determined by an optimizing algorithm.

In the case of oxygen, overall volumetric gas/liquid transfer coefficients were calculated by monitoring the dissolved oxygen concentration in the bulk two-liquid phase with an oxygen electrode in time. $k_l a_{gl}$ values were obtained from eq. 6:

$$\ln \frac{\left(\frac{C_{gin}}{m_{gl}} - C_l(t)\right)}{\left(\frac{C_{gin}}{m_{gl}} - C_l(t_0)\right)} = - k_l a_{gl} \, (t - t_0) \tag{6}$$

where $t_0$ is the time at which the step change in the inlet gas composition occurred (s) and $t$ is the elapsed time from the introduction of the step change in the inlet gas composition (s).

This equation is a simplification of eq. 2; $C_{gout}$ is assumed to be constant and equal to $C_{gin}$. This is valid in the case of oxygen due to its very low

solubility in the liquid phase (even in the dispersions with the largest solvent volume fractions tested) and the small residence time of the gas in the reactor[20].

The response time of the oxygen electrode was found to be 6.3 s. Since the characteristic time for mass transfer ($1/k_l a_{gl}$) was approximately 60 s (as will be shown below), a delay in the oxygen readings was not taken into consideration[26].

Oxygen concentrations were calculated from electrode partial-pressure readings and with the partition coefficient of oxygen between air and the dispersion calculated from eq.4.

***Prediction of the mass transfer rate enhancement***

Using the values of $k_l a_{gl}$ obtained during the studies in transient state and the values of $m_{gl}$, the enhancement of the mass transfer rate by solvent addition can be predicted. The potential mass transfer enhancement ($E$) is given by the ratio between the mass transfer rate in the presence and absence of solvent:

$$E = \frac{[F_g\ (C_{gin}-C_{gout})]_l}{[F_g\ (C_{gin}-C_{gout})]_w} \tag{7}$$

where $l$ and $w$ stand for overall liquid and water, respectively.

The mass transfer rate was calculated from a mass balance over the gas phase in steady-state conditions:

$$F_g\ (C_{gin}-C_{gout}) = k_l a_{gl}\ (\frac{C_{gout}}{m_{gl}}-C_l)\ V_l \tag{8}$$

When the transfer rate from gas to liquid is rate limiting, the concentration of the substrate in the liquid can be neglected ($C_l = 0$). With this simplification, eq. 8 was rearranged and $C_{gout}$ was calculated as a function of $k_l a_{gl}$ and $m_{gl}$ yielding:

$$C_{gout} = \frac{C_{gin}}{1 + \frac{k_l a \; V_l}{F_g \; m_{gl}}} \tag{9}$$

Substituting eq. 9 in the numerator and denominator of eq. 7 (for the dispersion and for the water phase, respectively) the potential mass transfer enhancement for each dispersion can be calculated as a function of known parameters only:

$$E = \frac{m_{gw} + (\frac{k_l a \; V_l}{F_g})_w}{m_{gl} + (\frac{k_l a \; V_l}{F_g})_l} \tag{10}$$

*Steady-state mass transfer experiments*

Batch experiments were carried out with continuous supply of gaseous substrate by sparging. As long as the substrate transfer rate to the broth exceeds the rate of consumption by the cells and no other nutrient is limiting, cells grow at their maximum specific rate. At some critical cell concentration, however, the gaseous substrate can no longer be transferred fast enough to meet the cell requirements. Under this condition, the substrate becomes depleted in the liquid, and linear cell growth occurs. A pseudo-steady state is assumed with respect to the gaseous compound concentration. During the experiments with toluene, because of the low values of $C_{gin}$ and the relatively good solubility of toluene in the culture medium, $C_{gout}$ was very low and therefore difficult to be measured accurately . Larger gaseous inlet concentrations were not used for reasons that will be explained below. For that reason, the mass transfer rate was determined from measurements of the

cell growth rate using a steady state mass balance over the liquid phase:

$$k_l a \left(\frac{C_{gout}}{m_{gl}} - C_l\right) V_l = \frac{dX}{dt} \frac{1}{Y_{x/s}} V_l \qquad (11)$$

with $X$ the biomass concentration (kg/m$^3$ liquid) and $Y_{x/s}$ the specific yield of biomass on substrate (kg biomass/ mol substrate).

Eq. 11 can be combined with eq. 8 yielding:

$$F_g \left(C_{gin} - C_{gout}\right) = \frac{1}{Y_{x/s}} \frac{dX}{dt} V_l \qquad (12)$$

This equation was used to calculate the enhancement factor ($E_r$) from measurements under steady-state conditions:

$$E_r = \frac{\left[\frac{1}{Y_{x/s}} \frac{dX}{dt} V_l\right]_l}{\left[\frac{1}{Y_{x/s}} \frac{dX}{dt} V_l\right]_w} \qquad (13)$$

Observed enhancements (eq. 13) were compared with potential enhancements calculated by equation 10.

## Materials and methods

### *Transient-state mass transfer experiments*

*Experiments with toluene*

Experiments were carried out in a 2 dm$^3$ Applikon stirred-tank reactor with a working volume of 1.7 dm$^3$ equiped with a 4-blade turbine stirrer. The temperature in the reactor was kept at 22°C and the stirring speed was 800 rpm. The gas was sparged through the reactor at a rate of $2\times10^{-5}$ m$^3$/s

containing toluene in a concentration of 0.029 mol/m$^3$. With respect to the liquid phase the reactor was operated batchwise. When solvent was used it was dispersed by mechanical agitation of the aqueous and organic phases in the reactor.

Toluene-in-air mixtures were prepared by mixing air saturated with toluene with pure air. Toluene-saturated air was prepared by passing air at a controlled rate through a bubble column containing liquid toluene. The temperature of the column was kept at 22°C. The gas flow rates were controlled using Brooks 5850 TR Mass-Flow Controllers (Rosemount, Schiedam, The Netherlands).

Mass transfer coefficients were determined by first sparging toluene-free air and then imposing a step change in toluene concentration at $t = t_0$. The toluene concentration in the outlet gas flow was monitored on-line until it equaled the inlet concentration, indicating saturation of the liquid phase with toluene. $k_l a_{gl}$ values were obtained with the help of a computer program as explained above.

The overall mass transfer coefficient in the presence of solvent was determined in triplicate at five solvent volume fractions, namely 0, 1, 3, 5 and 10 % (v/v).

*On-line measurement of toluene in the outlet gas*

The outlet gas toluene concentration was monitored on-line. This was done by injecting, by means of a small centrifugal gas pump, a fraction of the gas leaving the reactor directly through the detector of the gas chromatograph. Before entering the detector, the gas passed through a heated block (250°C), to prevent vapour condensation, where it was split manually to a flow of 30 ml/min by two needle valves. This splitt-off flow passed through the detector.

*Experiments with oxygen*

Measurements of the oxygen transfer coefficients were carried out in the same reactor set-up used during the measurements for toluene. Mass transfer coefficients were measured at 25°C and 1 atm by equilibrating the fermenter with sparged nitrogen at a flow rate of $2\times10^{-5}$ $m^3/s$, and then imposing a step-change at $t = t_0$ by switching from nitrogen to air. The dissolved oxygen tension was monitored versus time using a Scott Gerade membrane oxygen electrode which was connected to an oxygen analyser (Scott Gerade) the output of which was recorded on a chart recorder. The overall mass transfer coefficients were determined in triplicate at five different solvent volume fractions namely 0, 1, 3, 5 and 10 % (v/v). $k_l a_{gl}$ values were obtained from eq. 6.

***Steady-state mass transfer experiments***

*Micro-organism and cell cultivation*

*Pseudomonas putida* GJ40 was kindly supplied by Dr. S. Hartmans (Department of Industrial Microbiology, Wageningen, The Netherlands). This strain was maintained on yeast-extract/glucose agar-slants at room temperature.

Experiments were done with biomass harvested from batch cultures grown on toluene. The cells were cultivated in batch at 30°C in mineral-salts medium[5] with toluene supplied through the gas phase. A 2 $dm^3$ Applikon fermentor with a working volume of 1.2 $dm^3$ and a 6-blade turbine stirrer was used. A second stirrer was placed above the liquid level to break the foam produced during the fermentation. The pH was maintained at 7.0 by controlled addition of 1 M NaOH and the impeller speed was 800 rpm. Aeration and substrate supply were accomplished by sparging air through the culture with a gas flow of $8.3\times10^{-6}$ $m^3/s$ and a toluene inlet concentration of 0.0085 $mol/m^3$. After a dense culture was achieved, the cells were harvested

by centrifugation, washed with 50 mM phosphate buffer (pH 7.0) and stored at -20°C until use.

*Mass transfer experiments*

The cells were grown on toluene as described above; a 4-blade turbine stirrer was used instead of the 6-blade one for later comparison with the experiments in transient state. The cell concentration was followed in time before and after a certain amount of FC40 was added to the system. Six different solvent volume fractions were tested, namely 0, 2, 3, 4.5, 6 and 9 % (v/v). A different batch run was carried out for each solvent amount.

*Analytical methods*

Toluene was determined by analysing 100 $\mu$l head-space samples on a Chrompack 9000 gas chromatograph equiped with a Poropack R column (100-120 mesh) and a flame ionization detector. The oven temperature was 210°C and the carrier gas $N_2$ was supplied at 30 ml/min.

Toluene-in-air calibration standards were prepared by adding an exact volume of liquid toluene in the range 0.5 to 2.0 $\mu$l to 250 ml volume flasks containing 100 ml of water and fitted with Teflon Mininert valves. With the partition coefficient (0.21 at 22°C) and the volumes of the gas and the water phases in the flask, the toluene concentration in the gas phase could be calculated.

The partition coefficients of toluene in the systems gas/water and gas/solvent-in-water dispersions were determined at 22°C according to the EPICS method (Equilibrium Partitioning In Closed Systems[10]).

Bacterial growth was determined by monitoring the absorbance at 660 nm with a Beckman Du 640 spectrophotometer. In agreement with the non-hydrophobic character of the bacterial strain, attachment of cells to the solvent phase droplets was not observed. Therefore, under gravitational

sedimentation, samples of the solvent-in-water dispersion separated into discrete solvent and water phases. An aliquot of the upper aqueous broth phase was then easily withdrawn. The possible influence of FC40 on the absorbance measurements was checked for and it was concluded that the presence of the solvent was not significant.

*Chemicals*

Toluene (99.5 %) was obtained from Janssen Chimica (Geel, Belgium) and FC40 was purchased from 3M (The Netherlands). Its properties are: density (25°C) 1850 kg/m$^3$; surface tension (25°C) 16 mN/m; boiling point 165-185°C; molecular weight 0.65 kg/mol; dynamic viscosity (25°C) 4.5 mPa.s.

## Results and discussion

The effect of the solvent on the gas/liquid mass transfer rate is both dependent on the overall volumetric mass transfer coefficient ($k_l a_{gl}$) and on the gas/liquid driving force, the latter being dependent on the partition coefficient gas/liquid ($m_{gl}$). Once these two variables are known, the mass transfer rate enhancement can be predicted by means of eq. 10.

***$k_l a$ determination from transient state measurements***

The overall volumetric toluene transfer coefficient was determined for dispersions containing different solvent amounts. In the systems with two liquid phases, the dispersion was treated as a single homogeneous liquid phase, which is equivalent to the assumption that an equilibrium exists between the solvent and water phases during the experiment. The validity of this assumption was verified based on calculation of the characteristic times for mass transfer gas/liquid and solvent/water (appendix 2).

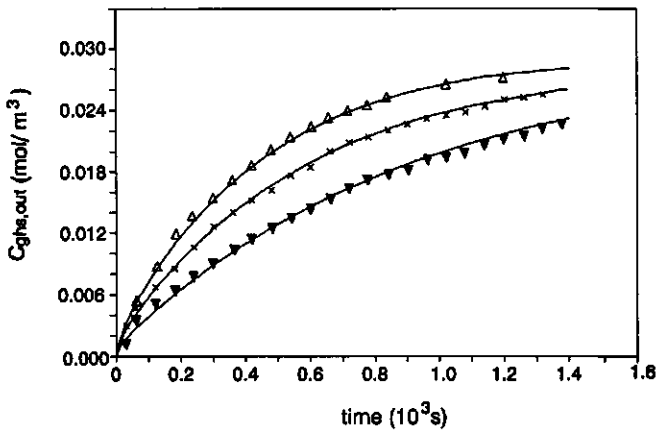


Figure 1. Toluene outlet gaseous concentration in time for different FC40-in-water dispersions. The points represent the experimental results and the line the best fit of the data with the model. ▵, water; ×, 1 % (v/v) FC40; ▾, 5 % (v/v) FC40.

Fig. 1 shows the toluene outlet gaseous concentrations versus time for some of the FC40-in-water dispersions. It is observed that saturation of the liquid is slower in dispersions containing larger amounts of FC40. This apparent paradox between the anticipated enhancement of the transfer with larger solvent volume fractions and the delay in approaching equilibrium in these experiments, can be explained by the high toluene solubility in the solvent, taking therefore longer for this phase to become saturated. Fig. 1 also gives the best fit of the data by eqs 1-5. For all dispersions tested, a good fit of the model calculation to the experimental points was found by using a specific $k_l a_{gl}$ value in the model. The input parameters used for $k_l a_{gl}$ calculations are listed in Table 1.

The overall mass transfer coefficients gas/liquid $(k_l a)_{gl}$ obtained for the different dispersions tested are given in Fig. 2. The data suggest $k_l a_{gl}$ to be

constant with the different solvent volume fractions.

Table 1. Parameters used for the determination of the $k_l a_{gl}$ values

| Parameters | Value | Unit |
|---|---|---|
| Gas volume | $8.5\times10^{-6}$ | $m^3$ |
| Liquid volume | $1.7\times10^{-3}$ | $m^3$ |
| Inlet gas concentration | 0.029 | $mol/m^3$ |
| Gas flow rate | $2\times10^{-5}$ | $m^3/s$ |
| Head-space volume | $0.3\times10^{-3}$ | $m^3$ |
| Partition coefficient gas/liquid | experimental[a] | (-) |

[a] Determined for each emulsion and given in Table 2.

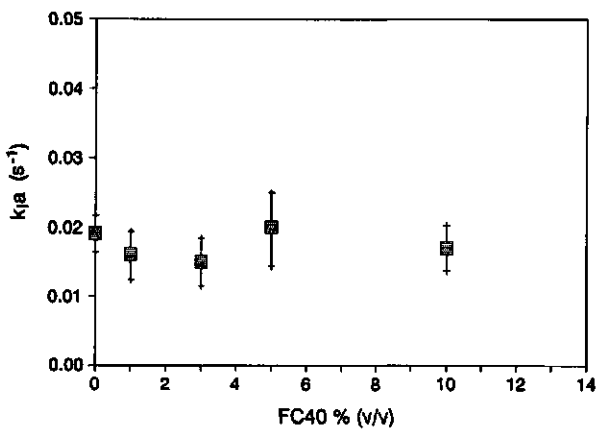


Figure 2. Effect of FC40 volume fraction on $k_l a_{gl}$ for toluene. Error bars represent the standard deviation of the mean.

Dynamic experiments were also carried out with oxygen in order to study the influence of the solvent volume fraction on the $k_l a_{gl}$. From Fig. 3 it is observed that the overall oxygen transfer coefficient is essentially constant as the amount of FC40 in the dispersion increases. The $k_l a_{gl}$ values are very similar to the ones found for toluene ($\approx 1.7 \times 10^{-2}$ s$^{-1}$).

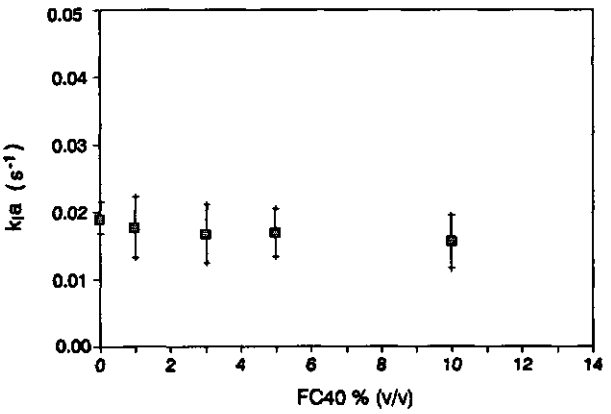


Figure 3. Effect of FC40 volume fraction on $k_l a_{gl}$ for oxygen. Error bars represent the standard deviation of the mean.

Though Ju *et al.*[13] studied mainly emulsions of FC40-in-water with larger solvent volume fractions, insignificant changes of $k_l a_{gl}$ up to 10% (v/v) FC40 were observed from measurements of the transfer gas/liquid in transient state, agreeing therefore with our results.

Based on the definition of $k_l a$, little or no changes of the $k_l a_{gl}$ value for different solvent volume fractions are in fact expected. The overall volumetric mass transfer coefficient, $k_l a_{gl}$, is the product of $(k_l)_{gl}$, the overall mass transfer coefficient and of $a_{gl}$, the specific area for mass transfer between the gas and the overall liquid. $(k_l)_{gl}$ is given by:

$$\frac{1}{(k_l)_{gl}} = \frac{1}{k_l} + \frac{1}{k_g\, m_{gl}} \tag{14}$$

with $k_g$ and $k_l$ the gas and the liquid partial mass transfer coefficients, respectively (m/s).

Table 2. Experimental values of $k_l a_{gl}$ and $m_{gl}$ for toluene and oxygen for dispersions with different FC40 volume fractions

| | toluene | | oxygen | |
|---|---|---|---|---|
| %FC40 (v/v) | $k_l a_{gl}$ ($s^{-1}$) | $m_{gl}$ (-) | $k_l a_{gl}$ ($s^{-1}$) | $m_{gl}$ (-) |
| 0 | $1.8\times10^{-2}$ | 0.21 | $1.9\times10^{-2}$ | 32.7 |
| 1 | $1.6\times10^{-2}$ | 0.17 | $1.8\times10^{-2}$ | 29.6 |
| 3 | $1.6\times10^{-2}$ | 0.13 | $1.7\times10^{-2}$ | 24.9 |
| 5 | $2.0\times10^{-2}$ | 0.10 | $1.7\times10^{-2}$ | 21.4 |
| 10 | $1.7\times10^{-2}$ | 0.076 | $1.6\times10^{-2}$ | 15.9 |

Regarding the values of $m_{gl}$ (Table 2), it is observed that in the case of oxygen the main resistance for mass transfer is located in the liquid film while for toluene both the gas and the liquid phase film resistances are important. The partial gas mass transfer coefficient is not expected to change in the presence of solvent. The partial liquid mass transfer coefficient is given by the film theory:

$$k_l = \frac{D_l}{\delta} \tag{15}$$

where $D_l$ is the diffusion coefficient of the compound in the liquid film around the gas bubbles ($m^2/s$) and $\delta$ is the liquid film thickness. In this liquid

film either water or solvent might be found since FC40 has a positive spreading coefficient ($S_p = + 0.57 \times 10^{-3}$ kg/s$^2$), i.e. the solvent droplets have the tendency to spread on the gas/liquid interface[11,15,22,23].

The presence of a solvent film partially covering the gas bubble surface is not expected to influence significantly the value of $k_l$ as the value of the diffusion coefficient in the solvent, $D_{FC40}$ ($7.2 \times 10^{-10}$ m$^2$/s for toluene and $1.7 \times 10^{-9}$ m$^2$/s for oxygen) is very similar to the one in the water, $D_w$ ($8.2 \times 10^{-10}$ m$^2$/s for toluene and $2.2 \times 10^{-9}$ m$^2$/s for oxygen). Moreover, the film thickness is not expected to change appreciably, since the hydrodynamic conditions are maintained constant in the experiments with and without solvent and the overall viscosity of the dispersions with FC40 amounts up to 10% (v/v) should be very similar to the one of water (the viscosity of FC40 is $4.5 \times 10^{-3}$ kg/m s).

Regarding the influence of the solvent on the specific area between the gas and the liquid, although there is some evidence that a dispersed phase with a positive spreading coefficient[11,23], can increase the interfacial area by reducing the gas/water interfacial tension, this contribution is in general very small to the total enhancement[23].

For all the reasons pointed above, the value of $k_l a_{gl}$ is not expected to change appreciably in the range of solvent volume fractions tested.

Most studies in literature present $k_l a$ based on water phase concentrations and not on the total liquid phase as it is defined in this paper. Defined on water only, a general increase of the $k_l a_{gw}$ with the solvent volume fractions for solvent-in-water dispersions and for solvents with a positive spreading coefficient ($S_p$), is found[15,21,23,29]. $k_l a_{gw}$ values can be calculated from $k_l a_{gl}$ (appendix 3):

$$(k_l a)_{gw} = (f_s \frac{m_{gw}}{m_{gs}} + f_w) (k_l a)_{gl} \quad (16)$$

When $k_l a_{gw}$ is calculated for toluene and oxygen from the values of $k_l a_{gl}$ obtained experimentally, an increase with the $f_s$ is observed, agreeing with the pattern often found in literature and mentioned above.

***Theoretical prediction of the mass transfer rate enhancement***

The influence of $m_{gl}$ and consequently of $m_{gw}$ and $m_{gs}$ (eq. 4) on the mass transfer enhancement when adding an organic solvent to the fermentation medium was studied under steady-state conditions. The mass transfer rate enhancement was predicted theoretically using eq. 10. The $k_l a_{gl}$ values used were the ones obtained during the study in transient-state. The values of $k_l a_{gl}$ and $m_{gl}$ used are given in Table 2 for toluene and oxygen.

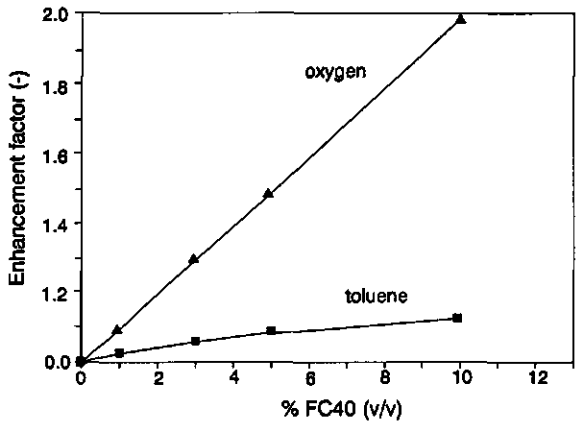


Figure 4. Theoretical predictions of the mass-transfer-rate enhancement of toluene and oxygen at different FC40 volume fractions.

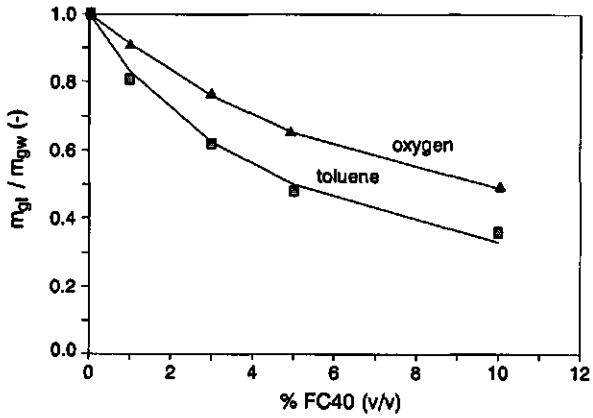


Figure 5. Influence of the FC40 volume fraction on the ratio of partition coefficients gas/liquid and gas/water for toluene and oxygen.

Because the $k_l a_{gl}$ does not change significantly with the solvent volume fraction a constant value of $1.7\times10^{-2}$ $s^{-1}$ for toluene and oxygen was used in the calculations. The theoretically calculated mass transfer rate enhancement for toluene and oxygen to dispersions containing different amounts of FC40 are shown in Fig. 4. It is observed that the enhancement expected for toluene is much lower than the enhancement expected for oxygen. While for the former an enhancement factor of 1.1 for 10% FC40 is predicted, an improvement of approximately a factor 2 is expected for oxygen at the same solvent volume fraction. This is because of the larger values of $m_{gl}$ for oxygen. Although for oxygen $m_{gl}$ changes less than for toluene with the solvent volume fraction (Fig. 5), the absolute values of $m_{gl}$ are larger and so is $C_{gout}$ (eq. 9), causing a greater variation of the mass transfer rate (numerator of eq. 10). It is therefore expected that the larger the $m_{gl}$, the greater the effect of the solvent on the mass transfer rate enhancement.

In order to validate these theoretical predictions, steady-state experiments

in the presence of a microbial reaction were carried out for toluene. For oxygen, experimental results from other authors were used.

*Steady-state mass transfer experiments*

To test whether the addition of FC40 enhances the transfer rate of toluene to the medium, FC40 should neither be used as a carbon source, nor be toxic to the cells. In preliminary experiments the biodegradability and toxicity of FC40 towards *P. putida* was tested. From these experiments it was concluded that FC40 is not consumed by the bacteria and also no toxicity effect could be found (own unpublished results). The inlet gas concentration was chosen in such a way that toluene and not oxygen transfer was the rate-limiting step in the system.

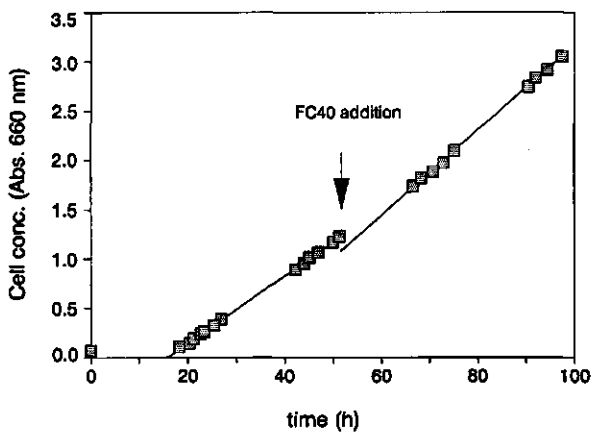


Figure 6. Change of the linear cell growth rate upon addition of 4.5 % (v/v) FC40 to the fermentation medium.

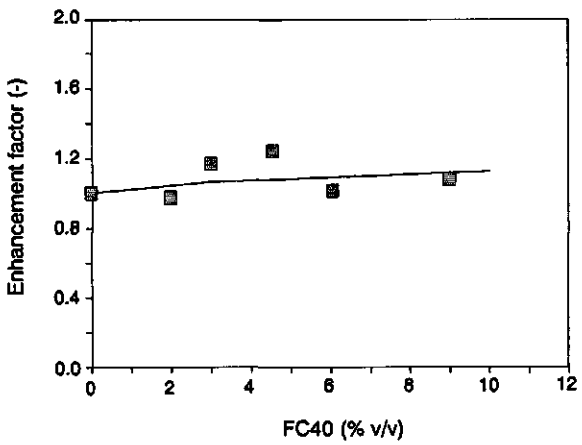


Figure 7. Comparison of the toluene-transfer-rate enhancement experimentally (■) and theoretically predicted (solid line) at different FC40 amounts.

The study of the solvent effect on the toluene transfer rate should take place in a system where the mass transfer rather than the conversion rate is the limiting step in the overall process. The effect of the solvent was studied by following the change of the cell growth rate upon solvent addition to the aqueous medium. The cell concentration was followed in time during a batch experiment with a continuous addition of toluene via the gas phase. At higher cell concentrations a linear cell growth is observed indicating that the mass transfer became rate limiting. Fig. 6 shows the change of cell concentration in time before and after 4.5 % FC40 was added to the suspension. The linear curve changes slightly, by a factor of 1.2, after addition of solvent took place. This experiment was repeated with several FC40 volume fractions. The enhancement factor was calculated for each case using eq. 13. It was assumed that $Y_{x/s}$ is constant in the presence or absence of solvent. Fig. 7 shows the enhancement of the linear growth rate for the different solvent

amounts and the theoretically predicted enhancement calculated with equation 10. Both results are in good agreement. As expected, the toluene mass transfer hardly increases by the addition of solvent to the aqueous medium. This is due to the relative good solubility of this compound in water ($m_{gw}$= 0.21 mol/m$^3$ gas/ mol/m$^3$ water).

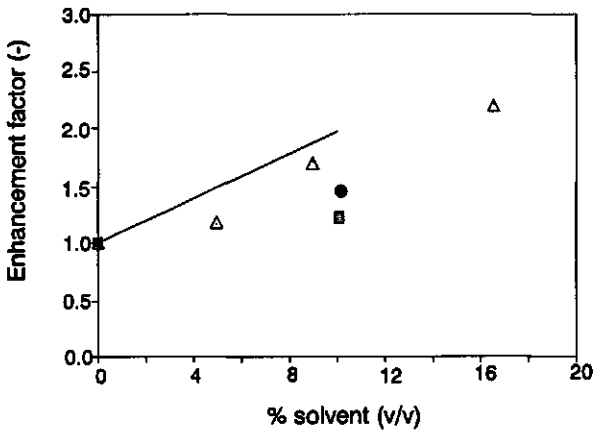


Figure 8. Comparison of the oxygen-transfer-rate enhancement experimentally and theoretically predicted (solid line) at different solvent volume fractions. The experimental points are from literature: (■), McMillan *et al.*[17], with FC40; (•), Junker *et al.*[14], with FC40; (▵) Rols *et al.*[23], with n-dodecane. Prior to comparison, the $k_La$'s obtained by those authors have been recalculated based on overall liquid-phase concentrations and total liquid volume.

The same study was done for oxygen. Fig 8 shows both the enhancement factor predicted theoretically and calculated from experimental results as a function of the solvent volume fraction. The experimental points are values from studies mentioned in literature[14,17,23] which used FC40 and n-dodecane

to enhance the transfer of oxygen to oxygen-limited fermentations. Those studies were carried out under similar hydrodynamic conditions and used the solvent dispersed mechanically as we have done during our experiments in transient state. Because the range of FC40 volume fractions covered by Junker *et al.*[14] and McMillan *et al.*[17] is much larger than the one used in our study, the results obtained by Rols *et al.*[23] with n-dodecane were also compared with our theoretical predictions. This comparison is valid since this solvent also has a positive spreading coefficient ($S_p = + 0.6 \times 10^{-3}$ kg/s$^2$) and the partition coefficient solvent/water is similar to the one of FC40 ($m_{sw}$= (4.8 mol/m$^3$ n-dodecane)/ (mol/m$^3$ water)). A good agreement between the predicted and the experimental results is observed for the range of solvent volume fractions tested. The enhancement observed for oxygen is much larger than the one obtained for toluene as it was predicted.

Since for both compounds tested a good correlation between the predicted and the observed results was found, the theoretical model was used to predict for which values of $m_{gw}$ and $m_{gs}$, the use of a solvent is most advantageous. Aiming at this, eq. 10 was used. $k_l a_{gl}$ was assumed constant within the considered range of solvent volume fractions (up to 10% v/v) and only $m_{gl}$ was varied. This assumption is valid since for solvents with a positive spreading coefficient only a slight decrease of $k_l a_{gl}$ within this narrow range is found in literature. The enhancement factor was calculated as a function of $f_s$ for a constant $m_{gw}$ value and various $m_{gw}/m_{gs}$ combinations, as depicted in Fig.9. A very poorly water-soluble compound as hexane with $m_{gw}$= 71 (mol/m$^3$gas)/ (mol/m$^3$ water)[28] and a moderately poor water-soluble compound like toluene with $m_{gw}$= 0.21 (mol/m$^3$ gas)/ (mol/m$^3$ water) were chosen. From this figure it is observed that the mass transfer increases with increasing amounts of solvent dispersed in the medium and with increasing solubility of the compound in the solvent (higher $m_{gw}/m_{gs} = m_{sw}$ values). Remarkable is the great enhancement that can be achieved for very poorly

water-soluble compounds while for moderately poor water-soluble ones the use of a solvent is hardly significant.

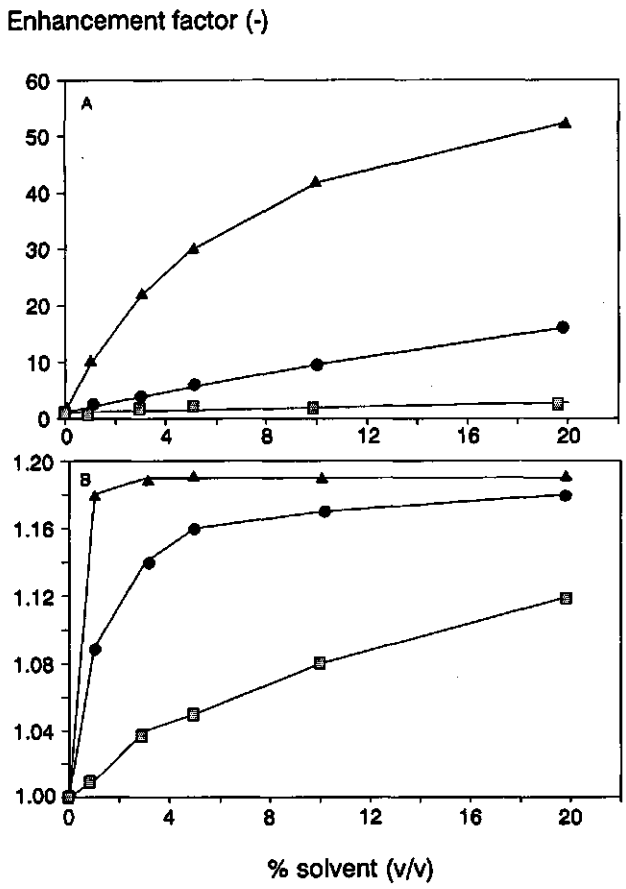


Figure 9. Influence of the solvent volume fraction, the partition coefficient solvent/water ($m_{sw}=m_{gw}/m_{gs}$) and the solubility of the compound in the water ($m_{gw}$) on the mass-transfer-rate enhancement. **A.** hexane; **B.** toluene.; (▲), $m_{sw}$= 1000; (●), $m_{sw}$= 100; (■), $m_{sw}$= 10.

The influence of the compound's solubility in water on the mass transfer rate enhancement was already shown experimentally for toluene and for oxygen, namely in figs 7 and 8. The transfer enhancement as a function of the compound's solubility in the solvent is shown in Fig. 10. This study was done for oxygen and used results from literature[21,23]. The solvents tested were n-dodecane and soybean oil, both with a positive spreading coefficient and with partition coefficients for oxygen in the system solvent/water ($m_{sw}$) of 7.9 and 1.8 (mol/m$^3$ solvent)/(mol/m$^3$ water), respectively. Both experiments were done under similar hydrodynamic conditions and both used the solvent dispersed mechanically. From this figure it is observed that the oxygen transfer enhancement is larger as the solubility of the compound in the solvent is larger, as it was predicted theoretically.

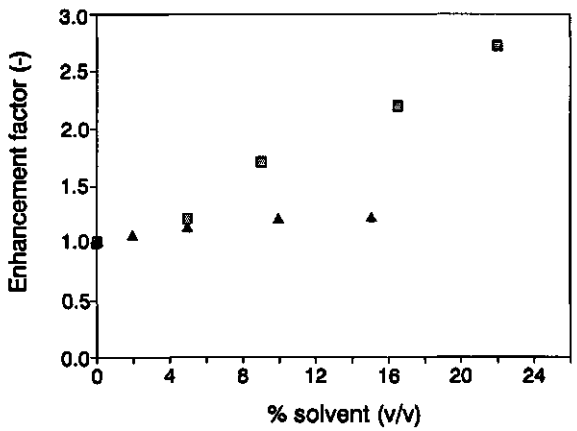


Figure 10. Influence of the solvent volume fraction and of the solvent/water oxygen partition coefficient ($m_{sw}$) on the mass transfer rate enhancement. The data is from: (■), $m_{sw}$= 7.9, Rols *et al.*[23]; (▲), $m_{sw}$= 1.8, Rols and Goma[21]. The $k_La$'s obtained by those authors have been recalculated based on overall liquid-phase concentrations and total liquid volume.

## Conclusions

The overall volumetric mass transfer coefficient ($k_l a_{gl}$) from the gas phase to FC40-in-water dispersions systems was determined in transient state for two different apolar compounds, namely toluene and oxygen. For both compounds an essentially constant $k_l a_{gl}$ with increasing solvent volume fractions up to 10 % (v/v) was found. This behaviour is similar to the one found in literature for solvents with a positive spreading coefficient.
Once the $k_l a_{gl}$ and the partition coefficient in the system gas/dispersion ($m_{gl}$) were known, the enhancement of the mass transfer rate upon addition of solvent to the fermentation medium could be predicted with a simple mass balance over the gas phase for steady-state conditions. The theoretical predictions agreed well with the experimental results for both toluene and oxygen. While for toluene an enhancement of 1.1 for 10 % (v/v) FC40 was predicted, an improvement of approximately a factor 2 for the same solvent volume fraction was found for oxygen.

From this study it was concluded that the mass transfer enhancement upon addition of a second liquid phase is negligible for moderately poor water-soluble compounds ($m_{gw} < 1$) while it can reach large values for very poorly water-soluble compounds. The increase of the mass transfer is larger the greater the solubility of the compound to the solvent (larger partition coefficients solvent/water).

## Appendices

### *Appendix 1*

From a mass balance for the compound over the gas, water and solvent phases:

$$M = C_w V_w + C_g V_g + C_s V_s \qquad \text{(A1.1)}$$

with $M$ the total mass of the compound (mol) and $V_s$ the solvent volume ($m^3$).

When the three phases are in equilibrium eqs. (A1.2) and (A1.3) are valid:

$$m_{gs} = \frac{C_g}{C_s} \qquad \text{(A1.2)}$$

$$m_{gw} = \frac{C_g}{C_w} \qquad \text{(A1.3)}$$

Substituting eqs. (A1.2) and (A1.3) in eq. (A1.1) yields:

$$M = \frac{C_g}{m_{gw}} V_w + C_g V_g + \frac{C_g}{m_{gs}} V_s \qquad \text{(A1.4)}$$

$f_s$ and $f_w$ are given respectively by:

$$f_s = \frac{V_s}{V_s + V_w} \qquad \text{(A1.5)}$$

$$f_w = \frac{V_w}{V_s + V_w} \qquad \text{(A1.6)}$$

Rearranging eq. (A1.4) yields:

$$\frac{\dfrac{C_w V_w + C_s V_s}{V_w + V_s}}{C_g} = \frac{f_w}{m_{gw}} + \frac{f_s}{m_{gs}} \qquad \text{(A1.7)}$$

Since:

$$C_l = \frac{C_w V_w + C_s V_s}{V_w + V_s} \qquad \text{(A1.8)}$$

Eq. (A1.7) can be simplified to:

$$\frac{1}{m_{gl}} = \frac{f_s}{m_{gs}} + \frac{f_w}{m_{gw}} \qquad \text{(A1.9)}$$

*Appendix 2*

For the two liquids to be in equilibrium, the characteristic time for mass transfer gas/liquid, $(t_c)_{gl}$, should be much greater than the characteristic time for mass transfer solvent/water, $(t_c)_{sw}$.

Characteristic times for solvent-to-water and gas-to-dispersion mass transfer were calculated and are given respectively by:

$$(t_c)_{sw} = \frac{1}{(k_w a)_{sw}} \qquad \text{(A2.1)}$$

and

$$(t_c)_{gl} = \frac{1}{(k_l a)_{gl}} \qquad \text{(A2.2)}$$

with $(k_w a)_{sw}$ the overall volumetric mass transfer coefficient between the solvent and the water ($s^{-1}$). This coefficient was calculated by:

$$\frac{1}{(k_w a)_{sw}} = \frac{1}{k_w\, a_{sw}} + \frac{1}{k_s\, a_{sw}\, m_{sw}} \qquad \text{(A2.3)}$$

where $k_w$ and $k_s$ are the partial mass transfer coefficients on the water and solvent side (m/s), respectively, $a_{sw}$ the interfacial area solvent/water ($m^{-1}$) and $m_{sw}$ the partition coefficient between the solvent and the water phases (mol/$m^3$ solvent)/(mol/$m^3$ water). $a_{sw}$ can be calculated from:

$$a_{sw} = \frac{6\, f_s}{d_p} \qquad \text{(A2.4)}$$

with $d_p$ the solvent droplet diameter (m). $d_p$ may be estimated from[30]:

$$d_p = 0.047 \left(\frac{\sigma_{sw}^{0.6}}{\rho_w^{0.6}\, N^{1.2}\, D^{0.8}}\right) (1 + 2.5\, f_s) \qquad \text{(A2.5)}$$

with $\sigma_{sw}$ the interfacial tension between solvent and water ($kg/s^2$), $\rho_w$ the density of water ($kg/m^3$), $N$ the stirring speed ($s^{-1}$) and $D$ the stirrer diameter (m).

The calculated average droplet diameter ranges from 66 to 81 $\mu$m for $f_s$ values in the range 0.01 to 0.1. These values agree well with those of other authors using similar hydrodynamic conditions[14,17]. With this size, the droplets behave like rigid spheres (no internal circulation)[12] and the partial mass transfer coefficients on the water and on the solvent side can be calculated respectively from eqs. (A2.6) and (A2.8)[3]:

$$\frac{k_w\, d_p}{D_w} = 2 + 0.47\,\left[\frac{d_p^{4/3}\, R^{1/3}\, \rho_w}{\mu_w}\right]^{0.62}\, [D/T]^{0.17}\, Sc_w^{0.36} \qquad \text{(A2.6)}$$

with :

$$R = \frac{5\, N^3\, D^5}{V_l} \qquad \text{(A2.7)}$$

$\mu_w$ is the viscosity of water (kg/m s), $T$ the tank diameter (m) and $Sc$ the Schmidt number (-).

$$Sh_s = \frac{k_s\, d_p}{D_s} = 6.5 \qquad \text{(A2.8)}$$

The values of $k_s$ and $k_w$ were approximately $6.1\times10^{-4}$ and $1.4\times10^{-4}$ m/s, respectively, for toluene and $1.4\times10^{-4}$ and $2.8\times10^{-4}$ m/s, respectively, for oxygen. Substituting these values in eq. (A2.3) together with $m_{sw} = m_{gw}/m_{gs} = 17.5$ for toluene and $m_{sw}=11.6$ for oxygen, $(k_w a)_{sw}$ can be calculated. The values obtained were 0.11 $s^{-1}$ and 0.92 $s^{-1}$ for toluene and 0.21 $s^{-1}$ and 1.77 $s^{-1}$ for oxygen, for 1% and 10% FC40 (v/v), respectively. Substituting these values in eq. (A2.1), and the average $(k_l a)_{gl}$ value found experimentally ($(k_l a)_{gl} = 1.7\times10^{-2} s^{-1}$) in eq. (A2.2) it is observed that the characteristic time for mass transfer between the two liquid phases is a factor 10 to 100 smaller than the characteristic time for mass transfer gas/dispersion. The assumption of equilibrium between the two liquid phases is thus legitimate. This result agrees with the observations of other authors[14].

*Appendix 3*

Since the compound is not consumed in the solvent phase, it can be assumed under steady-state conditions that the net transport is to the water phase. Eq.

8 can therefore also be written as:

$$F_g\,(C_{gin}-C_{gout}) = k_l a_{gw}\,(\frac{C_{gout}}{m_{gw}} - C_w)\,V_l \qquad \text{(A3.1)}$$

Combining eq. 8 and eq. A3.1 yields:

$$k_l a_{gl}\,(\frac{C_{gout}}{m_{gl}} - C_l)\,V_l = k_l a_{gw}\,(\frac{C_{gout}}{m_{gw}} - C_w)\,V_l \qquad \text{(A3.2)}$$

The right side of eq. A3.2 can be rearranged when combined with eqs. 3 and 4. The result is:

$$k_l a_{gl}\,[f_s\,(\frac{C_{gout}}{m_{gs}} - C_s) + f_w\,(\frac{C_{gout}}{m_{gw}} - C_w)] = k_l a_{gw}\,(\frac{C_{gout}}{m_{gw}} - C_w) \qquad \text{(A3.3)}$$

When equilibrium between solvent and water exists:

$$C_w m_{gw} = C_s m_{gs} \qquad \text{(A3.4)}$$

Substituting eq. A3.4 in eq. A3.3 yields:

$$k_l a_{gl}\,(f_s\,\frac{m_{gw}}{m_{gs}} + f_w) = k_l a_{gw} \qquad \text{(A3.5)}$$

Depending on the ratio $m_{gw}/m_{gs}$ an increase of $k_l a_{gw}$ with $f_s$ might induce a different behaviour of $k_l a_{gl}$ with $f_s$.

## Acknowledgements

This work was supported by a grant (BD/740/90-IF) from the Junta Nacional de Investigação Científica e Tecnológica, Lisbon, Portugal. The authors want to thank H.M. van Sonsbeek for his valuable help in the first stages of this work and J.J. Wesselink for carrying out the preliminary experiments with *Pseudomonas putida*.

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# Chapter 4

## New technique for $k_l a$ measurement between gas and water in aerated solvent-in-water dispersions


### Summary

A new technique is presented to determine gas-to-water overall volumetric mass transfer coefficients ($k_l a$) in a stirred-tank reactor containing solvent-in-water dispersions. The compound to be transferred from the gas to the water was toluene; the water-immiscible organic solvent was FC40, a perfluorocarbon. The $k_l a$ was determined in steady-state conditions in the absence of biological consumption. Toluene removal was achieved by passing a continuous flow of toluene-free water through the reactor. When solvent was present it was separated from the water at the reactor outlet by means of a small settler and recycled back to the vessel. The $k_l a$ was found to increase with the FC40 volume fraction. An enhancement of a factor 1.6 on an aqueous-phase-volume basis was found at 15 % (v/v) FC40.



This chapter has been published in a modified form in Biotechnology Techniques 1996, 10, 195-198 by the authors M.T. Cesário, H.L. de Wit, J. Tramper and H.H. Beeftink

## Introduction

The transport of poorly water-soluble gaseous substrates towards the water phase is often the rate-limiting step in many microbial cultivation processes. A common example is the supply of oxygen in aerobic fermentations[4,5,7]. Analogously, the removal of apolar pollutants from the gas towards the water phase is often the critical factor during the biological treatment of waste gases[1,2,6]. One way to diminish this transport limitation is through addition to the aqueous medium of a water-immiscible organic solvent in which the compound shows a better solubility. Several researchers have shown an improvement of the overall volumetric oxygen transfer coefficient between the gas and the water ($k_la$) by dispersing an organic solvent in the broth of oxygen-transfer-limited fermentations[4,5,7].

To determine overall volumetric mass transfer coefficients from the gas to the water phase, dynamic and steady state methods can be used. In the dynamic method, the change of the compound concentration is monitored in time after a step-change of the concentration in the inlet gas. In the steady-state method, the concentration measurements are done at one moment after steady state has been reached. In order to use the dynamic method, a quick and accurate measurement of the compound concentration is of crucial importance. This is possible in case of oxygen, where a continuous monitoring of the dissolved oxygen can be accomplished using an oxygen electrode but it is problematic with other compounds. Frequent sampling and analysis is an alternative. Another option is measuring the change of concentration in time in the outlet gas phase. However, when a solvent is dispersed in the water phase no distinction can be made between the transport to the water or to the solvent but only towards the overall liquid. For this reason, a new and simple steady-state technique to measure the overall mass transfer coefficient ($k_la$) of apolar compounds between the gas and the water

in the presence of a dispersed solvent phase is proposed. There are two ways to achieve steady-state conditions: via a biological consumption reaction in the water phase or, in the absence of cells, via an artificial removal of the compound from the aqueous phase by passing a continuous flow of water through the reactor. We have chosen the second alternative in order to avoid any influence of the presence of micro-organisms, since these can produce surface-active agents and thus modify mass transfer interfacial areas.

The experiments were carried out in a stirred-tank reactor with a continuous flow of gas and water through the reactor. The solvent was kept in batch in the vessel, by means of a small settler placed inside the reactor which separates both liquid phases at the liquid outlet (Fig. 1).

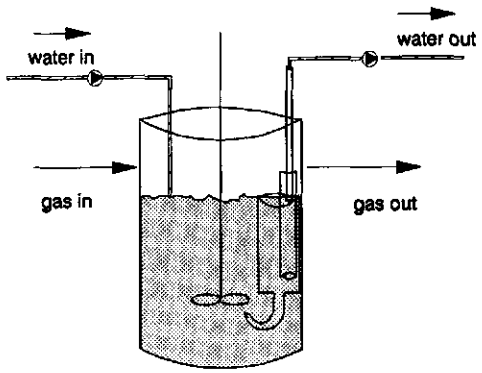



Figure 1. Set-up for stationary transfer measurement. Gas and water phases: continuous-flow; solvent: batch with the aid of settling device.

The influence of a second liquid phase on the $k_l a$ was studied for different solvent volume fractions. This technique is specially applicable in case the

density difference between the two liquid phases is large enough to accomplish a fast separation of the two liquids. In this study a perfluorocarbon (FC40) nearly twice as heavy as water (density= 1870 kg/m$^3$) was used as solvent. The model compound chosen was toluene ($m_{gw}^{22°C}$= 0.21 (mol/m$^3$gas) / (mol/m$^3$ water)).

## Theory

The transfer of the pollutant from the gas to the water can take place directly or indirectly via the solvent. In steady state there is no net transport of the compound to the solvent, but only towards the water phase from where it is discharged with the effluent. The $k_la$ was calculated from a stationary mass balance over the gas phase:

$$F_g\ (C_{gin} - C_{gout}) = k_la\ (\frac{C_{gout}}{m_{gw}} - C_{wout})\ V_w \qquad (1)$$

with $F_g$ the gas flow rate (m$^3$/s), $C_{gin}$ and $C_{gout}$ the inlet and outlet concentrations of ethene in the gas (mol/m$^3$), respectively, $C_{wout}$ the ethene concentration in the effluent water (mol/m$^3$), $k_la$ the overall volumetric mass transfer coefficient between gas and water (s$^{-1}$), $m_{gw}$ the partition coefficient of ethene between gas and water (mol/m$^3$gas)/(mol/m$^3$ water) and $V_w$ the water volume (m$^3$).

In the presence of solvent, the overall mass transfer coefficient between gas and water ($k_la$) is a composite parameter including gas/solvent, gas/water and solvent/water transfer coefficients and specific areas. The three possibilities for transport between the gas and the water in the presence of the solvent are depicted in the appendix.

The toluene concentration in the water phase ($C_{wout}$) can be eliminated

from eq. 1 with an overall stationary mass balance over the reactor and considering that the water entering the system is toluene free. This results in:

$$k_l a = \frac{\frac{F_g}{V_w}}{\frac{C_{gout}/C_{gin}}{1 - C_{gout}/C_{gin}} \frac{1}{m_{gw}} - \frac{F_g}{F_w}} \quad (2)$$

with $F_w$ the water flow rate ($m^3/s$).

In order to derive accurate $k_l a$ values, $C_{gin}$ and $C_{gout}$ should deviate at least 20%[8]. Furthermore, $C_{wout}$ should deviate at least 20 % from $C_{gout}/m_{gw}$. With these constraints and with eq. 2, the minimum water flow and a relation between the gas and the water flows is derived, eqs 3 and 4, respectively.

$$F_w \geq 0.25\ V_w\ k_l a \quad (3)$$

$$Fg \leq \frac{5}{\frac{1}{k_l a\ V_w} + \frac{1}{F_w}} \frac{1}{m_{gw}} \quad (4)$$

It is important that the water flow leaving the reactor allows a good separation of the two liquids in the settler since this is an important factor for the adequate working of this system.

## Materials and methods

After start-up, $C_{gout}$ was monitored until a constant value was achieved, which then was used to calculate $k_l a$ (eq.2).

*Experimental set-up*

A 2-$dm^3$ fermenter was used (liquid volume 1.3-$dm^3$, 4-blade turbine stirrer at 800 rpm). The temperature was kept at 22°C. Head-space aeration at $1.7\times10^{-7}$ $m^3/s$ was used, with a toluene inlet concentration of 0.25 $mol/m^3$; the water flow was $6.7\times10^{-7}$ $m^3/s$. Toluene-in-air mixtures were prepared from toluene-saturated and pure air. Toluene-saturated air was prepared by passing air through liquid toluene at 22°C. The gas flow rates were controlled with Brooks 5850 TR Mass-Flow Controllers (Rosemount, Schiedam, The Netherlands).

A small settler (Fig. 1) was placed inside the reactor. It consisted of two concentric cylinders between which the two liquids were separated by gravity. The liquid levels in the settler and in the reactor were the same. Solvent settled back into the reactor through a bended tube in the bottom of the settler; water was discharged at the desired flow rate from the top. Solvent discharge through the tube into the reactor was enhanced by suction from the stirrer. No losses of FC40 from the system were found when examining the outlet aqueous phase.

*Analytical methods*

Toluene was determined in 100-$\mu$l gas samples on a Chrompack 9000 gas chromatograph (Poropack R column, 100-120 mesh; flame ionization detector; oven temperature 210°C, carrier gas $N_2$ at 30 ml/min). Toluene-in-air calibration standards were prepared by adding an exact amount of toluene to flasks partially filled with water and fitted with Teflon Mininert valves (Phase Separation). After equilibration overnight at 22°C, head-space toluene concentrations were calculated from an overall mass balance and the partition coefficient (0.21 $mol/m^3$gas / $mol/m^3$ water at 22°C). Toluene partition coefficients were determined with the EPICS method[3].

*Chemicals*

FC40 was purchased from 3M, The Netherlands; the properties are: density (25°C) 1850 kg/m$^3$; surface tension (25°C) 16 nN/m; boiling point 165-185 °C; molecular weight 0.65 kg/mol; dynamic viscosity (25°C) 4.5 mPa.s. Toluene with a purity of 99.5 % was obtained from Janssen Chimica, Belgium.

## Results and discussion

Headspace aeration was chosen instead of liquid sparging. Sparging would mean larger $k_la$ values, and thus would require larger water flows to obtain a 20 % difference in $C_{wout}$ and $C_{gout}/m_{gw}$ (eq. 3). Consequently, phase separation in the settler would have been more difficult.

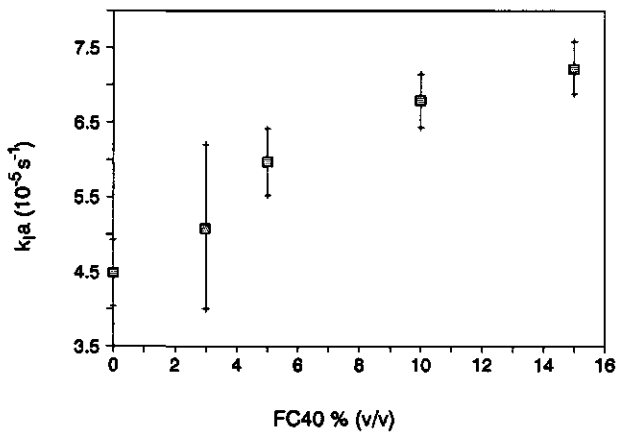



Figure 2. Gas-to-water transfer coefficient $k_la$ as a function of FC40 hold-up.

The effect of FC40 hold-up on $k_l a$ was studied at hold-ups of 0, 3, 5, 10 and 15% (v/v) (Fig. 2). Experiments were carried out in triplo at each hold-up; $k_l a$ values were calculated with eq. 2.

Volumetric toluene transfer coefficients gas/water increased with the solvent hold-up. An 1.6-fold increase was observed at 15 % (v/v) FC40. These results show that the gas/water transfer of poorly water-soluble substances can indeed be improved by dispersing adequate amounts of a water-immiscible organic solvent in the liquid.

## Conclusions

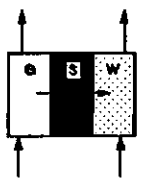
Steady-state determination of $k_l a$ between gas and water is very suitable and can be a good alternative for the dynamic method when overall mass transfer coefficients are to be determined in emulsion systems.

Conditions for the use of this technique are a good phase separation, and an adequate size of the settler when a particular gas and water flow rate are to be used.

## Appendix

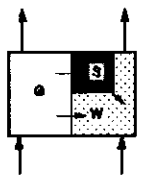
In Fig.3 the overall mass transfer coefficients are represented by the letter $T$ and are given for each case. They are obtained by eliminating the solvent concentration from the mass balances for the gas, solvent and water phases, assuming continuous steady-state operation and ideal mixing of each phase. These balances equations involve two (A) or three (B and C) driving forces; elimination of the solvent concentration yields two equations with the gas/water concentration difference as sole driving force and $T$ as the overall

mass transfer coefficient. $T_A$ and $T_C$ are special cases of $T_B$.



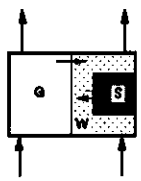

**A**

$$\frac{1}{T_A} = \frac{1}{k_{sw}a_{sw}} + \frac{1}{m_{sw}k_{gs}a_{gs}}\frac{V_w}{V_s}$$




**B**

$$T_B = \frac{1}{\frac{1}{k_{sw}a_{sw}} + \frac{1}{m_{sw}k_{gs}a_{gs}}\frac{V_w}{V_s}} + k_{gw}a_{gw}$$




**C**

$$T_C = k_{gw}a_{gw}$$

Figure 3. 3-phase gas-to-water toluene transfer (**G**: gas; **S**: solvent; **W**: water). A, serial transport gas→solvent→water; B, direct gas→water transport and serial transport gas→solvent→water; C, no direct gas/solvent. All systems: continuous gas and water flows, batch solvent phase. $k_{gs}$: overall gas→solvent mass transfer coefficient on solvent basis (m/s), $k_{gw}$: overall transfer coefficient gas→water on water basis (m/s), $k_{sw}$: overall transfer coefficient solvent→water on water basis (m/s), $a_{gs}$: specific area gas/solvent ($m^2$ gas/$m^3$ solvent), $a_{gw}$: specific area gas/water ($m^2$ gas/$m^3$ water), $a_{sw}$: specific area solvent/water ($m^2$ solvent/$m^3$ water), $m_{gs}$: toluene partition coefficient between gas and solvent (-), $m_{sw}$: toluene partition coefficient between solvent and water = $m_{gw}/m_{gs}$ (-) and $V_s$: solvent volume ($m^3$).

## Acknowledgements

This work was supported by a grant (Praxis XXI/BD/3636/94) from the Junta Nacional de Investigação Científica e Tecnológica, Lisboa, Portugal.

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# Chapter 5

## Dispersed organic solvent to enhance the overall gas/water mass transfer coefficient of apolar compounds Modeling and validation


### Summary

Dispersed water-immiscible organic solvents can be used to improve the mass transfer of poorly water-soluble pollutants in the biological treatment of waste gases.

A mathematical model was derived for predicting the potential enhancement of the overall gas/water mass transfer coefficient of different apolar compounds upon dispersion of an organic solvent in the aqueous medium. The mass transfer coefficient was calculated as a function of the solvent hold-up in the reactor and of the compound's solubility in water. The model assumed continuous steady-state operation, all phases to be ideally mixed and the solvent to be homogeneously dispersed in the aqueous phase.

The solvent used in model evaluation was FC40 - a perfluorocarbon. Solvent-in-water dispersions up to 15 % (v/v) FC40 were tested. Two compounds with different solubilities in water were studied, namely toluene and oxygen, being moderately and poorly-water soluble, respectively. The overall volumetric mass transfer coefficient from the gas to the water was measured in steady state. Removal of the compound was achieved by passing



This chapter has been accepted for publication in Biotechnology Progress by the authors M.T. Cesário, H.L. de Wit, J. Tramper and H.H. Beeftink

a continuous flow of compound-free water or gas through the reactor.

An increase of the mass transfer coefficient with increasing solvent amounts was found. The experimentally determined values of the enhancement factor, defined as the ratio between the mass transfer coefficient in the systems with and without solvent, compared well with the theoretical model predictions for the range of dispersions tested. While for oxygen a 2.2-fold increase of the overall mass transfer coefficient was found at 15 % (v/v) FC40, an enhancement of circa 1.15 was observed for toluene at the same solvent amount.

## Introduction

Dispersion of water-immiscible organic solvents in aqueous medium is used to improve the oxygen transfer rate in oxygen-limited biological processes[1,7,9,13,17-19,23,24]. The same technique was applied to enhance the removal of poorly-water soluble pollutants from waste gases during biological degradation[3,4].

The use of organic solvents as mass transfer enhancers is described in several papers[7,15,17,19,23,24], but in the majority of these studies the capacity of a second liquid phase to improve the mass transfer is only tested in an empirical manner. The aim of the work presented here was to generate knowledge to be able to predict theoretically at which solvent volume fractions and for which gaseous compounds a relevant intensification of the gas/water transfer rate can be expected. Aiming at this, a mathematical model was set-up by assuming a number of different possible paths for gas/water transfer in a 3-phase system (Fig. 1). For each path a characteristic composite overall mass transfer coefficient was obtained. This transfer coefficient is a function of the amount of solvent in the system and of the

affinity of the compound for the water and the solvent.

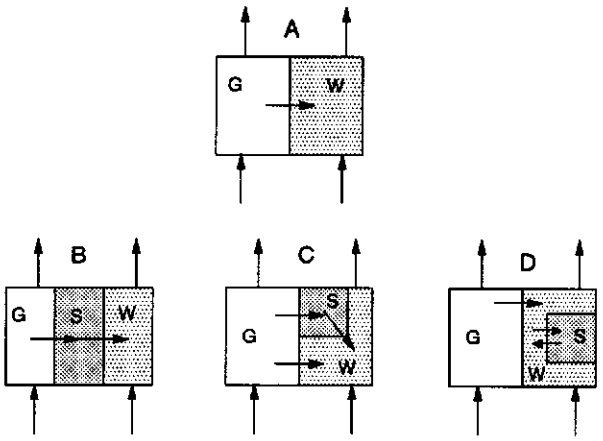



Figure 1. Possible pathways for gas/water transfer in a two-phase system (**A**) and in a three-phase system (**B, C, D**). **A.** direct gas/water transport; **B.** serial gas-solvent-water transport; **C.** serial transfer through the solvent plus direct gas/water transfer; **D.** transport to the water including the solvent. G: gas; S: solvent; W: water.

In the present work, a specific system configuration was chosen and the change of the overall mass transfer coefficient for various solvent volume fractions and for different compounds predicted theoretically by means of the model. Validation of model predictions was done by carrying out steady-state experiments in the absence of microorganisms. Removal of the compound was in this case achieved by passing a continuous flow of compound-free water or gas through the reactor. The solvent was kept in the vessel by a small settler placed inside the reactor, which separated both liquid phases at the liquid outlet[2]. Experiments were carried out in a stirred-tank reactor with surface aeration.

This study was carried out with two model compounds having different solubilities in water, namely toluene and oxygen. The partition coefficients in the system gas/water at 22°C are 0.21 and 32.7 (mol/m$^3$gas)/ (mol/m$^3$water), respectively. The water-immiscible organic solvent was FC40, a perfluorocarbon. This solvent was chosen because it has a good affinity for toluene and oxygen, the partition coefficient in the system gas/solvent being 0.012 and 2.8 mol/m$^3$ gas/ mol/m$^3$ solvent, respectively. Furthermore it has a density almost twice as large as water (density= 1870 kg/m$^3$). This large density difference is desirable for a faster separation of the two liquids in the settler.

## Theory

### Model development

A steady-state model is used to describe the mass transfer mechanism in each of the systems in Fig. 1. It is assumed that all phases are ideally mixed and that the solvent (if present) is homogeneously dispersed in the aqueous phase. In these systems the solvent is kept in the reactor while the only phases that receive or discharge external flows are the gas and the water phase. This is equivalent to say that under stationary conditions, there is no net transport to or from the solvent, the only net transfer being between the gas and the water.

*Gas/water mass transfer in a 2-phase system (Case A)*

In the absence of solvent, the transfer takes place directly between the gas and water phase (case A, Fig. 1). In continuous steady-state operation with both phases ideally mixed, the mass balances over the gas and the aqueous phase are:

$$F_g\ (C_{gin} - C_{gout}) = T_A\ (\frac{C_{gout}}{m_{gw}} - C_{wout}) \quad (1)$$

$$T_A\ (\frac{C_{gout}}{m_{gw}} - C_{wout}) = F_w\ (C_{wout} - C_{win}) \quad (2)$$

with $F_g$ and $F_w$ the gas and the water flow rate ($m^3/s$), respectively, $C_{gin}$ and $C_{gout}$ the concentration in the inlet and in the outlet gas phase ($mol/m^3$), respectively, $C_{win}$ and $C_{wout}$, the concentration in the inlet and in the outlet aqueous phase ($mol/m^3$) and $m_{gw}$ the partition coefficient between the gas and the water phase ($mol/m^3$ gas/ $mol/m^3$ water).

The overall mass transfer coefficient gas/water ($k_{gw}$, m/s) and the total interfacial area gas/water ($A_{gw}$, $m^2$) are combined into one transport parameter $T_A$:

$$T_A = k_{gw}\ A_{gw} \quad (3)$$

***Gas/water mass transfer in a 3-phase system***

When a gas is introduced into a solvent-in-water dispersion in a well mixed vessel (STR), various paths for mass transfer between the gas and the water phase are possible (Fig. 1). The solvent phase can be completely in-between the gas and the water phase (case B), partly in-between the gas and the water (case C), or entirely included in the water (case D). In the first case mass transfer towards water takes place exclusively through the solvent, while in the second case indirect (gas→solvent→water) as well as direct transfer (gas→water) occur simultaneously. In the third case, the solvent does not contact the gaseous phase and thus transfer to the water takes place exclusively from the gas.

Each case can be described by a set of three mass balance equations. In all systems, a simplification of these equations is possible resulting in each case

in a set of two equations similar to eqs. 1 and 2, featuring the gas/water concentration difference as the sole driving force for overall interface transfer and an overall mass transfer coefficient T. This parameter is a function of various interfacial areas, transfer coefficients and partition coefficients.

*Indirect transfer through the solvent compartment (case B)*
The mass balances over the gas, the solvent and the water are given by:

$$F_g\ (C_{gin} - C_{gout}) = k_{gs}\ A_{gs}\ (\frac{C_{gout}}{m_{gs}} - C_s) \tag{4}$$

$$k_{gs}\ A_{gs}\ (\frac{C_{gout}}{m_{gs}} - C_s) = k_{sw}\ A_{sw}\ (\frac{C_s}{m_{sw}} - C_{wout}) \tag{5}$$

$$k_{sw}\ A_{sw}\ (\frac{C_s}{m_{sw}} - C_{wout}) = F_w\ (C_{wout} - C_{win}) \tag{6}$$

with $C_s$ the concentration in the solvent (mol/m$^3$), $k_{gs}$ the overall mass transfer coefficient gas/solvent based on solvent concentrations (m/s), $k_{sw}$ the overall mass transfer coefficient solvent/water based on aqueous concentrations (m/s), $A_{gs}$ the interfacial area gas/solvent (m$^2$), $A_{sw}$ the interfacial area solvent/water (m$^2$), $m_{gs}$ the partition coefficient of the compound between the gas and the solvent ((mol/m$^3$ gas)/ (mol/m$^3$ solvent)) and $m_{sw}$ the partition coefficient of the compound between the solvent and the water phases= $m_{gw}/m_{gs}$ ((mol/m$^3$solvent)/ (mol/m$^3$water)).

This set of three balance equations involves two driving forces. It may be simplified by elimination of the variable $C_s$ to a set of two equations (similar to eqs 1 and 2) with a single driving force, namely the gas/water concentration difference and, instead of $T_A$, $T_B$ as the overall mass transfer coefficient. $T_B$ is given by:

$$\frac{1}{T_B} = \frac{1}{k_{sw} A_{sw}} + \frac{1}{m_{sw} k_{gs} A_{gs}} \tag{7}$$

*Indirect transfer through the solvent plus direct gas/water transfer (case C)*
The mass balances over gas, solvent and water are respectively:

$$F_g (C_{gin} - C_{gout}) = k_{gs} A_{gs} \left(\frac{C_{gout}}{m_{gs}} - C_s\right) + k_{gw} A_{gw} \left(\frac{C_{gout}}{m_{gw}} - C_{wout}\right) \tag{8}$$

$$k_{gs} A_{gs} \left(\frac{C_{gout}}{m_{gs}} - C_s\right) = k_{sw} A_{sw} \left(\frac{C_s}{m_{sw}} - C_{wout}\right) \tag{9}$$

$$k_{gw} A_{gw} \left(\frac{C_{gout}}{m_{gw}} - C_{wout}\right) + k_{sw} A_{sw} \left(\frac{C_s}{m_{sw}} - C_{wout}\right) = F_w (C_{wout} - C_{win}) \tag{10}$$

In analogy to case B, $C_s$ may be eliminated from these equations resulting in a set of two equations (again similar to eqs 1 and 2) with the gas/water concentration difference as driving force and, instead of $T_A$, $T_C$ as the overall mass transfer coefficient. $T_C$ is given by:

$$T_C = \frac{1}{\frac{1}{k_{sw} A_{sw}} + \frac{1}{m_{sw} k_{gs} A_{gs}}} + k_{gw} A_{gw} \tag{11}$$

*Transfer to the water phase including the solvent (case D)*
In this system, since the mass transfer rate solvent/water is equal to the transfer rate water/solvent, the mass balances over the gas, the solvent and the water reduce immediately to a system of two equations as for the case with no solvent. The overall transfer parameter $T_D$, is similar to $T_A$ although it might not have the same value:

$$T_D = k_{gw} A_{gw} \tag{12}$$

*Mass transfer enhancement*

The transfer enhancement created by addition of the solvent is given by the enhancement factor ($E_f$), which is the ratio between the overall mass transfer coefficients ($T$ parameter) in the solvent containing systems (cases B, C and D) and in the biphasic system (case A):

$$E_f = \frac{T}{T_A} \tag{13}$$

## Model description

Since in a 3-phase system the mass transfer coefficient is studied at different solvent volume fractions ($\alpha_s$), any influence of $\alpha_s$ on the quantities given under parameter $T$ such as interfacial areas and mass transfer coefficients should be specified.

The following analysis is for case C because both case B and D are particular cases of C and because in the system configuration used for model validation this is the most probable mechanism.

This study is done based on the total reactor volume ($V$). Because surface aeration is used, transfer between the gas and the liquid takes place from the reactor head-space across the surface of the liquid. It is assumed that the head-space volume is constant and so is the gas hold-up ($\alpha_g$) in the system. Any increase in the solvent volume is thus at the expense of the water volume only. Consequently:

$$1 = \alpha_g + \alpha_s + \alpha_w \tag{14}$$

As a simplification, it is assumed that all partial mass transfer coefficients are independent of $\alpha_s$, the only $\alpha_s$-dependent quantities in eq. 11 being the exchange areas $A_{gw}$, $A_{gs}$ and $A_{sw}$. The total gas exchange area ($A_{gw} + A_{gs}$) in this specific system configuration (surface aeration) is constant. More generally, in the case of gas sparged-systems, there is some evidence that a dispersed phase with a positive spreading coefficient[7] like FC40, can increase the interfacial area by reducing the gas/water interfacial tension[7,17]. However, in general this contribution to the total enhancement is relatively small[17].

As a consequence of a constant gas hold-up ($\alpha_g$), a constant volume-to-surface ratio for the gas phase ($r_g$) follows:

$$r_g = \frac{V_g}{A_{gw} + A_{gs}} = constant \tag{15}$$

The area available for the transfer gas → solvent is assumed to be directly proportional to the solvent hold-up in the liquid phase ( i.e. proportional to $\alpha_s/(1-\alpha_g)$):

$$A_{gs} = \frac{\alpha_s}{1-\alpha_g} (A_{gs} + A_{gw}) \tag{16}$$

Together with eq. 15 and with $V_g = \alpha_g$ V this yields:

$$\frac{A_{gs}}{V} = \frac{\alpha_s}{(1-\alpha_g)} \frac{\alpha_g}{r_g} \tag{17}$$

The gas/water interface is then given by:

$$A_{gw} = [1 - \frac{\alpha_s}{(1-\alpha_g)}] (A_{gs} + A_{gw}) \tag{18}$$

Again combination with eq. 15 yields:

$$\frac{A_{gw}}{V} = [1 - \frac{\alpha_s}{(1-\alpha_g)}] \frac{\alpha_g}{r_g} \tag{19}$$

Also for the solvent phase, a constant ratio volume-to-surface ($r_s$) is assumed:

$$r_s = \frac{V_s}{A_{sw} + A_{gs}} \tag{20}$$

The area of the solvent-water interface is calculated as the remainder of the total solvent area, i.e.:

$$A_{sw} = (A_{sw} + A_{gs}) - A_{gs} = \frac{V_s}{r_s} - A_{gs} \tag{21}$$

Combining this with eq. 17 gives:

$$\frac{A_{sw}}{V} = \frac{\alpha_s}{r_s} - \frac{\alpha_s}{(1-\alpha_g)} \frac{\alpha_g}{r_g} \tag{22}$$

All exchange areas, $A_{gw}$, $A_{gs}$ and $A_{sw}$ have been written as a function of $\alpha_s$. This can be used in eq. 11 to represent the overall transfer coefficient $T_C$ as a function of the solvent hold-up in the liquid.

Dividing eq. 11 by the total system volume (V) and substituting eqs. 17, 19 and 22 yields:

$$\frac{T_C}{V} = \frac{1}{\left[\frac{1}{k_{sw}}\right]\left[\frac{1}{\frac{\alpha_s}{r_s} - \frac{\alpha_s}{(1-\alpha_g)}\frac{\alpha_g}{r_g}}\right] + \left[\frac{1}{m_{sw}\, k_{gs}}\right]\left[\frac{1}{\frac{\alpha_s}{(1-\alpha_g)}\frac{\alpha_g}{r_g}}\right] + k_{gw}\left[1 - \frac{\alpha_s}{(1-\alpha_g)}\right]\frac{\alpha_g}{r_g}} \qquad (23)$$

Equation 23 was further developed by substituting overall mass transfer coefficients by partial mass transfer coefficients; this is given in Appendix 1. Two different hold-ups are present: the gas hold-up ($\alpha_g$) and the solvent hold-up ($\alpha_s$). Since the former is a constant, $T_C/V$ is a function of the solvent hold-up only. The derivative of $T_C/V$ with respect to $\alpha_s$ is independent of the later (equation not shown), indicating that $T_C/V$ should vary linerarly with the solvent hold-up.

Eq. 23 is used to study the influence of the different partition coefficients and of the solvent hold-up on $T_C/V$. This is possible after calculation of the parameters: total gas exchange area ($A_{gs} + A_{gw}$), total solvent exchange area ($A_{sw} + A_{gs}$) and the various partial mass transfer coefficients by means of empirical correlations (Appendix 2).

## Experimental determination of the overall mass transfer coefficient

Validation of the overall volumetric gas/water mass transfer coefficient calculated theoretically by the model ($T_C/V$) was done by carrying out experiments in steady state.

***Toluene***

The overall transfer coefficient for toluene was determined from the transfer from gas to water. Consumption of toluene was achieved by passing a continuous flow of toluene-free water through the reactor. In steady state and when solvent is present, there is no net transport of toluene to the solvent, but only towards the water phase from where it is discharged with the effluent. The overall volumetric mass transfer coefficient ($T/V$) was calculated from a stationary mass balance over the gas phase:

$$F_g\ (C_{gin} - C_{gout}) = (\frac{T}{V})\ (\frac{C_{gout}}{m_{gw}} - C_{wout})\ V \qquad (24)$$

with $T/V$ ($s^{-1}$) the overall volumetric mass transfer coefficient based on water phase concentrations and on the total reactor volume. The concentration in the water phase ($C_{wout}$) can be eliminated from eq. 24 with an overall stationary mass balance over the reactor:

$$F_g\ (C_{gin} - C_{gout}) = F_w\ (C_{wout} - C_{win}) \qquad (25)$$

Substituting eq. 25 in eq. 24 and considering that the water entering the system is toluene free ($C_{win} = 0$):

$$\frac{T}{V} = \frac{F_g / V}{\frac{C_{gout}/C_{gin}}{1 - C_{gout}/C_{gin}} \frac{1}{m_{gw}} - \frac{F_g}{F_w}} \qquad (26)$$

This equation was used to determine the coefficient T/V both in the presence and absence of solvent. In the absence of solvent T equals $T_A$ while in its presence it is given by $T_B$, $T_C$ or $T_D$ depending on the mechanism involved.

In order to derive accurate $T/V$ values, $C_{gin}$ and $C_{gout}$ should deviate at least

20 %[20]. Furthermore, $C_{wout}$ should deviate at least 20 % from $C_{gout}/m_{gw}$. To meet these constraints, the flow of gas and water through the system should be kept within certain limits[2].

### *Oxygen*

As opposed to toluene, the overall transfer coefficient for oxygen was determined from the transfer from water to gas (instead of gas→ water). Oxygen-free gas (nitrogen) was used to remove oxygen from the liquid. In this case the mass balance over the gas phase is:

$$F_g\ (C_{gout} - C_{gin}) = (\frac{T}{V})\ (C_{wout} - \frac{C_{gout}}{m_{gw}})\ V \qquad (27)$$

Just as for toluene, the concentration in the water phase ($C_{wout}$) can be eliminated from eq. 27 with an overall stationary mass balance over the reactor and considering in this case that the gas entering the system is oxygen free ($C_{gin}$= 0). This results in:

$$\frac{T}{V} = \frac{F_g\ /V}{\frac{C_{win}}{C_{gout}} - (\frac{F_g}{F_w} + \frac{1}{m_{gw}})} \qquad (28)$$

## Materials and Methods

### *Toluene transfer experiments*

Experiments were carried out in a 2-dm$^3$ fermenter with a working volume of 1.3 dm$^3$ equiped with a 4-blade turbine stirrer and a head-space volume of 0.7 dm$^3$. The temperature was kept at 22 °C and the stirring speed was 800

rpm. The gas and the water flow were $1.7\times10^{-7}$ $m^3/s$ and $6.7\times10^{-7}$ $m^3/s$, respectively. Head-space aeration was carried out with a toluene inlet concentration in the gas of 0.25 $mol/m^3$. Toluene-in-air mixtures were prepared by mixing air saturated with toluene with pure air. Toluene-saturated air was prepared by passing air at a controlled rate through a bubble column containing liquid toluene at 22°C. The gas flow rates were controlled with Brooks 5850 TR Mass-Flow Controllers (Rosemount, Schiedam, The Netherlands). Separation of the two liquids was accomplished in a small settler placed inside the reactor[2]. No losses of FC40 from the system were found when examining the outlet aqueous phase.

After starting the experiment, $C_{gout}$ was measured in time until a constant value was achieved. This value was used to calculate the mass transfer coefficient with eq. 26.

***Oxygen transfer experiments***

The same reactor configuration described above was used for experiments with oxygen. Instead of measuring the oxygen transfer from air to water (requiring the use of oxygen-free water), the oxygen transfer from water to an oxygen-free gas was measured. Therefore, water presaturated with air at 22°C was used. The oxygen concentration in the inlet water stream ($6.7\times10^{-7}$ $m^3$ water/s) was 0.27 mol oxygen/$m^3$ water. Nitrogen ($1.7\times10^{-7}$ $m^3$gas/s) was blown over the liquid surface.

After start-up, $C_{gout}$ was monitored until a constant value was achieved which was then used to calculate $T/V$ by eq. 28. The outlet oxygen concentration was measured by means of a paramagnetic oxygen meter (Cervomex, type OA-540).

***Analytical methods***

Toluene was determined by analyzing 100 $\mu$l gas samples on a Chrompack

9000 gas chromatograph fitted with a Poropack R column (100-120 mesh) and a flame ionization detector. The oven temperature was 210°C and the carrier gas $N_2$ was supplied at 30 ml/min.

Toluene-in-air calibration standards were prepared by adding an exact amount of toluene to flasks partially filled with water and fitted with Teflon Mininert valves (Phase Separation). After equilibration overnight at 22°C the toluene concentration in the head-space was calculated from an overall mass balance and the partition coefficient value (0.21 mol/m$^3$gas/ mol/m$^3$ water at 22°C). The partition coefficient of toluene between gas and water was determined according to the EPICS method described by Gossett[6].

***Chemicals***

FC40 was purchased from 3M, The Netherlands; the properties are: density (25°C) 1850 kg/m$^3$; surface tension (25°C) 16 nN/m; boiling point 165-185 °C; molecular weight 0.65 kg/mol; dynamic viscosity (25°C) 4.5 mPa.s. Toluene with a purity of 99.5 % was obtained from Janssen Chimica, Belgium. Nitrogen was obtained from Hoekloos B.V., The Netherlands.

## Results and Discussion

The system configuration was a stirred-tank reactor with a continuous water flow and a continuous gas flow via the reactor head-space. Blowing the gas over the liquid surface was chosen instead of sparging the gas through the liquid because the latter would induce larger T/V values. Larger mass transfer coefficient values would require larger water flows in order to assure a 20% difference between $C_{wout}$ and $C_{gout}/m_{gw}$ in steady-state necessary for an accurate determination of the mass transfer coefficient. Because a larger water flow would hinder a good separation of the two liquid phases in the

settler, surface aeration and thus lower overall mass transfer coefficient values were chosen in this study.

In case toluene-containing air is blown over a homogeneous solvent-in-water dispersion, the gaseous toluene is transferred both to the water bulk phase and to the solvent droplets adjacent to the gas/liquid interface. In the case of oxygen, this compound will be transferred both to the gas and to the solvent droplets dispersed in the water phase. The most probable path for mass transfer between water and gas in both cases is therefore, serial transfer through the solvent plus direct transfer gas/water, in other words case C. The overall volumetric gas/water mass transfer coefficient as a function of the solvent volume fraction was therefore calculated theoretically by means of eq. 23.

***Model calculations***

Aiming at calculating theoretically the overall mass transfer coefficient ($T_C/V$), the total solvent exchange area ($A_{sw}+ A_{gs}$) and the partial mass transfer coefficients for the transfer between gas/water, gas/solvent and solvent/water were calculated by means of empirical correlations given in Appendix 2. The total exchange area between the gas and the overall liquid ($A_{gs}+ A_{gw}$) is in this configuration equal to the total liquid surface area of the tank (0.01 $m^2$). Since the head-space volume is constant and equal to $7\times10^{-4}$ $m^3$ the volume-to-surface ratio, $r_g$, (eq. 15) is equal to 0.07 m and the gas hold-up ($\alpha_g$) is 0.35.

All the other parameters used to calculate the overall gas/water mass transfer coefficient ($T_C/V$) as a function of the solvent volume fraction (eq. 23) are calculated in Appendix 2 and given in Table 1.

Table 1. Parameters used to calculate $T_C/V$ for toluene and oxygen.

| | toluene | oxygen | units |
|---|---|---|---|
| $m_{gw}^{22°C}$ | 0.21 | 32.6 | $mol.m^{-3}/ mol.m^{-3}$ |
| $m_{gs}^{22°C}$ | 0.012 | 2.8 | $mol.m^{-3}/ mol.m^{-3}$ |
| $m_{sw}^{22°C}$ | 17.5 | 11.6 | $mol.m^{-3}/ mol.m^{-3}$ |
| $k_{Gw}$, $k_{Gs}$ | $4.0\times10^{-4}$ | $4.8\times10^{-4}$ | $m.s^{-1}$ |
| $k_{gW}$ | $8.42\times10^{-5}$ | $1.38\times10^{-4}$ | $m.s^{-1}$ |
| $k_{gS}$ | $7.9\times10^{-5}$ | $1.21\times10^{-4}$ | $m.s^{-1}$ |
| $k_{Sw}^{*}$ | $6.15\times10^{-5}$ | $1.45\times10^{-4}$ | $m.s^{-1}$ |
| $k_{sW}^{*}$ | $1.47\times10^{-4}$ | $2.94\times10^{-4}$ | $m.s^{-1}$ |
| $r_g$ | 0.07 | 0.07 | m |
| $\alpha_g$ | 0.35 | 0.35 | (-) |

* calculated for an average value of solvent droplet of 78 $\mu$m (see Appendix 2).

The overall volumetric mass transfer coefficient $T_C/V$ is given by the sum of two terms (eq. 23): the first term illustrates the mass transfer through the solvent and the second the direct transfer between gas and water. The change of each term of eq. 23 as a function of the solvent hold-up in the liquid $(\alpha_s/(1-\alpha_g)$ is shown in Fig. 2. This was done for toluene and oxygen. For both compounds, the direct gas/water mass transfer coefficient decreases with a decrease of the interfacial area gas/water which is caused by an increase of the amount of solvent. Reversely, an increase of the solvent volume fraction provokes an increase of the interfacial areas gas/solvent and solvent/water and a subsequent increase of the composite mass transfer coefficient from the gas to the water through the solvent. The sum of those two volumetric mass transfer coefficients gives $T_C/V$. It is observed that the change of $T_C/V$ is more pronounced for oxygen than for toluene.

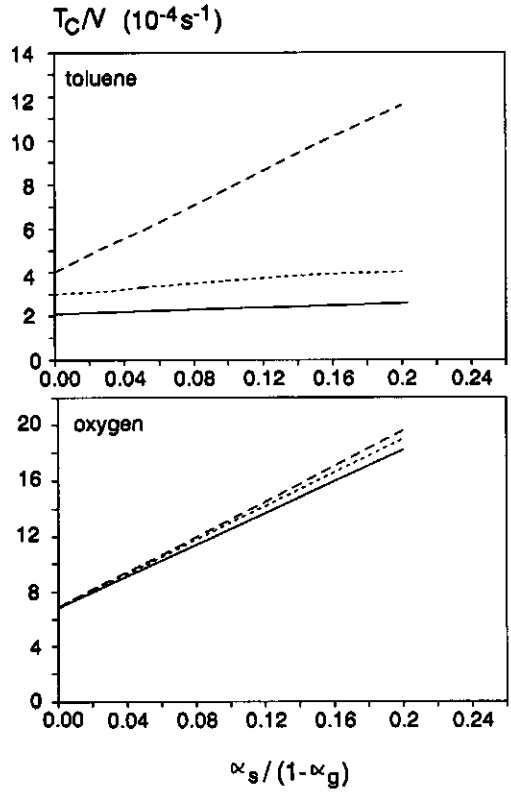



Figure 4. Influence of the partial mass transfer coefficient on the gas side ($k_g$) on the change of the overall gas/water mass transfer coefficient at different solvent hold-ups in the liquid for toluene and oxygen.(—), $k_g$= $4\times10^{-4}$; (...), $k_g$= $1\times10^{-3}$; (---), $k_g$= $1\times10^{-2}$.

the resistance in the gas film is larger than the resistance in the water film boundary layer. Under these circumstances, the addition of solvent to the

water has hardly any influence on the overall mass transfer coefficient ($T_C/V$), as expected here ($k_g = 4\times10^{-4}$ m/s). The partial gas mass transfer coefficient is very low because of surface aeration and the low value of the gas flow rate used; the typical value for $k_g$ being $\approx 1\times10^{-2}$ for gas/liquid dispersions[22].

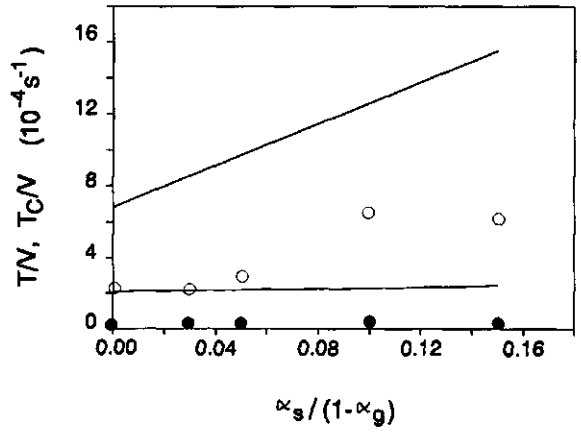



Figure 5. Comparison of the overall volumetric gas/water mass transfer coefficient theoretically predicted (solid line) and experimentally obtained at different solvent hold-ups in the liquid: (●), toluene; (○), oxygen.

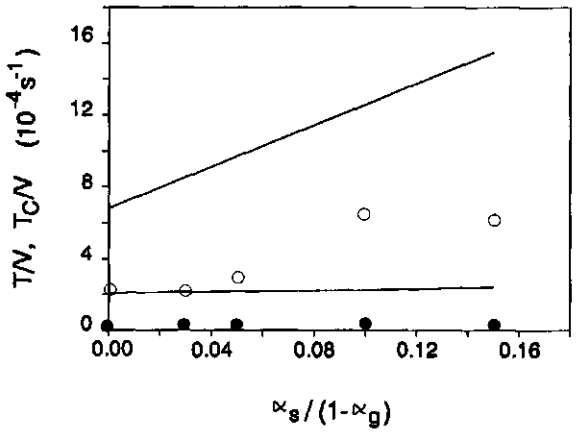
***Model validation***

Overall volumetric gas/water mass transfer coefficients were determined in steady state both in the presence and absence of solvent using the system configuration described above. This was done for both toluene and oxygen at different solvent volume fractions. Fig. 5 shows the $T/V$ values determined experimentally and the $T_C/V$ values calculated with the model. It is observed that for all solvent volume fractions and for both compounds, the mass

transfer coefficient values predicted by the model are larger than the values obtained experimentally. Because this difference is also found for 0 % (v/v) FC40, it must be related to the value used for either $k_{Gw}$ or $k_{gW}$. For lower partial mass transfer coefficients, the theoretical calculated $T_C/V$ approach the $T/V$ values determined experimentally. The difference between the calculated and the experimentally determined values might be due to the fact that both partial mass transfer coefficients were not determined experimentally for this particular system set-up, but calculated by means of general empirical calculations, being therefore only approximate estimations of the real value. However it is observed that the model predicts well the influence of the solvent amount on the gas/water mass transfer coefficient for both toluene and oxygen. For a better comparison, the experimental and theoretically calculated enhancement factor calculated with eq. 16 are shown in Fig. 6. It is important to emphasize that all theoretical and experimental $T/V$ parameters are based on the total reactor volume and not on the aqueous phase volume. This way an apparent increase of the overall mass transfer coefficient with the solvent volume fraction solely caused by a decrease of the aqueous phase volume is avoided. A reasonably good agreement between the theoretically predicted and the experimentally obtained enhancement factors is observed. This supports the assumptions made concerning the mechanism proposed for the transfer between the gas and the water in the presence of a dispersed solvent within this system configuration.

This study was done for a particular system configuration, namely a well-mixed liquid phase and surface aeration. If, instead, the gas would have been sparged through the dispersion all the three mechanisms depicted in Fig. 1 would have been possible, depending on the value of the solvent spreading coefficient ($S_p$). For $S_p < 0$, the solvent forms droplets that are homogeneously dispersed in the aqueous phase and do not contact directly

water has hardly any influence on the overall mass transfer coefficient ($T_C/V$), as expected here ($k_g = 4\times10^{-4}$ m/s). The partial gas mass transfer coefficient is very low because of surface aeration and the low value of the gas flow rate used; the typical value for $k_g$ being $\approx 1\times10^{-2}$ for gas/liquid dispersions[22].

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Overall volumetric gas/water mass transfer coefficients were determined in steady state both in the presence and absence of solvent using the system configuration described above. This was done for both toluene and oxygen at different solvent volume fractions. Fig. 5 shows the $T/V$ values determined experimentally and the $T_C/V$ values calculated with the model. It is observed that for all solvent volume fractions and for both compounds, the mass

transfer coefficient values predicted by the model are larger than the values obtained experimentally. Because this difference is also found for 0 % (v/v) FC40, it must be related to the value used for either $k_{Gw}$ or $k_{gW}$. For lower partial mass transfer coefficients, the theoretical calculated $T_C/V$ approach the $T/V$ values determined experimentally. The difference between the calculated and the experimentally determined values might be due to the fact that both partial mass transfer coefficients were not determined experimentally for this particular system set-up, but calculated by means of general empirical calculations, being therefore only approximate estimations of the real value. However it is observed that the model predicts well the influence of the solvent amount on the gas/water mass transfer coefficient for both toluene and oxygen. For a better comparison, the experimental and theoretically calculated enhancement factor calculated with eq. 16 are shown in Fig. 6. It is important to emphasize that all theoretical and experimental $T/V$ parameters are based on the total reactor volume and not on the aqueous phase volume. This way an apparent increase of the overall mass transfer coefficient with the solvent volume fraction solely caused by a decrease of the aqueous phase volume is avoided. A reasonably good agreement between the theoretically predicted and the experimentally obtained enhancement factors is observed. This supports the assumptions made concerning the mechanism proposed for the transfer between the gas and the water in the presence of a dispersed solvent within this system configuration.

This study was done for a particular system configuration, namely a well-mixed liquid phase and surface aeration. If, instead, the gas would have been sparged through the dispersion all the three mechanisms depicted in Fig. 1 would have been possible, depending on the value of the solvent spreading coefficient ($S_p$). For $S_p < 0$, the solvent forms droplets that are homogeneously dispersed in the aqueous phase and do not contact directly the gas bubbles (case D). If $S_p > 0$, the solvent tends to spread as a thin film

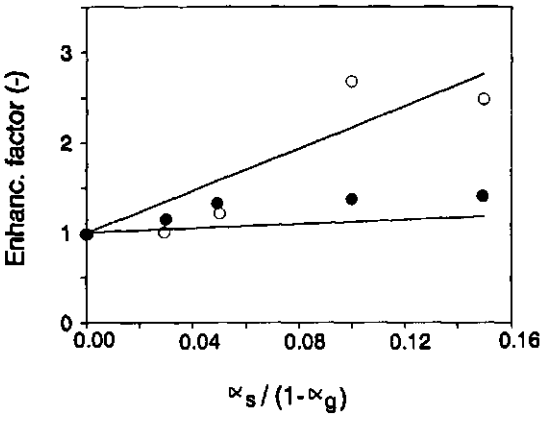


Figure 6. Overall volumetric gas/water mass transfer coefficient enhancement factor theoretically predicted ($T_C/V$/ $T_A/V$, solid line) and experimentally obtained at different solvent hold-ups in the liquid: (●), toluene; (○), oxygen.

covering totally or partially the gas/aqueous interface, cases B and C, respectively[7,17]. In the former case no enhancement of the overall volumetric gas/water mass transfer coefficient in the presence of the solvent is expected; this was observed by several authors[7,12,24]. For solvents with a positive spreading coefficient a general increase of mass transfer coefficient with increasing solvent volume fractions is usually found[9,10,13,17]. In this case, the effectiveness of the interactions between the gas bubbles and the solvent droplets is an important factor, the latter being dependent upon the local degree of turbulence, the gas residence time and the physico-chemical properties of the phases[16]. For this type of systems (gas-sparged systems with positive spreading coefficient), the mathematical model derived in this study and similar assumptions[11], could also be applied to predict the mass transfer coefficient enhancement factor.

## Conclusions

A mathematical model was used to describe the mass transfer between the gas and the water in the presence of a dispersed solvent for a particular system configuration, namely a stirred-tank reactor with surface aeration. It is shown that the model predicts well the overall volumetric gas/water mass transfer coefficient enhancement factor for both toluene and oxygen at increasing solvent volume fractions. However, a good agreement between the mass transfer coefficient values calculated theoretically by the model and the ones obtained experimentally was not found, because of the partial mass transfer coefficients, $k_{Gw}$ and $k_{gW}$ used in the model. These parameters were calculated by means of empirical correlations being therefore only approximate estimations of the real value.

The mass transfer coefficient increases more pronouncedly for oxygen than for toluene with an increase of the solvent volume fraction. This is because of the combined effect: low partition coefficient values ($m_{gw}$ and $m_{gs}$) for toluene and low partial gas mass transfer coefficient ($k_{Gw}$ and $k_{Gs}$) characteristic of this system. For systems with larger partial gas mass transfer coefficients a significant enhancement of the toluene transfer might also be achieved.

Theoretical prediction of the gas/water mass transfer coefficient enhancement by solvent addition and for compounds with different solubilities in water is therefore possible by using the model presented in this work. This model can be applied to estimate whether a particular dispersed solvent system may enhance the removal rate of a specific pollutant in the biological treatment of waste gases.

## Appendix 1

Substituting overall by partial mass transfer coefficients in eq. 23 yields:

$$\frac{T_C}{V} = \frac{1}{\left[\frac{1}{k_{sW}} + \frac{1}{m_{sw}k_{Sw}}\right]\left[\frac{1}{\frac{\alpha_s}{r_s} - \frac{\alpha_s}{(1-\alpha_g)}\frac{\alpha_g}{r_g}}\right] + \left[\frac{1}{k_{gS}} + \frac{1}{m_{gs}k_{Gs}}\right]\left[\frac{1}{\frac{\alpha_s}{(1-\alpha_g)}\frac{\alpha_g}{r_g}}\right]\frac{1}{m_{sw}}} + \frac{1}{\left[\frac{1}{k_{gW}} + \frac{1}{m_{gw}k_{Gw}}\right]}\left[1 - \frac{\alpha_s}{(1-\alpha_g)}\right]\frac{\alpha_g}{r_g} \quad \text{(A1)}$$

Partial mass transfer coefficients are refered to by writing with a capital letter the pertinent phase; e.g. $k_{gS}$ is the partial mass transfer coefficient in the solvent phase at the gas/solvent interface and $k_{sW}$ is the partial mass transfer coefficient in the water phase at the solvent/water interface.

## Appendix 2

### Calculation of the total solvent exchange area ($A_{sw}+A_{gs}$)

The total solvent exchange area ($A_{sw}+A_{gs}$) is calculated from the product of the solvent droplet surface area and the number of droplets ($N_d$); the latter being the total volume of solvent divided by the volume of a single droplet, yielding:

$$A_{sw} + A_{gs} = 6 \frac{V_s}{d_d} \qquad \text{(A2.1)}$$

The solvent droplet diameter ($d_d$) is among others a function of the solvent hold-up in the dispersion and may be estimated by Zuiderweg[25]:

$$d_d = 0.047 \left(\frac{\sigma_{sw}^{0.6}}{\rho_w^{0.6} N^{1.2} D^{0.8}}\right) \left(1 + 2.5 \left(\frac{\alpha_s}{1 - \alpha_g}\right)\right) \qquad \text{(A2.2)}$$

Combining eq. A2.2 with eq. A2.1 and substituting the values of the various parameters, yields for the total exchange area:

$$A_{sw} + A_{gs} = \frac{6 V_s}{6.5 \times 10^{-5} \left(1 + 2.5 \frac{\alpha_s}{1 - \alpha_g}\right)} \qquad \text{(A2.3)}$$

Combining eq. A2.3 and eq. 20, $r_s$ can be written as:

$$r_s = \frac{1 + 2.5 \left(\frac{\alpha_s}{1 - \alpha_g}\right)}{9.2 \times 10^4} \qquad \text{(A2.4)}$$

**Calculation of the partial mass transfer coefficients**

***A. Transfer across the gas-liquid interface***

*A1. Partial gas mass transfer coefficient.*

The partial mass transfer coefficient on the gas side both for the transfer gas/water ($k_{Gw}$) or gas/solvent ($k_{Gs}$) was calculated from an empirical correlation for laminar flow in tubes[8]:

$$Sh_g = \frac{k_g R_h}{D_g} = 3.66 \qquad \text{(A2.5)}$$

This correlation is valid when:

$$Gz = \frac{D_g l}{R_h^2 v_g} > 0.1 \qquad \text{(A2.6)}$$

The reactor head-space was considered a flat tube with the dimensions: $l \times d \times h = 0.115 \times 0.09 \times 0.067$ m with $l$ the length, $d$ the width and $h$ the tube height (m). The hydraulic diameter ($R_h$) given as: $2 \times d \times h/(d + h)$ equals 0.077 m. With this value and the value of the diffusion coefficient in the gas (Table A1), the partial mass transfer coefficient in the gas side was calculated for toluene and oxygen.

**Table A1.** Diffusion coefficients in air, water and solvent

| Compound | $D_g^{22°C}$ ($m^2/s$)[a] | $D_w^{22°C}$ ($m^2/s$)[b] | $D_s^{22°C}$ ($m^2/s$)[b] |
|---|---|---|---|
| toluene | $8.4\times10^{-6}$ | $8.2\times10^{-10}$ | $7.2\times10^{-10}$ |
| oxygen | $1\times10^{-5}$ | $2.2\times10^{-9}$ | $1.7\times10^{-9}$ |

[a] estimated according to Fuller *et al.*[5].

[b] estimated according to Wilke and Chang[14].

*A2. Partial solvent and water mass transfer coefficients.*

The partial mass transfer coefficients on the solvent ($k_{gS}$) and on the water sides ($k_{gW}$) were calculated using the Higbie penetration theory[21]. Calculation of the partial mass transfer coefficient will be exemplified for water (the calculation for solvent being identical):

$$k_{gW} = 2 \sqrt{\frac{D_w}{\pi \tau}} \qquad \text{(A2.7)}$$

with $\tau$ the contact time (s) of a small water volume element with the gas phase. The contact time can be calculated from the liquid velocity ($v_w$) as:

$$\tau = \frac{T/2}{v_w} \qquad \text{(A2.8)}$$

with T/2 the tank radius. The liquid velocity, $v_w$, is given by the ratio between the length of the circulation loop ($l_c$) and the time necessary for a total circulation loop ($t_c$):

$$v_w = \frac{l_c}{t_c} \qquad \text{(A2.9)}$$

Vonken and coworkers[21] found that the liquid in the loop causes a mixing time $t_m$, given by:

$$t_m = 4\, t_c \qquad \text{(A2.10)}$$

For Re > 10,000:

$$N\, t_m = 50 \qquad \text{(A2.11)}$$

with Re:

$$Re = \frac{\rho_w\, N\, D^2}{\mu_w} \qquad \text{(A2.12)}$$

In our case $Re$= 26,932 yielding a mixing time ($t_m$) of 3.76 s and a circulation time ($t_c$) of 0.95 s. This means that a small liquid volume element

will take approximately 1 s to undergo a complete circulation loop in the stirred vessel.

By sustituting $t_c$ in eq. A2.9, the liquid velocity can be calculated. The total circulation length of one loop is given by $2\times T/2 + 2H_l$ and amounts to 0.365 m. The liquid velocity results in 0.39 m/s and the contact time of a liquid element with the gas is $\tau = 0.15$ s. Substituting this value in eq. A2.7, $k_{gW}$ can be calculated.

The same procedure [A2.7]-[A2.12] was followed to calculate the partial mass transfer coefficient in the solvent phase ($k_{gS}$) for both compounds.

***B. Transfer between the solvent and the water***

According to the Levich criterion[8] droplets with size $d_d = 66\text{-}90$ $\mu$m behave like rigid spheres (no internal circulation) and the partial mass transfer coefficients on the solvent ($k_{Sw}$) and on the water side ($k_{sW}$) can be calculated respectively by:

$$Sh_s = \frac{k_{Sw}\, d_d}{D_s} = 6.5 \qquad \text{(A2.13)}$$

$$\frac{k_{sW}\, d_d}{D_w} = 2 + 0.47\, \left[\frac{d_d^{4/3}\, R^{1/3}\, \rho_w}{\mu_w}\right]^{0.62} [D/T]^{0.17}\, Sc_w^{0.36} \qquad \text{(A2.14)}$$

with:

$$R = \frac{5\, N^3\, D^5}{V_l} \qquad \text{(A2.15)}$$

## List of symbols

| | | |
|---|---|---|
| $A_{gw}$ | total interfacial area gas/water | ($m^2$) |
| $A_{gs}$ | total interfacial area gas/solvent | ($m^2$) |
| $A_{sw}$ | total interfacial area solvent/water | ($m^2$) |
| $C_{gin}$, $C_{gout}$ | inlet and outlet gas concentration | ($mol.m^{-3}$) |
| $C_s$ | solvent concentration | ($mol.m^{-3}$) |
| $C_{win}$, $C_{wout}$ | inlet and outlet water concentration | ($mol.m^{-3}$) |
| $d_d$ | solvent droplet diameter | (m) |
| $D$ | stirrer diameter | (m) |
| $D_g$, $D_s$, $D_w$ | diffusion coefficient in gas, solvent and water | ($m^2.s^{-1}$) |
| $F_g$ | gas flow rate | ($m^3.s^{-1}$) |
| $F_w$ | water flow rate | ($m^3.s^{-1}$) |
| $Gz$ | Graetz number | (dimensionless) |
| $H_l$ | liquid height | (m) |
| $k_{gw}$ | overall mass transfer coefficient gas/water based on water concentrations | ($m.s^{-1}$) |
| $k_{gs}$ | overall mass transfer coefficient gas/solvent based on solvent concentrations | ($m.s^{-1}$) |
| $k_{sw}$ | overall mass transfer coefficient solvent/water based on water concentrations | ($m.s^{-1}$) |
| $k_{Gw}$, $k_{gW}$ | partial gas and water mass transfer coefficient in the transfer gas/water | ($m.s^{-1}$) |
| $k_{Gs}$, $k_{gS}$ | partial gas and solvent mass transfer coefficient in the transfer gas/solvent | ($m.s^{-1}$) |
| $k_{Sw}$, $k_{sW}$ | partial solvent and water mass transfer coefficient in the transfer solvent/water | ($m.s^{-1}$) |
| $l$ | diameter of the reactor head-space | (m) |
| $l_c$ | length of the circulation loop | (m) |

| | | |
|---|---|---|
| $m_{gw}$ | partition coefficient between gas and water | (mol.m$^{-3}$gas)/(mol.m$^{-3}$water) |
| $m_{gs}$ | partition coefficient between gas and solvent | (mol.m$^{-3}$gas)/(mol.m$^{-3}$solvent) |
| $m_{sw}$ | partition coefficient between solvent and water | (mol.m$^{-3}$solvent)/(mol.m$^{-3}$water) |
| $N$ | stirring speed | (s$^{-1}$) |
| $r$ | volume-to-surface ratio | (m) |
| $Re$ | Reynolds number | (dimensionless) |
| $R_h$ | hydraulic diameter | (m) |
| $Sc$ | Schmidt number | (dimensionless) |
| $Sh$ | Sherwood number | (dimensionless) |
| $t_c$ | total circulation loop | (s) |
| $t_m$ | mixing time | (s) |
| $T$ | overall mass transfer coefficient based on water phase concentrations and on the total reactor volume | (m.s$^{-1}$) |
| $T/V$ | overall volumetric mass transfer coefficient based on water phase concentrations and on the total reactor volume | (s$^{-1}$) |
| $T$ | tank diameter | (m) |
| $v_g$ | superficial gas velocity | (m.s$^{-1}$) |
| $v_w$ | circulating liquid velocity | (m.s$^{-1}$) |
| $V$ | total reactor volume | (m$^3$) |
| $V_g$, $V_s$ | gas and solvent volume | (m$^3$) |
| $V_l$ | liquid volume | (m$^3$) |
| $\alpha_g$, $\alpha_s$, $\alpha_w$ | gas, solvent and water volume fractions based on the total reactor volume | (-) |
| $\mu_w$ | water viscosity | (kg.m$^{-1}$.s$^{-1}$) |
| $\rho_w$ | density of water | (kg.m$^{-3}$) |
| $\sigma_{sw}$ | solvent water interfacial tension | (kg.s$^{-2}$) |

| | | |
|---|---|---|
| $\tau$ | contact time | (s) |

**Acknowledgements**

This work was supported by a grant (BD/740/90-IF) from the Junta Nacional de Investigação Científica e Tecnológica, Lisbon, Portugal. The authors want to thank Fred van den End for his suggestions concerning the settler design.

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# Chapter 6

## Enhancement of the gas-to-water ethene transfer coefficient by a dispersed water-immiscible solvent: effect of the cells


### Summary

For a mass-transfer-limited system, it was demonstrated that the volumetric ethene transfer coefficient ($k_l a$) from gas to water could be enhanced by dispersing adequate amounts of a water-immiscible organic liquid, namely the perfluorocarbon FC40, in the aqueous phase. When 26 % (v/v) FC40 was dispersed in a culture of *Mycobacterium parafortuitum* an enhancement of the $k_l a$, calculated on a total liquid volume basis, of 1.8 times was found. Steady-state experiments in the absence of microorganisms, however, showed a 1.2-fold enhancement of the $k_l a$ at 18.5 % (v/v) FC40.

At all FC40 volume fractions tested, enhancement factors with cells were higher than enhancements without cells; apparently, the microorganisms or their excretion products affected the interfacial areas or characteristic phase dimensions.



This chapter has been published in Appl. Microbiol. Biotechnol. 1996, 46, 497-502 by the authors M.T. Cesário, M. Turtoi, S.F.M. Sewalt, H.H. Beeftink and J. Tramper

## Introduction

The biological treatment of waste gases containing organic pollutants has gained increasing interest from the industry during the last years[9,13]. The three main techniques are the trickling-filter, the biofilter and the bioscrubber[11,12]. In all these systems water is used as absorbent. The compound to be removed is first transferred to the water phase and then converted by the microorganisms. The mass transfer of the pollutant from the gas phase to the aqueous phase is therefore an important aspect in the removal efficiency. If the compound to be removed is poorly water-soluble, biological degradation is often limited by the rate of transfer towards the water phase.

To improve the absorption rate of apolar pollutants, a water-immiscible organic liquid in which these compounds show a high solubility may be used. An example is the enhancement of the oxygen transport in oxygen-transfer-limited fermentations by introducing a second liquid phase into the broth[6,7,10,14,15].

If a water-immiscible solvent is used, an additional or alternative route for transport between gas and water is introduced. From a previous study[2] it was concluded that the use of organic solvents can be advantageous if the specific area for mass transfer between solvent and water is large enough. Hence a bioreactor providing an intense contact between the two liquid phases should be used, such as a stirred-tank reactor (STR).

In this paper, the effect of a dispersed water-immiscible solvent on the gas-to-water overall volumetric mass transfer coefficient ($k_La$) was investigated in an STR containing gas, solvent and water. The transfer of the pollutant towards the water phase can happen directly, or indirectly through the solvent, or be a combination of these two mechanisms (see appendix).

Ethene was chosen as model pollutant because of its poor solubility in

water. The water-immiscible organic solvent was FC40, a perfluorocarbon. FC40 was chosen since it is known to be biologically inert[8,15] and because ethene is 10 times better soluble in this solvent than in water; the partition coefficient of ethene between air and FC40 was found to be 0.9 (mol/m$^3$ air)/(mol/m$^3$ FC40), while in the system air/mineral medium it was 8.8 (mol/m$^3$ air)/(mol/m$^3$ medium), both measured at 30°C.

The effect of FC40 on the enhancement of the overall ethene transfer coefficient ($k_la$) was studied in steady state, either in a consuming system with *Mycobacterium parafortuitum* utilising ethene as the only carbon source, or in the absence of microorganisms. In the former case, short-term experiments at constant cell concentration were carried out. In the absence of cells, virtual consumption of ethene was achieved by passing a continuous flow of water through the reactor. In this paper, the $k_la$ enhancements in both systems are compared and the influence of the cells on the enhancement is discussed.

## Theory

***Overall mass transfer coefficient ($k_la$) in the absence of microorganisms***

The experiments were carried out in a stirred-tank reactor (STR), with continuous flows of gas and water. If organic solvent was used, it was homogeneously dispersed in the aqueous medium and kept batch-wise inside the reactor.

The transport of the gaseous pollutant towards the water phase can take place directly, or indirectly via the solvent (the solvent as intermediary). In steady state there is no net transport of the compound to the solvent, but only towards the water phase from where it is discharged with the effluent.

The $k_la$ was determined from a stationary mass balance for the pollutant

over the gas phase:

$$Q_g\ (C_{gin} - C_{gout}) = k_l a\ (\frac{C_{gout}}{m_{gw}} - C_{wout})\ V_l \qquad (1)$$

with $Q_g$ the gas flow rate ($m^3/s$), $C_{gin}$ and $C_{gout}$ the inlet and outlet concentrations of ethene in the gas ($mol/m^3$), respectively, $C_{wout}$ the ethene concentration in the effluent water ($mol/m^3$), $k_l a$ the overall volumetric mass-transfer coefficient ($s^{-1}$), $m_{gw}$ the partition coefficient of ethene between gas and water ($mol/m^3$ gas)/($mol/m^3$ water), and $V_l$ the total liquid volume ($m^3$). The $k_l a$ was based on the total liquid volume and on the gas/water driving force.

Equation 1 is valid both in the presence and absence of solvent. In the former case, the volumetric mass transfer coefficient ($k_l a$) between the gas and the water phase is a composite parameter depending on gas/solvent, gas/water and solvent/water transfer coefficients and specific areas (see appendix).

The aqueous ethene concentration ($C_{wout}$) can be eliminated from eq. 1 with an overall stationary mass balance over the reactor. Considering the water inlet to be free of ethene, this results in:

$$k_l a = \frac{\frac{Q_g}{V_l}}{\frac{C_{gout}/C_{gin}}{1 - C_{gout}/C_{gin}}\ \frac{1}{m_{gw}} - \frac{Q_g}{Q_w}} \qquad (2)$$

with $Q_w$ the water flow ($m^3/s$) through the reactor.

***Overall mass transfer coefficient ($k_l a$) in the presence of microorganisms***

The experiments were carried out in an STR, with a continuous addition of ethene (substrate) via the gas phase. The water phase containing the

microorganisms and the solvent phase were kept batch-wise in the reactor.

At low biomass concentrations, the substrate transfer rate is not limiting and cell growth is exponential. At higher cell concentrations, however, growth becomes limited by the transfer of substrate. Under these circumstances, the transfer rate attains a constant maximum value since the ethene aqueous concentration is virtually zero. A pseudo steady state is assumed with respect to all ethene concentrations.

When solvent is present in the reactor under such steady state conditions, there is no net transport of the pollutant to the solvent, since the pollutant is not consumed in the solvent; the only net transport is to the water phase.

When the ethene transfer rate is the limiting step, one can assume the ethene aqueous concentration ($C_w$) to be negligibly low. Under these conditions, $k_l a$ may be calculated from an ethene balance over the gas phase:

$$k_l a = \frac{Q_g}{V_l} \left(\frac{C_{gin}}{C_{gout}} - 1\right) m_{gw} \qquad (3)$$

It requires measurements of the ethene concentration in the inlet and outlet gas.

## Materials and methods

### *Microorganisms*

*Mycobacterium parafortuitum* E3[5] was kindly supplied by Dr. S. Hartmans (Department of Industrial Microbiology, Wageningen Agricultural University, Wageningen, The Netherlands). It was maintained on yeast-extract/glucose agar slants at room temperature.

Experiments were done with biomass from batch cultures grown on ethene (see below). Cells were harvested by centrifugation, washed with 50 mM

phosphate buffer (pH 7.0) and stored at -20 °C until use.

*Growth on ethene*

Cells were cultivated in batch culture at 30°C in mineral-salts medium[4] with ethene supplied via the gas phase. A 2-dm$^3$ Applikon fermentor with a total liquid volume of 1.3 dm$^3$ and a 6-blade turbine stirrer (800 rpm), was used. The pH was maintained at 7.0 $\pm$ 0.05 with 1 M NaOH. Aeration and ethene supply were accomplished by sparging of 0.3 mol/m$^3$ ethene in air at a flow rate of $6.7\times10^{-6}$ m$^3$/s. Ethene-in-air mixtures were supplied to the fermentor using Brooks 5850 TR Mass-Flow Controllers (Rosemount, Schiedam, The Netherlands).

*Mass-transfer experiments in the absence of cells*

Experiments were carried out at 22° C in a 2-dm$^3$ Applikon fermentor with a constant total liquid volume of 1.3 dm$^3$, equiped with a 6-blade turbine stirrer (800 rpm). Air containing an ethene concentration of 0.28 mol/m$^3$ was sparged through the reactor at a rate of $3.0\times10^{-7}$ m$^3$/s. The water flow was $6.7\times10^{-7}$ m$^3$/s. Samples of the outlet gas phase were withdrawn in time until a constant ethene concentration was attained, indicating steady state. With the values of $C_{gin}$ and $C_{gout}$ and $m_{gw}^{22°C}$= 6.8 mol (ethene/m$^3$gas)/ (mol/m$^3$water), the $k_la$ was determined from eq. 2.

When solvent was used, the aqueous phase volume decreased correspondingly and the total liquid volume was maintained constant. The two liquid phases were separated at the reactor outlet by means of a small settler[3]. In this way, the solvent was kept in batch inside the vessel while water flew continuously through. A good separation of the two liquid phases in the settler is dependent on the water flow leaving the reactor. The water flow used was the maximum possible flow still allowing a good phase separation.

*Mass-transfer experiments in the presence of cells*

Cells were grown in a batch liquid phase with a continuous supply of gaseous ethene (see above) at a flow rate of $6.7 \times 10^{-6}$ $m^3/s$ (ethene concentration 0.14 $mol/m^3$). When a biomass dry weight of 9 g/l was reached, FC40 was added to the system. Subsequently, the ethene outlet concentration was measured in time until a constant value was found. This value was used to calculate the overall volumetric mass transfer coefficient (eq. 3). Because these were short-term experiments, the cell concentration remained essentially constant. The total liquid volume was constant, the water volume decreased with increasing volume of the solvent.

Since FC40 should not be used as a carbon source and neither be toxic to the microorganisms, its biodegradability and toxicity towards *M. parafortuitum*, were tested. From these experiments, FC40 was found to be biologically inert (data not shown).

It should be pointed out that the experiments were designed in such a way that the fermentations were limited by ethene and not by oxygen.

*Analytical methods*

Ethene was determined in 100-$\mu$l gas samples on a Chrompack 9000 gas chromatograph equiped with a Poropack R column (100-120 mesh) and a flame ionization detector. The oven temperature was 210°C and the carrier gas $N_2$ was supplied at 30 ml/min.

Ethene-in-air calibration standards were prepared by adding an exact volume of pure ethene in the range 500 - 2000 $\mu$l to 250 ml volume flasks fitted with Teflon Mininert valves.

For dry weight measurements, 10 ml of the cell suspension was centrifuged during 20 min at 4000 rpm, washed with 50 mM phosphate buffer and centrifuged again. The pellet was dried at 110°C for 24 hours.

*Partition coefficient*

Determination of the gas/water partition coefficient of ethene involved measurement of ethene concentrations in the head-space of a series of 250-ml flasks fitted with Teflon Mininert valves, containing 210 ml of water. Various amounts (290 - 440 $\mu$l) of pure ethene were added to the flasks. After equilibration overnight at 22 or 30°C, the ethene concentrations in the head-space were determined. The partition coefficient was then calculated from an overall ethene mass balance.

The same procedure was followed for the determination of the partition coefficient of ethene between gas and solvent. In this case, 40 ml flasks containing 20 ml of FC40 were used. The ethene volumes added to the flasks were in the range 150-250 $\mu$l.

*Chemicals*

Ethene with a purity of 99.95% was obtained from Hoekloos, Schiedam, The Netherlands. FC40 was purchased from 3M, The Netherlands; the properties are: density (25°C) 1850 kg/m$^3$; surface tension (25°C) 16 mN/m; boiling point 165-185 °C; molecular weight 0.65 kg/mol; dynamic viscosity (25°C) 4.5 mPa.s.

## Results

*Ethene transfer coefficients without cells*

The effect of the solvent on the enhancement of the overall mass transfer coefficient ($k_La$) was studied in steady state without biological consumption. Aqueous ethene removal was achieved by passing a continuous flow of ethene-free water through the reactor. The gas and the water flows were chosen so that accurate $k_La$ values could be derived using equation 2. Van

Sonsbeek *et al.*[17] recommend that $C_{gin}$ and $C_{gout}$ should differ at least 20%.

The ethene transfer coefficient, $k_la$, was calculated from $C_{gin}$ and $C_{gout}$ measurements in steady state and it was found to increase slightly with the FC40 volume fraction (Fig. 1). An enhancement of 1.2 times was found at 18.5 % (v/v) FC40. The $k_la$ was based on the total liquid volume instead of the aqueous volume to avoid an apparent increase in the $k_la$ solely caused by a decrease of the aqueous phase volume.

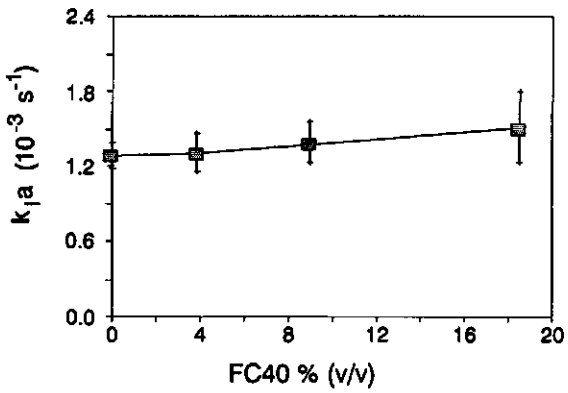


Figure 1. Influence of the FC40 volume fraction on the $k_la$. Experiments in triplicate for each amount of solvent. Error bars: standard deviation of the mean.

These results show that the volumetric ethene transfer coefficient from the gas to the water may be enhanced, although moderately, by dispersing an immiscible organic solvent in the aqueous phase.

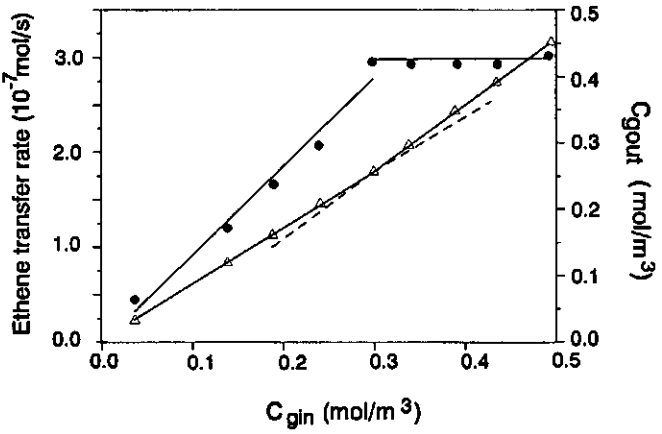


Figure 2. Change of the ethene transfer rate (●) and ethene outlet concentration (△) with the ethene inlet concentration. Gas flow: $6.7 \times 10^{-6}$ m$^3$/s; cell concentration: 9 g/l.

***Ethene transfer coefficients with cells***

The influence of the solvent was studied during short-term batch experiments, i.e. at a constant cell concentration. To perform this experiment, the ethene flow rate into the system ($Q_g.C_{gin}$) had to be such that the microbial reaction was not rate-determining, but rather the ethene transfer rate to the aqueous medium. Aiming at finding a mass transfer-limited system, short-term batch experiments were carried out at a constant arbitrary cell concentration of 9 g/l, a constant gas flow rate and at a number of ethene inlet concentrations ($C_{gin}$, tested in random order). After each change in $C_{gin}$, the outlet concentration ($C_{gout}$) was measured in time until a constant value was found, indicating pseudo steady state. The ethene transfer rate (ETR) was then calculated as $Q_g$ ($C_{gin}$-$C_{gout}$). Fig. 2 shows the ETR and $C_{gout}$ as a function of $C_{gin}$. Two regions can be distinguished. Up to $C_{gin}$= 0.3 mol/m$^3$, the ETR increased linearly with the ethene inlet concentration,

indicating the ethene transfer to be rate-limiting. At higher $C_{gin}$ values, a slightly faster increase of $C_{gout}$ with $C_{gin}$ was observed, resulting in constant ETR and indicating the conversion to be rate limiting.

On the basis of the above results, a mass-transfer-limited system was chosen to study the influence of FC40 on the transfer enhancement. In this system a constant $C_{gin}$ of 0.14 mol/m$^3$, a constant cell concentration of 9 g/l and a constant gas flow of $6.7\times10^{-6}$ m$^3$/s were used. $k_la$ values were determined upon addition of different FC40 amounts to the system.

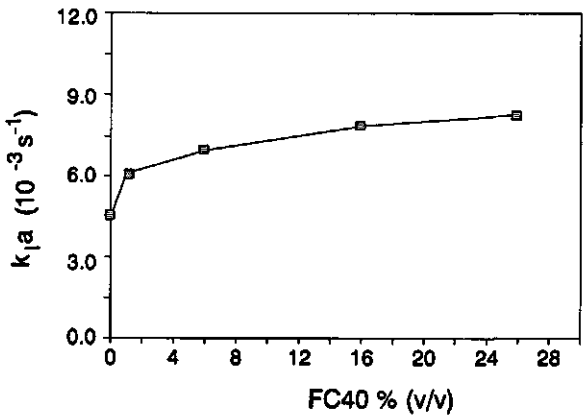


Figure 3. Effect of amount of FC40 on the $k_la$.

The overall volumetric ethene transfer coefficient ($k_la$) was found to increase significantly with the solvent hold-up (Fig. 3). An enhancement of 1.8 times on a total liquid volume basis was observed at 26 % (v/v) FC40. At higher solvent volume fractions, the $k_la$ increased only slightly.

The $k_la$ enhancement factors given by:

$$E_f = \frac{[k_l a]_{\alpha_s}}{[k_l a]_{\alpha_s=0}} \qquad (4)$$

with $\alpha_s$ the solvent volume fraction (-), were determined for the experiments with and without microorganisms (Fig. 4).

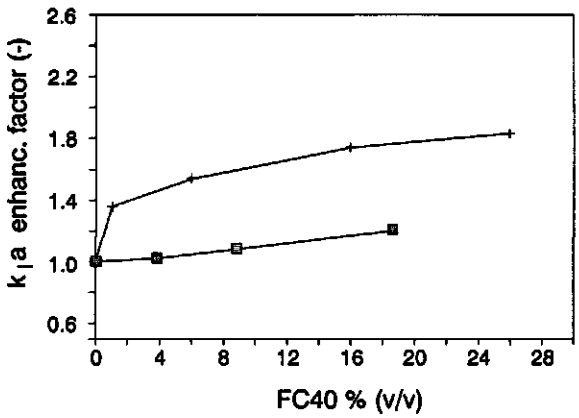


Figure 4. Effect of the FC40 volume fraction on the $k_l a$ enhancement in the presence and absence of cells: + with cells and ■ no cells, respectively.

The results show that the enhancement increases with the solvent volume fraction both in the presence or absence of cells. Nevertheless, the enhancement in the presence of cells is appreciably higher than in their absence at corresponding FC40 volume fractions.

## Discussion

Dispersed FC40 in the aqueous phase was shown to enhance the mass transfer coefficient ($k_la$) of a poorly water-soluble model pollutant- ethene- between the gas and the water. Comparing Figs. 1 and 3 it is observed that the overall volumetric ethene transfer coefficients ($k_la$) obtained in the absence of cells are lower than the $k_la$'s obtained in their presence. One reason for this might be the lower gas flow rate in the experiments without microorganisms. The $k_la$ for the lower gas flow rate ($3\times10^{-6}$ $m^3/s$) was recalculated with an empirical correlation[18] for the larger gas flow rate ($6.7\times10^{-6}$ $m^3/s$), for the case with no solvent (0% v/v FC40). The value obtained ($4.45\times10^{-3}$ $s^{-1}$) is identical to the one found experimentally under the same conditions in the presence of cells ($4.5\times10^{-3}$ $s^{-1}$). This indicates that the major difference between the $k_la$'s of the two different experiments is due to a different gas flow rate and is not caused by a fast homogeneous reaction by microorganisms in the stagnant liquid film at the gas/liquid interface as described by the Hatta theory[19].

Similar $k_la$ enhancements by water-immiscible solvents have also been observed by other authors for other apolar compounds. Rols *et al.*[14] have found an increase of the oxygen transfer coefficient u 3.5 times on an aqueous phase basis (2.6 on a total liquid volume basis) when adding 25 % (v/v) n-dodecane to a culture of *Aerobacter aerogenes*. These slightly larger enhancements may be ascribed to differences in partition coefficients (results to be published).

In the presence of cells, the $k_la$ levels off at higher solvent volume fractions (Fig. 3). That behaviour is not found in the absence of microorganims. Although this phenomenon is not yet fully understood, it might be explained by an increase of the overall liquid viscosity at larger solvent amounts and in the presence of cells[6,14].

An increase of $k_l a$ in both the presence or absence of cells was found. However, the enhancement in the presence of microorganisms is far more pronounced than in their absence at corresponding FC40 volume fractions. An explanation for the extra enhancement of $k_l a$ in the presence of cells might be the emulsifier effect of the microorganisms or their excretion products. Accumulation of cells or their fermentation products around the solvent droplets might hinder droplet coalescence, and might create a stable, fine emulsion and a larger specific area solvent/water. Similar results have been found by several authors[1,16]. Van der Meer *et al.*[16] observed an enhancement of the gas/water oxygen transfer coefficient by dispersing n-octane in the presence of cells and of surfactants, but not in their absence. He concluded that the enhancement of mass transfer is possible when the solvent droplet size is smaller than the water film thickness around the the gas bubbles where the main transfer resistence is located. A similar effect might explain the higher enhancement found in the presence of cells during our experiments with ethene.

## Appendix

***Transfer gas/water in the presence of solvent***

When a perfectly mixed solvent phase is present in the reactor it can either be completely or partly inbetween the gas and the water phases or it can be entirely included in the water phase. These three possibilities are depicted below (Fig. 1A).

Situation B will be described by means of mass balances over the gas, the water and the solvent phases assuming continuous steady-state operation and ideal mixing of the three phases. The balances over the gas, the solvent and the water are respectively:

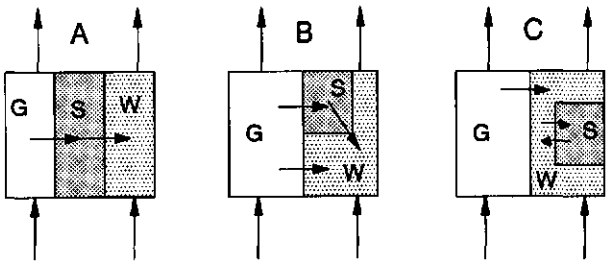


Figure 1A. Pathways for ethene transfer from gas to water in a 3 phase-system: A, serial transport gas-solvent-water; B, direct transport gas-water as well as serial transport gas-solvent-water; C, transport to water including solvent. All systems feature continuous gas and water flows; solvent: batch.

$$Q_g\ (C_{gin} - C_{gout}) = k_{gs}a_{gs}\ (\frac{C_{gout}}{m_{gs}} - C_s)\ V_l + k_{gw}a_{gw}\ (\frac{C_{gout}}{m_{gw}} - C_{wout})\ V_l \quad \text{(A1)}$$

$$k_{gs}a_{gs}\ (\frac{C_{gout}}{m_{gs}} - C_s)\ V_l = k_{sw}a_{sw}\ (\frac{C_s}{m_{sw}} - C_{wout})\ V_l \quad \text{(A2)}$$

$$k_{gw}a_{gw}\ (\frac{C_{gout}}{m_{gw}} - C_{wout})\ V_l + k_{sw}a_{sw}\ (\frac{C_s}{m_{sw}} - C_{wout})\ V_l = Q_w\ (C_{wout} - C_{win}) \quad \text{(A3)}$$

with $k_{gs}$ the overall mass transfer coefficient gas/solvent based on solvent phase concentrations (m/s), $k_{gw}$ the overall mass transfer coefficient gas/water based on water phase concentrations (m/s), $k_{sw}$ the overall mass transfer

coefficient solvent/water based on water phase concentrations (m/s), $a_{gs}$ the specific area gas/solvent on a total liquid volume basis ($m^{-1}$), $a_{gw}$ the specific area gas/water on a total liquid volume basis ($m^{-1}$), $a_{sw}$ the specific area solvent/water on a total liquid volume basis ($m^{-1}$), $m_{gs}$ the partition coefficient of the pollutant between the gas and the solvent (-), $m_{sw}$ the partition coefficient of the pollutant between the solvent and the water phases= $m_{gw}/m_{gs}$ (-), $C_s$ the concentration of the pollutant in the solvent phase ($mol/m^3$).

This system of three balance equations involves three driving forces. It may be simplified by elimination of the variable $C_s$ to a system of two equations with one driving force, namely the gas/water concentration difference and $T_B$ as the overall mass transfer coefficient.

$$Q_g\ (C_{gin} - C_{gout}) = T_B\ (\frac{C_{gout}}{m_{gw}} - C_{wout})\ V_l \tag{A4}$$

$$T_B\ (\frac{C_{gout}}{m_{gw}} - C_{wout})\ V_l = Q_w\ (C_{wout} - C_{win}) \tag{A5}$$

$T_B$ is given by:

$$T_B = \frac{1}{\frac{1}{k_{sw}a_{sw}} + \frac{1}{m_{sw}k_{gs}a_{gs}}} + k_{gw}a_{gw} \tag{A6}$$

Similar derivations can be made for situations A and C.

## Acknowledgements

This work was supported by a grant from the Junta Nacional de Investigação Científica e Tecnológica, Lisbon, Portugal

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# Chapter 7

## Ethene removal from gas by recycling a water-immiscible solvent over a packed absorber and a bioreactor


### Summary

Hydrophobic pollutants in waste gases are difficult to remove with the conventional biological treatment techniques because of the slow gas/water mass transfer rate. A two-stage system with a water-immiscible solvent as intermediate liquid was developed. This system consisted of a packed absorber for transfer of the model pollutant, ethene, from gas to solvent and a stirred-tank reactor (mixer) for solvent/water transfer and subsequent degradation by *Mycobacterium parafortuitum*. The solvent, FC40 a perfluorocarbon, was recycled between these two compartments.

The stability of the system was shown during a run of 10 days. The elimination efficiency was found to be a function of the solvent flow: a 9% and 15% elimination were obtained at solvent flows of $6\times10^{-8}$ $m^3/s$ and 11.3 $\times10^{-8}$ $m^3/s$, respectively. Ethene removal remained constant at increasing solvent hold-ups up to 50 % (v/v). In spite of the low elimination efficiencies caused by an inefficient use of the column, the feasibility of the system to remove ethene has been demonstrated. The system's performance was described by a steady-state mathematical model. Simulated ethene removal



This chapter has been submitted for publication by the authors M.T. Cesário, J.B. Brandsma, M.A. Boon, J. Tramper and H.H. Beeftink

efficiencies agreed well with the experimental data. Based on this, the model was used to optimize the dimensions and operating conditions. The optimized two-compartment system was compared with a STR in terms of removal efficiency and it was found to performe better; a 35 % elimination efficiency was found against a 15 % removal for the STR. Furthermore, the model was used to compare the performance of the combined system (PA/MS) with the performance of a similar system without solvent. It was found that the system with solvent only performs better than the system with water if the contaminant has a higher solubility in the solvent than in water.

## Introduction

In the biological treatment of waste gases the removal of apolar pollutants is often a problem due to their poor solubility in water. The three conventional biological techniques for waste gas treatment are the biofilter, the trickling filter and the bioscrubber[11,12]. In all these systems the contaminants are directly transferred to the water phase and then converted by the microorganisms. If the compound to be removed is poorly water-soluble, biological degradation is often limited by the rate of transfer. To achieve reasonable removal efficiencies, long gas/liquid contact times and large equipment volumes are thus necessary. To diminish the resistance to mass transfer, alternative systems have been proposed. Examples are the modified trickling filter[5], and the membrane bioreactor[14]. Another way to diminish the transport limitation in the water layer is by contacting the gas with an intermediary water-immiscible solvent in which the contaminant is better soluble. This way, the removal of apolar pollutants from the gas phase can be significantly enhanced due to an increase of the driving force gas/solvent. However, since degradation will take place in the aqueous phase, the mass

transfer between solvent and water should not be rate-limiting. From a previous study[2], was concluded that the use of solvents is advantageous if the area for solvent/water transfer is large enough to compensate for the extra resistance created by solvent addition. Hence, a bioreactor providing an intense contact between the two liquid phases should be used, for instance a stirred-tank reactor (STR). Stirred-tank reactors with well dispersed phases (gas and two liquids) have been used to improve the oxygen transfer in oxygen-limited fermentations[8,9,10,15,16]. The same bioreactors were used to enhance the mass transfer of ethene[1] and other apolar compounds[3] from gas to water at increasing solvent volume fractions. A mechanically agitated reactor is, however, not the appropriate reactor configuration for gas-treatment since the fractional removal of the contaminant from the gas is lower in comparison to a reactor in which the gas approaches plug flow. Moreover, a STR shows hydrodynamic constraints at high gas flows due to flooding. For these reasons, a reactor configuration featuring the gas and liquid in plug flow and allowing larger gas flow rates was tested in the present study.

This paper reports the use of a two-compartment system consisting of a packed absorber for transfer of the pollutant from the gas to the solvent and a stirred-tank reactor (mixer) featuring solvent/water transfer and subsequent biological degradation (Fig. 1). The aim of the study presented here was to test the working and stability of this system with a hydrophobic model compound and to describe its performance by means of a steady-state mathematical model. The model predicts the outlet gas concentration as a function of the solvent flow, the solvent hold-up in the reactor and the affinity of the contaminant for the solvent. Model predictions were validated with experiments in steady state.

The removal efficiency attained in the two-compartment system with gas and solvent moving in plug flow and counter-current was compared to the one achieved in a stirred- tank reactor with well mixed phases.

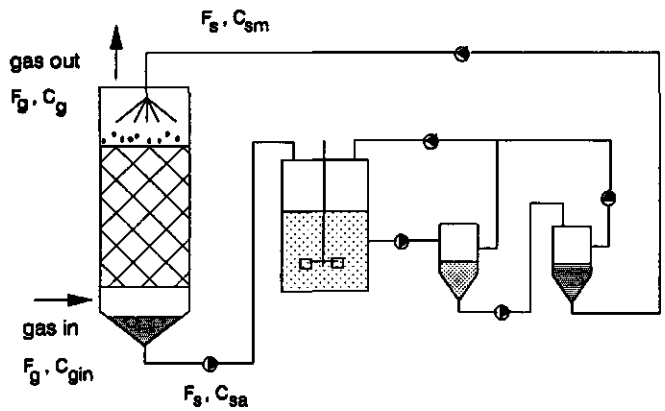


Figure 1. Packed absorber/ Mixer-settler: experimental set-up

The performance of this system was studied with ethene and ethene-degradation by *Mycobacterium parafortuitum* as a model reaction. FC40, a perfluorocarbon, was chosen as water-immiscible solvent because ethene dissolves approximately 9 times better in this solvent than in water ($m_{gw}$= 8 (mol/m$^3$gas)/ (mol/m$^3$ water); $m_{gs}$= 0.9 (mol/m$^3$gas)/ (mol/m$^3$FC40)). Furthermore it is non-biodegradable, non-toxic to the cells, has a low vapour pressure and a density almost twice as large as water (density= 1870 kg/m$^3$). This large density difference is desirable for a faster separation of the two liquids in the settler.

## Theory

### *Model description*

A steady-state model was used to describe mass transfer in each compartment of the system Packed absorber/ Mixer-settler (PA/MS) as depicted in Fig. 1. It predicts the outlet gas concentration as a function of known process variables such as: gas and solvent flows, absorber and mixer volume, inlet gas concentration, partition coefficients gas/solvent and gas/water and solvent hold-up in the mixer.

In this system, the gas flows continuously through the absorber, while the solvent and the water are maintained in the system. The solvent is recycled between the absorber and the mixer. Counter-current plug flow is assumed for gas and solvent in the absorber; the solvent and the aqueous phases in the mixer are assumed to be ideally mixed; no mass transfer occurs in the settler. Further, it is assumed that the cell concentration in the bioreactor is such that biological conversion is not rate limiting but rather the mass transfer (either in the absorber or in the mixer). In other words, the cell growth is limited by the supply of ethene.

The performance of the packed absorber is described by setting-up differential mass balances over the gas and the solvent phases while the mixer performance is described by a mass balance over the solvent phase assuming an ideally mixed solvent and a negligible ethene concentration in the water phase ($C_w = 0$). For simplification, dimensionless groups and variables have been introduced.

The mass balances over gas and solvent in the absorber and the mass balance over the solvent in the mixer are given by eqs. 1, 2 and 3, respectively:

$$\frac{dc_g}{dz} = -A(c_g - c_s) \tag{1}$$

$$\frac{dc_s}{dz} = -\frac{A\,(c_g - c_s)}{\Lambda} \tag{2}$$

$$c_{sa} = \left(\frac{M}{\Lambda} + 1\right) c_{sm} \tag{3}$$

with:

$$c_g = \frac{C_g}{C_{gin}} \;; \quad c_{sa} = \frac{m_{gs}\, C_{sa}}{C_{gin}} \;; \quad c_{sm} = \frac{m_{gs}\, C_{sm}}{C_{gin}} \;; \quad z = \frac{Z}{H} \tag{4}$$

and:

$$A = \frac{k_{gs}\, a_p\, V_a}{F_g} \;; \quad M = \frac{k_{sw}\, a_m\, V_m}{m_{gs}\, F_g} \;; \quad \Lambda = \frac{F_s}{m_{gs}\, F_g} \tag{5}$$

$c_g$ is the dimensionless concentration in the gas leaving the absorber, $c_{sa}$ and $c_{sm}$ the dimensionless concentrations in the solvent leaving the absorber and the mixer, respectively, and $z$ the dimensionless height of the absorber. The dimensionless group $\Lambda$ is the absorption factor and the dimensionless parameters $A$ and $M$ are a function of the absorber and the mixer characteristics, respectively.

Equations (1) and (2) were solved for the gas and solvent concentrations at the absorber inlet ($z=0$) and outlet ($z=1$) and combined with eq. (3), yielding solutions for the concentration in the outlet gas ($c_g$), the solvent leaving the absorber ($c_{sa}$) and the solvent leaving the mixer ($c_{sm}$) as a function of the dimensionless parameters $\Lambda$, $A$ and $M$. In the following only the solution for the outlet gas concentration is given, because this was the

variable measured during the experiments:

$$c_g = \frac{(-\Lambda M + \Lambda + M)\, e^{\left(-A + \frac{A}{\Lambda}\right)} - \Lambda}{(M + \Lambda)\, e^{\left(-A + \frac{A}{\Lambda}\right)} - \Lambda M - \Lambda} \qquad (6)$$

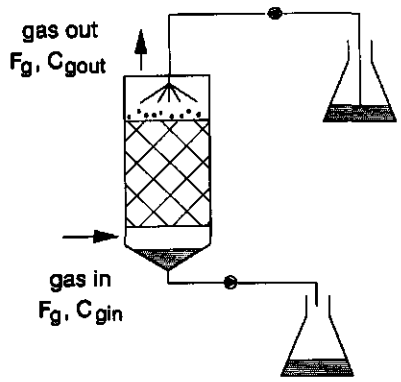


Figure 2. Experimental set-up for $k_{gs}a_p$ determination

***Mass transfer coefficient in the absorber ($k_{gs}a_p$)***

The overall volumetric mass transfer coefficient in the absorber ($k_{gs}a_p$) was determined in steady state with the experimental set-up given in Fig. 2. Ethene-free solvent was added continuously on the top of the column and collected at the bottom in a separate vessel. The overall volumetric mass transfer coefficient was calculated from eq. (7).

This equation was obtained by solving eqs (1) and (2) for the concentration in the gas and solvent at the inlet ($z = 0$) and outlet of the absorber ($z = 1$) and considering that the concentration in the solvent entering the absorber is zero ($z = 1$; $c_{sm} = 0$):

$$A = \frac{\ln\left[\frac{1 + \frac{(\Lambda - 1)}{c_g}}{\Lambda}\right]}{(1 - \frac{1}{\Lambda})} \qquad (7)$$

The transfer coefficient $k_{gs}a_p$ is calculated from the dimensionless group $A$ (eq. 5).

***Mass transfer coefficient in the mixer ($k_{sw}a_m$)***

The overall mass transfer coefficient in the mixer ($k_{sw}$) and the specific area for mass transfer solvent/water ($a_m$) were calculated by means of empirical correlations from literature as given in Appendix 2. The solvent hold-up in the mixer ($h_s$), one of the independent variables in this study, is introduced in the definition of the specific area $a_m$ (eq. A2.5, Appendix 2).

## Materials and methods

***Organism and growth medium***

*Mycobacterium parafortuitum* E3[6] was kindly supplied by Dr. S. Hartmans (Department of Industrial Microbiology, Wageningen Agricultural University, Wageningen, The Netherlands). It was maintained on yeast-extract/glucose agar slants at room temperature. Experiments were done with biomass harvested from batch cultures grown on ethene[1]. Cells were harvested by centrifugation, washed with 50 mM phosphate buffer (pH 7.0) and stored at -20°C until use.

***Packed absorber***

The absorber consisted of a glass cylinder with a diameter of 3.5 cm and a

height of 40 cm. It was packed to a height of 37.5 cm with 6-mm diameter metal Raschig rings (specific area of 900 $m^2/m^3$ rings). The solvent was added through a small nozzle at the top of the column and collected in a tiny reservoir at the bottom from where it was pumped towards the mixer. The liquid level in this reservoir was controlled by an electronic photocell. The gas was added directly under the packing. A perforated plate allowed the gas to distribute evenly over the area of the column. The gas flow rate was $6.7 \times 10^{-7}$ $m^3/s$ and the ethene inlet concentration 0.29 $mol/m^3$. Ethene-in-air mixtures were supplied to the fermentor using mass-flow controllers (Brooks 5850 TR Mass-flow Controller, Brooks Instruments, Veenendaal, The Netherlands). A sample port was located both at the influent and effluent of the gas stream. The temperature of the column and of the sample ports was maintained at 25°C.

*Mixer*

The mixer was a 2-$dm^3$ Applikon stirred-tank reactor with a working volume of 1.3 $dm^3$ equiped with a 6-blade turbine stirrer (800 rpm, diameter 4.5 cm). The temperature of the reactor was kept at 25°C. Cells were cultivated in mineral-salts medium[4] with ethene supplied from the solvent phase leaving the absorber. The pH was maintained at 7.0 $\pm$ 0.05 with 1 M NaOH. A maximum solvent hold-up of 0.45 was used because the pH value at larger solvent hold-ups is difficult to control.

*Settler*

To separate the solvent from the cell suspension at the mixer outlet, two glass settlers in series were used. In the first settler separation of the bulk aqueous phase containing the cells (lighter phase) from a solvent-rich emulsion (heavier phase) was obtained. This solvent phase consisted of a very stable dispersion of solvent, cells and interstitial water. The cells or cell

products attached to the FC40 droplets prevented the droplets from coalescing[1]. This dispersion was pumped to a second settler while the aqueous phase was recycled to the mixer. In the second settler immediate separation of the solvent from the cells and water occured. A very clear FC40 phase was obtained in the bottom of the settler while the aqueous phase with cells spread at the surface. The latter was pumped to the reactor and the solvent recycled over the absorber.

***Start-up and operation***

The experiment was started with a cell concentration of 1 g/l dispersion containing circa 10 % (v/v) FC40. The gas flow through the absorber was $6.7\times10^{-7}$ $m^3/s$ with an ethene concentration of 0.29 $mol/m^3$. Under these circumstances, the ethene transfer is the rate-limiting step in the whole process[1]. Samples of the outlet gas stream were withdraw in time until a constant ethene concentration was attained indicating pseudo-steady state.
The system performance was tested at solvent flows of $6\times10^{-8}$ and $11.3\times10^{-8}$ $m^3/s$, and at different solvent hold-ups in the mixer in the range 0.1 - 0.45 ($m^3$solvent/ $m^3$liquid). The solvent hold-up in the mixer was changed by temporarily stopping the run, withdrawing a certain volume of the aqueous phase and adding the same amount of solvent. After each change the system was allowed to reach steady state. Samples of the outlet gas phase were withdrawn several times to confirm steady-state conditions. The cell concentration was also monitored in time. Since these were short-term experiments the cell concentration remained essentially constant.

***Set-up for $k_{gs}a_p$ determination***

For the determination of the overall volumetric mass transfer coefficient in the packed absorber, the latter was uncoupled from the mixer (Fig. 2). This measurement was done in steady-state conditions by pumping pure FC40

continuously through the absorber in counter current with the gas. A constant gas flow rate of $6.7\times10^{-7}$ $m^3/s$ with an ethene concentration of 0.29 $mol/m^3$ was used. The transfer coefficient was determined at solvent flow rates of $3\times10^{-8}$, $6\times10^{-8}$, $9\times10^{-8}$ and $12\times10^{-8}$ $m^3/s$. For each solvent flow rate, the ethene outlet concentration was measured in time until a constant value was achieved. This value was used to calculate $k_{gs}a_p$ with eq. (7).

***Analytical methods***

Ethene was determined in 100-$\mu$l gas samples on a Chrompack 9000 gas chromatograph equiped with a Poropack R column (100-120 mesh) and a flame-ionization detector. The oven temperature was 210°C and the carrier gas $N_2$ was supplied at 30 ml/min.

Ethene-in-air calibration standards were prepared by adding an exact volume of pure ethene in the range 500 - 2000 $\mu$l to 250 ml volume flasks fitted with Teflon Mininert valves.

The determination of the gas/water and gas/solvent partition coefficient of ethene[1] was done at 25°C.

The inversion point of FC40/water emulsions was determined experimentally in the mixer at 800 rpm, in the absence of cells. This was done by monitoring the conductivity of the liquid phase when adding increasing amounts of FC40. Since the conductivity of FC40 is virtually zero, the inversion point is the point where the conductivity of the overall liquid becomes negligible[17].

***Chemicals***

An ethene-in-air mixture with a concentration of 0.697 % v/v (0.29 $mol/m^3$) and ethene with a purity of 99.95% were obtained from Hoekloos, Schiedam, The Netherlands. FC40 was purchased from 3M, The Netherlands; the properties are: density (25°C) 1850 $kg/m^3$; surface tension (25°C) 16 mN/m;

boiling point 165-185 °C; molecular weight 0.65 kg/mol; dynamic viscosity (25°C) 4.5 mPa.s.

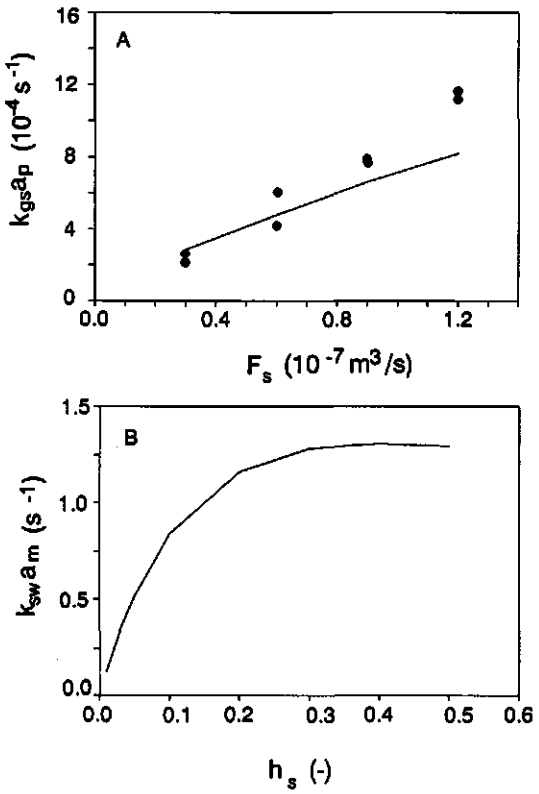


Figure 3. **A.** Overall mass transfer coefficient in the absorber at different solvent flow rates. Comparison between the experimental values (points) and the calculations from empirical correlations (solid line). **B.** Overall mass transfer coefficient in the mixer at different solvent hold-ups.

## Results

### *Overall mass transfer coefficient in the absorber ($k_{gs}a_p$) and in the mixer ($k_{sw}a_m$)*

The overall volumetric mass transfer coefficient in the absorber was determined from experimental measurements and calculated according to eq. 7. This was done at various solvent flows, in duplicate. Fig. 3A shows the $k_{gs}a_p$ values determined experimentally and the ones calculated by means of the empirical correlations given in Appendix 2. A linear increase of the $k_{gs}a_p$ with increasing solvent flows within the tested range is observed. The values obtained experimentally agree fairly well with the ones calculated from empirical correlations.

Fig. 3B gives the values of the overall volumetric mass transfer coefficient in the mixer ($k_{sw}a_m$) at different solvent hold-ups. These were calculated from empirical correlations given in Appendix 2. Both $k_{sw}$ and $a_m$ are a function of the solvent hold-up and not of the solvent recycling flow. For the calculation of $k_{sw}a_m$, the inversion point must be taken into consideration. The inversion point was measured experimentally and was found at a solvent hold-up of 0.45. In literature[9] this value was 0.55. This difference might be due to different experimental conditions such as the presence of cells in the experiments mentioned in literature.

It is observed that $k_{sw}a_m$ increases up to a solvent hold-up of circa 0.3 and it remains essentially constant at larger solvent hold-ups. This is because the droplet diameter increases with higher $h_s$ values (eq. A2.6, Appendix 2) causing a less pronounced increase on the specific area solvent/water ($a_m$) and thus on $k_{sw}a_m$.

***Ethene removal with the Packed absorber/Mixer-settler (PA/MS)***

The performance of the Packed absorber/Mixer-settler was studied in steady state at a constant gas flow rate and ethene inlet concentration, and with different solvent flows and solvent hold-ups in the reactor. The concentration of biomass in the mixer was such that the system was working under ethene-transfer-limiting conditions.

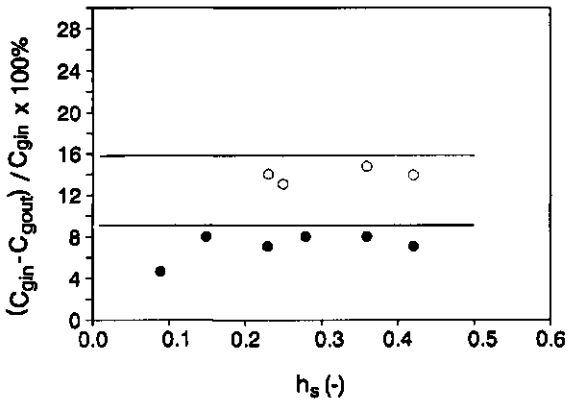


Figure 4. Influence of the solvent hold-up ($h_s$) and of the absorption factor ($\Lambda$) on the ethene removal efficiency. Comparison between the theoretical predictions (solid lines) and the experimental values (points): ●, $\Lambda = 0.1$; ○, $\Lambda = 0.19$

Fig. 4 shows the ethene removal efficiency as a function of the solvent hold-up in the mixer for two solvent recycling rates, namely $6\times10^{-8}$ and $11.3\times10^{-8}$ $m^3/s$ which correspond to absorption factors $\Lambda$ of 0.1 and 0.19, respectively. It is observed that the elimination efficiency, calculated as $(C_{gin}-C_{gout})/C_{gin}$ increases with the solvent recycling flows. An elimination of approximately 9 % was obtained at a solvent flow of $6\times10^{-8}$ $m^3/s$ ($\Lambda = 0.1$)

while a removal of 15 % was observed at $11.3\times10^{-8}$ $m^3/s$ ($\Lambda = 0.19$). Furthermore, it was found that the removal efficiency was independent of the solvent hold-up in the mixer in the range of solvent volume fractions tested.

Fig. 4 also shows the results of the model predictions. The effect of the solvent hold-up in the mixer ($h_s$) and of the solvent recycling rate ($F_s$) on the ethene elimination efficiency was calculated by eq. 6. Aiming at this, the values of $k_{gs}a_p$ determined experimentally and the values of $k_{sw}a_m$ calculated by means of empirical correlations were used; the latter being a function of the solvent hold-up in the mixer. A good agreement between the theoretical predictions and the experimental results is observed and therefore the model was used to interpret these results.

## Discussion

The constant value of the ethene removal efficiency with the solvent hold-up indicates that the mass transfer rate in the mixer is not limiting in the whole process. If this would have been the case, a better ethene elimination would have been found at increasing solvent hold-ups. Since the biological conversion is also not rate-limiting, the efficiency of the system is entirely limited by the mass transfer in the absorption column. This is shown in Fig. 5. In this figure, the dimensionless concentration in the outlet gas ($c_g$) is given as a function of the dimensionless parameters $M$ and $A$, characteristic of the mixer and absorber, respectively, and of the absorption factor $\Lambda$. The chosen range of $M$ and $A$ values includes the values of our experimental system ($1800 < M < 2800$; $A = 0.28$ and $A = 0.64$). The different surfaces shown in Fig. 5 correspond to different $\Lambda$ values, namely 0.1, 0.19, 1.0 and 2.5. The maximum $\Lambda$ of 2.5 corresponds to the maximum value of $F_s$ above which flooding in the column occurs[13]. For the $M$ and $A$ values of our

system, it is observed that $c_g$ is independent on the $M$ value and decreases with $A$ and $\Lambda$. This is equivalent to say that the mass transfer in the mixer is not rate limiting and that the removal efficiency can be improved by increasing $A$ or $\Lambda$.

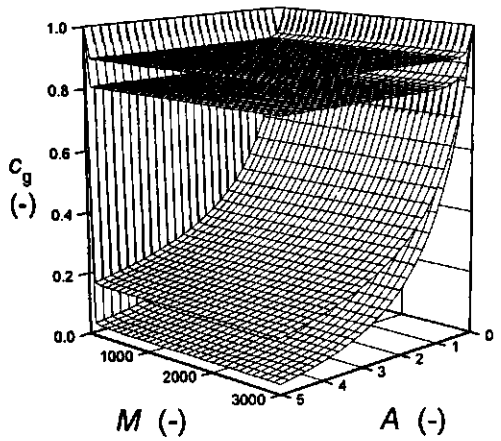


Figure 5. Model predictions for the dimensionless pollutant concentration in the gas leaving the experimental system as a function of the dimensionless parameters $M$, $A$ and $\Lambda$; $\Lambda$= 0.1; 0.19; 1.0; 2.5.

In the present system, the capacity of the mixer thus largely exceeds the capacity of the absorber; i.e. the mixer is oversized. Fig. 6 illustrates the example of a system where the dimensions of the mixer and the absorber are better in balance, i.e. both the mixer and the absorber performance might be limiting. This is done for $\Lambda$= 1.0. For lower $M$ values the outlet gas concentration changes much stronger with $M$ than with $A$ while for larger $M$ values the reverse occurs. This means that in the former case a better removal efficiency can be achieved by using a larger mixer while in the latter case a better elimination can be accomplished with a larger absorber.

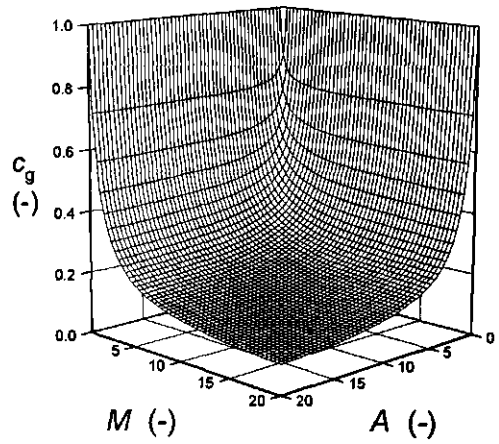


Figure 6. Dimensionless concentration in the outlet gas as a function of the dimensionless parameters $M$ and $A$ in a balanced system ($\Lambda = 1$).

The maximally achievable removal efficiency in our system was calculated from Fig. 5. Aiming at this, the parameter $A$ was calculated (eq. 5) for the maximum value of $\Lambda$ of 2.5 ($F_s = 1.5\times10^{-6}$ m$^3$/s), yielding a value of 2.8. The value of $k_g a_p$ in those conditions was calculated by the empirical correlations given in Appendix 2. Fig. 5 shows that for a $\Lambda = 2.5$ and $A = 2.8$ the maximum removal efficiency attainable in our system is approximately 88 %.

***Comparison between the performance of a two-compartment (PA/MS) and a one-compartment system (STR)***

The ethene removal efficiency obtained in the Packed Absorber/Mixer-settler was compared with the one accomplished in a one-compartment system, namely the stirred-tank reactor, with the gas and the two-liquid phases well mixed. The performance of the STR has been described in a previous work[1].

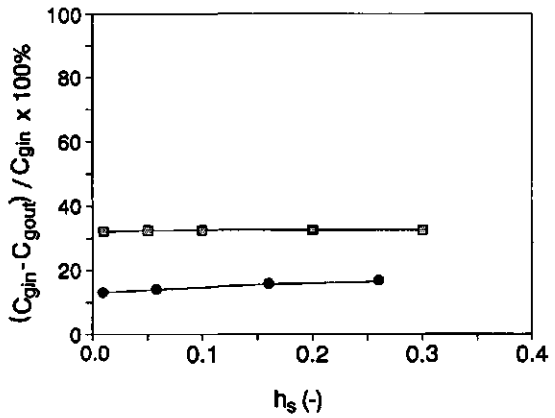


Figure 7. Ethene removal efficiency at different solvent hold-ups: ■, model predictions for the PA/MS; ●, experimental results with the STR

In that study a constant gas flow rate ($F_g$) of $6.7\times10^{-6}$ $m^3/s$ and different solvent hold-ups up to 26 % were used. In order to compare both systems, the elimination efficiency obtained by the present PA/MS was simulated with the model for a gas flow of $6.7\times10^{-6}$ $m^3/s$. With that $F_g$, a maximum solvent flow of $3.7\times10^{-6}$ $m^3/s$ corresponding to an absorption factor of 0.61, was calculated from the flooding line[13]. The maximum removal efficiencies calculated for these conditions and the results obtained with the STR are given in Fig. 7. It is observed that while in an STR an elimination of circa 15 % is obtained, this value is about 35 % in a PA/MS. The essentially constant value of the removal efficiency with the solvent hold-up in the case of the PA/MS, is because the mass-transfer-rate limiting step in that system is located in the absorber and not in the mixer. At this system dimensions and operating conditions (gas and solvent flows), $k_g a_p = 1.04\times10^{-2}$ $s^{-1}$ and $A = 0.56$. Larger mixer volumes or larger solvent hold-ups do not result in better removal efficiencies as can be deduced from Fig. 5. A better

elimination would be accomplished in a larger absorber. By increasing the column diameter, a larger liquid flow and consequently a larger Λ could be used resulting in a better elimination efficiency.

***Performance of the two-stage system with and without solvent***

The elimination efficiency in the two-compartment system with various intermediate solvents was calculated using eq. (6) and compared with the removal efficiency achieved in the same system but using water as absorbent (eq. A1.3, Appendix 1). In this system the aqueous reaction medium itself is recycled between the absorber and the mixer. Different solvents and therefore different partition coefficients gas/solvent ($m_{gs}$) and solvent/water ($m_{sw}$) were considered. The overall mass transfer coefficient in the absorber ($k_{gs}a_p$) is assumed to be independent of the partition coefficient between the gas and the liquid (either water or solvent). The systems with and without solvent were compared at a constant Λ value of 1.0 which implies that as the solvent flow ($F_s$) changes with $m_{gs}$ (eq. 5), the water flow will change as well. Fig. 8 shows the performance of the two systems at four different $m_{sw}$ values namely: 1.0, 2.0, 5.0 and 8.8. In this figure the elimination efficiency of the system containing solvent is independent of the $m_{sw}$ value and is similar to the one in Fig. 6. The removal efficiency of the system with water is represented by the surface parallel to the M-axis. The performance of the latter improves at increasing A values and is independent of the mixer characteristics (since the mass transfer in the mixer is not existent). For $m_{sw}$= 1, i.e. when the contaminant has an equal solubility in both solvent and water, ($m_{gs}$= $m_{gw}$), the system with water performs better than the one with solvent. This is because of the extra mass transfer resistance step (in the mixer) created by addition of the solvent. At higher $m_{sw}$'s, the system with solvent performs increasingly better compared to the system with water. At $m_{sw}$= 8.8, the partition coefficient of ethene between FC40 and water, the

model predicts that the system with solvent performs practically always better than the system without solvent.

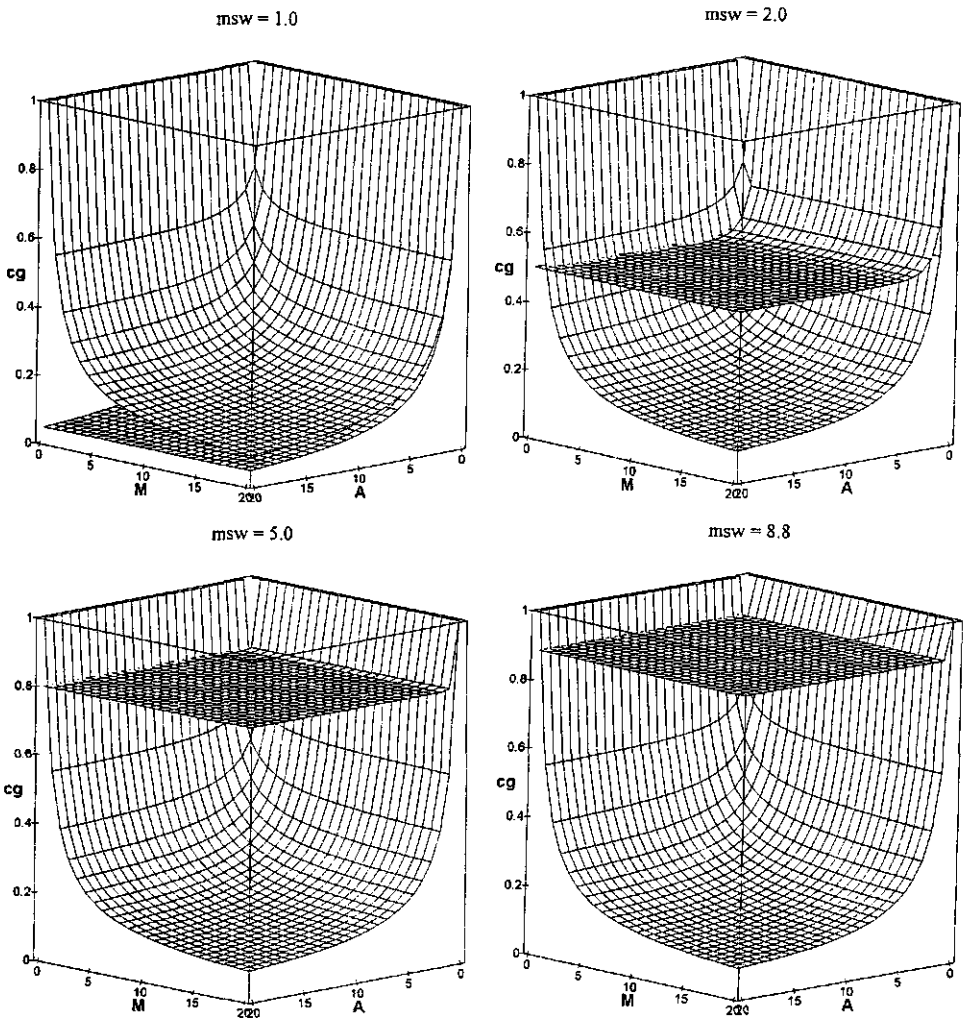


Figure 8. Ethene removal in a two-stage system as a function of the dimensionless parameters $M$ and $A$ at a constant $\Lambda$. Comparison between the removal in the system with and without solvent at different $m_{sw}$ values.

## Conclusions

The ethene removal efficiency in the combined system Packed absorber/ Mixer-settler increased with larger solvent recycling rates while it remained constant at increasing solvent hold-ups. The theoretical model predictions agreed well with the experimental results. From the model predictions it was concluded that in present system dimensions and operating conditions, the limiting step was the mass transfer in the absorber.

The performance of the PA/MS and of an STR were compared and it was concluded that under similar working conditions the fractional removal of the contaminant is larger in the two-compartment system than in a one compartment-system with all the phases ideally mixed.

The model was used to predict the elimination efficiency accomplished in a two-compartment system with and without solvent. From the results it was concluded that the system with solvent only performs better than the system with water for values of $m_{sw} > 1$. This is dependent however on the dimensions of the system (absorber and mixer volume) and on the operating conditions (gas and liquid flows). The range of $A$ and $M$ values where the system with solvent is better than the system with water is larger with higher $m_{sw}$ values. In the case of the model pollutant and the solvent used in this study, ethene and FC40, respectively, the model predicts that the system with solvent is for a broad range of $A$ and $M$ values more efficient than the system with water.

## Appendix 1

***Two-stage system with water***

If in the two-stage system, water instead of solvent is recycled between the absorber and the mixer, the concentration in the outlet gas can be derived from two differential mass balances over the gas and the water phase similar to eqs. 1 and 2, respectively:

$$\frac{dc_g}{dz} = -A\ (c_g - c_w) \qquad \text{(A1.1)}$$

$$\frac{dc_s}{dz} = -\frac{A\ m_{sw}\ (c_g - c_s)}{\Lambda} \qquad \text{(A1.2)}$$

$c_g$ is a function of the partition coefficient solvent/water ($m_{sw}$).

Solving eqs. A1.1 and A1.2 for the concentration in the outlet gas ($z = 1$) yields:

$$c_g\ (1) = \frac{e^{\left(\frac{A\ m_{sw}}{\Lambda}\right)}\ (-\Lambda + m_{sw})}{m_{sw}\ e^{\left(\frac{A\ m_{sw}}{\Lambda}\right)} - \Lambda\ e^{A}} \qquad \text{(A1.3)}$$

## Appendix 2

***Overall volumetric mass transfer coefficient in the absorber ($k_{gs}a_p$)***

The overall mass transfer coefficient $k_{gs}$ and the effective specific area for mass transfer in the packed column ($a_p$) were calculated theoretically with empiric correlations.

*A. Effective specific area in the absorber ($a_p$)*

Only the wetted surface of the packing material is involved in the gas/liquid transfer. This effective area for mass transfer is a function of the solvent flow and of the area of the column according to the following equation[13]:

$$a_p = a\ (1 - \exp\ [-1.45\ (\frac{F_s \rho_s}{A_a a \mu_s})^{0.1}\ (\frac{F_s^2 \rho_s}{A_a^2 a \sigma_s})^{0.2}\ (\frac{\sigma_c}{\sigma_s})^{0.75}\ (\frac{F_s^2 a}{A_a^2 g})^{-0.05}\ ]\ ) \qquad \text{(A2.1)}$$

with $\sigma_c$ the critical surface tension of the packing material ($75 \times 10^{-3}$ N/m)[13]. Under optimal conditions, the column is designed to work below the flooding line, i.e. in the loading point. This is the point where the gas and the liquid flowing in counter current start impeding one another. In these conditions the packing material is nearly completely wetted ($a_p \approx a$) and the column works the most efficiently[13].

*B. Overall mass transfer coefficient ($k_{gs}$)*

The overall mass transfer coefficient in the absorber is given by:

$$\frac{1}{k_{gs}} = \frac{1}{k_g} + \frac{m_{gs}}{k_{sa}} \qquad \text{(A2.2)}$$

The partial gas and solvent mass transfer coefficients ($k_g$ and $k_{sa}$) in a packed column are given by the correlations of Onda *et al*[13]:

$$\frac{k_g}{a\ D_g} = 2\ (\frac{\rho_g\ F_g}{a\ \mu_g\ A_a})^{0.7}\ (\frac{\mu_g}{\rho_g\ D_g})^{0.33}\ (a\ d_p)^{-2} \qquad \text{(A2.3)}$$

$$k_{sa}\ (\frac{\rho_s}{\mu_s\ g})^{0.33} = 0.0051\ (\frac{\rho_s\ F_s}{a_p\ \mu_s\ A_a})^{0.66}\ (\frac{\mu_s}{\rho_s\ D_s})^{-0.5}\ (a\ d_p)^{0.4} \qquad \text{(A2.4)}$$

The equation for the partial gas mass transfer coefficient (eq. A2.3) is valid for Raschig rings with a diameter smaller than 0.013 m while the one for the

solvent (eq. A2.4) can be used for $0.0063 < d_p < 0.051$. The Raschig rings used have a $d_p = 0.006$ m.

***Overall volumetric mass transfer coefficient in the mixer ($k_{sw}a_m$)***

The overall mass transfer coefficient $k_{sw}$ and the effective specific area for mass transfer in the mixer ($a_m$) were calculated theoretically with empiric correlations.

*A. Specific area for mass transfer in the mixer ($a_m$)*

The specific area in the mixer is a function of the droplet diameter and of the solvent hold-up:

$$a_m = \frac{6\ h_s}{d_m} \tag{A2.5}$$

The droplet diameter[18] is given by:

$$d_m = 0.047\ \left(\frac{\sigma_{sw}^{0.6}}{\rho_c^{0.6}\ N^{1.2}\ D^{0.8}}\right)\ (1 + 2.5\ h_s) \tag{A2.6}$$

*B. Overall mass transfer coefficient in the mixer ($k_{sw}$)*

The overall mass transfer coefficient is given by:

$$\frac{1}{k_{sw}} = \frac{1}{k_{sm}} + \frac{m_{sw}}{k_w} \tag{A2.7}$$

The empiric correlations found in literature to determine the partial mass transfer coefficients in the mixer ($k_{sm}$ and $k_w$), are given for the dispersed and for the continuous phase[18]. Because this study was carried out below the inversion point, the solvent is the dispersed phase while the water the continuous phase. The partial solvent ($k_{sm}$) and water ($k_w$) mass transfer

coefficients are determined for rigid droplets[7] and are given by:

$$\frac{k_{sm}\, d_m}{D_s} = 6.5 \qquad \text{(A2.8)}$$

and

$$\frac{k_w\, d_m}{D_w} = 2 + 0.47\, \left(\frac{d_m^{1.33}\, R^{0.33}\, \rho_w}{\mu_w}\right)^{0.62} (D/T)^{0.17}\, \left(\frac{\mu_w}{\rho_w\, D_w}\right)^{0.36} \qquad \text{(A2.9)}$$

with:

$$R = \frac{5\, N^3\, D^5}{V_m} \qquad \text{(A2.10)}$$

## List of symbols

| | | |
|---|---|---|
| $a$ | specific area of the packing | ($m^{-1}$) |
| $a_p$ | specific wetted area of the packing | ($m^{-1}$) |
| $a_m$ | specific area solvent/water in the mixer | ($m^{-1}$) |
| $A_a$ | cross-sectional area of the absorber | ($m^2$) |
| $A$ | dimensionless absorber parameter | (-) |
| $C_{gin}$, $C_{gout}$ | ethene concentration in the inlet and outlet gas | ($mol.m^{-3}$) |
| $c_g$ | dimensionless concentration in the gas leaving the absorber | (-) |
| $C_{sm}$, $C_{sa}$ | ethene concentration in the solvent leaving the mixer and the absorber, respectively | ($mol.m^{-3}$) |
| $c_{sm}$, $c_{sa}$ | dimensionless concentration in the solvent leaving the mixer and the absorber, respectively | (-) |
| $C_w$ | ethene concentration in water | ($mol.m^{-3}$) |

| | | |
|---|---|---|
| $d_m$ | solvent droplet diameter | (m) |
| $d_p$ | diameter of the Raschig rings | (m) |
| $D$ | stirrer diameter | (m) |
| $D_a$ | diameter of the absorber | (m) |
| $D_g$, $D_s$, $D_w$ | diffusion coefficient in gas, solvent and water | ($m^2.s^{-1}$) |
| $F_g$ | gas flow rate | ($m^3.s^{-1}$) |
| $F_s$ | solvent flow rate | ($m^3.s^{-1}$) |
| $g$ | gravity constant | ($m.s^{-2}$) |
| $h_s$ | solvent hold-up | (-) |
| $H$ | height of the absorber | (m) |
| $k_{gs}$ | overall mass transfer coefficient gas/solvent based on gas concentrations | ($m.s^{-1}$) |
| $k_{sw}$ | overall mass transfer coefficient solvent/water based on water concentrations | ($m.s^{-1}$) |
| $k_g$, $k_{sa}$ | partial gas and solvent mass transfer coefficient in the absorber | ($m.s^{-1}$) |
| $k_{sm}$, $k_w$ | partial solvent and water mass transfer coefficient in the mixer | ($m.s^{-1}$) |
| $m_{gw}$ | partition coefficient between gas and water | ($mol.m^{-3}$gas)/($mol.m^{-3}$water) |
| $m_{gs}$ | partition coefficient between gas and solvent | ($mol.m^{-3}$gas)/($mol.m^{-3}$solvent) |
| $m_{sw}$ | partition coefficient between solvent and water ($= m_{gw}/m_{gs}$) | ($mol.m^{-3}$solvent)/($mol.m^{-3}$water) |
| $M$ | dimensionless mixer parameter | (-) |
| $N$ | stirring speed | ($s^{-1}$) |
| $T$ | mixer diameter | (m) |
| $V_a$ | absorber volume | ($m^3$) |
| $V_m$ | mixer volume | ($m^3$) |

| | | |
|---|---|---|
| $z$ | dimensionless height of the absorber | (-) |
| $\mu_w$, $\mu_s$, $\mu_g$ | water, solvent and gas viscosity | ($kg.m^{-1}.s^{-1}$) |
| $\rho_w$,$\rho_s$,$\rho_g$ | water, solvent and gas density | ($kg.m^{-3}$) |
| $\sigma_{sw}$ | solvent water interfacial tension | ($kg.s^{-2}$) |
| $\Lambda$ | absorption factor | (-) |

## Acknowledgements

This work was supported by a grant (BD/740/90-IF) from the Junta Nacional de Investigação Científica e Tecnológica, Lisbon, Portugal. The authors want to thank Ido Wolters for his valuable help concerning the design of the Packed absorber/Mixer-settler.

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# Chapter 8

# General discussion

## Introduction

The removal of hydrophobic gaseous pollutants by absorption in an organic liquid with a high solving capacity, is a conventional physical-method for waste gas treatment[3]. After absorption, the contaminant is subsequently recovered in another compartment by stripping with water and the cleaned absorbent recycled to the absorber. This is, however, a temporary solution since a new waste stream is created, namely a wastewater stream. When the compound is biodegradable, this problem can be avoided by biological consumption in the water phase. This was thus the underlying idea of this project.

Aiming at the biological treatment of large volumes of gas containing poorly water-soluble pollutants a two-compartment system was proposed, namely a packed absorber for gas/solvent transfer and a bioreactor for solvent/water transfer and subsequent biodegradation. Initially, a Liquid-impelled Loop Reactor (LLR) was considered because there was experience within our group with this type of liquid/liquid contactor[5]. After preliminary experiments and calculations it was concluded that the LLR was not

appropriate because the maximum achievable solvent/water mass transfer rate was very low. The overall efficiency of the whole system was thus limited by the stripping rate in this compartment and therefore the use of a solvent was not advantageous compared to a set-up featuring direct gas/water transfer. These considerations lead to the study presented in chapter 2 where different types of solvent-containing bioreactors are compared with bioreactors without solvent. From this analysis it was concluded that the use of a solvent is advantageous only in a bioreactor configuration featuring large solvent/water exchange areas and mass transfer coefficients, such as in a stirred-tank reactor (STR). The STR was therefore used in further experiments.

Since the study described in this thesis aimed at analysing the effect of the solvent in terms of mass transfer enhancement, experiments were carried out in such conditions that the biological degradation was in all cases not rate-limiting.

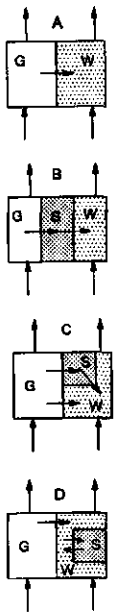
## Mechanisms for gas/water transfer in the presence of solvent

The use of water-immiscible solvents in the treatment of waste gases containing aromatic compounds has been first reported by Schippert (1989)[4] and was tested in a bioscrubber. The solvent was added to the suspended activated sludge in the range of 10-40% (v/v) and the mixture was sprayed over the scrubber compartment. In a cascade of stirred-tank reactors the compound was subsequently biodegraded. Toluene[1] ($m_{gw}^{25°C}$= 0.26) and styrene[1] ($m_{gw}^{25°C}$= 0.13) were the model pollutants used. $m_{gw}$ is the partition coefficient between the gas and the water; ($g/m^3$gas) per ($g/m^3$water). A steady-state mathematical model was developed considering the solvent/water

dispersion an homogeneous liquid; i.e. the solvent and the water are in equilibrium. In this study, data on the removal efficiency upon solvent addition is only shown for toluene. The solvent used in those experiments is not mentioned nor is the partition coefficient of toluene between the gas and the solvent. In view of the limited information concerning values of $m_{gw}$ and $m_{gs}$, and types of bioreactors for which the use of solvent is advantageous further investigation on this topic was needed.

We have set-up a steady-state mathematical model which predicts the influence of quantities such as the gas/solvent, gas/water and solvent/water exchange areas, mass transfer coefficients and partition coefficients on the contaminant removal efficiency. This is described in chapter 5 of this thesis. Different mechanisms for gas/water transfer in the presence of the solvent were considered (Fig. 1). Each mechanism represents a different system configuration. Mass balances over the gas, the solvent and the water were set-up for each mechanism. For each case, the three mass balance equations could be simplified resulting in a set of two equations featuring the gas/water concentration difference as common driving force for overall interface transfer and an overall mass transfer coefficient (T). This parameter is a function of exchange areas, mass transfer coefficients and partition coefficients (Fig. 1) and is different for each mechanism. Since the driving force is the same for all cases, the system performance may be assessed on the basis of the (T) parameter.

This model was set-up and validated in a stirred-tank reactor containing a solvent-in-water-dispersion. This study was done for two model pollutants namely a moderately water-soluble (toluene) and a poorly water-soluble (oxygen) pollutant. For both compounds an enhancement of the overall gas/water mass transfer coefficient (T) was observed, however, a greater improvement was found for the less water-soluble compound, i.e oxygen.




$$T_A = k_{gw} A_{gw}$$

$$\frac{1}{T_B} = \frac{1}{k_{sw} A_{sw}} + \frac{1}{m_{sw} k_{gs} A_{gs}}$$

$$T_C = \frac{1}{\frac{1}{k_{sw} A_{sw}} + \frac{1}{m_{sw} k_{gs} A_{gs}}} + k_{gw} A_{gw}$$

$$T_D = k_{gw} A_{gw}$$

Figure 1. Gas-to-water transfer in a 2-phase (A) and in a 3-phase system (B, C, D). **G**: gas; **S**: solvent; **W**: water. A, direct gas/water transfer; B, serial transport gas→solvent→water; C, direct gas→water transport and serial transport gas→solvent→water; D, no direct transport gas/solvent. All systems: continuous gas and water flows, batch solvent phase. $k_{gs}$: overall gas/solvent mass transfer coefficient on solvent basis (m/s), $k_{gw}$: overall transfer coefficient gas/water on water basis (m/s), $k_{sw}$: overall transfer coefficient solvent/water on water basis (m/s), $A_{gs}$: exchange area gas/solvent ($m^2$), $A_{gw}$: exchange area gas/water ($m^2$), $A_{sw}$: exchange area solvent/water ($m^2$), $m_{gs}$: partition coefficient between gas and solvent (-), $m_{sw}$: partition coefficient between solvent and water = $m_{gw}/m_{gs}$ (-).

As initially proposed, a two-compartment system was tested for the removal of a model hydrophobic compound from a gas stream. This is described in chapter 7. The model compound was ethene ($m_{gw}^{25°C}$= 8.0) and the solvent FC40. The two-stage system consisted of a packed absorber and a stirred-tank reactor. A settler separated both liquids downstream the bioreactor. The pure solvent and the aqueous phase containing the bacterial suspension were recycled back to the absorber and bioreactor, respectively. Although the removal efficiencies obtained in the experiments were low due to an inefficient use of the absorber, the feasibility of the system to remove ethene has been demonstrated. Furthermore, it has been shown theoretically that higher removal efficiencies can be obtained by using a solvent as intermediate phase, rather than by recycling the aqueous suspension between the absorber and the bioreactor. One of the conditions is, however, that the compound dissolves better in the solvent than in the water phase.

## Concluding remarks

The study described in this thesis has shown that the use of an intermediate solvent can improve the removal of hydrophobic compounds from waste gases. Conditions are, however, that both the absorber and the bioreactor work efficiently and that the pollutant dissolves better in the solvent than in water ($m_{sw} > 1$).

Compared to the system of Schippert (1989)[4], where the solvent-water dispersion is sprayed over the scrubber compartment, our system which contacts the gas with the pure solvent has both advantages and disadvantages. Spraying the pure solvent in the absorber is advantageous because a smaller column is needed. This must be weighted, however, against the need for a

settler. When solvent and water are separated downstream the bioreactor, a large density difference between both liquids is needed for a fast separation. This reduces the number of possible solvents that can be used for waste-gas treatment, and excludes the emulsion-forming ones as silicone or parafin oils (density of 937 and 840 kg/m$^3$, respectively)[5]. On the other hand, when a settler is used and the bacterial suspension is separated from the solvent, the origin of a new waste stream consisting of water/solvent/surplus biomass[2], can be prevented. This mixture is difficult to clean biologically and is seen as the major disadvantage of the technique. The use of a settler is, moreover, economically attractive because it reduces solvent losses to a minimum.

The packed absorber/mixer-settler was tested during a run of 10 days with a constant ethene removal. The operational stability of this system should however be tested for longer periods before it can be used in practice.

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# Summary

In conventional biological systems for the treatment of waste gases, contaminants are transferred directly to the aqueous phase and then converted by the micro-organisms. When poorly water-soluble pollutants are to be removed, biological degradation is often limited by the slow transport from the gas to the aqueous phase. This transport limitation can be circumvented by contacting the gas directly with an intermediate water-immiscible organic solvent with a high affinity for these contaminants.

The study described in this thesis evaluates at which conditions the use of an intermediate solvent is advantageous compared to systems featuring direct gas/water transfer. Aiming at this, different bioreactor configurations and different pollutants were considered and compared.

In a review, the current state of the art concerning new biotechniques for a better removal of hydrophobic pollutants from waste gases is given. The transfer rate of these compounds is often improved either by reducing the water layer between the gas and the micro-organisms, or by augmenting the gas/water exchange area. An alternative strategy mentioned in literature involves the use of a water-immiscible solvent. However, limited information is given on the conditions at which the use of a solvent is beneficial.

This research started with a preliminary theoretical study in which three solvent-containing systems were compared to bioreactor configurations with

direct gas/water transfer. Because this study aimed at characterizing the systems in terms of mass transfer, the biological degradation was considered not rate-limiting. The systems with solvent consisted of a two-compartment system with a packed absorber for gas/solvent transfer and a bioreactor for solvent/water transfer and subsequent biological conversion. Three types of bioreactors were considered namely the liquid-impelled loop reactor (LLR), the packed-bed reactor and the stirred-tank reactor. From this study it was concluded that the use of a solvent as intermediate phase is advantageous in a bioreactor configuration featuring large solvent/water exchange areas and mass transfer coefficients such as in a stirred-tank reactor. This was therefore the type of bioreactor chosen to carry out the experiments.

Initially, the effect of the solvent volume fraction and of the partition coefficients gas/water ($m_{gw}$) and gas/solvent ($m_{gs}$) on the mass transfer rate, was studied in a one-compartment system, namely the stirred-tank reactor. The gas containing the contaminant was sparged directly through the solvent-in-water dispersion. The effect of the solvent on the gas-to-water transfer rate was tested during steady-state experiments in the presence of biological conversion. This was done at increasing solvent volume fractions by measuring the change of the outlet gaseous concentration or of the linear cell growth rate. The model pollutants tested were toluene ($m_{gw}^{22°C}$= 0.21) and oxygen ($m_{gw}^{22°C}$= 32.7) and FC40 was the solvent used. An enhancement of the mass transfer rate of a factor up to 1.1 was found for toluene at 10 % (v/v) of FC40, while the oxygen transfer rate increased by a factor 2 at the same solvent volume fraction.

To be able to predict theoretically at which solvent hold-ups and for which gaseous compounds an enhancement of the gas/water mass transfer rate is expected, a steady-state mathematical model was set-up. This was done for different system configurations and therefore different mechanisms for

gas/water transfer through the solvent were considered. An overall gas/water mass transfer coefficient, characteristic of each mechanism, was derived. Since the driving force is the same for all the system configurations, namely the gas/water driving force, the performance of the different systems can be assessed on the basis of this overall gas/water mass transfer coefficient. For a particular configuration, this coefficient is a function of gas/water, gas/solvent and solvent/water exchange areas, mass transfer coefficients and partition coefficients. The model predictions were validated by carrying out steady-state experiments in a stirred-tank reactor containing a solvent-in-water dispersion. The overall gas/water mass transfer coefficient was determined in the absence of biological conversion to avoid the influence of the cells or their products. Removal of the compound was achieved by passing a continuous flow of compound-free gas or water through the reactor. The solvent was kept in the vessel by means of a small settler. This study was carried out with toluene and oxygen. As found out in the aforementioned experiments with cells, the mass transfer enhancement found for oxygen was larger than the one for toluene at increasing solvent volume fractions. While for oxygen a 2.2-fold increase of the overall gas/water mass transfer coefficient was found at 15 % (v/v) FC40, an enhancement of circa 1.2 was observed for toluene at the same solvent amount. The enhancement factors predicted by the model agreed well with the experimentally determined values.

The effect of the cells on the enhancement of the overall gas/water mass transfer coefficient at increasing solvent volume fractions was studied. This was done with ethene and the ethene-degrading bacterium *Mycobacterium parafortuitum*. At all solvent volume fractions tested, enhancement factors with cells were higher than enhancements without cells. In the presence of cells, a 1.8-fold increase of the $k_la$ value was found at 26 % (v/v) FC40,

whereas this value increased of a factor 1.2 in the absence of cells at approximately 19 % (v/v) FC40. The emulsifier effect of the microorganisms or their excretion products was suggested as a possible cause for this difference.

A two-compartment system consisting of a packed absorber for gas/solvent transfer and a stirred-tank reactor for solvent/water transfer and microbial degradation was tested with ethene as model pollutant. The solvent was recycled between absorber and bioreactor. A 9 % and a 15 % elimination efficiency was obtained at solvent flows of $6\times10^{-8}$ $m^3/s$ and $11.3\times10^{-8}$ $m^3/s$, respectively. Although the removal efficiencies obtained were low due to an inefficient use of the column, the feasibility of the system to remove ethene has been demonstrated. The systems's performance was described by a steady-state mathematical model. Simulated ethene removal efficiencies agreed well with the experimental results. It was concluded that with the system dimensions and operational conditions used during the experiments, the limiting step was the mass transfer in the absorber. Furthermore it has been shown theoretically that higher removal efficiencies can be obtained by using a solvent as intermediate phase than by recycling the aqueous suspension between the absorber and the bioreactor, if the contaminant has a higher solubility in the solvent than in water.

# Samenvatting

Bij de conventionele biologische behandeling van vervuilde gasstromen worden de te verwijderen componenten rechtstreeks overgedragen vanuit het gas naar een waterfase, en aldaar omgezet door micro-organismen. Als deze verbindingen echter slecht oplossen in water, wordt de biologische omzettingssnelheid vaak beperkt door de lage overdrachtssnelheid vanuit het gas naar het water. Een dergelijke transportbeperking kan vermeden worden door het gas rechtstreeks in contact te brengen met een intermediaire fase zoals een organisch solvent dat niet met water mengt. Daarbij dient deze solventfase een hoge affiniteit voor de te verwijderen verbinding te hebben.

Het onderzoek in dit proefschrift richt zich op de vraag onder welke voorwaarden de toepassing van een dergelijke intermediaire solventfase gunstig is (in vergelijking tot systemen zonder solventfase, met uitsluitend overdracht van gas naar water). In dit kader werden verschillende bioreactorconfiguraties en verschillende verbindingen geëvalueerd en vergeleken.

In een algemeen overzicht wordt de actuele stand van zaken gegeven aangaande nieuwe technieken voor de efficiënte biologische verwijdering van hydrofobe verbindingen uit gasstromen. De overdrachtssnelheid van dergelijke verbindingen tracht men in veel gevallen te verhogen, bijvoorbeeld door de

waterlaag tussen de gasfase en de micro-organismen te reduceren, of door het uitwisselingsoppervlak tussen gas en water te vergroten. Daarnaast wordt sinds kort het toevoegen van een aparte solventfase genoemd als zinvolle strategie. De theoretische grondslagen echter, van waaruit afgeleid zou kunnen worden of de toepassing van een dergelijke solventfase zinvol is, bleken slechts in zeer beperkte mate voorhanden te zijn.

Het in dit proefschrift beschreven werk begon met een theoretische vergelijking tussen enerzijds een drietal systemen met een additionele solventfase en anderzijds solvent-loze bioreactoren met uitsluitend gas/water-overdracht. De nadruk lag daarbij op de stoftransporteigenschappen; van de biologische omzettingscapaciteit werd verondersteld dat deze in overmaat voorhanden was. De solvent-bevattende systemen bestonden uit twee compartimenten: een gepakte absorptiekolom voor de overdracht van de gas- naar de solventfase, en een bioreactor voor overdracht van solvent naar water en voor aansluitende biologische omzetting. Drie bioreactoren werden hierbij in beschouwing genomen: een vloeistof-aangedreven lusreactor (liquid-impelled loop reactor), een gepakt-bed-reactor, en een ideaal geroerd vat. Uit deze vergelijking werd geconcludeerd dat een intermediaire solventfase zinvol kan zijn, vooropgesteld dat de transportcoëfficiënt en het uitwisselingsoppervlak tussen solvent- en waterfase groot genoeg zijn. Op grond van deze criteria werd een geroerd vat gekozen voor verdere experimenten.

In eerste instantie werd een één-compartimentssysteem (een geroerd vat) gebruikt voor onderzoek naar de stoftransportsnelheid als functie van de volumefractie van de solventfase, en als functie van de verdelingscoëfficiënten van de te verwijderen verbinding over gas en water ($m_{gw}$) en over gas en solvent ($m_{gs}$). Gas met daarin de modelverbindingen tolueen ($m_{gw}^{22°C} = 0.21$) of zuurstof ($m_{gw}^{22°C} = 32.7$) werd daarbij geleid door solvent-in-water-dispersies, met FC40

als solventfase. Het effect van de hoeveelheid solvent op de uitwisselingssnelheid tussen gas en water werd gemeten in experimenten onder stationaire omstandigheden waarin zich gelijktijdig een biologische omzetting in de waterfase voltrok. Als maatstaf werden de uitgangsconcentratie van de modelverbinding in de gasfase en de lineaire groeisnelheid van de micro-organismen in de waterfase gemeten. Een verbetering van de stoftransportsnelheid van tolueen ten opzichte van een solvent-loos systeem met een factor 1.1 werd gemeten bij een volumefractie FC40 van 10% (v/v); voor zuurstof verbeterde de stoftransportsnelheid met een factor 2.0, eveneens bij een volumefractie FC40 van 10% (v/v).

Om theoretisch te kunnen voorspellen bij welke volumefractie solvent en voor welke gasvormige verbindingen een verbetering van de gas/water-transportsnelheid te verwachten is, werd een wiskundig model voor stationaire omstandigheden opgesteld. Dit werd gedaan voor verschillende systeemconfiguraties en daarmee voor verschillende wegen (of mechanismen) van overdracht vanuit gas naar water via de solventfase. Hierbij werd, voor elk van deze mechanismen afzonderlijk, een overall gas/water-stoftransportcoëfficiënt afgeleid met telkens een identieke drijvende kracht: het 'concentratieverschil' tussen gas- en waterfase. Gezien deze gemeenschappelijke drijvende kracht konden de prestaties van de verschillende systemen vergeleken worden op basis van de respectievelijke overall gas/water-stoftransportcoëfficiënten. Voor elk van de configuraties was deze overall-coëfficiënt telkens een configuratie-specifieke functie van de gas/water, gas/solvent en solvent/water uitwisselingsoppervlakken, stoftransportcoëfficiënten en verdelingscoëfficiënten. De modelvoorspellingen werden geverifieerd met experimenten onder stationaire omstandigheden in een geroerd vat met een solvent-in-water-dispersie. De overall

gas/watertransportcoëfficiënt werd bepaald in afwezigheid van een biologische reactie, teneinde een complicerende invloed van (producten van) cellen op deze coëfficiënten te vermijden. Met het oog op de gewenste stationaire omstandigheden diende de overgedragen verbinding desalniettemin verwijderd te worden; hiertoe werd de waterfase of de gasfase continu ververst. De solventfase werd daarbij in de reactor gehouden met behulp van een kleine bezinker. De experimenten werden uitgevoerd met tolueen en zuurstof. Net als in de eerdergenoemde experimenten in àànwezigheid van cellen, bleek ook nu het toevoegen van solvent een sterkere verbetering te bewerkstelligen van de gas/water-overdracht van zuurstof (een factor 2.2 bij een FC40-gehalte van 15% v/v) dan van de overdracht van tolueen (een factor 1.2 bij eenzelfde FC40-gehalte). De theoretisch berekende verbeteringen waren in goede overeenstemming met de experimenteel bepaalde waarden.

De invloed van cellen op de solvent-gestuurde verbetering van de overall gas/water-massatransportcoëfficiënt werd onderzocht aan de hand van etheen-overdracht in aanwezigheid van de etheen-afbrekende bacterie *Mycobacterium parafortuitum*. Bij al de onderzochte volumefracties FC40 bleek de solvent-afhankelijke transportverbetering verder versterkt te worden door de aanwezigheid van cellen. In afwezigheid van cellen bleek een 1.2-voudige verbetering van de overall transportcoëfficiënt gerealiseerd te kunnen worden door 19 % (v/v) FC40 toe te voegen; in aanwezigheid van cellen werd een 1.8-voudige verbetering bereikt bij een FC40-gehalte van 26 % (v/v). Emulgerende effecten van de (producten van) cellen werden geacht deze verschillen te kunnen verklaren.

Een 2-compartimentensysteem werd getest met etheen als modelverbinding; het systeem bestond uit een gepakte absorptiekolom voor gas/solvent-overdracht en een geroerd vat (bioreactor) voor solvent/water-overdracht en aansluitende

microbiële afbraak. De solventfase werd gerecirculeerd over de kolom en de bioreactor. Een etheenconversie van 9 % werd gevonden bij een recirculatiedebiet van $6.0\times10^{-8}$ $m^3/s$; bij een FC40-debiet van $11.3\times10^{-8}$ $m^3/s$ was de conversie 15 %. De lage conversiewaarden konden worden toegeschreven aan de inefficiëntie van de absorptiekolom, en laten de principiële geschiktheid van het systeem voor de verwijdering van etheen onverlet. De prestaties van het 2-compartimentensysteem onder stationaire omstandigheden werden beschreven met een mathematisch model; de hiermee verkregen voorspellingen waren in goede overeenstemming met de experimentele bevindingen. Op grond hiervan werd geconcludeerd dat, gegeven de systeemdimensies en -bedrijfsvoering, de stofoverdracht in de absorptiekolom de snelheidsbeperkende stap voor het gehele proces vormde. Bovendien werd theoretisch aannemelijk gemaakt dat het recirculeren van een waterige celsuspensie - in afwezigheid van een solventfase - een veelal ongunstige invloed zou hebben op de conversie, vooropgesteld dat de over te dragen verbinding beter oplost in solvent dan in water.

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## Curriculum vitae

Maria Teresa Cesário was born on the 2nd of October 1965 in Santiago do Cacém, Portugal. In 1988 she obtained a degree in Chemical Engineering at the Instituto Superior Técnico - Universidade Técnica de Lisboa. From March 1989 till December 1990 she worked as visiting researcher at the Department of Food Science of the Agricultural University of Wageningen (The Netherlands) in a project on plant cell cultures. In January 1991 she started the PhD in the subject described in this thesis at the same department.