

Designing CO₂ Absorption Columns with Activated Amine Solutions

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CO₂ absorption into chemical solvents has been a growing industrial market for decades. Currently, activated methyldiethanolamines (aMDEAs) in aqueous solutions are quite often used as solvents. There are several amine compositions available on the market, and most often these solvents are activated. For designing a CO₂ absorption tower with activated amine, the chemical reaction in the liquid phase must be considered properly. At the column top, the fully reactive amine enters the column, whereby at the column bottom, the solvent is almost inactive. The highly exothermic CO₂ reaction with the activated amine generates heat in the solvent, leading to temperature peaks along the tower. This paper will discuss especially structured and random packings used in industrial CO₂ chemisorption columns. It will disclose information about packing characteristics and parameters to look at for selecting the preferred device. The paper will also discuss prediction models recommended for use with such processes.

1. Introduction

For the prediction of chemisorption processes in packed columns currently, process simulators such as Aspen, Chemcad or Protreat, to name only a few, are used. They allow the prediction of the packed bed height with the help of non-equilibrium means, mass transfer or the rate-based calculations considering chemical reactions. These rate-based simulations require the selection of mass transfer equations, and if a chemical reaction occurs the description of reaction kinetics are required. Process simulators offer several equations to be selected by their users, whereby a large amount of experience is required to pick a proper model. Finally, either structured or random packing must be selected, offering surface area and flow capacities to the process. Depending on the choice of equations, the packing height simulated can differ noticeably.

This paper will especially study the impact of the mass transfer model selected by simulation users on CO₂ absorber designs. The models studied in this paper are the Olujic et. al. (2004) model for predicting the mass transfer of structured packings, Onda et. al. (1959, 1968) model for the prediction of mass transfer of random packings and the Billet Schultes (1999) model for the prediction of both random and structured packings. It is of importance to notice that the experimental data used to derive these models are quite far from high pressure CO₂ chemisorption processes, which is why these equations are used in an area they were never modeled for. To study the performance of all three models under high pressure conditions, first the physical CO₂ absorption in water will be predicted followed by the chemisorption of CO₂ in aMDEA solutions.

2. CO₂ absorption into water at high pressures

The following Table 1 shows the predictive results for all three authors for a CO₂ absorption process from natural gas into water at 55 bar (800 psia) and 80 °C (176 °F). This first comparison is made for a non-reactive system to study the impact of physical properties on the calculation results. For the random packing, a 50-mm metal Pall-Ring (2" PR) and a metal Raschig Super-Ring No. 2 (RSR #2.0) were chosen, and for the structured packing, a Mellapak 2X (M2X) was chosen. The relationship between the tabulated values can be described by the following equations of the HTU-NTU model. Comparing the results of the predictions between Onda and Billet Schultes leads to the comparison of random packings. The HTU_{OV} and HETP values predicted by Onda are more than two times as high as those according to Billet and Schultes.

$$HTU_{OV} = HTU_V + \lambda HTU_L = \frac{u_V}{k_V a_{eff}} + \frac{He/p_T}{L/V} \frac{u_L}{k_L a_{eff}} \quad (1)$$

One can see a huge difference also in the estimated height of transfer units HTU_L and HTU_V . On the liquid side, the exponents for the liquid velocity, viscosity and surface tension in the equations for the effective surface area and mass transfer coefficient are different, which is why these models generate different results. For both HTU_L and HTU_V , the impact of dry packing surface area is also differently correlated by the equations, leading to different results.

Table 1: Prediction of mass transfer efficiency according Olujic, Onda and Billet Schultes for 50 mm metal Pall-Rings (2" PR), metal Raschig Super-Ring No. 2 (RSR #2.0) and metal Mellapak 2X (M2X). System: CO₂ absorption from natural gas into water at 55 bar and 80 °C.

Packing	$k_V a_{eff}$ 1/s	$k_L a_{eff}$ 1/s	Onda Correlation		HTU_V m	HTU_L m	HTU_{OV} m	HETP m
			a_{eff}/a -	a_{eff} m ² /m ³				
2" PR	0.412	0.0218	0.955	100.2	0.623	1.038	42.47	3.99
RSR #2.0	0.435	0.0207	0.958	93.5	0.590	1.094	44.69	4.20
Olujic Correlation								
M2X	0.698	0.0482	0.971	199	0.367	0.470	19.29	1.81
Billet Schultes Correlation								
2" PR	1.512	0.0468	2.312	242.8	0.170	0.484	19.66	1.85
RSR #2.0	1.694	0.0513	2.520	245.9	0.151	0.441	17.93	1.69
M2X	1.198	0.0349	1.227	245.3	0.214	0.647	26.31	2.47

Comparing the results of the predictions between Olujic and Billet Schultes leads to the comparison of structured packing. In this case, Olujic predicts noticeably lower HETPs for Mellapak 2X than Billet Schultes. Again, this is a result of the difference in correlating physical properties in the equations, for example, gas density. Another major difference can be recognized in the effective surface area predicted by Billet Schultes. Billet and Schultes overpredict the effective surface area for the listed random and structured packings. This fact is not important for this physical absorption study as only the volumetric mass transfer coefficients $k_V a_{eff}$ and $k_L a_{eff}$ are required as defined by the different authors. This matter will change in the next sample for the CO₂ chemisorption process into activated amine solutions.

3. CO₂ absorption into activated amines at high pressures

For the CO₂ absorption into activated amine solutions, the reaction kinetics must be considered. One approach to this is the application of Dankwerts (1970) model by applying an enhancement factor. Incorporating the enhancement factor into the HTU-NTU model leads to Eq. (2).

$$HTU_{OV} = HTU_V + \lambda \frac{1}{E} HTU_L = \frac{u_V}{k_V a_{eff}} + \frac{He/p_T}{L/V} \frac{1}{E} \frac{u_L}{k_L a_{eff}} \quad (2)$$

Bishnoi and Rochelle (2002) have published a very detailed paper for the prediction of the enhancement factor for CO₂ absorption in aqueous solutions of piperazine (PZ) and methyldiethanolamine (MDEA). The authors recommend to split the enhancement factor E into two parts. One part describes the instantaneous reaction with piperazine $E^{PZ,INST}$ and the second part is the pseudo-first order reaction (PFO) of CO₂ with MDEA $E^{MDEA,PFO}$. For the determination of individual enhancement factors, the liquid side mass transfer coefficients of reaction product $k_{L,Prod}$ and CO₂ $k_{L,CO2}$ must be predicted. For this, the volumetric mass transfer coefficient ($k_{L,A} a_{eff}$) must be divided by the effective surface area a_{eff} which makes it relevant to determine the correct effective surface area in the chemisorption processes, s. Eq. (3).

$$k_{L,A} = \frac{(k_{L,A} a_{eff})}{a_{eff}} \quad (3)$$

For the Billet Schultes model, it was shown that the effective surface area is over predicted for the packings in this study, s. Table 1. A better approach for the effective surface area is the correlation provided by Tsai which was originally generated for structured packings only but can be re-written for random and structured packings in the form of Eq. (4), s. Tsai et.al. (2011) and Schultes M. (2013). For the calculation of the volumetric mass transfer coefficients $(k_L a_{eff})_{BS}$ and $(k_V a_{eff})_{BS}$ the Billet Schultes model according to Eq. (5) and (6) still must be applied considering the relative effective surface area equation of $(a_{eff}/a)_{BS}$ shown in Eq. (7). Eq. (8) and Eq. (9) describe the prediction of the gas and liquid side mass transfer coefficients k_V and k_L by combining the Billet Schultes equations for the volumetric mass transfer coefficients $(k_V a_{eff})_{BS}$ and $(k_L a_{eff})_{BS}$ and the Tsai

equation for $(a_{eff})_{TS}$. In Eq. (7), C_A is a packing constant which is 1.0 for metal structured packings and 1.15 for metal random packings.

$$\left(\frac{a_{eff}}{a}\right)_{TS} = C_A 1.34 \left[\frac{\rho_L}{\sigma_L} g^{1/3} u_L^{4/3} \left(\frac{\varepsilon}{a}\right)^{4/3} \right] \quad (4)$$

$$(k_L a_{eff})_{BS} = C_L 12^{1/6} \left(\frac{u_L}{h_L}\right)^{1/2} \left(\frac{D_L}{d_h}\right)^{1/2} a \left(\frac{a_{eff}}{a}\right)_{BS} \quad (5)$$

$$(k_V a_{eff})_{BS} = C_V \frac{1}{(\varepsilon - h_L)^{1/2}} \frac{a^{3/2}}{d_h^{1/2}} D_V \left(\frac{u_V}{a v_V}\right)^{3/4} \left(\frac{v_V}{D_V}\right)^{1/3} \left(\frac{a_{eff}}{a}\right)_{BS} \quad (6)$$

$$\left(\frac{a_{eff}}{a}\right)_{BS} = 1.50 (ad_h)^{-0.5} \left(\frac{u_L d_h}{v_L}\right)^{-0.2} \left(\frac{u_L^2 \rho_L d_h}{\sigma_L}\right)^{0.75} \left(\frac{u_L^2}{g d_h}\right)^{-0.45} \quad (7)$$

$$k_V = \frac{(k_V a_{eff})_{BS}}{(a_{eff})_{TS}} \quad (8)$$

$$k_L = \frac{(k_L a_{eff})_{BS}}{(a_{eff})_{TS}} \quad (9)$$

Before studying the mass transfer predictions with the 3 models mentioned, including the chemical reaction in a tabular form, the relevant conditions along the CO₂/aMDEA absorption tower are first discussed. Figure 1 shows a typical gas and liquid temperature profile and the CO₂ gas concentration along a packed bed. The mass transfer principles can be split in sections along the absorber. At the column top, the lean solvent out of the regenerator is fed to the absorber. The solvent is almost free of CO₂ and fully activated by piperazine and amine. The gas at the column top has a low partial pressure as almost all of the CO₂ is already absorbed out of the gas stream. This is the section of the tower that ensures the specified low CO₂ off-gas concentration. The enhancement factor is the highest in this column section. In the column section below the CO₂ partial pressure is increasing and so does the concentration driving force for CO₂ into the liquid. The CO₂ mass transfer rates are very high in this section and CO₂ is reacting with piperazine and amines. Noticeable amount of heat is generated in the liquid phase because of the exothermic reaction. Consequently, the liquid temperature rises up to the point where the reactivity of the liquid drops down and a temperature peak can be recorded.

This temperature peak is critical for the column design as the CO₂ solubility in the solvent drops with increasing temperature and the vapor pressure for piperazine and amine rises, generating a possible solvent loss. Additionally, the enhancement factor becomes noticeably reduced in this column section. Above this temperature peak, a fast reaction zone can be considered which is not valid below the temperature peak where the reactivity of the solvent is heavily reduced.

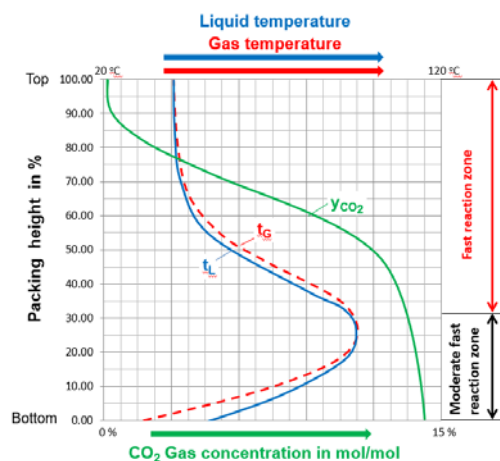


Figure 1: General gas and liquid temperature profile and CO₂ gas concentration profile along a packed column with activated amine as the solvent.

At the bottom of the column, the cold gas enters the column. The cold gas cools the liquid coming from the temperature peak zone. Consequently, the gas temperature rises on its way upwards. The gas temperature has its own peak point just above the liquid temperature peak and cools down flowing further upwards. This gas temperature peak is critical for the column design as the volumetric gas rate is the highest at this point, which determines the column diameter. Below the temperature peak, the absorption rate is low because the

liquid is much less reactive and the physical solubility of CO₂ in the solvent is low. The velocity of the reaction slows down for being moderately fast and the enhancement factor decreases as well.

The following Table 2 shows the predicted parameters for the Onda and Olujic models and for the combined Billet Schultes and Tsai models for the CO₂ absorption in the upper column section where a fast reaction zone can be considered. The gas is again natural gas with CO₂ for absorption into activated MDEA at 55 bar (800 psia) and 80 °C (176 °F). It can be recognized that for random packings, Onda predicts again much higher HTU_{OG}-values than Billet Schultes which makes the column much taller if designed according to Onda. The reaction velocity is high in the upper column section and so is the enhancement factor, but the magnitude of the enhancement factor is not high enough to shift the mass transfer resistance completely to the gas side. According to Onda, the gas side mass transfer resistance HTU_V/HTU_{OV} is app. 43-45 %, whereby according to Billet Schultes, the gas side mass transfer resistance is only 20-23 %.

Table 2: Predicted parameters for the Onda and Olujic models and for the combined Billet Schultes and Tsai models for a CO₂ absorption process from natural gas into activated MDEA at 55 bar (800 psia) and 80 °C (176 °F). The values are for the fast reaction zone just above the temperature peak.

Packing	Onda Correlation with Fast Chemical Reaction						HTU _V m	HTU _L m	HTU _{OV} m
	k _v a _{eff} 1/s	k _L a _{eff} 1/s	a _{eff} /a	a _{eff} m ² /m ³	E k _L a _{eff} 1/s				
2" PR	0.412	0.0218	0.955	100.2	1.203	0.623	0.0188	1.381	
RSR #2.0	0.435	0.0207	0.958	93.5	1.122	0.590	0.0202	1.402	
Olujic Correlation with Fast Chemical Reaction									
M2X	0.698	0.0482	0.971	199	2.388	0.367	0.0095	0.749	
Billet Schultes and Tsai Correlation with Fast Chemical Reaction									
2" PR	1.512	0.0468	1.248	131.1	1.573	0.170	0.0144	0.749	
RSR #2.0	1.694	0.0513	1.276	124.5	1.494	0.151	0.0151	0.761	
M2X	1.198	0.0349	1.087	217.5	2.610	0.214	0.0087	0.563	

Comparing the results for structured packings leads to the comparison of the models of Olujic and Billet Schultes. The high effective surface area a_{eff} for the structured packing generates lower HTU_{OV} values compared to random packings. Accordingly, a structured packing solution is favorable in the top column section as the height is reduced. Billet Schultes concluded the same, but the reduction in the column height is much less when compared to Olujic and Onda, and the question becomes which result to trust. An answer to this question can be provided by the experimental data available from Process Science and Technology Center (PSTC) in Austin, TX. PSTC used CO₂ absorption into a caustic solution as a test system to measure the effective surface area of packings. This test system has similarity to CO₂ absorption into activated amines because with the caustic solution, the CO₂ reaction can also be assumed to be fast and pseudo first order.

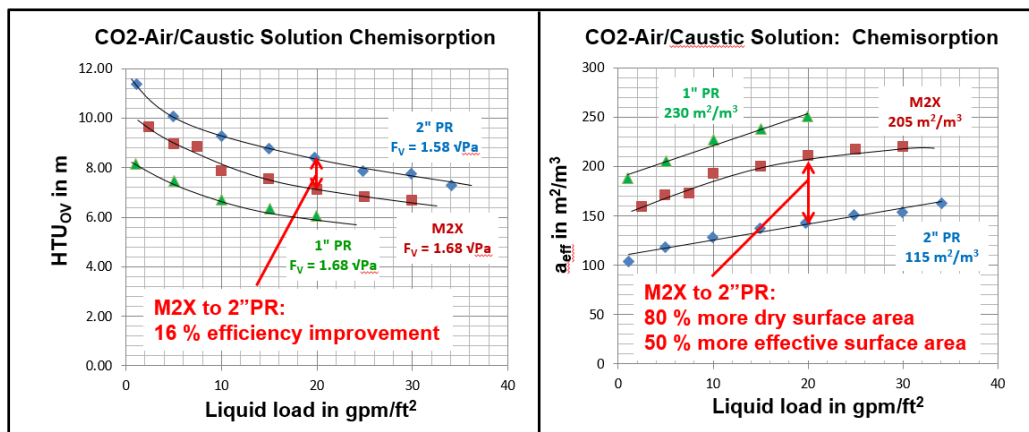


Figure 2: Experimental data for CO₂ absorption into a caustic solution from PSTC for metal 25 mm Pall-Rings, metal 50 mm Pall-Rings and metal Mellapak 2X. Left figure shows the height of a transfer unit HTU_{OV} over the liquid load. Right figure shows the effective surface area over the liquid load.

Figure 2 shows the experimental test results for metal 25 mm Pall-Rings, metal 50 mm Pall-Rings and metal Mellapak 2X under ambient conditions. One can see from Figure 2 on the right hand side that the packing with the highest dry surface area (25 mm Pall-Rings) also provides the highest effective surface area a_{eff}. The

lowest effective surface area in this comparison comes from the 50 mm Pall-Rings. Although the dry surface area of the structured packing is 80 % higher than that for 50 mm Pall-Rings, the effective surface area improvement for Mellapak 2X is only 50 %. If the plot is generated in terms of HTU_{OV} over the liquid load, the mass transfer coefficients become incorporated in the comparison, s. also Eq. (2). The higher the mass transfer coefficient, the smaller the HTU_{OV} value. A packing with a high turbulence of gas flow for example generates a high mass transfer coefficient k_G which is the case for 25 mm Pall-Rings. Of course, for the 25 mm Pall-Ring, this also results in a higher pressure drop compared to Mellapak 2X. The same is valid for 50 mm Pall-Rings and because of the higher gas side mass transfer coefficient k_G for 50 mm Pall-Rings, the advantage in HTU_{OV} for Mellapak 2X drops down to only 16 % and so does the packing height. These experiments demonstrate that the use of Onda's equation for random packing mass transfer first and then Olujic's equation for structured packing mass transfer can provide misleading results. The fundamental equations of both authors are too different; thus, for the high pressure CO_2 chemisorption process study in this paper, the difference in the predicted packing height is unrealistically high. It is more reasonable to stay with one model that allows the prediction of mass transfer for random and structured packings as shown in Table 2, i.e., using the Billet Schultes model in combination with the Tsai correlation for a_{eff} .

Table 3: Predicted parameters for the Onda and Olujic models and for the combined Billet Schultes and modified Tsai models for a CO_2 absorption process from natural gas into activated Amines at 55 bar (800 psia) and 80 °C (176 °F). The values are for the moderate fast reaction zone below the temperature peak.

Packing	Onda Correlation with Moderate Fast Chemical Reaction								
	$k_y a_{eff}$ 1/s	$k_L a_{eff}$ 1/s	a_{eff}/a -	a_{eff} m^2/m^3	$E k_L a_{eff}$ 1/s	HTU_V m	HTU_L m	HTU_{OV} m	
2" PR	0.412	0.0218	0.955	100.2	0.066	0.623	0.343	14.43	
RSR #2.0	0.435	0.0207	0.958	93.5	0.062	0.590	0.365	15.29	
Olujic Correlation with Moderate Fast Chemical Reaction									
M2X	0.698	0.0482	0.971	199	0.141	0.367	0.160	6.81	
Billet Schultes and Tsai Correlation with Moderate Fast Chemical Reaction									
2" PR	1.512	0.0468	1.248	131.1	0.125	0.170	0.181	7.46	
RSR #2.0	1.694	0.0513	1.276	124.5	0.133	0.151	0.170	7.00	
M2X	1.198	0.0349	1.087	217.5	0.115	0.214	0.197	8.14	

In the column bottom section, the reactivity of the solvent is very much reduced and the absorption of CO_2 is more and more affected by physical absorption. The enhancement factor is much smaller than at the column top and the resistance to mass transfer falls back into the liquid phase, meaning $HTU_V/HTU_{OV} < 5\%$.

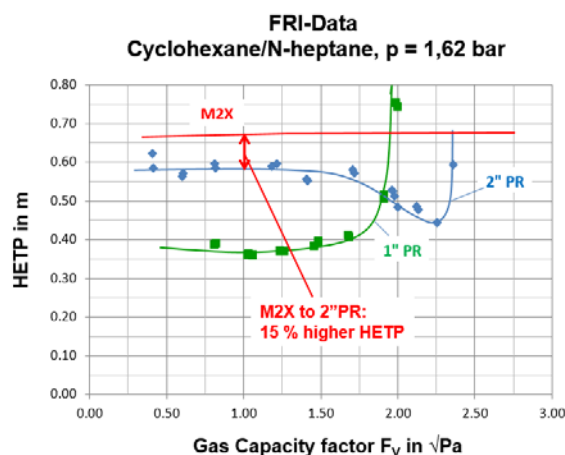


Figure 3: Distillation HETP data for 25 mm Pall-Rings and 50 mm Pall-Rings from FRI for a cyclohexane/n-heptane test system and from Sulzer's catalogue for an organic test system

Again, for random packings, Onda predicts noticeably higher HTU_{OV} values than Billet Schultes and much higher values than for structured packings according to Olujic. Only the Billet and Schultes model predicts a lower HTU_{OG} for random packings than for Mellapak 2X, which again raises the question which result to trust. As the reactivity is small in the bottom column section and the physical diffusion of molecules becomes important, one can look towards experimental investigations on physical absorption or distillation to receive an answer. Such information is available from Fractionation Research Inc. (FRI) and Sulzer's product catalogue. The Mellapak 2X efficiency data form Sulzer's product catalogue are typically based on in-house tests at Sulzer's facility, and the Pall-Ring data are published by FRI, s. Figure 3. This comparison demonstrates that both random packings have a better mass transfer efficiency (lower HETPs) than Mellapak 2X though the dry

surface area of the 50 mm Pall-Ring is nearly twice as small compared to Mellapak 2X. This comparison is in line with the CO₂ absorption prediction of Billet Schultes in Table 3 and demonstrates again that using different correlations can lead to misleading results in comparing random and structured packings. However, it also demonstrates that distillation data cannot be used for product efficiency evaluations in chemisorption processes with fast chemical reactions.

4. Conclusions

The paper demonstrates that for high pressure chemisorption processes, a proper validation of mass transfer model is required to receive proper information on mass transfer efficiencies and effective surface area. At the present, Eq. (4) from Tsai is recommended to predict the effective surface area a_{eff} , and the Billet Schultes model is recommended for the prediction of the gas and liquid side volumetric mass transfer coefficients $k_{V,a_{\text{eff}}}$ and $k_{L,a_{\text{eff}}}$, Eqs. (5) - (7). Eq. (8) and (9) must be considered to properly describe the liquid and gas side mass transfer coefficients k_L and k_V , whereby k_L is relevant for the prediction of the enhancement factor E.

Nomenclature			Greece Letters		
a	m ² /m ³	Spec. packing surface area	ε	m ³ /m ³	Packing void fraction
C _A , C _L , C _V	-	Constants	ρ	kg/m ³	Density
D	m ² /s	Diffusion coefficient	σ	N/m	Surface tension
d _h	m	Hydraulic diameter	λ	-	Stripping factor: (He/p _T)/(L/V)
E	-	Enhancement factor	ν	m ² /s	Kinematic viscosity
g	m/s ²	Acceleration	η	kg/ms	Dynamic viscosity
He	bar	Henry coefficient			
He*	Pa/(mol/l)	Henry coefficient	Indices		
HTU	m	Height of a transfer units	A		Component A
h	m ³ /m ³	Volumetric liquid hold up	BS		Billet Schultes
k	m/s	Mass transfer coefficient	eff		Effective for mass transfer
			T		Total
L	kmol/s	Molar liquid flow rate	TS		Tsai
V	kmol/s	Molar gas/vapor flow rate	L		Liquid
p	bar	Pressure	OV		Overall gas/vapor side
u	m ³ /m ² s	Velocity related to column cross section area	V		Vapor

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