GAS-LIQUID INTERFACIAL AREA IN OXYGEN ABSORPTION INTO OIL-IN-WATER EMULSIONS

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Abstract: Present work includes an exhaustive study about gas-liquid interfacial area between gas phase and liquid heterogeneous medium generated in an airlift bioreactor. The model system studied is composed by water, methyl ricinoleate and Tween 80, since it is the base of the medium used for the production of γ-decalactone through the biotransformation of ricinoleic acid, by the yeast *Yarrowia lipolytica*. Experimental results allow describing the hydrodynamic behavior of the gas phase into the biphasic medium. In the oil-in-water system used, a decrease of the gas-liquid interfacial area with the oil concentration increase was found, due to the redistribution of surfactant between interface and bulk phases.

Keywords: Air-lift bioreactor, methyl ricinoleate, emulsion, gas-liquid interfacial area

1. INTRODUCTION

Gas-liquid-liquid systems are encountered in many reactions and have gained special interest in chemical engineering with the introduction of homogeneous biphasic catalysis. Mass transfer modeling in biphasic media has been done by several authors using as a model, systems in which the second liquid phase (organic) is an additional inert and external compound (like perfluorocarbons and silicone oils, among others) added to the system on the purpose to improve mass transfer from the gas to the liquid aqueous phase (Dumont and Delmas, 2003). These systems are encountered in some biochemical applications where a hydrophobic compound with higher oxygen solubility than water is used to improve the oxygen transfer rate to the culture media. However, numerous biotechnological processes are based on the development of microorganisms within a biphasic medium formed by an oil-in-water emulsion where the oil is the substrate to be degraded. In these cases, the organic substrate can affect the gas-liquid mass transfer, thus influencing the overall productivity.

The system herein presented is an emulsion of water and methyl ricinoleate (MR), stabilized by Tween 80, which constitutes the medium used in the production of γ-decalactone (a peach-like aroma compound of industrial interest) through the biotransformation of ricinoleic acid (major constituent of methyl ricinoleate) by the yeast *Yarrowia lipolytica* (Aguedo *et al.*, 2005). The biochemical pathway leading to the production of the aroma has been extensively studied. However, crucial steps controlling the production ratio of γ-decalactone against derived non-aromatic lactones are not totally understood. The oxygen is believed to influence these side-reactions, but this point remains to elucidate. Since *Y. lipolytica* is an obligate aerobe, oxygen is a crucial operational parameter for the control of processes involving this yeast. Previous studies (Gomes *et al.*, 2007) have analyzed the influence of operating conditions on oxygen mass transfer and on γ-decalactone production in a bubbling stirred bioreactor. In the present work an airlift bioreactor was used and the main aim of this study was to study the influence of operating conditions and emulsion composition on oxygen mass transfer to the emulsion, especially the gas-liquid interfacial area, in this biphasic medium, in an airlift contactor.

2. EXPERIMENTAL DATA

1.1 Liquid velocity

The velocity of liquid circulation was determined with the neutral buoyancy flow follower technique. A small square piece of plastic (side length, 0.005m; specific gravity, 1.03) was used as a flow follower. The time taken by the follower to traverse a known vertical distance (0.2 m) in the downcomer was noted and the flow velocity was calculated from an average of 10 measurements. The density of the follower was very close to that of the liquid.

Figure 1 shows that the increase of the air flow rate leads to an improvement in the liquid velocity, although it seems to be a trend to become constant at the higher aeration rates tested.
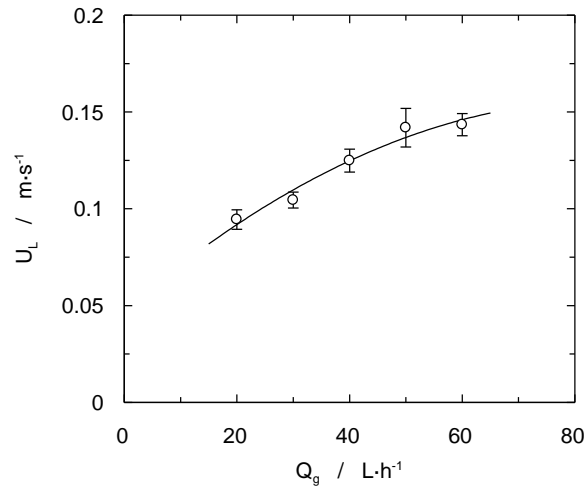

Figure 1. Liquid velocity (U_L) generated into the air-lift reactor at different aeration rates.

1.2 Gas-liquid interfacial area

To determine the gas-liquid interfacial area, a photographic method was used. Bubbles diameter was measured using a photographic method based on images of the bubbles taken along the height of the column, from the bottom to the top. A minimum number of 50 well-defined bubbles along the bubble column were used to evaluate the size distribution of the bubbles in the liquid phase for the different gas flow rates tested. The geometrical characteristics of air bubbles produced in the contactor enable to calculate the value of the gas-liquid interfacial area. The bubbles produced in the contactor have ellipsoidal shape and for this reason, major (E) and minor (e) axes of the projected ellipsoid (in two dimensions) must be determined. The diameter of the equivalent sphere was taken as the representative bubble dimension. Equation 1 allows determining the diameter distribution of a bubble present along the gas-liquid contactor.

$$d = \sqrt[3]{E^2 \cdot e} \tag{1}$$

Photographs in Figure 2 display clearly that when the methyl ricinoleate concentration increases in the liquid phase, an increase in bubbles size is produced.
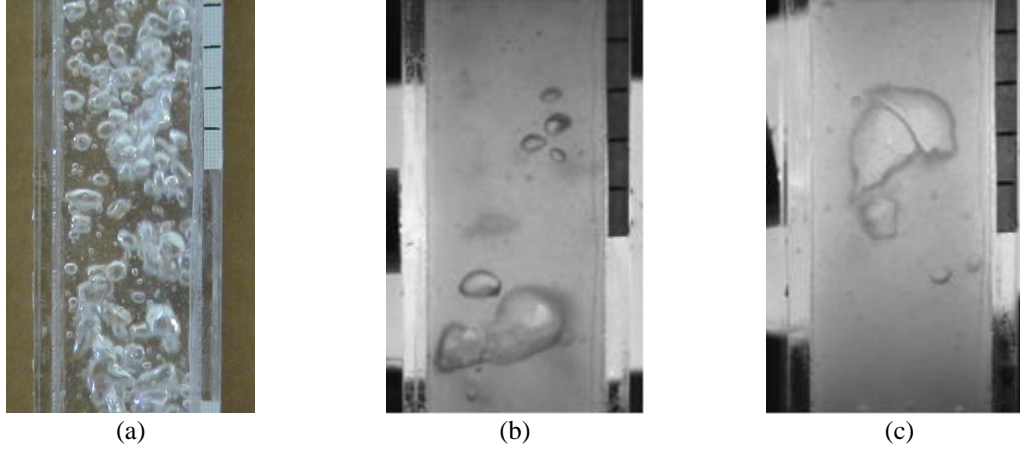
(a)   (b)   (c)

Figure 2. Photographs from the bubble column at an air flow rate of 1.35 L·min⁻¹ for different liquid phase compositions: (a) aqueous solution with 0.093 % (v/v) Tween 80; (b) emulsion with 0.3 % (v/v) MR and 0.093 % (v/v) Tween 80; (c) emulsion with 0.54 % (v/v) MR and 0.093 % (v/v) Tween 80.

The bubble diameter distribution along the bubble contactor has a direct influence upon the value corresponding to gas-liquid interfacial area. The interfacial area determination is developed on the basis of two important parameters: the Sauter mean diameter and the gas hold-up. An example of the bubble size distribution obtained in the present work is shown in Figure 3. An increase in the surfactant concentration decreases the bubbles size in the whole diameter range. This behavior has an important role in the value of the gas-liquid interfacial area. The decrease in the value of liquid phase surface tension caused by the presence of surfactant molecules at gas-liquid interface produces the decrease in the diameter of the bubbles generated into the gas-liquid contactor.
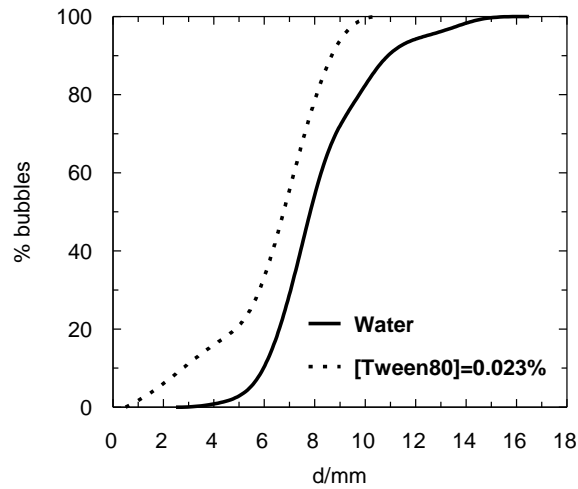

Figure 3. Influence of Tween 80 concentration in the liquid phase upon the bubble size. $Q_g = 0.5$ L·min⁻¹.

Different authors recommend the use of the Sauter mean diameter (d_{32}) (Shah *et al.*, 1982), that can be determined using the data calculated for the equivalent diameter by equation (2).

$$d_{32} = \frac{\sum_i \left(n_i \cdot d_i^3 \right)}{\sum_i \left(n_i \cdot d_i^2 \right)}$$
(2)

where n_i is the number of bubbles that have an equivalent diameter (d_i).

The gas hold-up was determined in a square bubble column contactor, due to the difficulty to measure the variations on the height of the liquid. This column has geometrical characteristics of 4 cm inside side-length and height of 65 cm. Since the diameter and height are similar to those of riser's airlift reactor, results can be extrapolated. The use of this methodology is possible due to bubbles are not present in the downcomer of the airlift reactor. Air was used as gas stream in the gas-liquid contactor and it was fed at the bottom of the bubble column using a five holes sparger.

The gas hold-up, ε_G, was calculated using the difference between the liquid height in the absence of gas in the bubble column and under the different experimental conditions of gas flow rate fed to the contactor (equation 3) (Vasconcelos *et al.*, 2003).

$$\varepsilon_G = \frac{\Delta V}{\Delta V + V_L} \tag{3}$$

where V_L is the ungassed liquid volume and ΔV is the volume expansion after gas dispersion, calculated from the liquid level change and the cross sectional area. The change of volume in the bubble column was calculated based on the change observed in the liquid level and the increase of this value after gassing.

The gas hold-up was determined for different liquid phase compositions (pure water, aqueous solution with 0.093 % (v/v) Tween 80, emulsions with 0.1 % (v/v) and 0.54 % (v/v) MR and 0.093 % (v/v) Tween 80, at different gas flow rates (or surface gas velocities).

The experimental results obtained for the gas hold-up in the bubble column are depicted in Figure 4. An increase in the gas flow rate (or surface gas velocity) produces a clear increase in the value of the gas hold-up with a linear trend. Also, it can be observed that no significant differences exist between the different liquid phases compositions tested, although for higher gas flow rates it seems that the gas hold-up starts to become greater for the aqueous medium. This can be explained by the increase of bubbles size in water and therefore, the decrease of its residence time.
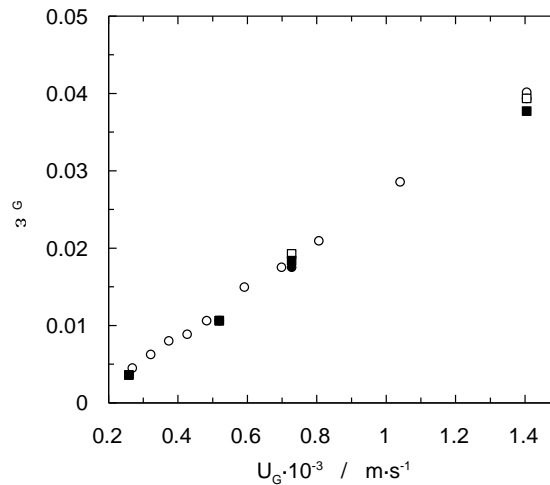

Figure 4. Influence of surface gas velocity (U_G) upon gas hold-up (ε_G). ($\bigcirc$) Pure water; ($\bullet$) 0.093 % (v/v) Tween 80; ($\square$) 0.1 % (v/v) of MR and 0.093 % (v/v) Tween 80; ($\blacksquare$) 0.54 % (v/v) of MR and 0.093 % (v/v) Tween 80.

The Sauter mean diameter and the gas hold-up values allow the calculation of the specific gas-liquid interfacial area using equation 4 (van't Riet and Tramper, 1991).

$$a = \frac{6 \cdot \varepsilon_G}{d_{32} \cdot \left(1 - \varepsilon_G\right)} \qquad (4)$$

This experimental methodology allows the determination of gas-liquid interfacial area under the different experimental conditions (liquid phase composition and gas flow rate) assayed in this work (Figure 5).
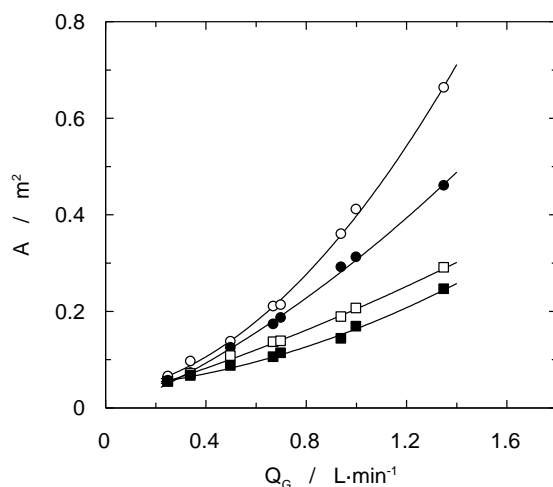

Figure 5. Influence of gas flow rate and methyl ricinoleate concentration on the interfacial area in the airlift bioreactor. (○) 0.093 % (v/v) Tween 80; (●) 0.1 % (v/v) of MR and 0.093 % (v/v) Tween 80; (□) 0.3 % (v/v) of MR and 0.093 % (v/v) Tween 80; (■) 0.54 % (v/v) of MR and 0.093 % (v/v) Tween 80.

Experimental results shown in figure 5 indicate the influence of liquid phase composition and gas flow rate upon the specific interfacial area generated in the bubble column. When gas flow rate increases, the interfacial area also increases due to the previously observed behavior caused by this variable upon the gas hold-up. The gas hold-up increases with the gas flow rate because a higher number of bubbles are generated in the sparger, increasing the interfacial area.

When pure water was employed as liquid phase in the bubble contactor at high values of gas flow rate, the increase in interfacial area was not observed because under those conditions there is a great number of bubbles that collide producing coalescence and therefore the increase in the bubbles diameter (data not shown).

The presence of surfactant in the liquid phase produces a clear increase in the value of the specific interfacial area, comparing to pure water, particularly noticed for high values of gas flow rate. This behavior is due to different reasons. One of them is the clear decrease in the liquid phase surface tension when the surfactant concentration increases (Gómez-Díaz et al., 2008) as it causes the formation of bubbles with minor size increasing the interfacial area (Painmanakul, 2005). Also, the presence of surfactant molecules in the liquid phase produces a decrease in the bubbles effective collisions and then the bubbles small size remains constant along the bubble column.

The experimental results obtained when emulsions were employed as liquid phases are presented in Figure 5 that shows a decrease in the specific interfacial area value when the oil concentration increases in the liquid phase. This effect is negligible for the lowest gas flow rate analyzed but when it increases, the presence of the organic phase has an important role on the values of interfacial area. This behavior is assigned to a change in the surfactant concentration at gas-liquid interface because when an organic phase is added to aqueous solutions with Tween 80, a new distribution of surfactant between interface and bulk phases is originated. This distribution affects the value of the liquid phase surface tension and consequently bubbles produced under these conditions have higher diameters than the ones formed in the absence of organic phase.

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