Step Up: Gas-liquid Mass Transfer Characterisation at Plant Scale using the Pressure Step Method

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1. Introduction

Characterisation of gas-liquid mass transfer is key to a number of industrial applications; in this example liquid phase hydrogenation in a stirred tank. Often these reactions are substantially mass-transfer limited. Successful prediction of plant performance and scale up relies on good knowledge of mass-transfer characteristics, as represented by the combined mass transfer constant, $k_L a$. However, prediction of mass transfer remains elusive.

For an industrial organisation in possession of a suite of reactors, experimental measurement of these gas transfer properties to build a library of known characteristics is an attractive alternative. This is moving towards plant selection in multi-product manufacturing plant based on the reactors' heat and mass transfer capability in addition to the vessel volume [1]. This presentation will demonstrate that this can be achieved using a modified pressure step methodology applied at production scale.

Numerous correlations have been proposed, with an emphasis towards lab scale equipment [2]. However, many authors also report the failure of these correlations [3]. Alternatively, some authors propose a CFD-derived route. These calculations are complex and time consuming. They still require some empirical correlations in order to either convert CFD flow-fields to usable $k_L a$ predictions or to adequately model the behavior of bubbles [4].

2. Methods

The method rests on the classic pressure step experiment, as well described by Teramoto and coworkers [5]. For this method, solvent and gas are equilibrated at a known pressure. Agitation is then ceased and the pressure increased. When the desired pressure is attained agitation is resumed. The resulting rate of pressure decline as the gas dissolves in the liquid is related to the rate of mass transfer. The measured rate of pressure change in the vessel can be used to estimate $k_L a$ and solubility, using the formula [6]:

$$\frac{dC_{L,g}}{dt} = k_L a \cdot \left(P \cdot H - C_{L,g} \right) \tag{1}$$

Where $C_{L,g}$ is the concentration of gas dissolved in the solvent, P, is the pressure and H is the Henry's coefficient for the solvent. Teramoto et al [5] in 1974 advocated a graphical route based on the analytical integral of Equation (1). Nowadays a numerical solution is more appropriate. In this study the both $K_L a$ and H were adjustable parameters in the equation fitting.

For the present study, this methodology was applied to a single 1.2 m^3 (TT = 1533 mm. D=900 mm) vessel, with a normal nominal fill level of 0.7 m^3, on a manufacturing plant using two different agitators; a Rushton Disc (RDT) with a draft tube and a twin down-pumping pitched-blade turbine (PBT) without draft tube. Both agitators rely on induced draft to drive to provide gas-liquid contacting. Three different charge volumes of water and acetic acid were also explored: 0.38, 0.7 and 0.8 m^3. The gas phase in all cases was hydrogen.

However, In the trial runs, it was found that at plant scale even very small losses of gas from the vessel (e.g. through control valves or flanges) caused pressure changes of the same order of magnitude as that of dissolution. It was thus necessary to account for this additional pressure loss term in the data analysis to obtain a better estimate of the mass transfer rate and coefficient. This was addressed by explicitly modelling this loss as a choked flow to atmosphere of unknown size [7].

$$G = P \cdot \sqrt{\left(\frac{2}{\gamma+1}\right)^{\frac{\gamma+1}{\gamma-1}} \cdot \left(\frac{\gamma M_w}{RT}\right)} \tag{2}$$

Non-linear least squares and the DDAPLUS integrator were used in Athena Visual Studio™ to solve and estimate the unknown parameters of the model.

3. Results and discussion

The unknown gas loss was separately modelled and estimated as being equivalent to that through a circle of approximately 200 µm over the 1.2 m³ volume vessel. Nevertheless, this represents between 50% and 100% of the pressure change measured. This illustrates the both implausibility of achieving total leak-tightness at plant scale and the necessity of explicitly modelling this effect.

The analysis of the experimental data was able to estimate the unknown parameters in all cases where mass transfer was detected. The quality of fit was assessed based on residual trends and the confidence intervals of estimated parameters, which were acceptable. The RDT and draft tube design was found to stall at low rotational speeds, giving no mass transfer at all. In contrast the PBT produced a measurable mass transfer at $Fr > 0.29$.

For those cases with significant mass transfer ($k_L a > 0.01\ s^{-1}$), the estimated Henry's law coefficient came close to that reported in the literature (e.g. for water $8.01 \times 10^{-4} \pm 0.2\%$ mol/kg.bar estimated compared to 8.29×10^{-4} mol/kg.bar [6])

No significant difference was found in $k_L a$ between the solvents; the Henry's Law coefficient was able to completely capture the change in solubility. However, the volume of solvent charged did result in significant changes in the performance of the PBT.

Each trial took about 5 minutes to complete. Including time to purge, charge and pressure the vessel, it was still possible to run 5 in a day, which could easily be improved with practice. This would be sufficient to profile a vessel with a known solvent at different agitation and charge levels.

Figure 1. Estimated $k_L a$ from experiment on the two agitators at different rotational speeds

4. Conclusions

The pressure step methodology can successfully be applied at plant scale, provided the unique pitfalls which arise from the scale and complexity of industrial plant is accounted for. This methodology is simple and fast to apply, making it suitable for building a profile of existing equipment. Knowledge of the mass transport characteristics of existing equipment enables businesses to confidently transfer production between equipment, without repeated experimentation.

References

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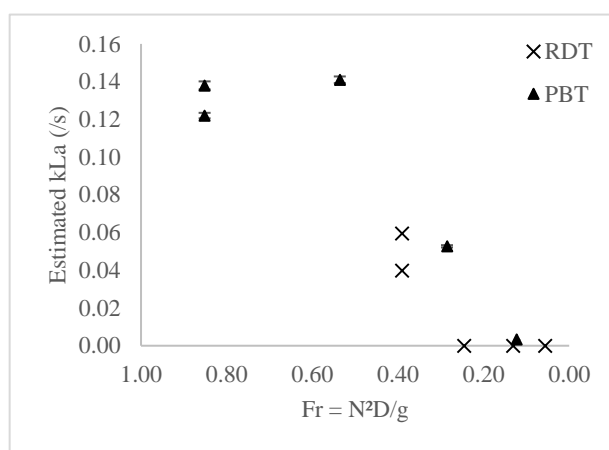[7] R.H. Perry, D.W. Green, J.O. Maloney, Eds., Perry's Chemical Engineers' Handbook, 7th ed., McGraw-Hill: New York, 1997.