Desorption of Isobutyl Acetate into Air as a Low-Cost Alternative System for the Measurement of Liquid Phase Mass Transfer Coefficients

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A study was conducted in enhancing the measurement of volumetric liquid phase mass transfer coefficients (K_La) in packed columns, by re-considering the application of conventional desorption and absorption of oxygen and carbon dioxide. The cost-effectiveness of this well-established system is hampered by reagent costs, in the form of oxygen and nitrogen, as well as plant footprint requirements. Therefore, aqueous desorption of isobutyl acetate into air (ADIBAA) is proposed as alternative to the conventional system. This ADIBAA-method utilises continuous dosing of isobutyl acetate with on-line ultraviolet quantification. This decreases reagent costs as only the desorbed component is dosed, thereby limiting related losses. Additional benefits of the newly proposed ADIBAA-method include minimal environmental impact and short experimental evaluation times, in the order of 20-30 min.

The ADIBAA-method was experimentally verified in a 400 mm ID column with a 1.1 m bed height. FlexiRings® sizes 1.5" and 2", and Intalox® Ultra™ size A, were evaluated over liquid loadings ranging from 6 to 96 $m^3.m^{-2}.h^{-1}$ and vapour flow factors between 0.6 and 2 $kg.m^{-0.5}.s^{-1}$. Liquid phase mass transfer coefficients (K_La) ranging from 0.0032 to 0.168 s^{-1} and 0.004 to 0.02 s^{-1} were measured for the 1.5" and 2" FlexiRings®, respectively. This is in agreement with the literature, with deviations limited to *ca* 10%. The liquid phase mass transfer coefficient evaluations of the Intalox® Ultra™ size A, yielded K_La values ranging from 0.00482 to 0.0242 s^{-1}. These results confirm the manufacturer statement that modern Intalox® Ultra™ packing provides similar mass transfer efficiency to smaller, and therefore higher apparent interfacial area packing from the second and third generations. This implies comparative mass transfer efficiencies between Intalox® Ultra™ A and 1" FlexiRings®, while providing decreased pressure drop and increased hydraulic capacity.

1. Introduction

Volumetric liquid phase mass transfer coefficients are commonly used as kinetic performance metrics in the design and modelling of stripping and absorption columns (Linek *et al.*, 1998). Related kinetic parameters are conventionally evaluated through the absorption or desorption of sparingly soluble vapours. The high relative volatility of the sparingly soluble liquid solutes result in negligible vapour phase resistance, thereby isolating the liquid resistive component.

The aforementioned experimental approach is well-established for both oxygen and carbon dioxide as sparingly soluble gasses (Rejl *et al.*, 2009). The conventional approach, however, opts for an indirect evaluation strategy, using fresh vapour reagents on a once-through basis (Hoffmann *et al.*, 2007). By doing so, significant vapour volumes are used to induce a ppm-level composition change within the liquid body. This amounts to sizable vapour wastage, since the excess vapour is expelled into the atmosphere.

Addressing the shortcomings of the conventional method, an alternative is proposed, stripping volatile organic compounds (VOC's) from an aqueous solution using air as stripping gas. This paper consequently proposes the aqueous desorption of isobutyl acetate using air (ADIBAA-method), for volumetric liquid phase mass transfer coefficient evaluations. The rationale is based on literature (Linek *et al.*, 1998) suggesting comparable VOC liquid phase mass transfer results to that of O_2 and CO_2, as the interfacial transport mechanism remains constant irrespective of component and direction. The aforementioned was validated by Linek *et al.* (1998)

and Wang *et al.* (2012) on the desorption of cyclic and halogenated hydrocarbons. These systems were used to generate stripping data for industrially applicable chemicals but introduce notable health and environmental risks as the solutes are both carcinogenic and bio-accumulating. The focus of this paper is the development of an accelerated, low-cost performance characterisation tool for pilot scale evaluation. The proposed ADIBAA-method consequently aims to reduce**:**

a) Excessive vapour reagent usage by replacing the sparingly soluble gas with a solute that remains liquid at room temperature, while using ambient air as the stripping gas;
b) Health risks through particular solute sections that exclude carcinogens and bioaccumulants; and
c) Plant footprint and costs through the use of a liquid circulation design.

1.1 Method Development- ADIBAA

The aqueous absorption or desorption of solutes with high Henry's volatility constants conventionally exhibit liquid phase mass transfer limiting behaviour (Cussler, 1984). Little quantitative data are, however, available in defining the transitional Henry's volatility constant at which the vapour phase resistance is negligible. The solute selection process for this paper was therefore based on a regression model of literature-defined, liquid phase mass transfer limiting systems. A systematic approach was developed using the Onda *et al.* (1968) correlations for the prediction of the ratio between vapour and liquid phase mass transfer coefficients in packed columns (k_G/k_L). A mathematical relationship, derived from the resistance analogy (Eq1) of mass transfer (Cussler, 1984), was employed in relating the mass transfer coefficient to a fraction of liquid resistance. The relationship is provided in Eq2.

$$\frac{1}{K_{OL}} = \frac{1}{k_L} + \frac{1}{k_G . H_c} = R_{Total} = R_{gas} + R_{Liquid} \tag{1}$$

$$\frac{R_{Liquid}}{R_{Total}} = \frac{100}{1 + \dfrac{1}{\left(\dfrac{k_G}{k_L}.H_c\right)}} \tag{2}$$

The Onda *et al.* (1968) correlations were chosen in accordance with the results presented by Rejl *et al.*(2009), suggesting agreement in K_La values when compared to Sahay & Sharama (1973), Billet & Schultes (1999) and Hoffmann *et al.* (2007) on both 1" and 2 " metal Pall Rings. Comparison of the volumetric vapour phase mass transfer coefficients illustrated an under-prediction of between 100-200% with the Onda *et al.* (1968) correlations compared to the aforementioned literature sources (with the exception of Billet & Schultes, 1999). This underprediction, however, acts as an included safety buffer, increasing the ratio of the coefficient (k_G/k_L) and subsequently the transitional Henry's volatility constant (Eq2).

Regression Inputs– Calculating k_G/k_L

- Hydrodynamic data were chosen at both the upper and lower limits of packed column operability (6 - 120 $m^3.m^{-2}.h^{-1}$, Fs>0.5) to provide boundaries for the regression.
- Diffusion coefficients were collected either from their relevant literature sources (Linek *et al.*, 1998), (Wang *et al.*, 2012) or the group contribution models in Perry's Chemical Engineers' (Green & Perry, 2007). The required parameters were approximated using the DIPPR (Design Institute for Physical Properties, 2005) database.
- The training data of experimentally validated liquid phase mass transfer limited systems were taken from Linek *et al.* (1998), Wang *et al.* (2012) and Rejl *et al.* (2009).

Regression Products

The Onda *et al.* (1968) correlations yielded a minimum ratio of vapour to liquid mass transfer coefficients (k_G/k_L) equal to 1307. This was found at the upper and lower boundaries of the respective liquid and vapour loadings for the desorption of dichlorobromomethane with air as the stripping gas (Linek *et al.*, 1998). Solving the relationship in Eq2 for a 95% confidence interval (R_{Liquid} / R_{Total} = 95) and k_G/k_L = 1307, provided the limiting Henry's volatility constant, above which desorption operations are approximated in excess of 95% liquid phase mass transfer limited. The transitional Henry's volatility constant was consequently calculated as 0.0142 (Dimensionless with respects to concentration) or $3.55 \cdot 10^{-4}$ atm.m^3.mol^{-1}.

1.2 Solute Selection

The solute selection process considered volatile organics above the transitional Henry's volatility constant ($H_{pc} \geq 3.55 \cdot 10^{-4}$ atm.m^3.mol^{-1}) and evaluated the solutes based on **a)** quantification technique**, b)**

environmental and health Impact, **c)** cost and **d)** ease of use. Based on the outlined criteria, a room temperature liquid was chosen for desorption with air, operated within a recycling liquid loop. Regarding quantification, UV-VIS spectrophotometry was chosen for the ADIBAA-method due to its fast, simplistic and cost-effective analysis. The quantification technique is sufficiently accurate, cost-effective and offers on-line sampling capabilities.

Isobutyl acetate was chosen for the ADIBAA-method, as it adequately satisfied the presented criteria. The solute shows no evidence of cariogenic or bio-accumulating effects with vapour phase OSHA PEL and CAL/OSHA PEL limits of 150ppm TWA (CDC. 2015) while having an experimentally verified Henry's volatility constant equal to $4.55 \cdot 10^{-4}$ atm.m^3.mol^{-1} (Abraham *et al.*, 2001). An atmospheric photochemical degradation half-life of 6 days is presented in literature (Howard, 1993), with aqueous hydrolysis half-lives of 3.1 years, 114 days and 11.4 days at 20°C with pH values of 7,8 and 9, respectively. The combination of biodegradability data with the lower flammability limits of 1.7v/v% (CDC. 2015) consequently motivates the choice of this solute. Accordingly, the solute is highly biodegradable when vaporised, but offers acceptable stability within the aqueous phase.

2. Experimental Setup

A two-part column was used for the acquisition of the experimental data. A schematic of the experimental setup is presented in Figure 1. The bottom section consisted of a 1 m length, 200 mm diameter Schott column, filled with 2.5" FlexiRings®. This section circulated potable water through two distributors, both above and below the packing, acting as a practical pre-treatment step to increase the humidity of the vapour entering the stripping section (top section). This was included to mitigate the effects of water vaporisation on the stripping experiments. Pressure readings above and below this section were continuously taken to illustrate any fluctuations in the flow of vapour.
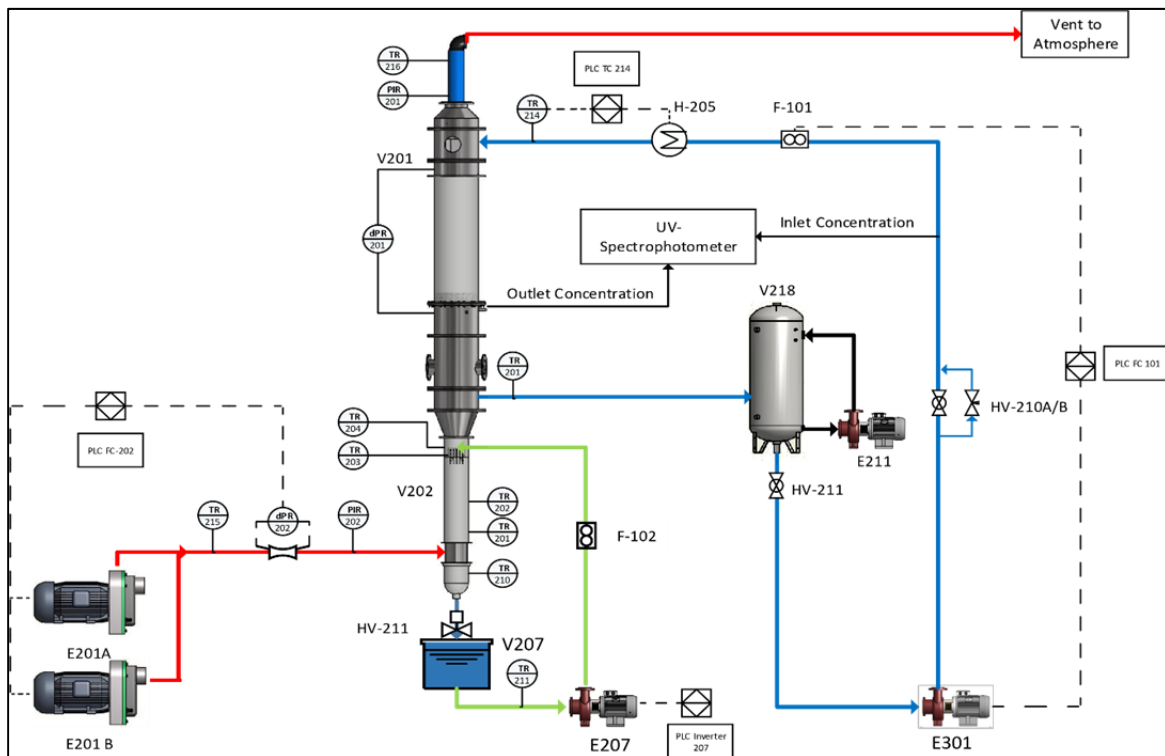

Figure 1: Packed Column Experimental Setup.

The stripping section was comprised of a single 1.1 m, 400 mm diameter, stainless spool piece. A liquid distributor, previously validated by Lamprecht (2010), was used. The distributor uses 19 pipes at a drip point density of 157 m^{-2}. The recirculating liquid loop of the stripping section was equipped with both flow and temperature control and liquid composition samples (UV-Spectrophotometer) were taken at 1-second intervals both at the inlet and directly below the packing. The inlet isobutyl acetate composition was kept constant at 400 ppm, through composition controlled dosing within an enclosed 200-litre sump. Isobutyl acetate compositions directly below the packing ranged from 80-200ppm. A UV-VIS spectrophotometer from PG

Instruments was used to quantify the composition of the liquid phase at the inlet and outlet of the stripping spool piece. The instrument offered variable spectral bandwidth with a wavelength accuracy of *ca* 0.3 nm and reproducibility of 0.2 nm. The spectrophotometer was fitted with an aftermarket eight cell changer and dual Hanna quartz flow cells for continuous measurement. The cells offered a 10 mm path length and 550 µl sampling volume. All ultraviolet absorbance were taken at 210 nm. A dual dosing pump system, operating at 100 ml/min, was used to continually refresh the liquid sampled in the flow cells. This translated to a refreshment time of 0.33 seconds, inhibiting contaminant accumulation in the quartz flow cells.

2.1 Experimental Evaluation Times

A 5-minute experimental evaluation time (translating to 300 independent data points) was used, with an additional 15-25 minutes awarded for steady-state stabilisation. The recirculation design and continual dosing mitigate the intermittent experimental downtimes that conventionally plague K_La evaluations. These downtimes are ordinarily incurred during the resaturation of the aqueous phase.

2.2 Composition Error Analysis

The absolute instrument error was quoted by the manufacturer to be within 0.3 nm and 0.002 A. This was neutralised, as a single measurement unit was used for both inlet and outlet quantification. The error was therefore limited to the instrument repeatability. The manufacturer wavelength reproducibility was quoted at 0.2 nm with photometric reproducibility amounting to 0.001 A. Spectral analysis for 400 ppm isobutyl acetate illustrated a maximum error of $2.84.10^{-4}$ within the band of 210 ± 0.2 nm. Summation consequently yielded a $1.284.10^{-3}$ A or 7 ppm error. This translates to a maximum deviation of 2% in K_La values.

3. Results

The experimental setup and ADIBAA-method were validated through comparison with four independent literature models. The models were regressed on O_2 and CO_2 absorption, as well as indirect evaluation from constant reflux data. The experimental validation was limited to the preloading range, as Rejl *et al.* (2009) suggested a consensus among literature sources within this band. Due to limited data on modern packing, verification was done on 2" FlexiRings®. For direct comparison, the models were translated to their isobutyl acetate equivalent, using penetration theory (Higbie, 1935). This approach was motivated by Linek *et al.* (1998) in producing K_La values within 10% of the experimental. The results of the verification experiments are presented in Figure 2.
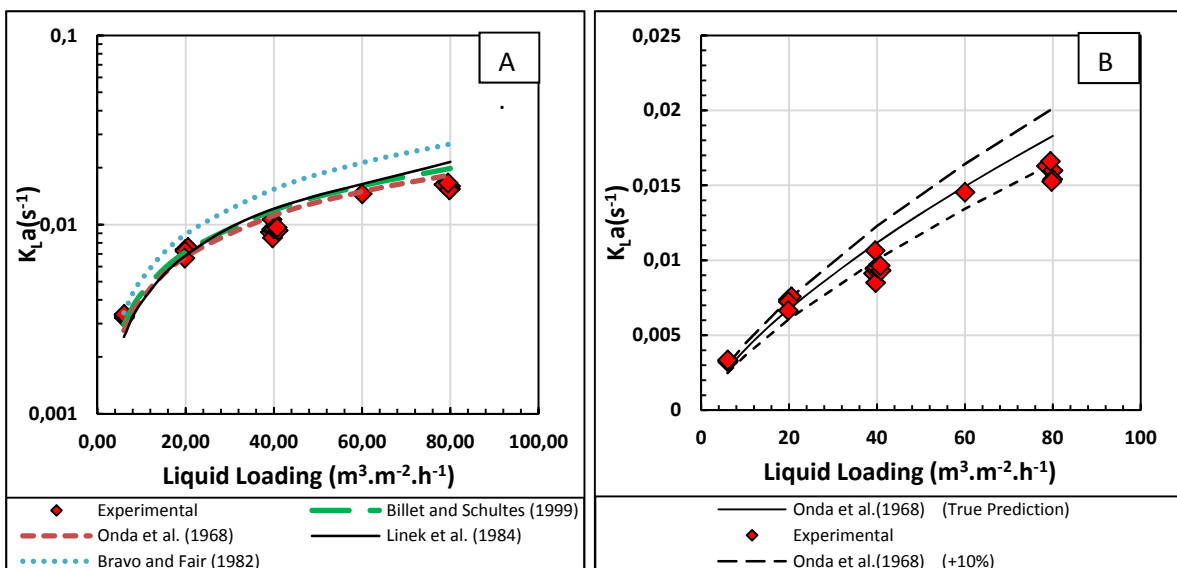

*Figure 2: Packed column experimental setup and method verification through **A)** comparison with literature sources and **B)** a deviation analysis of the experimental data and the Onda et al. (1968) predictions.*

The experimental setup and ADIBAA-method provided satisfactory replication of literature models with the exception of a slight curvature difference. This is attributed to the use of penetration theory (Higbie, *1935),* where high liquid loadings are expected to produce increased interfacial turbulence and renewal, contradicting the static phase assumption of the theory. The ADIBAA-method of liquid phase mass transfer coefficient

evaluation was further assessed through comparison of 1.5" and 2" FlexiRing®, presented in Figure 3. The results were found to be in agreement with literature sources (Linek *et al.*, 1984) regarding the relative influence of the liquid load, reflecting independence from packing size. This is in agreement with Linek *et al.* (1984) noting the constant influence of liquid loadings (power relationship 0.7-0.8) on Pall Rings, both 1" and 2". The numerical value of the relevant exponent, however, is the subject of debate, as Rejl *et al.* (2009) noted the effects of axial dispersion related to Linek *et al.*'s (1984) use of a 290 mm ID column. A maximum deviation ranging from 30% (Rejl *et al.*, 2009) at low liquid loadings to negligible at high liquid loadings is consequently given as motivation for the variation in exponent values.
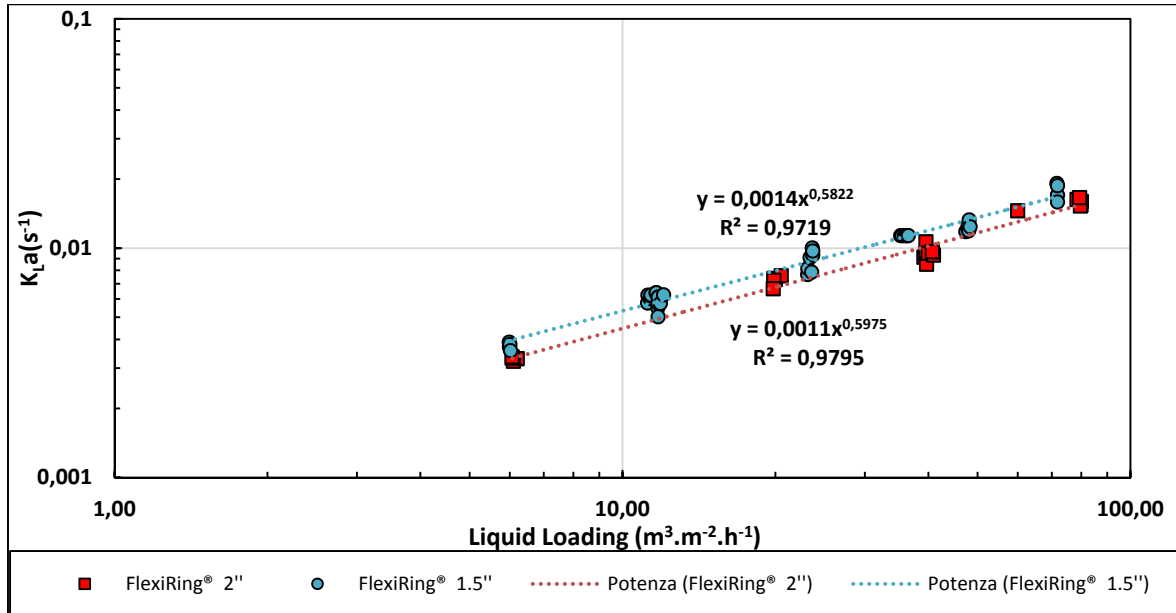

Figure 3: Volumetric Liquid Phase Mass Transfer Coefficients for FlexiRing®; 1.5 " vs 2".
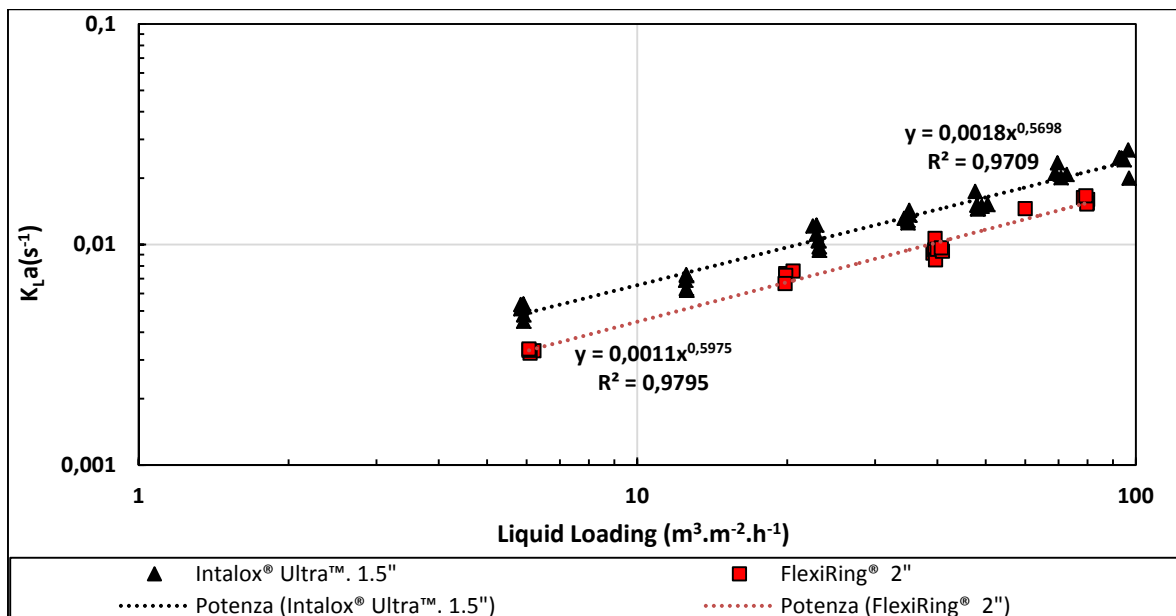

Figure 4: Volumetric Liquid Phase Mass Transfer Coefficients for Intalox® Ultra™ A (1.5" effective size) Packing vs 2" FlexiRing®.

Based on the K_La results across the pre-loading range (Figure 3), a 27% performance increase was recorded between the 1.5" and 2" FlexiRing®. This is attributed to the increased effective interfacial area, at the

expense of additional pressure drop (Lamprecht, 2010). With the modern advances in packing design, pressure drop trade-offs are mitigated through increased open area. The relevant advances were investigated using the ADIBAA-method on Intalox® Ultra™ *A* (with a 1.5" effective size) and 1.5" FlexiRings®. The Intalox® Ultra™ *A* experimental data is presented in Figure 4, compared to 2" FlexiRings®. This was done to provide better visual representation. A performance increase of 28% was subsequently recorded for the Intalox® Ultra™ A, compared to the 1.5" FlexiRings®. The performance of the Intalox® Ultra™ A consequently resembles that of 1" Pall Rings (Linek *et al.*, 1984) while producing greatly reduced pressure-drop compared to the 1.5" FlexiRings® (Lamprecht, 2010). The ADIBAA-method, therefore, confirms the manufacturer statements regarding the packing performance.

4. Conclusion

Aqueous desorption of isobutyl acetate with air (ADIBAA) is proposed as an alternative, cost-effective and simplistic method for K_La quantification. The ADIBAA-method improves upon currently accepted systems through decreased reagent costs, replacing the gaseous solute with a liquid alternative. Additional benefits include reduced plant footprint and costs, incorporating cost-effective on-line UV-spectrophotometry with liquid recirculation and continual dosing. The proposed combination of the ADIBAA-method and the experimental setup decreases evaluation times and limits downtime. The ADIBAA-method exhibits robustness with regards to composition control and system temperature, with adequate sensitivity to measure and identify efficiency differences between second and fourth generation random packing. It is therefore considered a viable alternative to the more cumbersome conventional evaluation techniques, and it shows good promise.

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