High Pressure CO2 Column With Structured Packing – From Concept To Successful Column Operation

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Abstract. Carbon dioxide **(**CO_2) is used in a broad application spectrum, e. g. beverage carbonation, food industry or health services. Linde has designed and supplied several CO_2 purification and liquefaction plants worldwide. Linde's standardized and modularized CO_2 plants comprise of prefabricated skids, which include piping, instrumentation, and equipment such as a preassembled random packing CO_2 Column operated at elevated pressure. For a new CO_2 plant in Mexico, a CO_2 Column was designed with structured packing for the first time. A systematic investigation was conducted, employing literature as well as in-house models and evaluating other high-pressure structured packing distillation columns, to determine the packing capacity and to predict the packing efficiency, especially under consideration of the loss of performance from the so-called hump occurrence. Finally, the CO_2 Column equipped with structured packing and applying the selected bed height was successfully put into operation, delivering liquid CO_2 product to the required purity level.

Keywords CO_2 Column, HETP Prediction, Efficiency Hump, Structured Packing

Introduction

A rising number of companies worldwide are looking for flexible solutions to reduce their CO_2 emissions. Recycling CO_2 from off-gas streams is one solution to avoid emitting the gas to the atmosphere. The benefits of CO_2 recycling are the low supply cost and the immediate availability of the gas. Liquid and gaseous CO_2 is used in a wide application spectrum, such as beverage carbonation, food industry, health services, chemical applications, and much more. Linde has engineered, supplied, and commissioned several CO_2 purification and liquefaction plants worldwide. Linde's CO_2 plants are designed to leverage the advantages of the standardization and off-site modular construction. A high degree of standardization and modularization increases quality, reduces on-site installation and commissioning time, while overall costs are reduced. All CO_2 plants comprise of prefabricated skids, which contain piping, valves, instrumentation, paint, insulation, cabling, and equipment such as preassembled scrubber and distillation columns.
In 2019, a contract was awarded to Linde for the engineering and procurement of such a modularized CO_2 purification and liquefaction plant in Mexico. The new CO_2 plant has a name plate capacity of 200 MTPD.

Figure 1 shows a simplified process flow diagram of a CO_2 purification and liquefaction plant. The feed gas is cooled down and water is separated before the gas is sent to the CO_2 compressor to increase the pressure to operating conditions. Subsequently, the compressed CO_2 gas is routed to the scrubber unit. The CO_2 raw gas is washed and cooled down in the Scrubber Column. In addition, water-soluble components are removed. Water and traces of other chemical components are further removed in the drying and adsorption unit. The dry CO_2 raw gas is sent to the rectification and liquefaction unit, which also comprises the CO_2 Column. A vent gas is leaving the column at the top. A high purity liquid CO_2 product is withdrawn from the column bottom and pumped to storage tank.

The process flow diagram of the rectification and liquefaction unit in Mexico is shown in more detail in figure 2. The CO2 raw gas coming from the drying and adsorption unit passes through the CO_2 Reboiler to generate the necessary strip gas for the CO2 Column. The CO_2 raw gas and the overhead gas, coming from the top of the CO_2 Column, are liquified in the CO_2 Condenser. The outlet stream from the CO_2 Condenser contains mainly liquid CO_2, but also non-condensable inert components, such as argon (Ar), methane (CH_4), nitrogen (N_2) and oxygen (O_2), which are separated

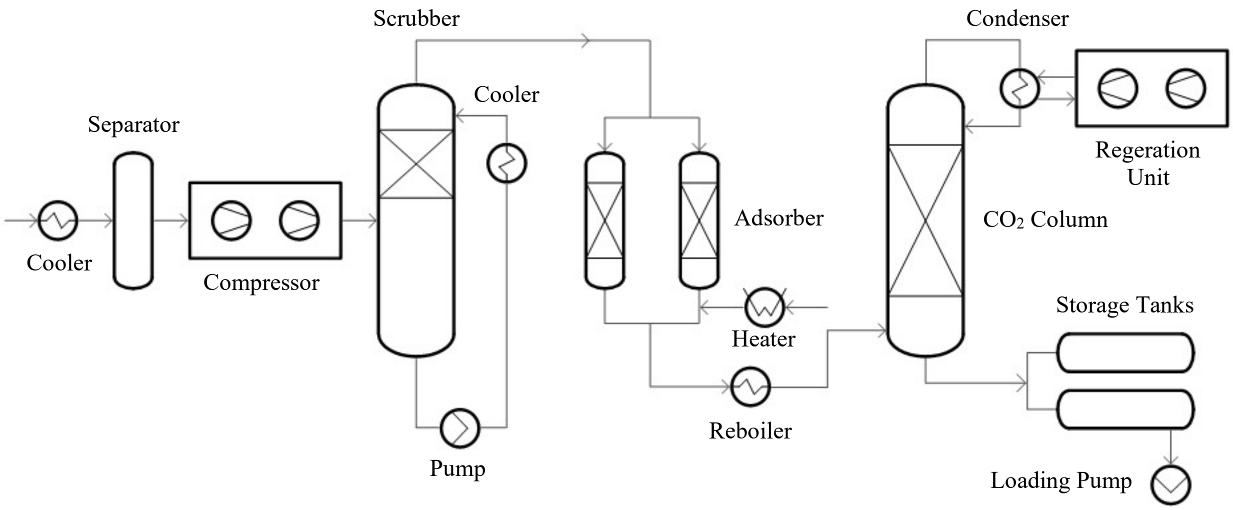

Fig. 1 Simplified process flow diagram of a Linde CO2 purification and liquefaction plant.

in the CO_2 Separator. The inert gases are sent to safe location, while the liquid CO_2 is pumped as reflux to the top of the column. In the CO_2 Column traces of components like Ar, CH_4, N_2, and O_2 are separated from the CO_2. A liquid CO_2 product with a purity level up to 99.99 vol.-% is drawn-off from the bottom of the column.

The CO_2 Column is operated at elevated pressure of around 16 bar(a) to 20 bar(a). In the past, the CO_2 Column was filled with random packing, because of the narrow column diameter, that is typically between 300 mm to 700 mm. Due to the high degree of modularization, all column internals, e. g. support plates, hold-down grids, liquid distributors and random packing are already installed at the pressure vessel manufacture's workshop. The random packing column is delivered in horizontal position to construction site, fully dressed with insulation, instrumentation and cabling. Caused by the permanent transport movement, a non-homogeneous random packing bed can occur, especially at larger column diameter, even though the rings are filled in the pressure shell in vertical position. A non-homogeneous random packing bed can lead to a deterioration of the mass transfer efficiency and capacity, caused by vapor and liquid maldistribution. Special constructive features and procedures are considered by Linde during design and installation of the random packing and the internals to prevent deterioration of packing efficiency.
Structured packings are better suited for off-site installation and the transport to construction site. The installation of structured packings in the pressure vessel manufacture's workshop and the shipment of preassembled columns, is a well-established procedure at Linde that was successfully performed in the last 30 years, e. g. in the air separation as well as in the hydrogen and synthesis gas business. However, the application of structured packings at high pressures is not recommended in the industry, because of the so-called hump phenomenon.

At elevated pressures above ~10 bar(a) and high flow parameters (>0.25) [1], a reduction of structured packing efficiency (HETP) is observed. The hump region typically starts at ~65% of flood and ends at ~90% flood [1]. Even if known for decades, the hump phenomenon is not yet fully understood and modelled. Generally, the hump phenomenon is explained in the literature by vapor and liquid back-mixing as well as by flow segregation [1] [2]. High liquid loadings at low vapor loadings can cause premature flooding of some of the structured packing's crimp channels, due to flow unevenness. Vapor is entrained and carried down by the liquid in this flooded crimp channels leading to vapor back-mixing. Likewise, high vapor loadings at high liquid loadings can promote liquid drop formation. The liquid drops are carried upwards with the ascending vapor leading to liquid back-mixing. Both, vapor, and liquid back-mixing result in the loss of structure packing efficiency and the formation of the hump occurrence.

A structured packing was installed in the CO_2 Column on client request and to benefit from its applicability for off-site installation as well as horizontal transport. At that time, efficiency data for structured packing CO_2 Columns operated at elevated pressure were not available. Hence, Linde conducted a thorough investigation to predict the column's efficiency and capacity without risk of malfunction, but also to avoid oversizing the equipment. The HETP prediction is described in more detail in the next section.

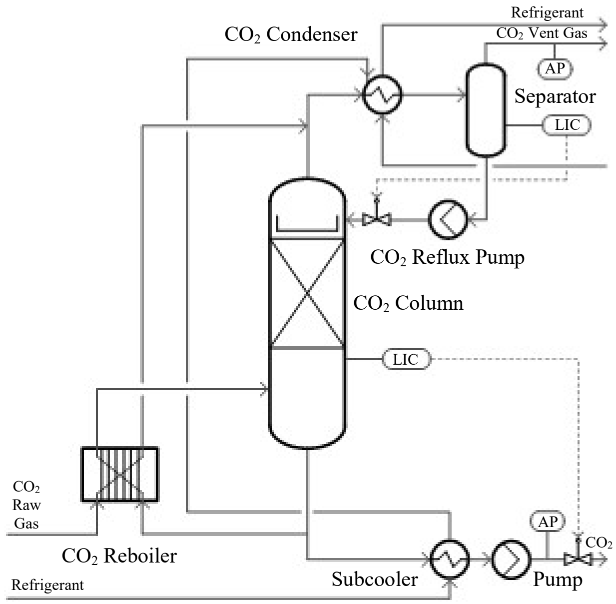

Fig. 2 Rectification and liquefaction unit of a CO2 plant in Mexico.

HETP Prediction

In general, when proven HETP data for a specific packing type are not available, the HETP values can be obtained from theoretical models, rules of thumb, and interpolation of experimental HETP data. The authors followed a comprehensive approach that comprised all three HETP prediction procedures. First, an available random packing design HETP value was converted into a structured packing HETP value. The conversion of the random packing design HETP value was done using a Linde in-house correlation, which considers e. g. the packing type, the packing surface area per unit volume, and the structured packing's crimp angle. The random packing design HETP value was successfully applied for many years. But, as typical for plant operational data, past evaluations of actual operational data from random packing CO_2 columns involved several uncertainness, due to lack of full set of measurement instruments. Thus, it was difficult to simulate the actual plant operation and to determine the actual random packing HETP value. Because of that, it is uncertain whether the applied random packing HETP is conservative or accurate.

For that reason, the random packing design HETP value was first checked against HETP values predict from different mass-transfer models and rules of thumb. A Linde in-house program was employed to predict the HETP values. The program comprises in total 12 HETP correlation for random packings and 15 HETP correlations for structured packings. The HETP prediction for many commercially available random and structured packings from various vendors is possible. Before a mass-transfer model or a rule of thumb is selected for predicting the HETP value for a new column service and a certain packing type, the reliability of the correlations is checked against HETP values derived from F.R.I. test data with similar physical properties (e. g. density difference, surface tension, viscosity) and packing geometry. Finally, four mass-transfer models and one rule of thumb, that produced the least discrepancies when compared to the F.R.I. test data, were selected for checking the random packing design HETP value of the CO_2 column. The HETP prediction was performed with the mass-transfer models from Onda et al. [3] [4], Hanley and Chen [5], F.R.I. topical report (TR) 152 [6] and Wagner et al. [7]. The rule of thumb published by Harrison and France [8] was used for predicting the random packing efficiency. All other correlations for random packing HETP prediction were excluded for the investigation, since these correlations produced large discrepancies when compared to the F.R.I. test data. For each of the selected correlations, the ratio of the predicted HETP value and the measured F.R.I. HETP values was used to obtain a design safety factor. These calculated design safety factors were multiplied with the predicted HETP values, to achieve a confidence level of 99%.

The predicted random packing HETP values are plotted against the random packing design HETP value in figure 3. As seen in figure 3, the HETP predictions from Onda et al. [3] [4], and Hanley and Chen [5] are in good agreement with the design HETP value. The HETP value obtained from the Harrison and France rule of thumb [8] has only a little discrepancy when compared with the applied design HETP value. On the other hand, the F.R.I. [6] and the Wagner et al. [7] models are deviating significantly from the design HETP value. Based on the above observations and considering the proven performance of random packing CO_2 Column, the authors concluded that the applied random packing design HETP value is accurate. Thus, the random packing design HETP value provided a sound basis for converting it into a structured packing HETP by means of Linde's in-house correlation.

The hydrodynamics that prevails in a structured packing differs from that in a random packing. For that reason, also the HETP value obtained from the conversion of the random packing design HETP value was checked against several correlations using Linde's in-house HETP prediction program. This was necessary to verify the reliability of the conversion procedure. Five mass-transfer models and one rule of thumb, that produced the least discrepancies when compared to the F.R.I. test data, were selected for checking the reliability of the converted structured packing HETP value. The HETP prediction was performed with the mass-transfer models from Rocha et al. [9] [10], Olujic et al. (Delft model) [11] [12] [13] [14], F.R.I. Handbook 2021, Hanley and Chen [5] as well as Xu et al. [15]. The rule of thumb published by Harrison and France [8], which was adapted by Kister and Larson [1] was used for predicting the structured packing efficiency. As described above design safety factors were considered to obtain predicted HETP values with a confidence level of 99%.

During conceptual design phase the decision was made to use a structured packing with a high surface area per unit volume, to obtain a bed and hence column height suitable for installation in a skid. On the one hand, since a structured packing with high specific area was selected and considering the high pressure of ~18 bar(a), the high liquid loading (flow parameter >0.2) as well as the low surface tension (<10 dyne/cm), the possibility of a hump occurrence could not be ruled out. Furthermore, empirical correlations developed by F.R.I. [2] predicted a high possibility of a hump formation caused by vapor back-mixing. On the other hand, the CO_2 Column is rather a stripping than a distillation system and having a relatively big difference in vapor and liquid density. These factors make a hump formation less likely. Finally, it was decided to take the hump effect on the structured packing efficiency into consideration, to avoid an incorrect column design.
Two correlations were suggested for predicting the HETP in the hump region. The hump HETP was calculated with the empirical correlation by F.R.I [2] and the shortcut method published by Wang et al. [16]. An unreasonably high hump HETP value was obtained from the Wang et al. [16] theoretical model. Thus, this hump HETP value was not considered for calculating the bed height. Also, F.RI.'s correlation predicted a HETP in the hump region that did not agree with F.R.I. test data for a system operated at 20.7 bar(a) having a similar packing geometry. Because of that, the elevated HETP derived from the F.RI. correlation was not considered for further column design. Instead of using the calculated hump HETPs, a different design procedure was chosen to obtain a reliable and reasonable design HETP value.

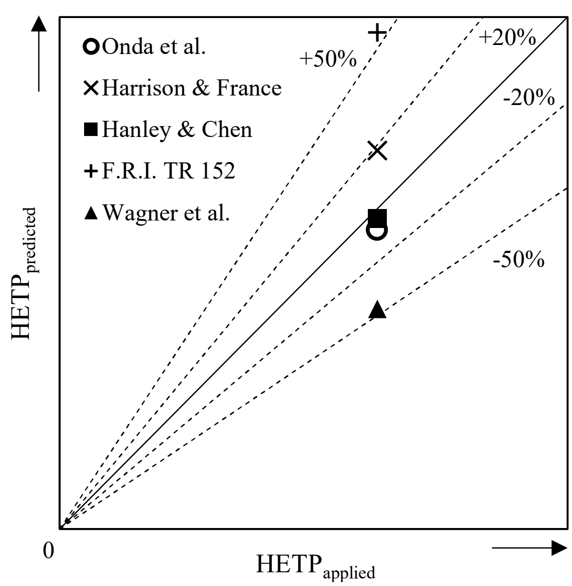

Fig. 3 Predicted random packing HETP values compared with a design HETP value used for the random packing CO2 Columns.

The predicted structured packing HETP values and the HETP value converted from the random packing CO_2 Column were multiplied with a safety factor. This safety factor was derived from Linde's experiences made with other distillation and stripping columns in the air separation as well as hydrogen and synthesis gas business, which are successfully in operation for many years. Some of these columns are operated at elevated pressure and equipped with a high specific area structured packing. In addition, the HETP in the hump region was measured and the loss of efficiency was determined by comparing with the normal design HETP value.
The safety factor was necessary to cover not the effect of possible hump occurrence, but also other factors that affect HETP and column performance. The selected structured packing type and the CO_2 system itself is not in the F.R.I. data range. Thus, the calculated safety factors for a confidence level of 99% may be incorrect, leading to underestimated HETP values. Due to the required high purity, the quality of the liquid CO_2 product is sensitive to maldistribution. Vapor and liquid maldistribution can significantly reduce the separation efficiency.
Finally, after the evaluation and comparison of all correlations, it was decided to use the HETP value derived from the conversion of the random packing HETP value including the safety factor. As demonstrated earlier, the converted HETP is a good basis for deriving the structured packing efficiency. Also, this HETP value was checked against several correlations and was in good agreement with the models from Hanley and Chen [2], Xu et al. [15] as well as with the rule of thumb suggested Kister and Larson [1] (fig. 4).
The authors also strongly focused on the evaluation of the packing hydraulics, bed height effects and liquid distributor design. In particular, the column was designed for a moderate percentage flood and useful capacity to avoid the hump region (typically at 65 % to 90 % of flood [1] and hence to prevent a reduction of the packing efficiency. Moreover, it was essential for achieving the predicted HETP, that the new liquid distributor for the structured packing column has the same very good quality of distribution as the random packing columns. Likewise, it was crucial to limit packing bed height, considering a reasonable number of theoretical stages per bed and checking height to diameter ratio.

The CO_2 Column in Mexico was successfully started up and has been reliably producing CO_2. In figure 4, the final HETP values are plotted against the actual HETP from the CO_2 Column plant data. Based on measurement data, several simulations of the actual plant operation were performed, considering different column feed compositions. Thus, slightly different HETP values were calculated. The most conservative HETP value obtained from the simulation was used for the parity plot. As described above a wide range of HETP values was calculated with the various correlations. However, when compared with the plant data, the correlations of Kister and Larson [1], Hanley and Chen [5] and Xu et al. [15] provide the best prediction. The mass-transfer models from Rocha et al. [9] [10] and Olujic et al. [11] [12] [13] [14] underestimated the packing efficiency, while an overestimated hump HETP was obtained with empirical correlation from F.R.I. [2].

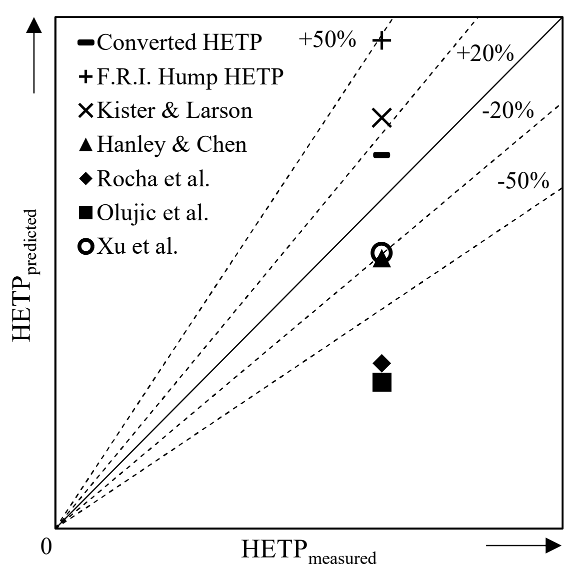

Fig. 4 Predicted structured packing HETP values compared with the HETP value for a CO2 Column operation in Mexico.

A good agreement with the measured HETP was achieved with the Linde's in-house approach for converted HETP values. It shows only little deviation to the measurement data. This observation led to the conclusion that certain hydraulic effects are reducing the packing efficiency. It is not unlikely, that the column is operated at the onset of the hump region, considering the elevated operational pressure and the type of packing. The converted HETP value without the extra safety factor would have been smaller than the actual measurement, which proves that a comprehensive equipment design can be done only based on a deep understanding of every step from conceptual design until plant operation.

Conclusions

A CO_2 Column, which is a key equipment of Linde's CO_2 purification and liquefaction plants was equipped with structured packings for the first time. A proven HETP for this new structured packing column, operated at elevated pressure was unavailable. A comprehensive design approach for the prediction of the structured packing HETP was presented. It comprised the calculation of HETP values derived from theoretical models and rules of thumb as well as the conversion of a HETP value used for the design of CO_2 Column containing random packings. Various factors that affect the HETP were examined. The possibility of a hump occurrence was checked. In addition, factors such as the type of packing, bed height, and system properties were considered. A converted HETP value was selected, which was checked against several HETP prediction methods. Finally, a first structured packing CO_2 Column was commissioned and proved Linde's capability of predicting packing efficiencies for new column services operated at elevated pressure. The investigation also showed the need for further improvement of the efficiency models and the need for developing correlations for the HETP hump prediction.

References

[1] H. Z. Kister, P. M. Mathias, D. E. Steinmeyer, W. R. Penny, V. S. Monical and J. R. Fair, "Equipment for Distillation, Gas Absorption, Phase Dispersion, and Phase Separation," in *Perry's Chemical Engineer's Handbook*, 9th ed., New York, McGraw-Hill Education, 2019, pp. 1-118.

[2] Fractionation Tray Design Handbook, Fractionation Research Inc., 2021.

[3] K. Onda, E. Sada and H. Takeushi, "Gas Absorption with Chemical Reaction," *J. Chem. Eng. Jpn.,* vol. 1, no. 2, pp. 62-66, 1986.

[4] K. Onda, H. Takeuchi and Y. Okumoto, "Mass Transfer Coefficients between Gas and Liquid Phases in Packed Columns," *J. Chem. Eng. Jpn.,* vol. 1, no. 1, pp. 56-62, 1968.

[5] B. Hanley and C. Chen, "New Mass-Transfer Correlations for Packed Towers," *AIChE Journal,* vol. 58, no. 1, pp. 132-152, 2012.

[6] Topical Report No. 152, Fractionation Research Inc., February 2004.

[7] I. Wagner, J. Stichlmair and J. R. Fair, "Mass Transfer in Beds of Modern, High-Efficiency Random Packings," *Ind. Eng. Chem. Res.,* vol. 36, no. 1, pp. 227-237, 1997.

[8] M. E. Harrison and J. J. France, "Download Distillation Column Troubleshooting Part 2: Packed Columns," *Chem. Eng.,* vol. 96, no. 4, pp. 121-128, 1989.

[9] J. A. Rocha, J. L. Bravo and J. R. Fair, "Distillation Columns Containing Structured Packings: A Comprehensive Model for Their Performance. 1. Hydraulic Models," *Ind. Eng. Chem. Res.,* vol. 32, no. 4, pp. 641-651, 1993.

[10] J. A. Rocha, J. L. Bravo and J. R. Fair, "Distillation Columns Containing Structured Packings: A Comprehensive Model for Their Performance. 2. Mass-Transfer Model," *Ind. Eng. Chem. Res.,* vol. 35, no. 5, pp. 1660-1667, 1996.

[11] Z. Olujic, A. B. Kamerbeek and J. d. Graauw, "A Corrugation Geometry Based Model for Efficiency of Structured Distillation Packing," *Chem. Eng. Process.,* vol. 38, no. 4-6, pp. 683-695, 1999.

[12] Z. Olujic, "Development of a Complete Simulation Model for Predicting the Hydraulic and Separation Performance of Distillation Columns Equipped with Structured Packings," *Chem. Biochem. Eng. Q.,* vol. 11, pp. 31-46, 1997.

[13] J. R. Fair, F. Seibert, M. Behrens, P. P. Sarabar and Z. Olujic, "Structured Packing Performance - Experimental Evaluation of Two Predictive Models," *Ind. Eng. Chem. Res.,* vol. 39, no. 6, pp. 1788-1796, 2000.

[14] Z. Olujic, M. Behrens, L. Colli and A. Paglianti, "Predicting the Efficiency of Corrugated Sheet Structured Packings with Large Specific Surface Area," *Chem. Biochem. Eg. Q.,* vol. 18, no. 2, pp. 89-96, 2004.

[15] Z. P. Xu, A. Afacan and K. T. Chuang, "Predicting Mass Transfer in Packed Columns Containing Structured Packings," *Chem. Eng. Res.,* vol. 78, no. 1, pp. 91-98, 2000.

[16] G. Q. Wang, X. G. Yuan, Z. L. Tang, J. B. Chen and K. T. Yu, "A Shortcut Method for Estimating the HETP of Structured Packed Distillation Columns at Elevated Pressure," *Chem. Eng. Technol.,* vol. 28, no. 7, pp. 767-772, 2005.