CHEMICAL ENGINEERING TRANSACTIONS
VOL. 117, 2025
A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.cetjournal.it
Guest Editors: Fabrizio Bezzo, Flavio Manenti, Gabriele Pannocchia, Almerinda di Benedetto

ISBN 979-12-81206-17-5; **ISSN** 2283-9216
DOI: 10.3303/CET25117150

Impact of Hydrophobic Surfaces on Mass Transfer in Structured Packings

Pietro Giustacori[a], Sara Marchini[b], Elisabetta Brunazzi[a, *], Uwe Hampel[c, d], Markus Schubert[b]

[a]Dipartimento di Ingegneria Civile e Industriale, Università di Pisa, Largo Lucio Lazzarino 2, Pisa, 56122, Italy
[b]Chair of Chemical Process Engineering, Technische Universität Dresden, Dresden, 01062, Germany
[c]Chair of Imaging Techniques in Energy and Process Engineering, Technische Universität Dresden, Dresden, 01062, Germany
[d]Institute of Fluid Dynamics, Helmholtz-Zentrum Dresden-Rossendorf, Dresden, 01328, Germany
elisabetta.brunazzi@unipi.it

This study investigates a potential alternative to traditional film flow in structured packings operating at low liquid loads, aiming to improve mass transfer performance by increasing the gas-liquid interfacial area. The potential of small droplet flow, which theoretically offers a significantly higher interfacial area compared to film flow, was investigated. The water affinity of the structured packing surface was modified by applying self-assembled monolayer (SAM) coatings. Contact angles, droplet behavior and coalescence tendencies were investigated on smooth, corrugated and embossed metal sheets to identify the best combination of SAM system and coating process. The mass transfer performance of SAM-coated packings was compared to standard packings by stripping isobutyl acetate with air. These tests showed that the SAM coated packings tested had lower liquid holdup and therefore lower mass transfer efficiency compared to uncoated packings. However, the study provides a valuable methodology and framework for evaluating the performance of other structured packing surface treatments.

1. Introduction

Thermal separations are the most widely used processes for separating and purifying mixtures in the chemical industry. These operations are usually carried out in columns where the liquid and gas phases are brought into contact. Inside the column, various elements promote the contact between the two phases. In recent years there has been significant development of structured packings, and many of the newly built columns now use this technology (Spiegel and Meier, 2003). In addition, structured packings have been used extensively to revamp random packed and tray columns (Shiveler et al., 2007). The purpose of structured packings is to provide a large contact area while minimizing pressure drop. For this reason, they are also widely used in vacuum operations where pressure drop must be minimized. Typically, structured packings operate in film flow, where the liquid, at best, covers the entire surface of the element to utilize all the available geometric area (Szulczewska et al., 2003). However, maldistribution within the packing and preferential paths usually prevents perfect wetting (Fitz et al., 1999). Furthermore, in the case of film flow, the interfacial area cannot exceed the geometric area provided by the packing.
Flow regimes other than film flow could potentially increase the interfacial area available for mass transfer, an even more important aspect for applications that require low liquid loadings where film flow and full wetting is also difficult to establish. Droplet flow is one such regime that could achieve this goal. In the extreme case of a spherical droplet contacting the packing at a single point, the interfacial area is nearly five times greater than for film flow, considering the same liquid volume.
The possibility of increasing the mass transfer performance of structured packings using hydrophobic coatings was investigated in this study. To induce changes in flow regimes, the surface of the packing elements was systematically modified to alter their interaction with the liquid phase. Specifically, these modifications were

Paper Received: 3 December 2024; Revised: 30 March 2025; Accepted: 22 April 2025
Please cite this article as: Giustacori P., Marchini S., Brunazzi E., Hampel U., Schubert M., 2025, Impact of Hydrophobic Surfaces on Mass Transfer in Structured Packings, Chemical Engineering Transactions, 117, 895-900 DOI:10.3303/CET25117150

designed to increase the liquid contact angle on the surface, thereby enhancing the hydrophobic properties of the material. By increasing surface hydrophobicity, the modifications promote film instability and the formation of discrete droplets on the surface. Self-assembled monolayers (SAMs) were selected for the surface modification to implement these flow destabilizations. SAMs offer a simple, yet highly effective method of tailoring surface properties, providing robust means of achieving desired contact angles. Their ease of application, combined with their ability to produce uniform and reproducible hydrophobic coatings, makes them an ideal approach for this study (Harm et al., 2002).

2. Materials and methods

2.1 Surface wettability modification

Samples were obtained from AISI 316 steel sheets (0.1 mm thick) used in the construction of Montz structured packings. The samples were first cleaned with deionized water and degreased with ethanol, dried with compressed air and then immersed in a chemical etching bath for half an hour. To enhance the effect of the chemical bath and to homogenize the concentration, the etching was performed in an ultrasonic cleaner. After the chemical bath, the samples were rinsed with deionized water and dried with compressed air. The samples were then immersed in a solution containing 1 mmol of SAM molecules for about 5 minutes at 60 °C. After this last immersion, the samples were rinsed with deionized water, dried with compressed air and stored in a closed container to avoid contact with dust and to allow self-organization of the SAM molecules. Self-organization consists of the reorganization of molecules adsorbed on the surface to maximize interactions with the substrate and to align their functional groups to interact with the substrate while their tail groups extend outward, imparting hydrophobic properties. A detailed description of the coating process can be found in Harm et al. (2002).
The wettability characterization of the surfaces was performed by determining the contact angles of ultrapure water droplets on the different surfaces analyzed. This analysis was performed using a Krüss DSA100S goniometer. The procedure for measuring contact angles using the goniometer sessile drop technique was the same as that typically used in the literature (e.g., Kwok et al., 1997). Static contact angle (CA) values were extracted using the ADVANCE software associated with the goniometer; while advancing and receding contact angles (ACA and RCA) were extracted from the video by the goniometer software and using a custom Python script.
Two different molecules were considered for the coating of steel samples: n-dodecylphosphonic acid (DPA) and heptadecafluorodecylphosphonic acid (17FPA). The tested systems have the advantage of forming SAMs at low concentrations and do not require complicated coating procedures. In addition, at the used concentrations, SAMs solutions are not classified as toxic or carcinogenic. Chemical etching of surfaces can be performed with different solutions. In the present study, two different etching temperatures and etching solutions containing 10 % of nitric acid (HNO_3) in water alone or in mixtures with 10 % of ferric chloride ($FeCl_3$) or 10 % hydrogen peroxide (H_2O_2) were considered (all percentages are by weight). The following procedure was chosen as the reference case: surface etching with HNO_3 solution for 5 minutes at room temperature, followed by coating with DPA for 2 minutes at 40 °C. All tests were compared with this system.

2.2 Fluid dynamic characterization

The dynamic of the liquid flows on the coated metal surfaces was investigated with a particular focus on droplet stability. An inclined plate with variable inclination was constructed to support the samples and to test typical contact angles of commercially available structured packings. Flat, embossed, and corrugated embossed sheets were used for these experiments. The sheets were placed on the inclined stand and liquid was supplied from above through three needles of approximately 1.8 mm OD. The supply system consists of a reservoir, a pump, and a valve to control the flow rate. A camera was used to capture the liquid patterns on the sheets for different flow rates. To obtain clearer and more distinct images of the liquid flow patterns on the sheets, a dye was used. Specifically, an aqueous solution of 0.02 g/L methylene blue was used. The physical properties of the dyed solution (i.e., viscosity, surface tension, density, etc.) remained identical to those of pure water.

2.3 Structured packing characterization

The performance of coated and uncoated packing elements was compared. A packed column with three Montz B1-500 structured packing elements (i.e. consisting of corrugated embossed metal sheets placed side by side) was used. The aim of these experiments was to explore the main differences between coated and uncoated packings, particularly in terms of holdup and mass transfer performance.
The experimental setup consists mainly of a DN 100 column with gas and liquid auxiliary circuits. The column is composed of several PMMA tube segments screwed together with PMMA flanges. The lower section is a bubble column that allows partial pre-saturation of the pressurized dry air entering the system; to prevent liquid entrainment, a demister is placed above this section. The upper part of the column is the actual test apparatus,

and this section is equipped with three 100 mm high structured packing elements. The overlapping elements are rotated 90° with respect to each other to allow liquid and vapor redistribution at the interfaces between the elements. A liquid distributor consisting of 36 1.8 mm OD needles is located at the top of the column. The number of irrigation points per square meter is close to the guidelines for ideal packing wetting (Green and Perry, 2007). In the system, the liquid is delivered at volumetric flow rates ranging from 0.25 to 2.0 L/min, corresponding to liquid loads (B) of 2 to 15 m^3/m^2h. In this work, a single gas flow rate of 200 SLPM was chosen, which corresponds to a gas superficial velocity ($u_{s,G}$) of 0.45 m/s, ensuring operation below the gas loading point. The focus was on understanding how the coating affects the behavior of the liquid phase. Figure 1 shows the process diagram of the mini-plant (left) and a picture of the setup (right); a more detailed description of experimental procedures follows.

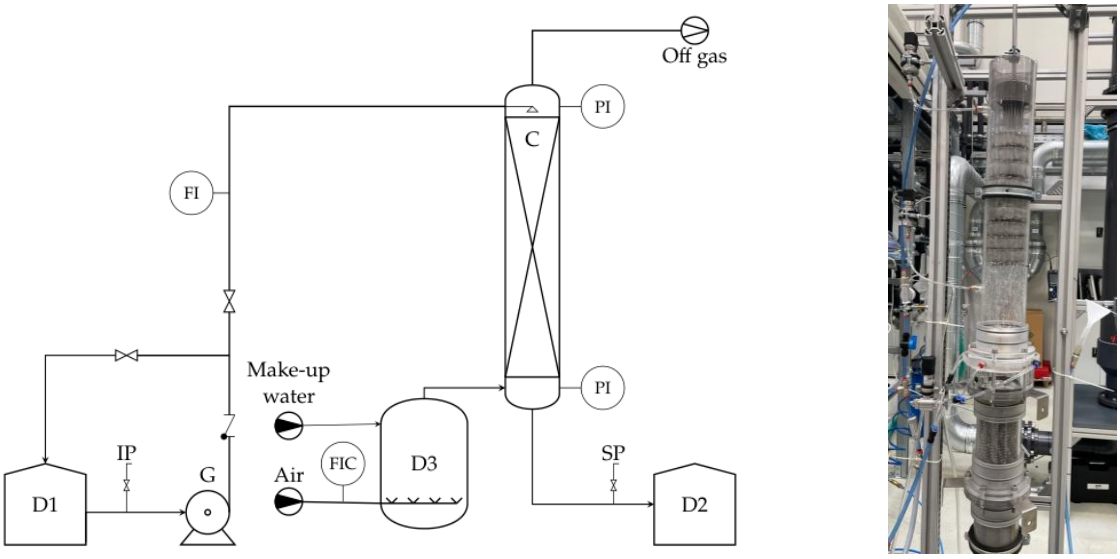

Figure 1: Experimental test rig details (left: PFD of the test rig, right: test rig).

The liquid circuit is operated by a centrifugal pump (G) which pumps the liquid from a buffer tank (D1) to the liquid distributor. The liquid leaving the packed bed is collected by a chimney tray element and sent to the outlet tank (D2), the outlet line is equipped with a sampling point (SP). The gas supply is provided by a compressed air line. The gas flow is controlled by a mass flow controller with a range of up to 250 SLPM with an accuracy of 0.8%. Air is introduced at the bottom of the pre-saturation section and, after bubbling through a batch of water, enters directly into the stripping section. After passing through the column, the gas is vented to the atmosphere at top of the column. An exhaust hood is placed above the column to collect gaseous emissions.
For mass transfer experiments, a 1000 ppm_v volatile organic compound (VOC) water solution must be prepared. To prepare the solution, the pump is used as a mixing device. Two valves allow switching between preparation and experimental modes. Pure VOC is injected at the pump inlet via the injection point (IP), and the liquid circulates to and from the tank. Liquid exact concentration was checked offline by UV spectroscopy. During the experiments, the gas and liquid temperatures above the packed bed and the gas humidity after the bubble column were measured at regular intervals.

Holdup measurement

For the sake of simplicity, the holdup determination in the present work was made by measuring the amount of liquid collected at the bottom of the column when the liquid inlet and outlet were closed, as used by Aferka et al. (2011). Liquid level changes were measured as pressure changes using a differential pressure sensor. The acquired pressure signals were then converted first to water column heights and then to liquid volumes by knowing the area of the liquid collection section. Dividing the collected water by the volume occupied by the packing elements, the holdup was derived. First, the packing was pre-wetted; after reaching a steady state at a given flow rate, the liquid inlet and outlet valves were closed simultaneously and the liquid was allowed to drain. The drain time was ten minutes for each test, a compromise between collecting most of the liquid from the packing and keeping the test times short. After the valves were closed, the water supply was immediately shut off due to the design of the distributor. At normal operating conditions of the specific experimental setup, the gas superficial velocity does not exceed 1 m/s. At this low superficial velocity, the column always operates in the preloading regime. In this regime, holdup is essentially independent from the gas velocity but is a strong

function of liquid flow rate and packing size. Therefore, for simplicity, it was decided to perform holdup measurements in the absence of countercurrent gas flow, as the effects were considered negligible.

Mass transfer tests

The present work uses air-led stripping of isobutyl acetate from an aqueous solution to measure the mass transfer performance of the structured packings. Isobutyl acetate is a colorless liquid with a fruity odor and moderate solubility in water. This test system has recently been used to measure liquid-side mass transfer coefficients in randomly packed columns by Lamprecht and Burger (2018), and to measure tray and point efficiencies in distillation columns by Marchini et al. (2021, 2023). This work represents the first application of this system for the determination of mass transfer parameters on structured packings.
An initial concentration of 1000 ppm isobutyl acetate in the liquid batch was selected based on preliminary tests. The physical properties of the resulting batch (i.e., viscosity, surface tension, density, etc.) remained identical to those of pure water. An offline UV spectrometer was used for sample analysis and data acquisition. During the experiments, solution samples were taken from the sampling point (SP) visible in Figure 2 (left). At first, mass transfer resistances were estimated for the considered physical system using the model of Brunazzi et al. (1995). It turns out that the resistance in the liquid phase is much higher than in the gas phase, so that the experimentally determined mass transfer coefficient corresponds to the liquid-side mass transfer coefficient. From the concentration values across the packed bed, the $k_L a$ values are derived as follows.

$$N = L(x_{IN} - x_{OUT}) = K_{OX} a A_C H \Delta x_{\mathrm{LM}} \quad (1)$$

As noted above, the gas phase resistance was considered negligible, so the total liquid-side coefficient is equal to the single liquid phase coefficient.

$$k_L a = \frac{K_{OX} a}{\rho_L / MM} = \frac{1}{\rho_L / MM}\left(\frac{L}{A_C H}\frac{(x_{IN} - x_{OUT})}{\Delta x_{LM}}\right) \quad (2)$$

3. Results and discussion

3.1 Surface wettability modification

Depending on the SAM system, the etching solution giving the best results was determined. For DPA, higher contact angles were obtained using HNO_3 + $FeCl_3$ solution, while for 17FPA greater contact angles were obtained using HNO_3 + H_2O_2 solution. The effect of the temperature of the etching bath was also studied. Two cases were considered: no heating and heating at 60°C. For the DPA-based system, the combination of HNO_3 + $FeCl_3$ and heating at 60°C gave the best results, while for 17FPA, heating at 60°C did not have a significant effect on the contact angle. The contact angle results are presented in Table 1. The degradation of the contact angle by immersion in water was also analyzed. Contact angles were compared before and after immersion in water for 72 hours. The degradation of contact angles under these conditions is less than 5% for both systems. This feasibility study showed that 17FPA gave the best results in terms of contact angle and hysteresis between ACA and RCA. Therefore, it was decided to use the system consisting of 17FPA with a pre-etch treatment at room temperature with nitric acid and hydrogen peroxide solution for the subsequent coatings. Figure 2 (left) shows the contact angle obtained for the chosen combination of SAMs and etching solution.

Table 1: Static contact angles for different surface treatment combinations (RT: room temperature)

Surface treatment combination	Average CA (°)
Non coated	80.3
DPA/HNO_3 @RT	93
DPA/(HNO_3 + $FeCl_3$) @ RT	101.5
DPA/(HNO_3 + H_2O_2) @ RT	95.9
17FPA/HNO_3 @ RT	109
17FPA/(HNO_3 + $FeCl_3$) @ RT	114.7
17FPA/(HNO_3 + H_2O_2) @ RT	121.9
DPA/(HNO_3 + $FeCl_3$) @ 60°C	106.2
17FPA/(HNO_3 + H_2O_2) @ 60°C	117.3

3.2 Fluid dynamic characterization

The most significant effect of the coating on wettability occurs on smooth surfaces, where the rivulet is unstable and tends to break into droplets even at high flow rates. Embossed surfaces are more wettable, but droplets can still form at lower flow rates. As the flow rate increases, the embossing provides more stability to the rivulets

that are much narrower and taller on the coated surface compared to the uncoated one. Figure 2 (right) shows the effect of coating on the behavior of the liquid flowing over the embossed sheet. It can be seen how the coating promotes droplet formation and enhances droplets stability.

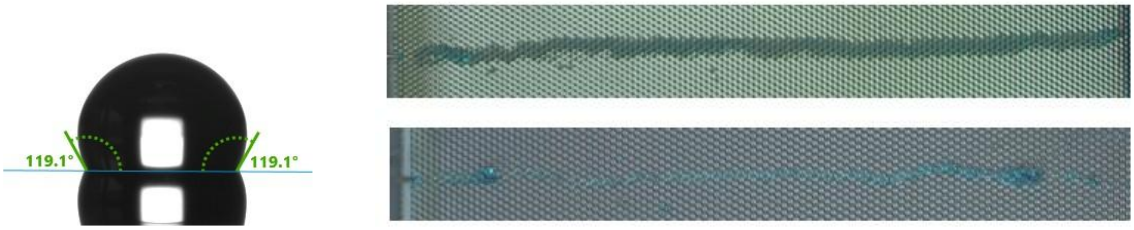

Figure 2: Feasibility study results (left: static contact angle measurement; right: Liquid behavior on embossed metal surface, top uncoated, bottom - coated).

3.3 Packing performance comparison

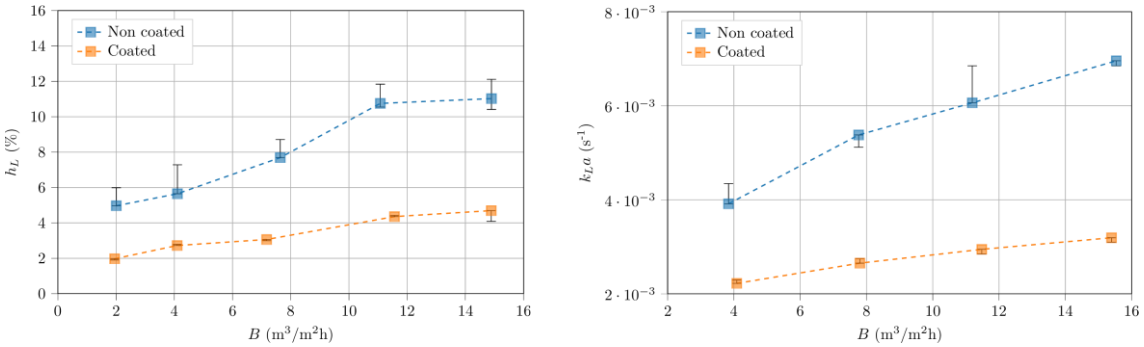

Figure 3: Comparison of experimental results for uncoated and coated structured packings (left: holdup; right: mass transfer coefficient).

Holdup results

Figure 3 (left) shows the holdup results for coated and uncoated packings. The coating significantly reduces the amount of liquid retained in the column during operation, this effect is most noticeable at high liquid flow rates. The coating reduces the wettability of the surfaces, causing the liquid to flow more rapidly through the packing, thereby reducing the amount of liquid instantly present in the packing. Over the range of liquid loads tested, the coating results in a macroscopic reduction of the holdup value by a factor of 2 to 3.

Mass transfer results

The product of the mass transfer coefficient and the specific interfacial area obtained during the experimental campaign is shown in Figure 3 (right). The results show that the mass transfer performance is degraded by the surface coating and may be partially due to the reduction in holdup. It is not yet clear whether the degradation is due to a reduction in the mass transfer coefficient or the specific interfacial area, or both. Further experiments to determine the interfacial area alone would be necessary to distinguish the effects. It should be noted that the applied liquid loading values were intentionally limited to study the effect of the hydrophobic coating at low liquid flow rates, where the packings operate at the lower limit of the nominal wetting rate.

4. Conclusions

The effects of hydrophobic coatings on liquid holdup and mass transfer in structured packings were systematically investigated. Self-assembled monolayers (SAMs) were chosen for their non-toxicity at low concentrations and ease of deposition on metal substrates. Among the tested systems, n-dodecylphosphonic acid (DPA) and heptadecafluorodecylphosphonic acid (17FPA) were evaluated, with 17FPA identified as the optimal coating due to its stability, compactness, and superior hydrophobic properties. The pre-treatment of metal surfaces using a solution of nitric acid and hydrogen peroxide at ambient temperature further enhanced the coating's effectiveness. The feasibility study demonstrated that the coated surfaces promoted droplet formation, potentially increasing the interfacial area within the packing.

To assess the impact of these coatings, an experimental packed column setup was developed, enabling direct performance comparisons between coated and uncoated packing sheets. Holdup measurements revealed that hydrophobic coatings significantly reduced liquid retention within the packing, thereby decreasing the available

liquid volume for mass transfer. Mass transfer experiments using air-led stripping of isobutyl acetate confirmed that reduced holdup led to shorter liquid residence times, ultimately lowering mass transfer efficiency.
Despite this reduction in mass transfer performance, the application of hydrophobic coating presents several practical implications. In industrial applications where minimizing holdup is advantageous, such as in processes requiring rapid phase disengagement, reduced solvent inventory, or enhanced gas flow capacity, hydrophobic coatings could be strategically employed. Additionally, in cases where fouling or corrosion due to excessive liquid retention is a concern, these coatings may help maintain long-term operational efficiency. However, further research is necessary to refine coating techniques and identify conditions where the trade-off between reduced holdup and mass transfer efficiency can be optimized for specific process requirements. Future studies should also focus on tailoring surface modifications to balance droplet formation with sufficient liquid residence time for effective mass transfer.

Nomenclature

a – specific interfacial area, m^{-1}
A_C – column cross-sectional area, m^2
B – liquid load, m^3/m^2h
H – packed bed height, m
k_L – liquid-side mass transfer coefficient, m/s
K_{OX} – overall mass transfer coefficient, $kmol/m^2s$
L – liquid molar flowrate, kmol/s
MM – molar mass, kg/kmol
N – molar flux, kmol/s
$u_{s,G}$ – gas superficial velocity, m/s
x_{IN} – liquid inlet molar fraction, -
x_{OUT} – liquid outlet molar fraction, -
Δx_{LM} – logarithmic mean driving force, -
ρ_L – liquid mass density, kg/m^3

References

Aferka S., Viva A, Brunazzi E., Marchot P, Crine M., Toye D., 2011, Tomographic measurement of liquid hold up and effective interfacial area distributions in a column packed with high performance structured packings, Chemical Engineering Science, 66, 3413-3422
Brunazzi E., Nardini G., Paglianti A., Petarca L., 1995, Interfacial area of Mellapak packing: absorption of 1,1,1-Trichloroethane by Genosorb 300, Chemical Engineering & Technology, 18, 248-255
Fitz C.W., King D.W., Kunesh J.G., 1999, Controlled Liquid Maldistribution Studies on Structured Packing, Chemical Engineering Research and Design, 77 (6), 482-486
Green, D.W., Perry R.H., Perry's Chemical Engineers' Handbook, Eighth Edition McGraw Hill professional, McGraw-Hill Education, 2007
Harm U., Bürgler R., Fürbeth W., Mangold K. M., Jüttner K., 2002, Novel protective coatings for steel based on a combination of self-assembled monolayers and conducting polymers, Macromolecular Symposia, 187 (1), 65-76
Kwok D. Y., Gietzelt T., Grundke K., Jacobasch H. J., Neumann A. W., 1997, Contact Angle Measurements by Axisymmetric Drop Shape Analysis and a Goniometer Sessile Drop Technique, Langmuir, 13 (10), 2880-2894
Lamprecht H., Burger A., 2018, Desorption of Isobutyl Acetate into Air as a Low-Cost Alternative System for the Measurement of Liquid Phase Mass Transfer Coefficients, Chemical Engineering Transactions, 69, 7-12
Marchini S., Vishwakarma V., Schubert M., Brunazzi E., Hampel U., 2021, Direct Tray and Point Efficiency Measurements Including Weeping Effects through a Convenient Add-On for Air-Water Simulators, Industrial & Engineering Chemistry Research, 60 (6), 2600–2612
Marchini S., Vishwakarma V., Schubert M., Brunazzi E., Hampel U., 2023, Effects of non-uniform weeping distributions on tray and point efficiencies, Results in Engineering, 19, 101238
Shiveler G., Solis G. S., Peña Gonzalez L. H., Bueno M. L., 2007, Retrofit of a H2S selective amine absorber using MellapakPlus structured packing, Asia-Pacific Journal of Chemical Engineering, 2 (4), 232-244
Spiegel L., Meier W., 2003, Distillation Columns with Structured Packings in the Next Decade, Chemical Engineering Research and Design, 81 (1), 39-47
Szulczewska B., Zbicinski I., Górak A., 2003, Liquid Flow on Structured Packing: CFD Simulation and Experimental Study, Chemical Engineering & Technology, 26 (5), 580-584