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New pilot data and Aspen Plus simulations for CO_2 capture with MDEA/PZ: A biogas upgrading case

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Abstract

This work introduces robust pilot-scale experimental campaigns to validate the predictive capabilities of the current rate-based ENRTL-RK Aspen Plus model for CO_2 capture using MDEA/PZ solvent blends under biogas upgrading conditions. The experiments were conducted in a pilot absorber column (height: 10.5 m, diameter: 0.1 m) equipped with 8.2 m Mellapak 250Y packing with an 84 mm packing diameter to upgrade gas streams containing roughly 40 vol% CO_2. Key operating parameters, including lean-to-gas flow rate, lean solvent temperature, and the PZ-to-MDEA ratio, were systematically varied to study their influence on CO_2 slip and mass transfer performance. The campaigns provided the first pilot-scale dataset available for validating this model, addressing a critical gap identified in the Aspen Plus model description. The model demonstrated good agreement with steady-state data, accurately predicting CO_2 absorption trends along the absorber column. However, sensitivity studies revealed opportunities to refine the mass transfer coefficient for improved prediction accuracy. These findings emphasize the value of validated simulations at the pilot scale in optimizing CO_2 capture processes for biomethane production.

Keywords: CO_2 capture; biogas upgrading; pilot scale, piperazine (PZ); methyldiethanolamine (MDEA); rate-based modelling

Introduction

Alternatives to traditional fossil fuels are essential to mitigate climate change, and biogas emerges as a promising carbon-neutral candidate [1, 2]. However, biogas typically contains 25–50 vol% CO_2, along with other impurities, which limits its direct use as a fuel [3, 4]. To enable its distribution, biogas must be upgraded to biomethane by removing CO_2 and impurities. Most countries enforce stringent purity standards for biomethane injection into natural gas grids, requiring a low CO_2 slip, which refers to the remaining CO_2 concentration in the upgraded biogas.

Upgrading biogas increases its energy density by more than half, achieving carbon neutrality and improving its sustainability and efficiency as an energy source [5]. Among available carbon capture technologies, chemical

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absorption using amines is considered the most mature and economically viable option for biogas upgrading [6]. Despite its advantages, the high energy demand for solvent regeneration remains a major challenge for scaling up this technology for efficient commercial deployment [7].
Among various amine solvents, the aqueous solvent blend of piperazine (PZ) activated methyldiethanolamine (MDEA) offers the potential for achieving high biogas upgrading capacities through enhanced reaction rates, while still maintaining a low heat of reaction [8, 9].
A robust absorber column model is critical for optimizing this process. The absorber's performance depends on both gas-liquid phase equilibrium and reaction kinetics, whereas the stripper's performance is primarily constrained by equilibrium. Accurate modeling of these interactions is vital for improving process efficiency. However, the current ENRTL-RK rate-based model for CO_2 capture with MDEA/PZ lacks validation against dedicated pilot-scale data, a limitation noted in the Aspen Plus model description [10].
This study addresses this gap by presenting the first pilot-scale experimental dataset for validating the ENRTL-RK rate-based model under biogas upgrading conditions. The findings contribute to the development of advanced models and the optimization of biogas upgrading processes using MDEA/PZ solvent blends, paving the way for more sustainable and efficient biomethane production.

Method

This work considers the pilot-scale absorber column at the Technical University of Denmark (DTU), configurated to mimic biogas upgrading conditions. The column (10.5 m height, 0.1 m diameter) operates with a recycle gas loop, processing gas streams containing 40 vol% CO_2 and 60 vol% N_2 at a total flow rate of approximately 13 kg/h. Sensitivity studies using the Aspen Plus model examined the most important process variables, including lean solvent temperature (T_{lean}), lean-to-gas flow ratio (L/G), and PZ-to-MDEA ratio, to assess their influence on CO_2 slip achieved. Experimental campaigns were conducted on the pilot absorber column, varying solvent formulations, PZ-to-MDEA ratios, T_{lean}, and L/G values to validate the model. Simulations of the obtained steady states were also performed to evaluate the model's accuracy against pilot-scale data.

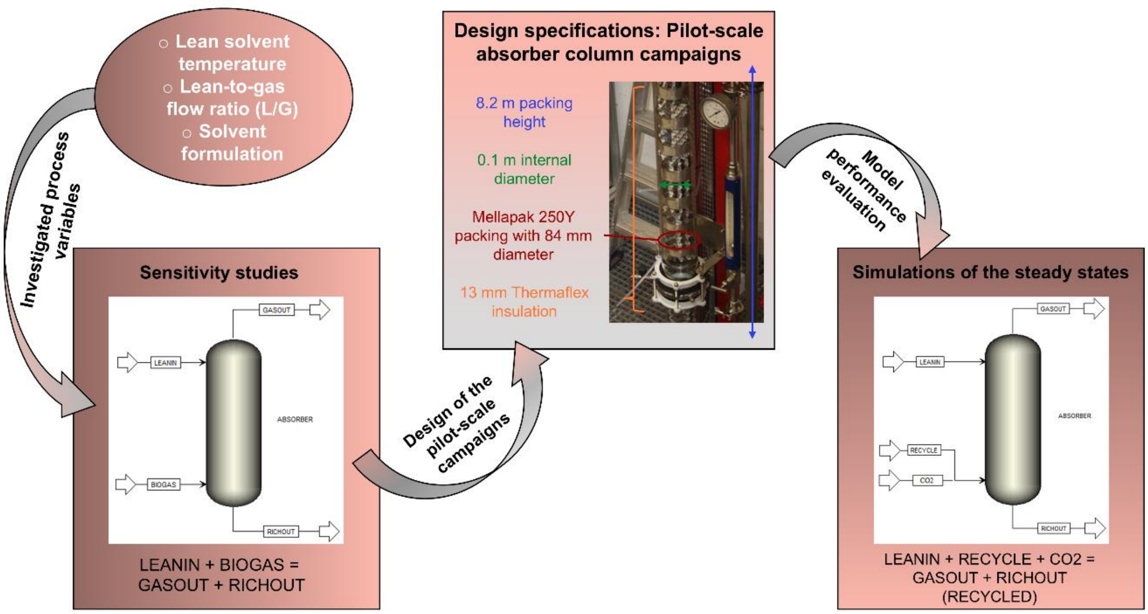

Figure 1. Methodology for pilot-scale validation of the ENTRL-RK rate-based Aspen Plus model for CO_2 capture using an MDEA/PZ solvent blend under biogas upgrading conditions.

Results

The influence of the L/G ratio, Tlean, and solvent blend formulation on CO_2 slip was investigated at a constant gas flow rate (G) of 13 kg/h. The solvent blends used had a fixed amine molality of 7.15 mol amine/kg water and a lean CO_2 loading of 0.05 mol CO_2/mol amine. The L/G ratio was varied from 6 kg/kg to 14 kg/kg in increments of 0.1 kg/kg. present the combined results for different T_{lean} values and solvent blend formulations, respectively. **Figure 2** and **Figure 3** present the combined results for various T_{lean} values and solvent blend formulations, respectively.

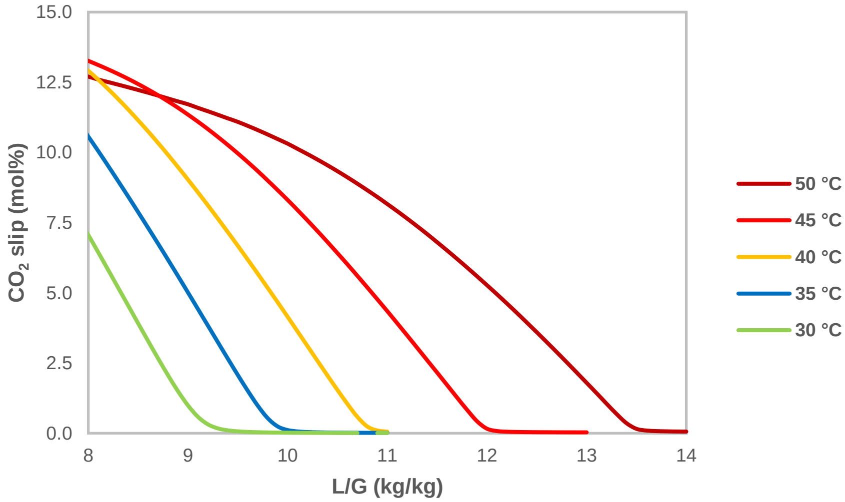

Figure 2. Sensitivity of CO_2 slip to L/G ratio at G = 13 kg/h using an MDEA/PZ formulation with a weight fraction of 5, amine molality of 7.15 mol amine/kg water, and lean CO_2 loading of 0.05 mol CO_2/mol amine at various lean temperatures.

At all lean temperatures studied, CO_2 slip decreases with increasing L/G ratio due to enhanced mass transfer from the gas phase to the liquid phase. Lower lean temperatures, however, allow for near-zero CO_2 slip at smaller L/G ratios. This occurs because CO_2 absorption into amines is exothermic; at higher lean temperatures, the temperature increase limits the solvent's capacity.

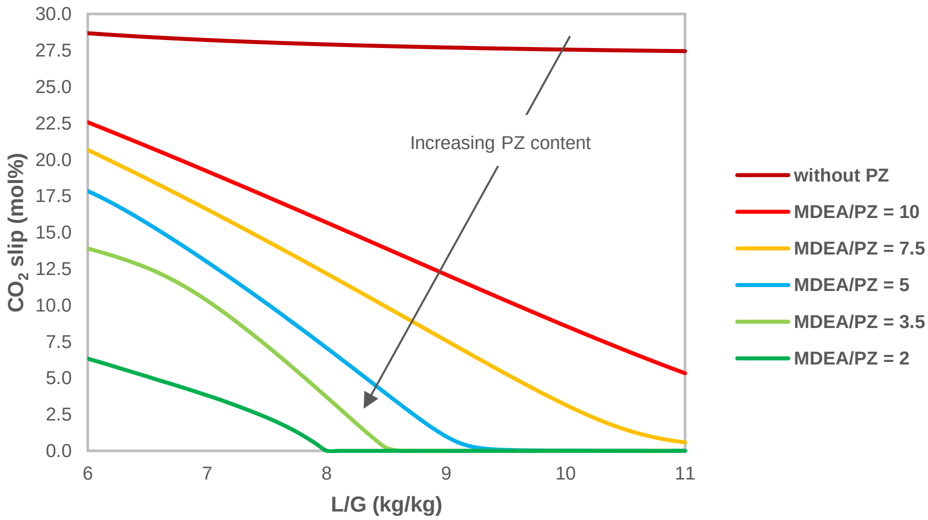

Figure 3. Sensitivity of CO_2 slip to L/G ratio at G = 13 kg/h and T_{lean} = 30 °C using different MDEA/PZ weight fractions, with an amine molality of 7.15 mol amine/kg water and lean CO_2 loading of 0.05 mol CO_2/mol amine.

The sensitivity studies with various solvent blend formulations show that increasing PZ concentrations enhance the CO_2 absorption capacity. This allows for achieving near-zero CO_2 slip with smaller L/G ratios as more PZ is present in the solvent blend.

The pilot plant campaigns employed three different aqueous solvent formulations, each with a CO_2 loading of 0.05 mol CO_2 / mol amine and similar amine molality values to those used in the sensitivity studies. Once the online measurements from temperature probes across the column, CO_2 slip data from the gas analyzer at the top, and lean and gas flow rates stabilized for at least a minute with a one-second sampling interval, steady-state regions were defined. The average of the measured parameters is provided in **Table 1**.

Table 1. The averages of the parameters, T_{lean}, L/G, and CO_2 slip, obtained at the experimental steady-state regions once three different solvent formulations of A, B, and C utilizing 0.05 mol CO_2/mol amine were tested in the pilot absorber column.

Formulation	Steady-state label	T_{lean} (°C)	L/G ratio (kg/kg)	Inlet CO_2 concentration (vol%)	CO_2 slip (vol%)
38.93 wt% MDEA + 5.14 wt% PZ + 55.17 wt% water	A1	30.67	9.27	39.16	2.50
	A2	38.23	13.04	43.56	0.96
	A3	37.94	12.36	40.02	0.02
	A4	37.99	10.31	39.09	0.01
	A5	37.97	10.31	39.20	0.03
35.00 wt% MDEA + 8.23 wt% PZ + 56.11 wt% water	B1	31.48	7.72	42.28	4.44
	B2	31.44	8.11	41.74	3.73
	B3	39.07	9.39	50.80	13.51
31.86 wt% + 9.22 wt% PZ + 58.24 wt% water	C1	32.11	7.56	37.98	0.00
	C2	31.99	7.44	41.08	4.51

Figure 4 shows the experimental CO_2 slip values plotted as a function of L/G ratio, demonstrating the predicted trend of decreasing CO_2 slip with higher L/G values, as indicated by the previous sensitivity studies.

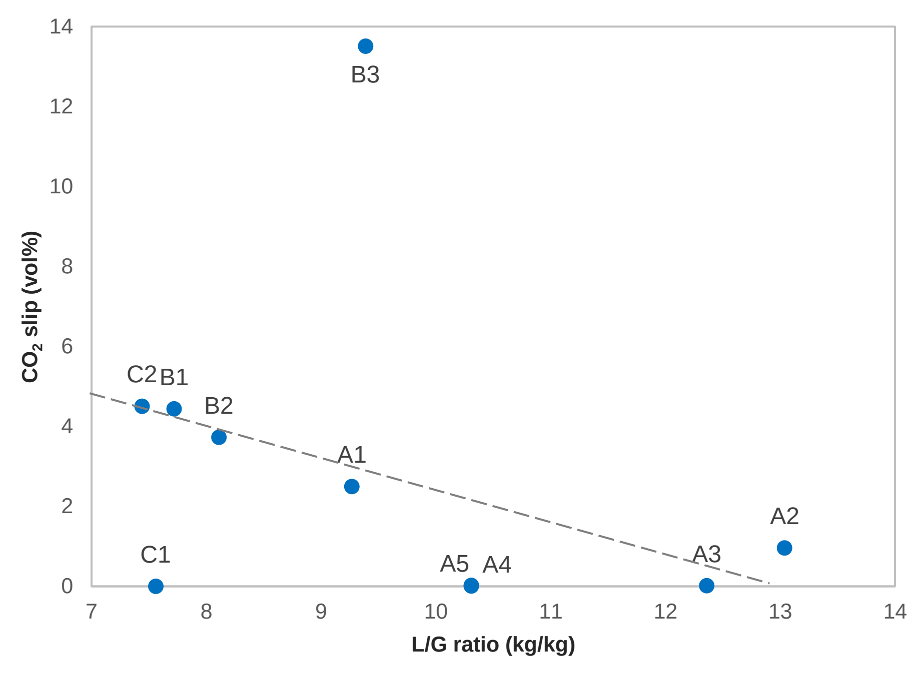

Figure 4. The trend of decreasing CO_2 slip with increasing L/G values observed across steady-state regions in the experimental campaigns.

CO_2 slip decreases with increasing L/G ratios across the steady states, as higher lean flow rates provide more solvent to capture CO_2, thereby enhancing absorption capacity. However, steady-state B3, which has a higher lean temperature compared to the cooler steady states B1 and B2, exhibits a higher CO_2 slip. Since CO_2 absorption is thermodynamically favored at lower temperatures, the lean flow rate in B3 is insufficient to achieve the required absorption capacity to align with the trend. Furthermore, the higher CO_2 slip leads to increased recycling of CO_2 back into the column, which further contributes to the deviation of B3 from the trend.
The performance of the model diminishes in some cases. Once the steady-state regions were simulated, the absorber temperature profiles did not align well with the model prediction in cases especially with higher temperature increases due to higher lean temperatures as demonstrated in **Figure 6**.

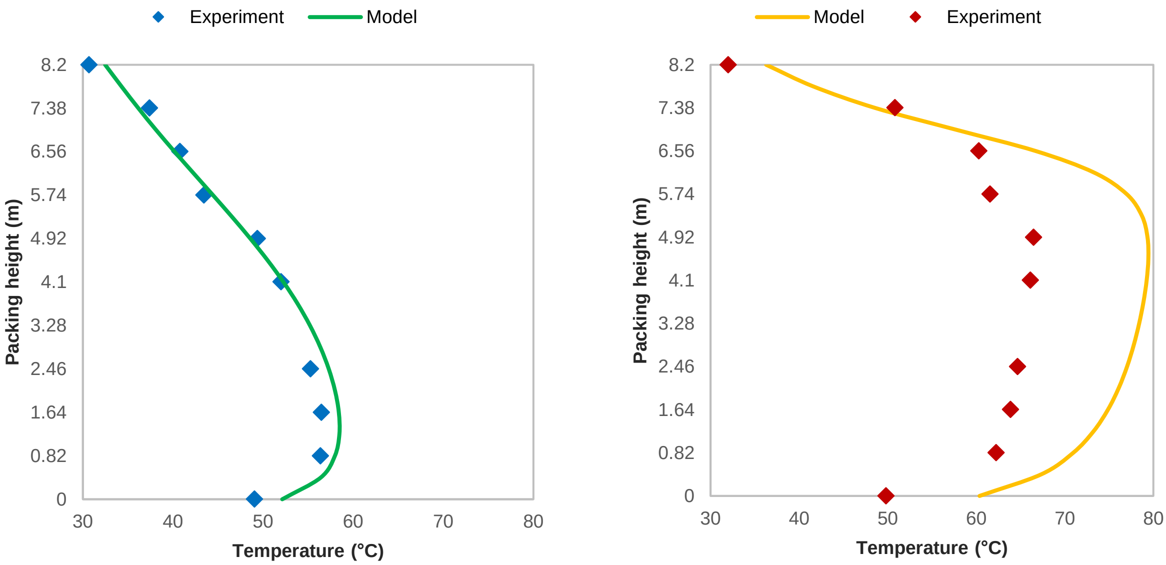

Figure 6. Simulation of steady states A1 (cool T_{lean}) vs. C2 (warm T_{lean}).

While the model accurately predicted the temperature profile measured by the probes along the column for steady-state A1, there are deviations for C2. This discrepancy may be attributed to potential heat loss from the column at higher temperatures and slight inaccuracies in the mass transfer coefficient used by the model.

Conclusion

The process parameters, including lean-to-gas flow rate, lean solvent inlet temperature, and PZ-to-MDEA ratio, were investigated through Aspen Plus sensitivity studies and validated with experimental campaigns. The model demonstrated good accuracy in predicting CO_2 mass transfer across the column for the experimental steady-state regions. However, discrepancies observed, such as those influenced by potential heat loss at higher temperatures and inaccuracies in the mass transfer coefficient, highlight areas for improvement. With these refinements, the model could serve as a powerful tool for designing and optimizing sustainable and economically viable biomethane production. Moreover, it holds promise for broader applications in carbon capture processes, such as post-combustion CO_2 capture using mixed PZ and MDEA formulations.

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