

An experimental investigation into the behaviour of antifoaming agents



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ABSTRACT

As part of an on-going research program into the development of accurate computational fluid dynamics models of industrial bubble column bio-reactors, the behaviour of a range of commercially available antifoaming compounds was investigated. Experimental data from a laboratory scale system showed that increasing the antifoam concentration led to a decrease in the Oxygen Transfer Rate (OTR) up to a critical value, hypothesised to be related to the monolayer coverage of the gas-liquid interface; further increases in antifoam concentration had no additional impact. Beyond this critical antifoam concentration, a 3–5 fold reduction in the OTR was found, this reduction being independent of the type of antifoam used or the superficial air velocity. The issue of antifoam 'deactivation' was also examined with the results obtained being consistent with the deactivation of polyethylene oxide type antifoams being caused by their displacement from the gas-liquid interface by more hydrophobic material.

1. Introduction

Many bioprocesses have problems with foam formation which is thought to arise due to the presence of a wide range of surface active compounds in the fermentation media used (Prins and van't Riet, 1987; Junker, 2007; Doran, 1995; Berenjian et al., 2014). As excessive foam formation is undesirable from an operational perspective, addition of chemical antifoams is generally necessary to prevent foaming (Prins and van't Riet, 1987; Doran, 1995). However, addition of such antifoams has its drawbacks, one of which is a significant reduction in the oxygen transfer rate (OTR). Such a reduction is commonly attributed to the accumulation of the antifoam at the gas-liquid interface where it creates an additional barrier for oxygen transfer as well as making the interface more rigid, thereby leading to a reduction in the liquid film mass transfer coefficient (k_L) (Doran, 1995).

Ensuring a sufficiently high OTR is often a key issue in industrial fermentations, hence reliable information regarding the quantitative impact of commercial antifoams is of obvious interest. With this in mind, a range of authors (Prins and van't Riet, 1987; Kawase and Moo-Young, 1990; Koch et al., 1995; Vasconcelos et al., 2003; Morão et al., 1999) have examined this issue. Vardar-Sukan (1998) reported an approximately threefold reduction in the volumetric mass transfer coefficient ($k_L a$) with the addition of vegetable oils (fatty acid esters); Kawase and Moo-Young (1990) found that the addition of a silicone emulsion type antifoam led to a three to fivefold reduction in the OTR;

while Koch et al. (1995) observed that polyether based antifoams have less impact than silicone based compounds. Aside from the work of Morão et al. (1999) little in the way of a systematic comparison between these three widely used classes of antifoams (i.e. fatty acid esters, polyethers, and silicone based oils/emulsions) could be identified in the open literature. Vasconcelos et al. (2003) have examined the effect of the antifoam concentration on mass transfer in bubble columns, finding that k_L was effectively constant above the critical micelle concentration for the antifoam used (Sigma 289). Similarly, Benedek and Heideger (1971) observed that the measured value of $k_L a$ was effectively constant in a stirred tank when Antifoam C was added at concentrations between 2 and 20 ppm (2×10^{-4} and $2 \times 10^{-3}\%$ (v/v)), while Bull and Kempe (1971) have also observed similar behaviour where addition of antifoam (polypropylene glycol P-2000) led to the rate absorption of oxygen at the free surface being essentially constant above some critical value (here 14 ppm – $14 \times 10^{-3}\%$ (v/v)). Such findings suggest that all antifoams behave in a similar way at the interface, leading to the observed reductions in oxygen transfer.

It is generally agreed that chemical antifoams work by destabilising the liquid film surrounding the air bubble inside the foam with three mechanisms having been proposed (Prins and van't Riet, 1987; Karakashev and Grozdanova, 2012). Firstly, that the antifoam agent displaces a surface active compound from the interface, thereby stopping it from stabilising the foam; secondly, that the antifoam acts to form hydrophobic 'bridges' between interfaces, causing the liquid

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Nomenclature

Units	Description	%Rise	Percentage rise of foam layer (dimensionless)
a	Interfacial area per unit volume of liquid (m^{-1})		
A_m	Molecular area ($\text{m}^2 \text{molecule}^{-1}$)		
$C_{\text{SO}_3^{2-}}$	Sulphite concentration (g L^{-1})		
H	Height (m)		
H_{foam}	Foam height (m)		
H_{liquid}	Liquid height (m)		

$M_{i,w}$	Molecular weight (g mol^{-1})
N_A	Avogadro's number (mol^{-1})
OTR	Oxygen transfer rate ($\text{g L}^{-1} \text{h}^{-1}$)
P	Octanol water partition coefficient (dimensionless)
t	Time (s)
ρ	Density (kg m^{-3})
$C_{\text{monolayer}}$	Concentration of antifoam needed for monolayer coverage (% (v/v))
k_L	Liquid film mass transfer coefficient (m/s)
$k_{L,a}$	Volumetric liquid film mass transfer coefficient (s^{-1})

film to rupture and hence collapsing the foam; thirdly, that droplets of antifoam can spread throughout the liquid film, thinning it and causing it to rupture. Of these possible mechanisms, it is a task of considerable experimental difficulty to determine which is most significant in any particular situation, particularly for a complex and poorly defined system such as fermentation media where there are a range of potential foamants and other surface active compounds present. It is thus almost impossible to determine from first principles which antifoam will be most effective for a given industrial fermentation in terms of maximising foam suppression and minimising any reduction in oxygen transfer.

Another issue with the industrial usage of antifoams is 'deactivation' whereby the antifoam loses its efficiency with time meaning that further additions are necessary (Rác et al., 1996). Denkov et al. (1999), Denkov (1999) and Denkov et al. (2000) have proposed that so-called 'mixed' antifoams become deactivated due to the segregation of the oil and solid components together with the emulsification of the oil. However, little information is available in the open literature regarding the deactivation of other classes of antifoams.

In this industrially-oriented context, the aims of this present study were to quantify the impact of a range of commercial antifoams in terms of foam suppression, OTR reduction, and time dependent deactivation.

2. Experimental method

A bubble column 190 mm in diameter and 1000 mm in height constructed from clear acrylic was used in this work. Air was introduced through a perforated plate sparger having 13 holes, each 3 mm in diameter, arranged in a cross pattern. Fig. 1 is a schematic diagram of the experimental set-up used; further details being available elsewhere (McClure et al., 2013).

The antifoams used were vegetable oil along with three commercially available antifoaming agents: Antifoam O-30 (a fatty acid ester); Disfoam (a polyether); and Antifoam Y-30 (a silicone based agent). Antifoams O-30 and Y-30 were sourced from Sigma Aldrich while Disfoam was obtained from the NOR Corporation.

The surfactants Sodium Dodecyl Sulphate (SDS) and Tween 80 were used as foaming agents, both being sourced from Sigma Aldrich.

The OTR for the antifoam-containing solutions was measured using the sulphite oxidation technique. Here sodium sulphite was added to give an initial 0.5 M concentration, together with cobalt sulphate (which acts as a catalyst) at a concentration of 1×10^{-5} M Co^{2+} . The OTR was calculated based on the rate of sulphite consumption:

$$OTR = -\frac{1}{2} \frac{dC_{\text{SO}_3^{2-}}}{dt} \quad (1)$$

Samples were taken at 10 min intervals with the sulphite concentration being measured using iodometric titration (Eaton et al., 1995; McClure et al., 2015). Here we have measured the OTR for the antifoams at concentrations between 1×10^{-6} and 1×10^{-2} % (v/v).

When measuring the OTR, the column was filled to an initial liquid height of 500 mm. Measurements were made at superficial air velocities between 0.03 and 0.11 m s^{-1} . Reported values are the mean of at

least three repeat measurements with error bars indicating one standard deviation about the mean value. The hold-up was measured using the level-swell method as detailed elsewhere (McClure et al., 2013).

In order to quantify the effect of the various antifoams, three different foaming agents were used. The first was molasses at a concentration of 6 g L^{-1} ; chosen as it is a substrate used in many fermentation processes and is thus likely to provide a foaming system that is broadly representative of the behaviour of industrial fermentation media. In addition, SDS and Tween 80 were also used as foamants, these having the advantage of being well characterised single compounds (unlike molasses which is a poorly characterised mixture of compounds). Experiments using these compounds were performed at a superficial velocity of 0.10 m s^{-1} .

The effect of antifoam addition was quantified by measuring the height of the foam layer as a function of time, as commonly described in the literature (Kulkarni et al., 1977; Etoc et al., 2006). Here, the percentage rise is reported, calculated as:

$$\% \text{Rise} = \frac{H_{\text{foam}} - H_{\text{liquid}}}{H_{\text{liquid}}} \times 100 \quad (2)$$

where H_{foam} is the height of the foam layer and H_{liquid} is the initial liquid height (200 mm). At least three measurements were made, with reported values being the mean, with error bars indicating one standard deviation about the mean. Some portion of this height will be due to the hold-up of air bubbles in the system, so the actual 'height' being measured is that of the foam layer plus this hold-up. However, it was felt that due to the difficulty of accurately identifying the interface between the two-phase gas-liquid mixture and the foam layer above, simply using the height of the foam layer was the more realistic option.

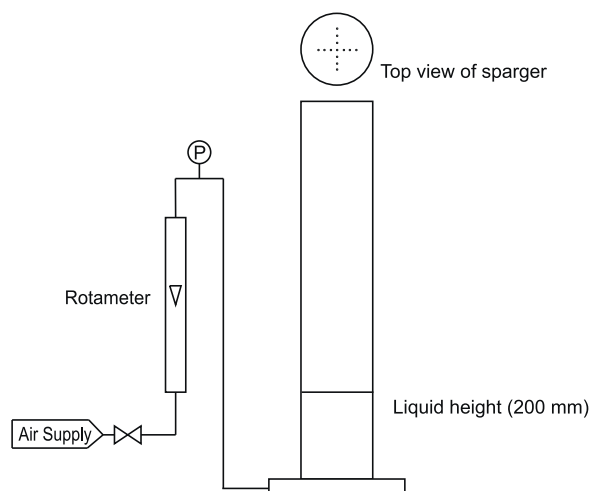


Fig. 1. Schematic diagram of the experimental bubble column system.

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