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Dynamic simulations of an amine-based absorption-regeneration CO₂ capture process applied to lime plant flue gases

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Abstract

The implementation of CCUS (Carbon Capture Utilization and/or Storage) in different industrial sectors (e.g. steel, cement, lime, glass, etc.) is still facing many challenges. Focusing on the application in the lime industry of the post-combustion CO₂ capture process by absorption-regeneration using amine-based solvent, one specific challenge appears. Indeed, in the lime production process, the flue gas generated is not stable in time and it is fluctuating both in terms of flow rate and composition (CO₂, O₂, H₂O, ...) due to inversion phenomenon inherent to the industrial process itself: a typical cycle of 15 min includes 11 min at nominal conditions (flue gas CO₂ concentration of 24 mol.%) and 4 min at 50% of the nominal gas flow rate value and 25% of the nominal CO₂ concentration value). Therefore, the following questions arise: what is the dynamic answer of the CO₂ capture process to these fluctuations and what are the solutions to keep a recovered CO₂ flow as stable as possible despite these flue gas variations? To answer these questions, different simulations were performed using Aspen Plus[®]/Dynamics[®] software combined to Matlab-Simulink[®] interface. Considering monoethanolamine (MEA) 30wt.% as solvent and a conventional process configuration (including the Direct Contact Cooler (DCC) for flue gas cooling), after having performed steady state simulations for validation purposes with micro-pilot scale results, dynamic simulations were developed considering PID controllers (DCC sump level, absorber inlet gas pressure, absorber sump level, stripper sump level, etc.). The PID parameters (gain, integral and derivative times) were optimized in order to keep an efficient regulation all along the process. These simulations allowed to highlight the temporal variation of the CO₂ production flow. Two solutions were then investigated (separately and combined) in order to smooth the CO₂ production curve, namely: the regulation of the reboiler duty and the addition of a solvent buffer tank on the rich solution line. Several simulations were performed in order to find the adapted volume (not oversized in order to avoid too much CAPEX increase, but sufficient to smooth the solvent CO₂ loading and therefore the CO₂ production flow). It was shown that acting only on the reboiler heat duty, especially in order to avoid any CAPEX increase, is possible but leads to an increase of up to almost 10% of the heat consumption during around 5 min. On the other hand, it is also possible to keep a stable captured CO₂ production flow by adding a rich-solution tank without any impact on the reboiler duty (e.g. a tank of 145 m³ leads to quite smooth CO₂ production flow with almost 20% of CAPEX increase). By combining the addition of a smaller rich solution tank (e.g. a tank of 19 m³) and a adequate heat duty regulation (e.g. temporary increase of only 4% of the nominal reboiler heat duty), the CO₂ production flow was kept very stable. Globally, this study shows that even if a lime plant generates a flue gas with some temporal fluctuations on its flow rate and CO₂ concentration, technical solutions allow to obtain a stable captured CO₂ production flow, leading to an increase of the total CO₂ capture costs from 1.4% to 4.8%.

Keywords: Post-combustion CO₂ capture; Absorption-regeneration amine-based process ; Aspen Dynamics[®] simulation; Lime plant flue gases.

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Nomenclature

| | |
|--|--|
| a | Installation lifetime (years) |
| A | Absorption rate (%) |
| ABS | Relative to the absorber |
| $\alpha_{\text{CO}_2, \text{rich/lean}}$ | Rich/Lean CO ₂ loading of the solvent (mol _{CO₂} /mol _{amine(s)}) |
| CAPEX | Capital Expenditures |
| CCUS | Carbon Capture Utilization and/or Storage |
| CEPCI | Chemical Engineering Plant Cost Index |
| DCC | Direct Contact Cooler |
| $D_{\text{columns}}/D_{\text{tank}}$ | Diameter of the columns/of the liquid tank (m) |
| E_{regen} | Solvent regeneration energy (MJ/kg _{CO₂} or GJ/t _{CO₂}) |
| EQU | Relative to the equilibrium mode |
| EXP | Relative to the experiments |
| G | Inlet gas flow rate in the absorber (m ³ /h) |
| $H_{\text{packing}}/H_{\text{tank}}$ | Height of the packing/of the Liquid tank (m) |
| i | Straight-line depreciation interest rate (%) |
| in | Relative to the absorber's inlet |
| K_{equ} | Reaction equilibrium constant |
| L | Inlet liquid flow rate in the absorber (m ³ /h) |
| MEA | Monoethanolamine |
| OPEX | Operational Expenditures |
| P | Pressure (kPa) |
| P_{boiler} | Reboiler heating power (GJ/h) |
| PFRK | Parallel Flow Regenerative Kiln |
| $Q_{\text{reboiler}}/Q_{\text{HEAT}}$ | Micro-pilot unit electrical reboiler/preheater heating power (kW) |
| RB | Relative to the rate-based mode |
| SIM | Relative to the simulations |
| STRIP | Relative to the stripper |
| T | Temperature (°C) |
| tpd | Metric tons per day |
| V_{tank} | Liquid tank volume (m ³) |
| $Y_{\text{CO}_2, \text{in}}$ | CO ₂ concentration of the absorber's inlet gas flow (mol.%) |

1. Introduction

In order to significantly decrease the carbon dioxide emissions from industrial sectors (e.g. steel, cement, glass, etc.) and especially from the lime industry, in parallel of other measures (e.g. energy efficiency improvement, alternative fuel use, etc.), implementing CCUS (Carbon Capture Utilization and/or Storage) is a complementary and necessary solution. Looking specifically at the CO₂ capture step, two main technological ways could be envisaged in the lime sector, namely: the oxy-fuel combustion (which requires many adaptations regarding the kiln and the burners, the use of large amount of pure oxygen, such as the implementation of a CO₂ purification unit – not investigated in the present study) and the post-combustion CO₂ capture process (end-of-pipe and most developed technology, requiring very limited adaptations for the upstream industrial process – considered in the present study, especially the absorption-regeneration process using amine-based solvent).

Lime production primarily involves the thermal decomposition of limestone in a kiln ($\text{CaCO}_{3(s)} \rightarrow \text{CaO}_{(s)} + \text{CO}_{2(g)}$). This process is known as calcination and occurs typically at temperatures above 900°C. Parallel Flow Regenerative Kilns (PFRK) are a popular type of kiln used in lime production. They are known for their efficiency and the quality of the lime they produce. Such kiln typically consists of two vertical shafts and operates on a regenerative principle. The process involves alternating between heating one shaft and cooling the other, which helps in recovering heat and improving fuel efficiency. This inversion phenomenon between the two operating modes leads to a fluctuation of the flue gas generated, both in terms of flow rate and in terms of composition (CO₂, O₂, H₂O, ...), as presented on Fig. 1.

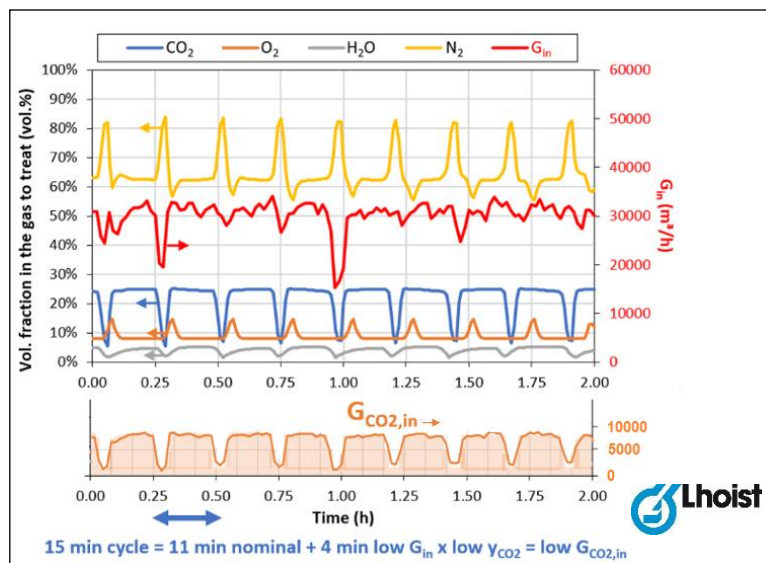


Fig. 1. Illustration of the flow rate and gas components volume fractions variations in a PFRK lime kiln flue gas (capacity of 230 tpd of lime, provided by the industrial lime producer partner, namely Lhoist).

The considered cycle of 15 min includes 11 min at nominal conditions and 4 min at low CO₂ concentration (6% corresponding to around 25% of the nominal value) leading to a low inlet CO₂ flow ($G_{CO_2,in}$, see Fig. 1). In view of the application in the lime industry of the post-combustion CO₂ capture process by absorption-regeneration using amine-based solvent, the following challenging questions have to be answered: what would be the dynamic answer of the CO₂ capture process to these fluctuations and what are the possible technical solutions to keep a captured CO₂ flow as stable as possible despite these flue gas variations? To answer these questions, different simulations were performed using Aspen Plus[®] and Aspen Dynamics[®] (V14.0) software considering monoethanolamine (MEA) 30wt.% as solvent and a conventional process configuration.

In a first step, Aspen Plus[®] steady state simulations were performed in order to validate the model used for the dynamic simulations based on micro-pilot results. Then, in a second step, the Aspen Plus[®] steady state model was converted to Aspen Dynamics[®] and combined to Matlab-Simulink[®] interface in order to manage the temporal evolution of all the simulation inputs and outputs.

The implementation of a gas holder (generally expensive and needing a lot of available space) to smooth the flue gas flow rate and composition was not considered in the present work. Two solutions were investigated (separately and combined) and compared on a techno-economic point of view in order to smooth the CO₂ production curve: the regulation of the reboiler duty and the addition of a solvent buffer tank on the rich solution line (absorber's outlet).

2. Simulation parameters and validation results

2.1. Aspen Plus[®] steady state simulations validation with micro-pilot scale results

When simulating the absorption-regeneration CO₂ capture process in Aspen Plus[®] software, it is conventional to use “RadFrac” columns parametrized in “Rate-based” calculation mode. “RadFrac” is a rigorous model for simulating various multistage vapor-liquid operations such as absorption and stripping. It can handle both liquid and/or vapor phase chemical reactions. The “Rate-based” calculation mode is a fundamental and rigorous approach which directly accounts for the mass and heat transfer rate processes in the system of equations representing the separation unit. It considers the multicomponent interactions between simultaneously diffusing species, including the influence of chemical reactions. In order to switch from Aspen Plus[®] steady state simulations to Aspen Dynamics[®] it is mandatory to perform the columns calculation in “Equilibrium” mode. Vaporization (used in the present study) or Murphree efficiencies are used to account for deviations from equilibrium for the vapor and liquid phases leaving any stage.

Therefore, in order to validate the simulation model in “Equilibrium” mode prior to the dynamic simulations, a validation step was performed based on micro-pilot scale results obtained for MEA 30 wt.% solvent. The micro-pilot unit used (see picture on Fig. 2 (a)) and the associated experimental procedure were completely described in [2-3].

The Aspen Plus[®] simulation model of the micro-pilot tests is presented on Fig. 2 (b), where the main dimensional and operating parameters are provided (c).

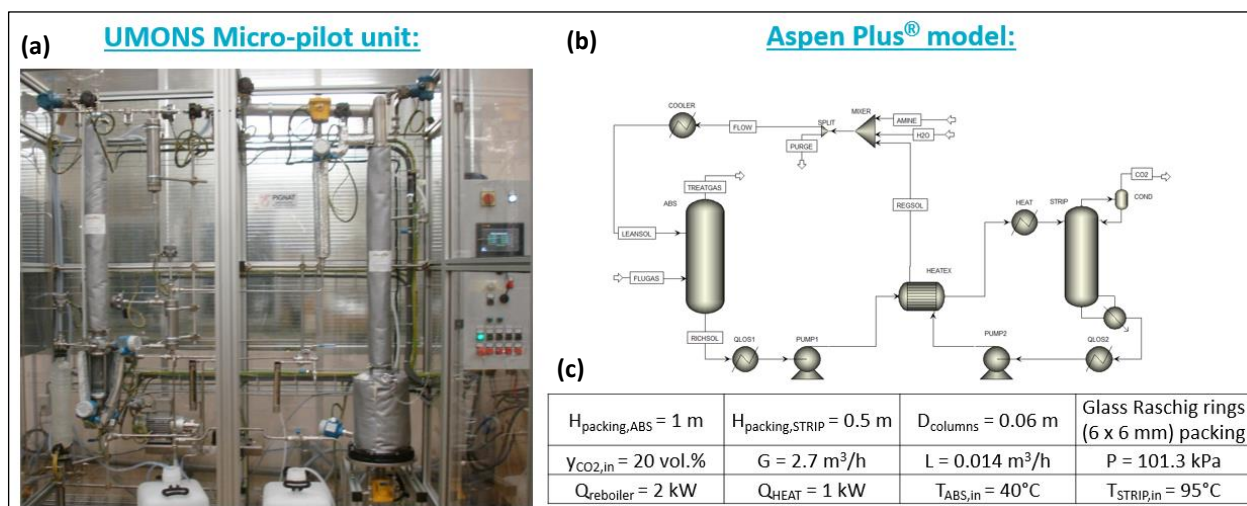


Fig. 2. Illustration of the UMONS micro-pilot unit (a) and the associated Aspen Plus® model (b), including micro-pilot data (c).

The thermodynamic models used are Redlich Kwong (RK) and Electrolyte Non-Random Two-Liquid (ELEC-NRTL) for the vapor and liquid phases respectively. The reaction set implemented in the columns (equilibrium reactions only allowed), corresponding to the CO_2 -MEA- H_2O chemistries, are the different dissociation equilibrium reactions, namely the formation of: H_3O^+ (K_{equ} from [3]), HCO_3^- (K_{equ} via Gibbs free energy minimization), CO_3^{2-} (K_{equ} from [3]), MEAH^+ (K_{equ} from [4]), and MEACOO^- (K_{equ} via Gibbs free energy minimization), K_{equ} corresponding to the equilibrium constant of the reaction. This mix between literature and calculated values of K_{equ} was the one leading to the lowest deviation in comparison with experimental results.

The experimental and simulation results are compared on Fig. 3 in terms of: absorption rate (CO_2 captured amount normalized to the inlet CO_2 content of the gas), regeneration energy (energy provided for the solvent regeneration divided by the CO_2 captured amount) and rich/lean CO_2 loading of the solvent (CO_2 content of the solvent per mol of MEA respectively at the outlet of the absorber and of the stripper). The results are provided parametrizing the absorption/regeneration columns (“RadFrac”) in “Equilibrium” (“SIM EQU”) or “Rate-based” (“SIM RB”) modes.

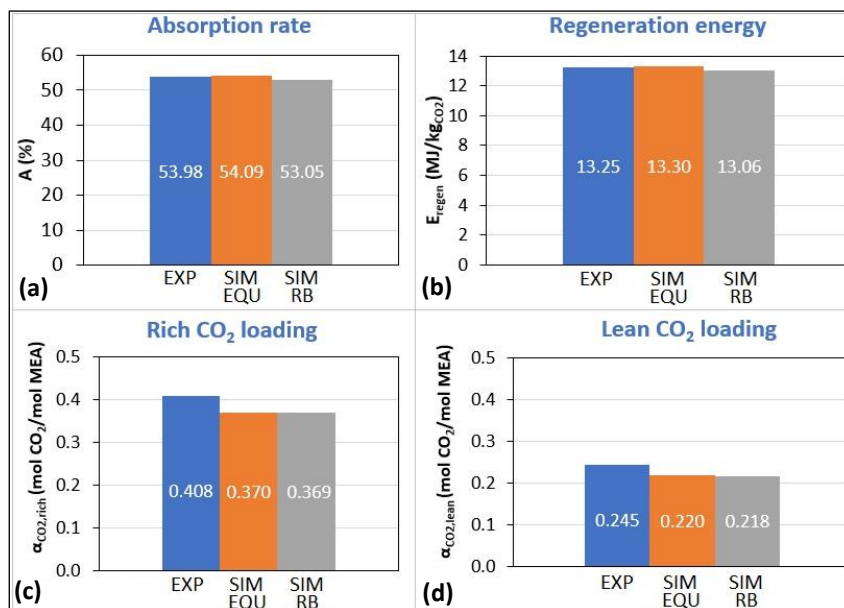


Fig. 3. Comparison between UMONS micro-pilot unit results (“EXP”) and associated Aspen Plus® simulation results with RadFrac columns in equilibrium (“SIM EQU”) and rate-based (“SIM RB”) modes in terms of A (a), E_{regen} (b) and $\alpha_{\text{CO}_2,\text{rich}}$ (c) / $\alpha_{\text{CO}_2,\text{lean}}$ (d) values.

It can be seen that globally the experimental and simulation values, both in “Equilibrium” or “Rate-based” modes, of the absorption rate and the regeneration energy are very close to each other (less than 2% relative difference). A bigger deviation ($\approx 10\%$) is observed for the rich and lean CO_2 loading values. This bigger difference could be partially explained by the CO_2 loading measurement method (namely using a TOC (Total Organic Carbon analyser)) which implies solution dilutions leading to higher standard deviation values. It can be also pointed out that “Equilibrium” and “Rate-based” results are very close to each other. The “Equilibrium” mode was therefore validated and used for the dynamic simulations.

2.2. Modeling parameters for the Aspen Dynamics[®] simulations of an industrial case

Using the simulation model validated at section 2.1, an industrial case corresponding to a PFRK lime kiln (capacity of 230 tpd of lime) was simulated. The operating, dimensional and simulation parameters are provided in Table 1. The system was designed based on the unit used in [5] for MEA 30 wt.%. The $L_{\text{in}}/G_{\text{in}}$ optimum volumetric ratio (minimizing the regeneration energy), corresponding to a liquid flow rate of 192 m^3/h , was determined as performed in [5] using the steady state Aspen Plus[®] simulations considering the nominal operating data. This ratio varied between $4.65 \cdot 10^{-3} \text{ m}^3/\text{m}^3$ and $1.08 \cdot 10^{-2} \text{ m}^3/\text{m}^3$ due to the temporal variation of the inlet gas flow rate (see Fig. 1). It has to be noted that other gaseous components (e.g. SO_x , NO_x , ...) and the CO_2 compression chain were not considered in the present study.

Table 1. Operating, dimensional and simulation parameters.

| | |
|--|---|
| Lime kiln flue gas flow rate (temporal variations, see Fig. 1) | 15000 m^3/h to 34000 m^3/h (at 110°C and 1 atm) |
| Flue gas composition (temporal variations, see Fig. 1) | N_2 : 55 vol.% to 84 vol.% |
| | CO_2 : 5 vol.% to 25 vol.% |
| | O_2 : 8 vol.% to 15 vol.% |
| | H_2O : 2 vol.% to 5 vol.% |
| Targeted recovered CO_2 flow rate | $\sim 12600 \text{ kg}_{\text{CO}_2}/\text{h}$ ($\sim 90\%$ of inlet CO_2 on average) |
| Recovered CO_2 purity | 99.0 wt.% |
| Solvent | Monoethanolamine (MEA) 30 wt.% in aqueous solution |
| Columns height | DCC: 8 m (8 stages x 1m) / Absorber: 17 m (17 stages x 1 m) |
| | Stripper: 10 m (10 stages x 1 m) |
| Columns (and sumps) diameter | DCC: 3 m / Absorber: 3.4 m / Stripper: 4.2 m |
| Columns sump height | $\approx 25\%$ of columns height (DCC: 2 m / Absorber: 4 m / Stripper: 2.5 m) |
| Columns packing | Random metal packing IMTP 50 |
| Inlet liquid temperature | DCC: 30°C / Absorber: 40°C / Stripper: 110°C |
| Columns bottom pressure | DCC: 1.2 bar / Absorber: 1.2 bar / Stripper: 2 bar |
| Liquid flow rate (absorber inlet) | 192 m^3/h |
| Nominal reboiler heating power (“P _{boiler-fix} ”) | 42.54 GJ/h ($E_{\text{regen}} = 3.38 \text{ GJ}/t_{\text{CO}_2}$) |
| Dynamic calculation step | 0.01 h |

The simulated Aspen Dynamics[®] flow sheet is provided in Fig. 4. The flue gas enters a first column (Direct Contact Cooler (DCC)) where it is cooled to 50°C thanks to a contact with water before entering the absorption column. It has to be pointed out that the cooling water circuit was simulated as an open loop even if, in practice, cooling water would be recirculated including a purge/make-up of water (as represented in [5]).

A conventional absorption-regeneration flow sheet was implemented including, in the upper part of Fig. 4, a “mixer-splitter” combination acting as make-up unit in the simulation allowing to maintain a good water and MEA balance in the system (losses compensation) while allowing fixing the desired MEA concentration and total liquid flow rate. It can be pointed out that for convergence reasons, the internal heat exchanger was implemented with two separate heaters (“HEXR” and “HEXL” on Fig. 4) including a “duty link” ensuring the heat provided for the solvent preheating is removed from the hot lean solution. Nevertheless, a real internal heat exchanger was considered for the techno-economic assessment (section 4.).

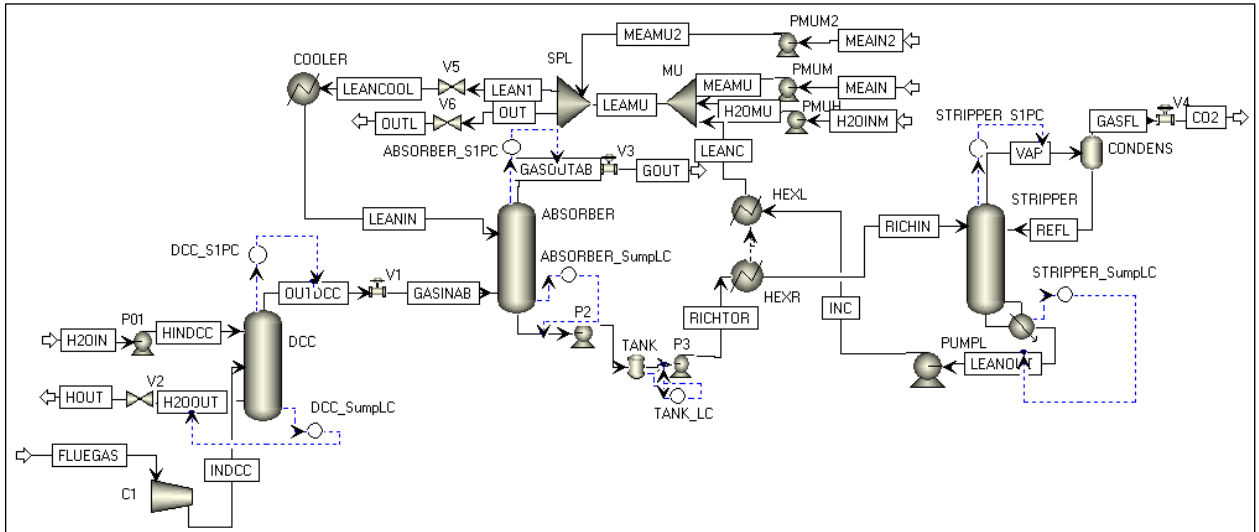


Fig. 4. Aspen Dynamics® simulation flow sheet using MEA 30wt.% as solvent (liquid tank included).

Two hours of operations (corresponding to Fig. 1. temporal profiles, provided as spreadsheet inputs to the simulation thanks to a Matlab-Simulink® interface) were simulated considering the following regulation loops comprising PID (Proportional-Integral-Derivative) controllers: the sump level (50%) and the outlet gas pressure of each column (DCC, absorber and stripper), such as the liquid tank level (50%) for the specific cases considering this tank. The PID parameter values (gain, integral and derivative times) were optimized (starting from Aspen Dynamics® default values) in order to keep an efficient regulation all along the process.

3. Aspen Dynamics® simulation results

3.1. Base case

Aspen Dynamics® simulation results of the base case (fixed value of reboiler duty and no liquid tank) in terms of absorption rate (a), produced CO₂ (b) and rich (c)/lean (d) CO₂ loading values are presented on Fig. 5.

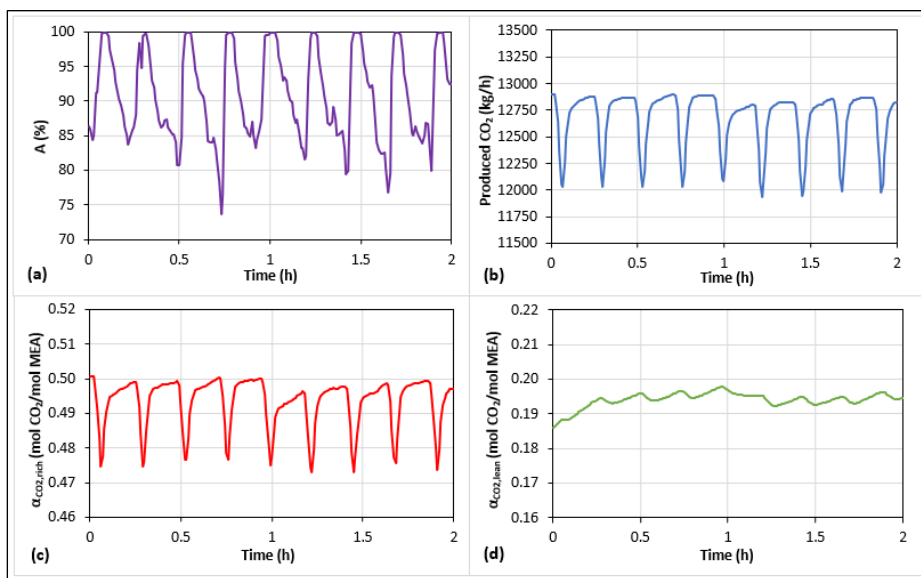


Fig. 5. Aspen Dynamics® simulation results of the base case (fixed value of reboiler duty and no liquid tank) in terms of absorption rate (a), produced CO₂ (b) and rich (c)/lean (d) CO₂ loading values.

It can be seen that due to the flue gas variations (both in terms of flow rate and composition, see Fig. 1), the absorption rate and the corresponding produced CO₂ flow are varying (e.g. the produced CO₂ flow is decreasing during ± 5 min, reaching a minimum value corresponding to a decrease of around 7% of the nominal value). Fig. 5. (c) and (d) illustrate the rich and lean CO₂ loading values variations. While the impact on the lean CO₂ loading values is quite limited, the rich CO₂ loading values are directly impacted by the flue gas variations (maximum decrease of $\pm 5\%$). In view of maintaining a CO₂ production flow as stable as possible for the next steps of a CCUS value chain, it is therefore necessary to investigate technical ways to smooth these temporal variations.

3.2. Comparison of CO₂ production smoothing paths

Two technical ways were investigated (separately and combined) for smoothing the CO₂ production flow, namely the regulation of the reboiler heat duty and the implementation of a liquid tank on the rich solvent line (outlet of the absorption column, see Fig. 4).

Fig. 6 (a) presents the regulated reboiler heating power (“Pboiler-vary-A”) leading to the produced CO₂ flow provided on Fig. 6 (b) without any liquid tank. It can be highlighted that thanks to this reboiler heating regulation (maximum 9.5% increase of the nominal heating power), a maximum of 1.5% of variation of the CO₂ production flow is obtained. Even if this CO₂ production is not perfectly stable yet, it is a clear improvement in comparison with the initial CO₂ production flow profile (Fig. 5. (b)).

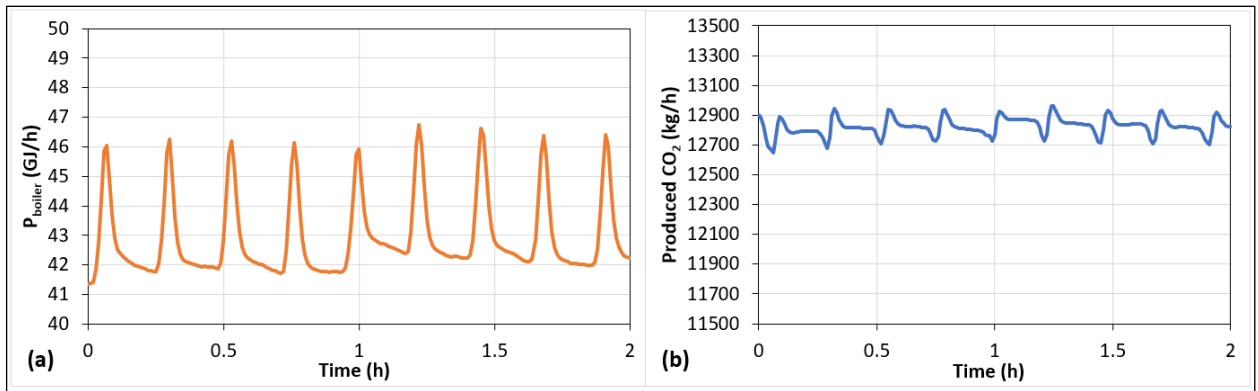


Fig. 6. Regulated reboiler heating power “Pboiler-vary-A” (a) and corresponding produced CO₂ flow (b) without liquid tank.

The simulation results (CO₂ production flow) corresponding to the second smoothing path investigated, namely the addition of a liquid tank on the rich solution line while keeping the nominal reboiler heating power, are provided on Fig. 7 for different cylindrical liquid tank volumes ($D_{\text{tank}} \times H_{\text{tank}}$): (a) $V_{\text{tank}} = 5 \text{ m}^3$ (2 m x 1.6 m); (b) $V_{\text{tank}} = 19 \text{ m}^3$ (2 m x 6 m); (c) $V_{\text{tank}} = 73 \text{ m}^3$ (3.4 m x 8 m); (d) $V_{\text{tank}} = 145 \text{ m}^3$ (6.4 m x 4.5 m). It can be seen that as the liquid tank volume is increased, the CO₂ production flow is progressively more smoothed. This smoothing can be directly related to the effect of the liquid on the solvent rich/lean CO₂ loading values (as well illustrated on Fig. 8 for the liquid volume tank of 145 m³). Indeed, for a liquid tank volume of 145 m³, the maximum variation of the CO₂ production flow is 0.5% of the nominal value and both the rich/lean CO₂ loading values are stabilizing respectively at 0.493 and 0.198 mol CO₂/mol MEA.

Finally, two smoothing paths were combined, namely the implementation of a liquid tank of a moderate volume (19 m³) and the regulation of the reboiler heating duty (see “Pboiler-vary-B” on Fig. 9 (a)). The resulting produced CO₂ flow is provided on Fig. 9 (b). It can be observed that the CO₂ production flow is even more smoothed in comparison with the previous CO₂ production flow profiles, the maximum variation of the CO₂ production flow being 0.3% of the nominal value. The resulting rich/lean CO₂ loading values are quite similar as the ones illustrated on Fig. 8 for the case of a liquid tank volume of 145 m³.

Different paths are therefore implementable to smooth the CO₂ production flow, the last solution (combination of a liquid tank and of the reboiler duty regulation) leading to the most stable CO₂ production.

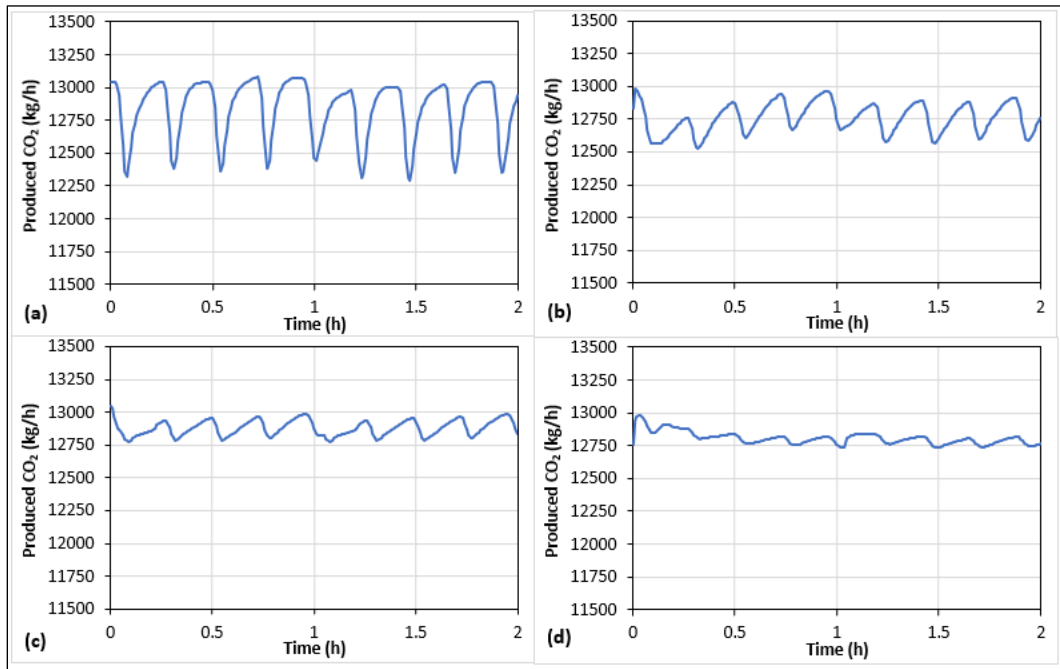


Fig. 7. Aspen Dynamics[®] simulation results (with $P_{\text{boiler-fix}}$) in terms of produced CO_2 flow rate for different liquid tank volume values: 5 m^3 (a), 19 m^3 (b), 73 m^3 (c) and 145 m^3 (d).

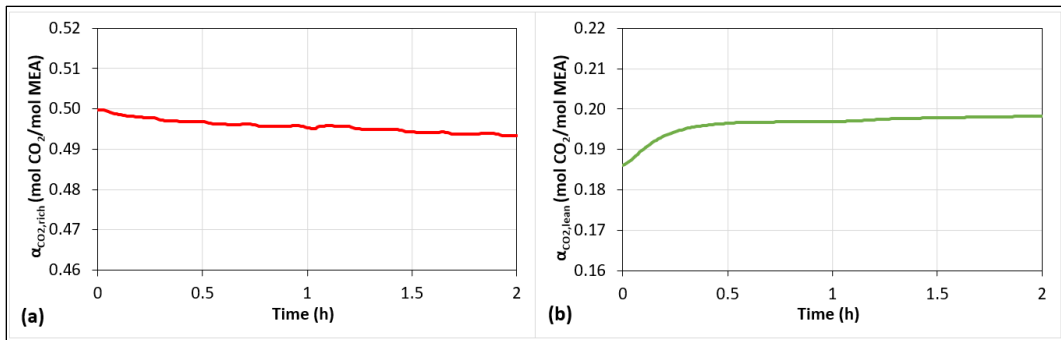


Fig. 8. Aspen Dynamics[®] simulation results (with $P_{\text{boiler-fix}}$) in terms of rich (a) and lean (b) CO_2 loading values for a tank volume of 145 m^3 .

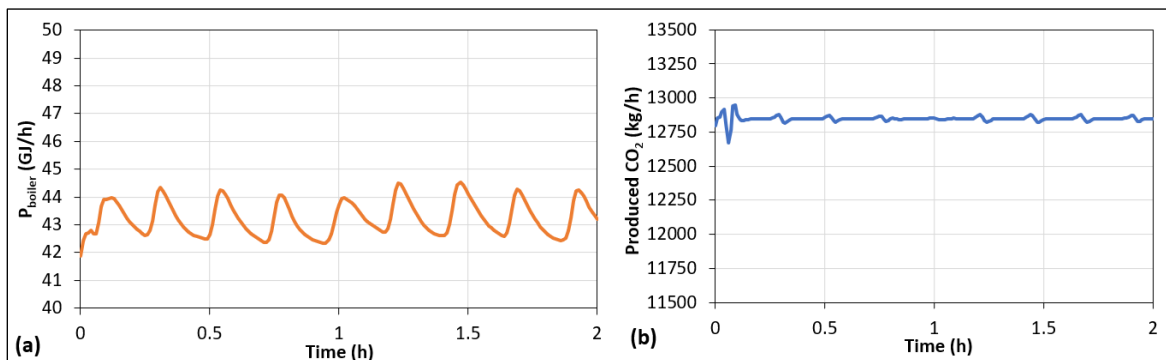


Fig. 9. Regulated reboiler heating power "Pboiler-vary-B" (a) and corresponding produced CO_2 flow (b) with a tank of 19 m^3 .

In order to compare the different technical solutions envisaged, a techno-economic assessment was performed considering five cases, namely: (i) the base case (no liquid tank and no reboiler duty regulation), (ii) the regulation of the reboiler duty (“Pboiler-vary-A”) without a liquid tank, (iii) the implementation of a big liquid tank (145 m³) without any reboiler duty regulation, (iv) the implementation of a moderate liquid volume (19 m³) without any reboiler duty regulation and (v) the regulation of the reboiler duty (“Pboiler-vary-B”) with a moderate liquid volume (19 m³).

4. Techno-economic assessment

4.1. CAPEX results

The equipment direct costs were evaluated for three cases: (i) the base case without any liquid tank, (ii) when a moderate liquid tank volume ($V_{\text{tank}} = 19 \text{ m}^3$) is implemented and (iii) when a large liquid tank volume ($V_{\text{tank}} = 145 \text{ m}^3$) is installed. The repartition of each equipment component in the total equipment direct costs is provided for these three cases on Fig. 10 (a), (b) and (c), while the CAPital EXpenditures (CAPEX) are detailed in Table 2.

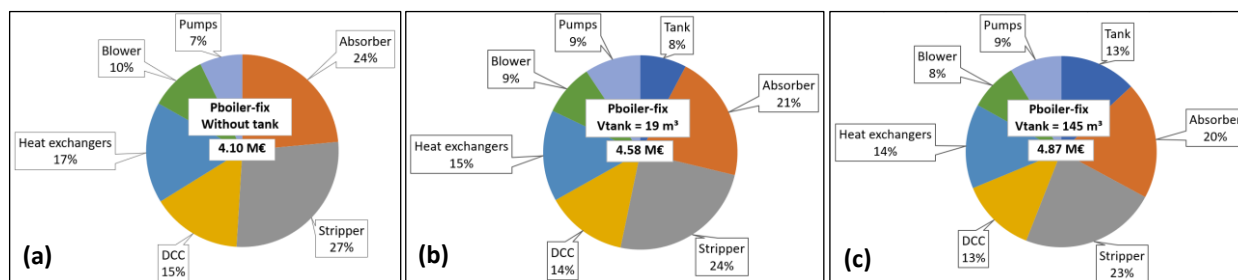


Fig. 10. Equipment direct costs repartition without liquid tank (a), with a liquid tank volume of 19 m³ (b) and 145 m³ (c).

Table 2. CAPEX details for the three different simulation cases.

| CAPEX | Without tank | $V_{\text{tank}}=19\text{m}^3$ | $V_{\text{tank}}=145\text{m}^3$ |
|--|--------------|--------------------------------|---------------------------------|
| Direct costs (M€) | 4.10 | 4.58 | 4.87 |
| Purchased Equipment | 1.73 | 1.94 | 2.06 |
| Equipment Setting | 0.03 | 0.03 | 0.03 |
| Piping | 0.68 | 0.76 | 0.81 |
| Civil | 0.13 | 0.15 | 0.16 |
| Steel | 0.07 | 0.08 | 0.09 |
| Others ⁽¹⁾ | 1.45 | 1.62 | 1.72 |
| Indirect costs (M€) ⁽²⁾ | 5.90 | 6.60 | 7.01 |
| Fixed Capital Investment (M€) ⁽³⁾ | 10.00 | 11.19 | 11.88 |
| Working capital (M€) ⁽⁴⁾ | 1.50 | 1.68 | 1.78 |
| CAPEX (M€) | 11.50 | 12.86 | 13.66 |
| Relative difference | | +12% | +19% |

⁽¹⁾Instrumentation, electrical, insulation, and paint categories. ⁽²⁾Cost of engineering and supervision, legal expenses, construction expenses, contractors fees and contingency. A ratio factor of 1.44 is applied across the direct purchased equipment cost for the indirect costs. ⁽³⁾Sum of the direct and indirect costs. ⁽⁴⁾Working capital = 15 % of the FCI.

It can be seen from Fig. 10 that the implementation of a liquid tank adds a contribution of 8% ($V_{\text{tank}} = 19 \text{ m}^3$) and 13% ($V_{\text{tank}} = 145 \text{ m}^3$) to the equipment direct costs, the main contributors to these costs corresponding to the three columns (namely Direct Contact Cooler (DCC), absorber and stripper). In terms of total CAPEX, Table 2 shows that relatively to the base case without any liquid tank, the CAPEX are increased from 12% to 19% depending on the liquid tank volume.

4.2. OPEX results

OPEX estimation implies the calculation of variable costs considering utilities costs (provided in Table 3). The variable costs (€/t_{CO2}) presented on Fig. 11, and the CAPEX provided in Table 4, were calculated using equation (1) as the sum of the variable costs related to each utility (variable cost_i), i corresponding to steam, electricity, water (cooling and process) and solvent:

$$\text{Variable costs} = \sum_i \text{Variable cost}_i = \sum_i \frac{\text{Cost}_i \times \text{Consumption}_i}{\text{Produced CO}_2} \quad (1)$$

where Cost_i and Consumption_i are respectively the cost and the consumption of the utility i

Table 3. Utilities costs considered for variable costs calculations.

| Utilities | Costs |
|---------------|---------------------------------|
| Electricity | 100.0 €/MWh [6] |
| Steam | 22.5 €/ton of steam [7] |
| Cooling water | 0.1165 €/t _{water} [5] |
| Process water | 0.4241 €/t _{water} [5] |
| Solvent price | 1.00 €/kg [8] |

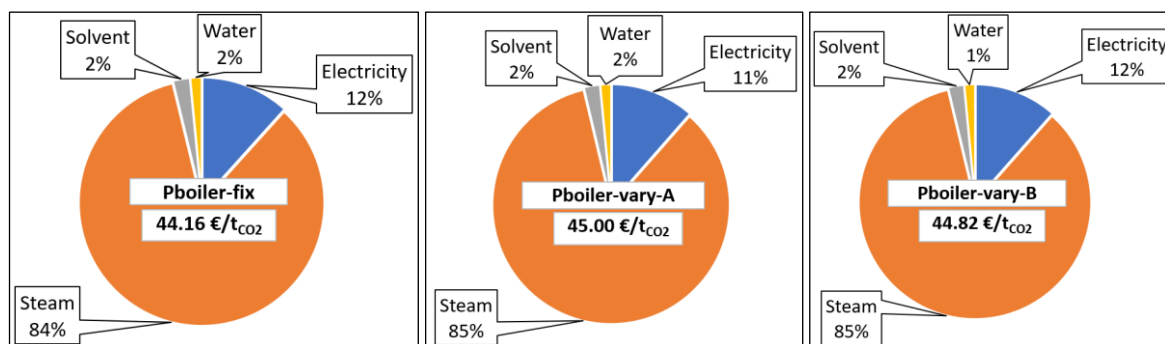


Fig. 11. Variable costs repartition for a fixed reboiler heating power (a), with the “Pboiler-vary-A” (b) and “Pboiler-vary-B” (c) reboiler duty regulations.

Table 4. OPEX details for different simulation cases.

| OPEX (€/tCO ₂) | Pboiler-fix | Pboiler-vary-A | Pboiler-vary-B |
|---------------------------------|--------------|----------------|----------------|
| Electricity | 5.17 | 5.17 | 5.17 |
| Steam | 37.32 | 38.16 | 37.97 |
| Chemicals | 1.00 | 1.00 | 1.00 |
| Other utilities | 0.67 | 0.67 | 0.67 |
| OPEX (€/tCO₂) | 44.16 | 45.00 | 44.82 |
| Relative difference | | +1.9% | +1.5% |

In all cases, the main contributor to the variable costs and the OPEX is the steam consumption linked to the solvent regeneration (around 85% of the total variable costs in all cases), the second main contribution being the electricity consumption (around 12%). The solvent and water consumptions represent globally from 3 to 4% of the variable costs. Regarding the OPEX, it can be pointed out from Table 4 that they are increased from 1.5% to 1.9% due to the regulation of the reboiler heat duty, increasing the steam consumption.

4.3. Total CO₂ capture costs comparison

In order to calculate the total CO₂ capture costs (detailed in Tab. 7 and summarized on Fig. 12), the CAPEX detailed in section 4.1 have to be annualized ($CAPEX_{annuity}$) taking into account the installation lifetime a (25 years was considered) and the interest rate i (straight-line depreciation, 6.5% in the present work):

$$CAPEX_{annuity} = CAPEX \times \frac{i \times (1+i)^a}{(1+i)^a - 1} \quad (2)$$

this amount being normalized to the amount of captured CO₂ over the entire lifetime of the installation (considering 8232 hours of annual effective capture operations). It is worth noting that all costs were obtained for 2023 as reference year (Chemical Engineering Plant Cost Index, $CEPCI_{2023} = 797.9$ [9]).

Table 5. Total CO₂ capture costs details for the different simulation cases.

| CO ₂ CAPTURE COSTS (€/t _{CO2}) | Pboiler-fix Without tank | Pboiler-vary-A Without tank | Pboiler-fix V _{tank} =145m ³ | Pboiler-fix V _{tank} =19m ³ | Pboiler-vary-B V _{tank} =19m ³ |
|---|--------------------------|-----------------------------|--|---|--|
| Variable cost | 44.16 | 45.00 | 44.16 | 44.16 | 44.82 |
| Fixed cost ⁽¹⁾ | 6.77 | 6.77 | 8.04 | 7.57 | 7.57 |
| OPEX | 50.92 | 51.77 | 52.19 | 51.73 | 52.39 |
| Capex annuity | 8.43 | 8.43 | 10.01 | 9.43 | 9.43 |
| TOTAL COSTS | 59.35 | 60.19 | 62.20 | 61.16 | 61.81 |
| Relative difference | | +1.4% | +4.8% | +3.0% | +4.2% |

(1) Fixed costs, corresponding to operation and maintenance expenses, are fixed to 7% of the CAPEX [8].

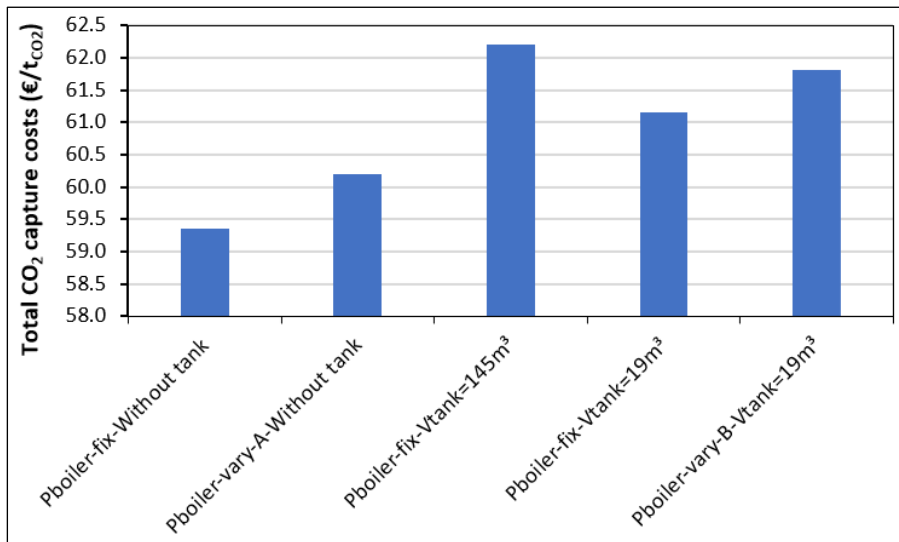


Fig. 12. Total CO₂ capture costs comparison for the different simulation cases.

Globally, it can be observed that the total CO₂ capture costs increase remains limited for all considered cases (maximum 4.8% when the biggest tank volume is considered, the total CO₂ capture costs increasing from 59.39 €/t_{CO2} to 62.20 €/t_{CO2}). The regulation of the reboiler heat duty leads to an increase of only 1.4% of the total CO₂ capture costs but as shown on Fig. 6 (b), the CO₂ production flow is not perfectly smoothed. The technical solution leading to the most stable CO₂ production flow is the combination of a moderate liquid tank volume (19 m³) with a reboiler duty regulation (“Pboiler-vary-B”), the total CO₂ capture costs being increased by only 4.2%.

5. Conclusions

In view of the application in the lime industry of the post-combustion CO₂ capture process by absorption-regeneration using amine-based solvent, one challenge is the management of the flue gas fluctuations, both in terms of flow rate and composition, especially to keep a stable CO₂ production flow. Considering MEA 30 wt.% as solvent, and thanks to Aspen Dynamics® simulations integrated in a Matlab-Simulink® interface, two solutions were therefore investigated (separately and combined) in order to smooth the CO₂ production curve, namely: the regulation of the reboiler duty and the addition of a solvent liquid tank on the rich solution line.

It was shown that acting only on the reboiler heat duty, especially in order to avoid any CAPEX increase, is possible but leads to an increase of up to almost 10% of the heat consumption during around 5 min. On the other hand, it is also possible to keep a stable CO₂ production flow by adding a rich-solution tank without any impact on the reboiler duty. Different tank volumes were considered and it was highlighted that a tank of 145 m³ leads to quite smooth CO₂ production flow but with a CAPEX increase of almost 20%. By combining a smaller rich solution tank (namely 19 m³) and a heat duty regulation, the CO₂ production flow can be kept very stable. This third possibility has the advantage to offer more flexibility to the CO₂ capture unit, especially if the flue gas fluctuations evolve with time. On a techno-economic point of view, the different solutions investigated have a limited impact on the total CO₂ capture costs (between 1.4% and 4.8% increase in comparison with the reference case).

Globally, this study shows that even if a lime plant generates a flue gas with some temporal fluctuations on its flow rate and composition (especially CO₂ concentration), obtaining a stable captured CO₂ production flow is possible with the different solutions investigated. The choice of the best solution relies on the economic strategy of the industrial CO₂ emitter (impacting only OPEX, only CAPEX or a part of both).

Acknowledgements

Wallonia is warmly acknowledged for the funding of the NKL project in the framework of the Recovery and Resilience Plan (PNRR), initiated and financed by the European Union. Lhoist company is also acknowledged for providing the data for the process simulations.

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Calgary (Alberta, Canada) – 22nd October 2024 – Session 5A PCC Process Modeling II


Dynamic simulations of an amine-based absorption-regeneration CO₂ capture process applied to lime plant flue gases

L. DUBOIS, G. DE WEIRELD AND D. THOMAS


Dr Lionel DUBOIS

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Chemical & Biochemical Process Engineering Unit
Faculty of Engineering - University of Mons (Belgium)
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UMONS CCUS Projects



CO₂ capture by adsorption with MOFs




CO₂ Purification Unit (CPU) modeling




CO₂ capture using demixing solvents

e-Posters by Prof. G. De Weireld

e-Poster by Ir D. Verdonck




CO₂ capture, purification, liquefaction & conversion Units




CO₂ capture application to different CO₂ emitters




CO₂ capture with MOFs & Microwave Swing Adsorption



Triphasic electrolyzer modeling



CO₂ capture & integration with conversion into e-kerosene




CO₂ capture using catalytic absorption process

Presentation by Dr L. Dubois


e-Poster by Ir C. Pasté



Micro-Gas Turbines & CO₂ capture unit integration

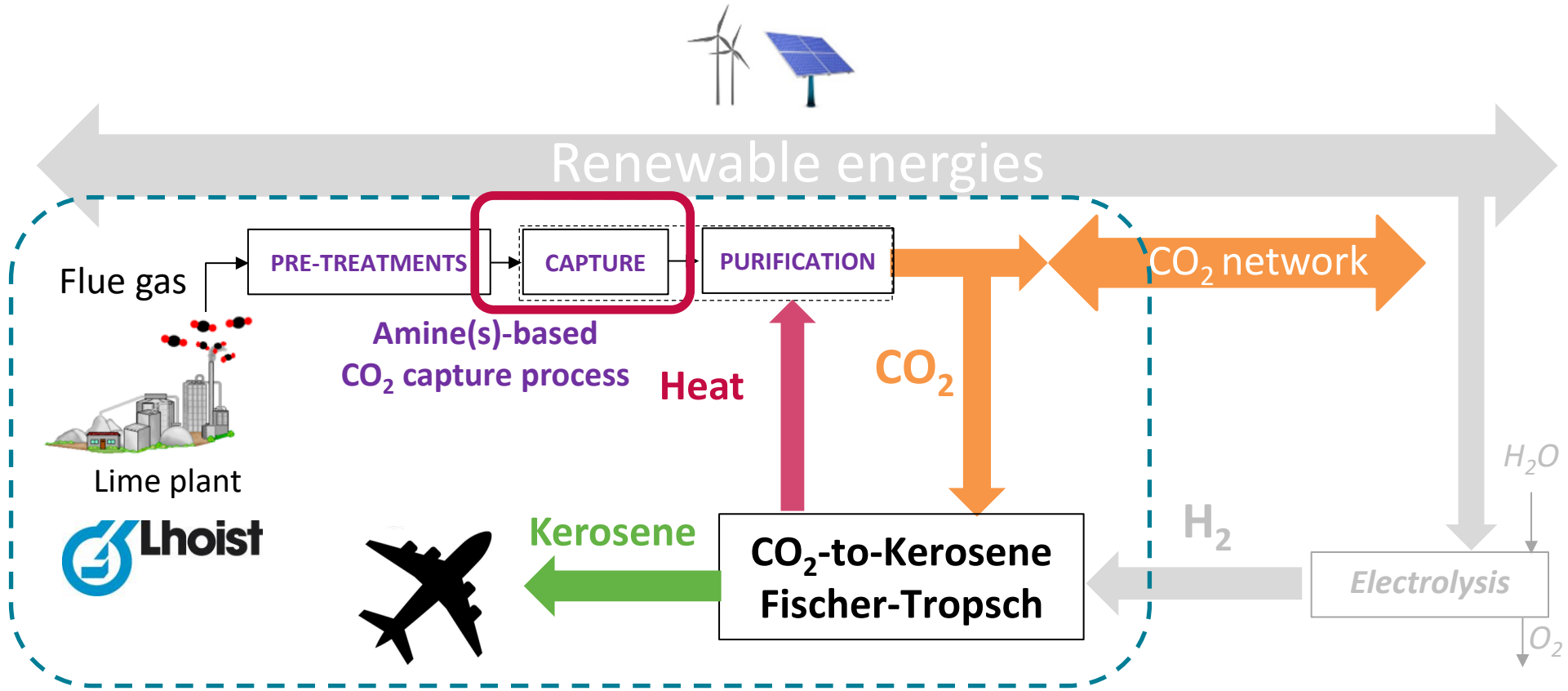


CO₂ capture in the Waste-to-Energy sector



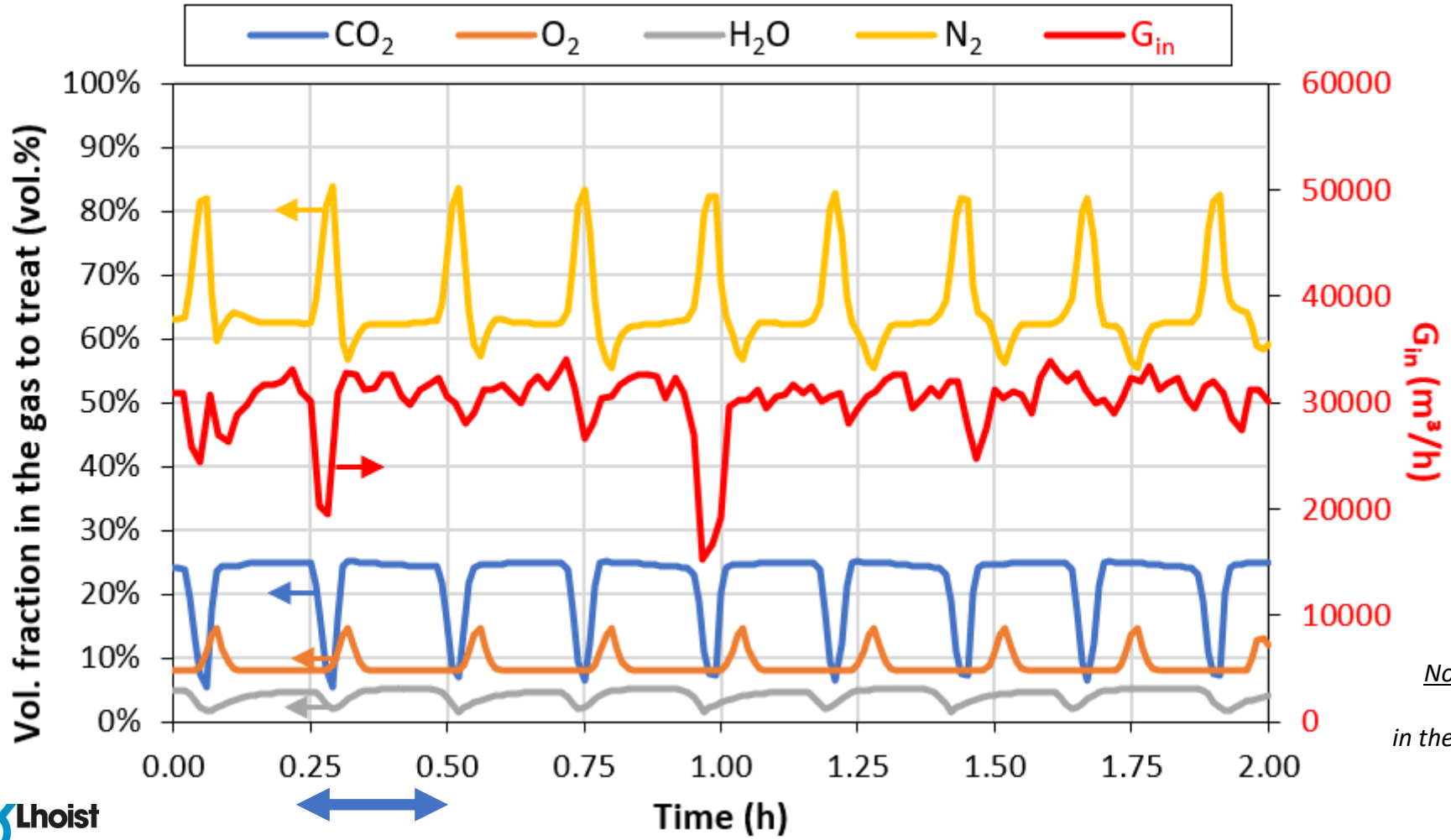
CO₂ capture using innovative adsorbents

NKL project scope

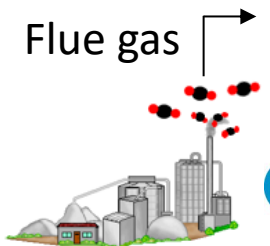


NKL SCOPE

Lime plant flue gas



Note: Measurement campaign at Lhoist Hermalle site in the framework of the NKL project.



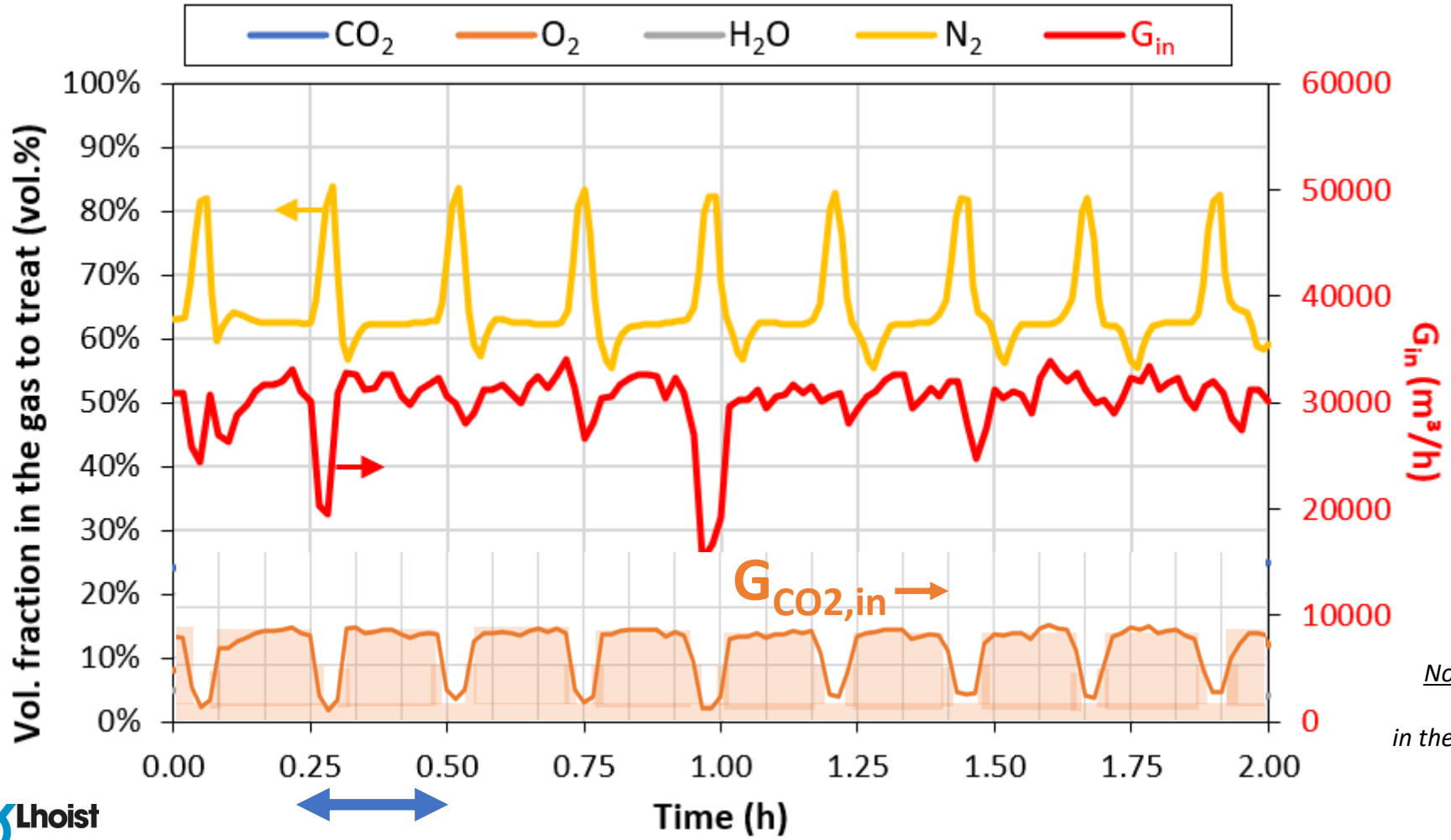
Lime production (230 tpd)



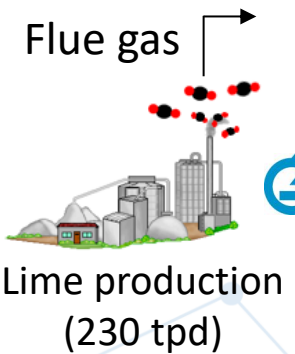
Parallel Flow Regenerative Kiln (PFRK)

15 min cycle = 11 min nominal + 4 min low G_{in} x low y_{CO_2} = low $G_{CO_2,in}$

Lime plant flue gas

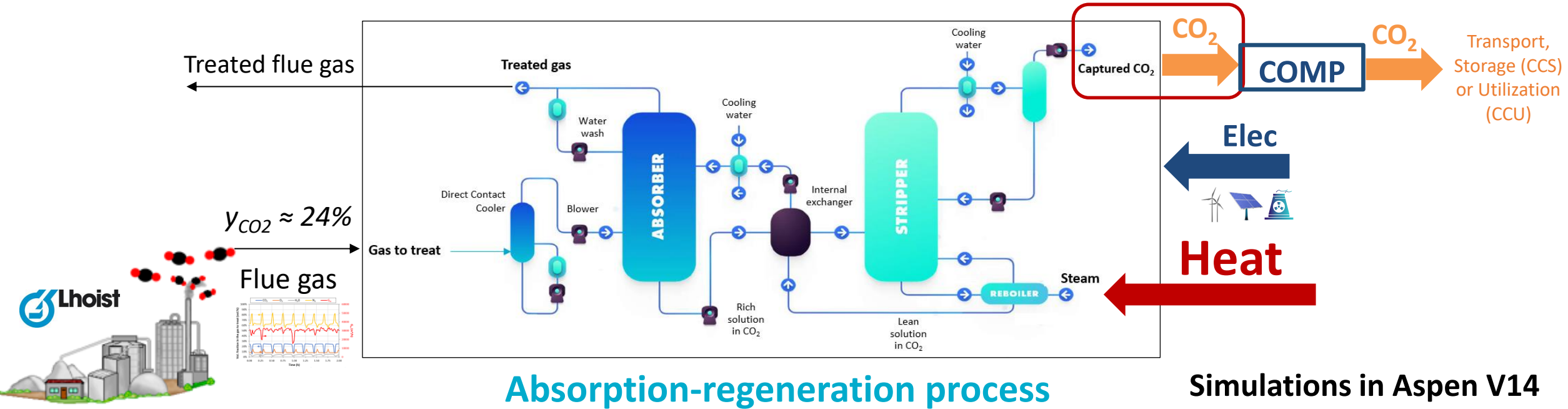


Note: Measurement campaign at Lhoist Hermalle site in the framework of the NKL project.



In terms of total CO_2 content in the gas ($G_{\text{CO}_2, in}$) \approx 15% decrease during a 15 min cycle

Study scope



Lime plant

What is the dynamic answer of the CO₂ capture process to the flue gas fluctuations?

What are the technical solutions to keep a recovered CO₂ flow as stable as possible?

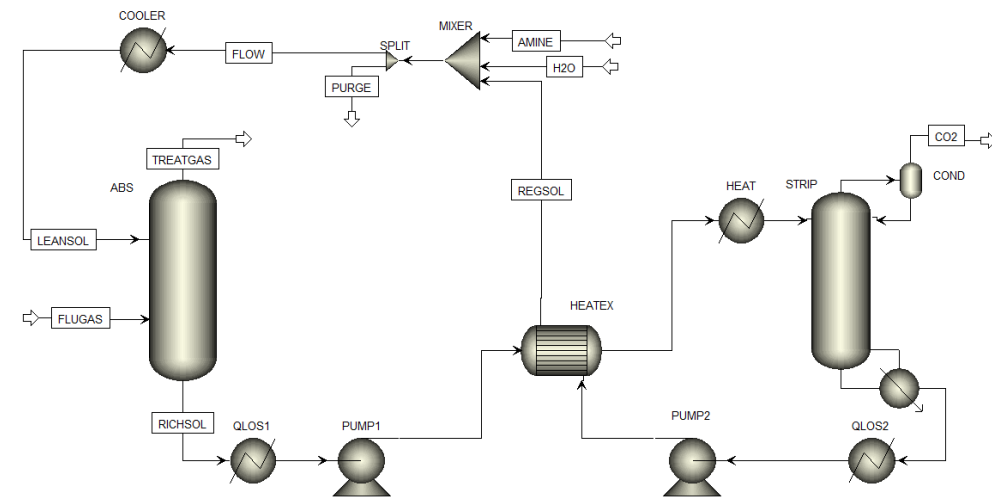
Micro-pilot scale model validation

**RadFrac columns in Aspen Dynamics®:
need to switch from « Rate based » mode to « Equilibrium » mode**

UMONS Micro-pilot unit:



Aspen Plus® steady state model:



| | | | |
|---|--|--|---|
| $H_{\text{packing,ABS}} = 1 \text{ m}$ | $H_{\text{packing,STRIP}} = 0.5 \text{ m}$ | $D_{\text{columns}} = 0.06 \text{ m}$ | Glass Raschig rings (6 x 6 mm) packing |
| $Y_{\text{CO}_2,\text{in}} = 20 \text{ vol.}\%$ | $G = 2.7 \text{ m}^3/\text{h}$ | $L = 0.014 \text{ m}^3/\text{h}$ | $P = 101.3 \text{ kPa}$ |
| $Q_{\text{reboiler}} = 2 \text{ kW}$ | $Q_{\text{HEAT}} = 1 \text{ kW}$ | $T_{\text{ABS,in}} = 40^\circ\text{C}$ | $T_{\text{STRIP,in}} = 95^\circ\text{C}$ |

Note: new unit working under pressure and with a decanter available soon.

Micro-pilot scale model validation

**RadFrac columns in Aspen Dynamics®:
need to switch from « Rate based » mode to « Equilibrium » mode**

UMONS Micro-pilot unit:



Aspen Plus® steady state model:

Solvent: monoethanolamine (MEA) 30 wt.%

| Type | Stoichiometry |
|-------------|---|
| Equilibrium | $2 \text{H}_2\text{O} \leftrightarrow \text{H}_3\text{O}^+ + \text{OH}^-$ |
| Equilibrium | $\text{CO}_2 + 2 \text{H}_2\text{O} \leftrightarrow \text{HCO}_3^- + \text{H}_3\text{O}^+$ |
| Equilibrium | $\text{HCO}_3^- + \text{H}_2\text{O} \leftrightarrow \text{CO}_3^{2-} + \text{H}_3\text{O}^+$ |
| Equilibrium | $\text{MEA}^+ + \text{H}_2\text{O} \leftrightarrow \text{MEA} + \text{H}_3\text{O}^+$ |
| Equilibrium | $\text{MEACOO}^- + \text{H}_2\text{O} \leftrightarrow \text{MEA} + \text{HCO}_3^-$ |

(Edwards et al., 1978)

Gibbs free energy minimization

(Edwards et al., 1978)

(Hamborg & Versteeg, 2009)

Gibbs free energy minimization

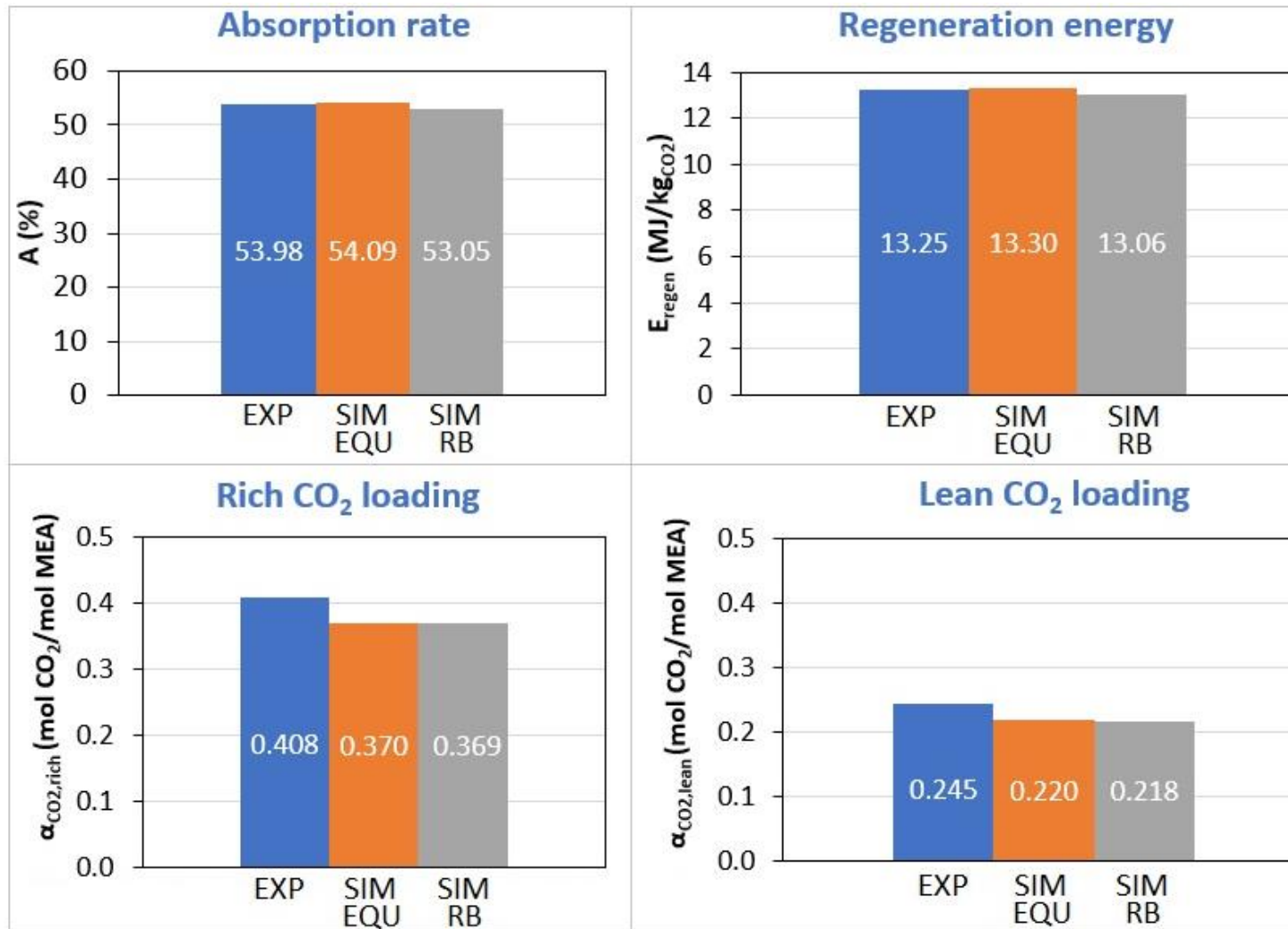
Thermodynamic models:

Vapor phase: Redlich Kwong (RK)

Liquid phase: Electrolyte Non-Random Two-Liquid (ELEC-NRTL)

Micro-pilot scale model validation

Aspen Plus®
steady state model



<2% relative difference

max ≈10% relative difference

“EXP”: UMONS micro-pilot unit results - “SIM EQU”: Aspen Plus® simulation results with RadFrac columns in equilibrium mode & “SIM RB” in rate-based mode

Dynamic simulations conditions

Lime kiln flue gas flow rate (temporal variations)

Flue gas composition (temporal variations)

Targeted recovered CO₂ flow rate

Recovered CO₂ purity

Solvent

Columns height

Columns (and sumps) diameter

Columns sump height

Columns packing

Inlet liquid temperature

Columns bottom pressure

Liquid flow rate (absorber inlet)

Nominal reboiler heating power (“P_{boiler-fix}”)

Dynamic calculation step

Dynamic simulations conditions

Lime kiln flue gas flow rate (temporal variations)

15000 m³/h to 34000 m³/h (at 110°C and 1 atm)

Flue gas composition (temporal variations)

N₂: 55 vol.% to 84 vol.% / CO₂: 5 vol.% to 25 vol.%
O₂: 8 vol.% to 15 vol.% / H₂O: 2 vol.% to 5 vol.%

Targeted recovered CO₂ flow rate

~12600 kg_{CO2}/h (~ 90% of inlet CO₂ on average)

Recovered CO₂ purity

99.0 wt.%

Solvent

Monoethanolamine (MEA) 30 wt.% in aqueous solution

Columns height

Columns (and sumps) diameter

Columns sump height

Columns packing

Inlet liquid temperature

Columns bottom pressure

Liquid flow rate (absorber inlet)

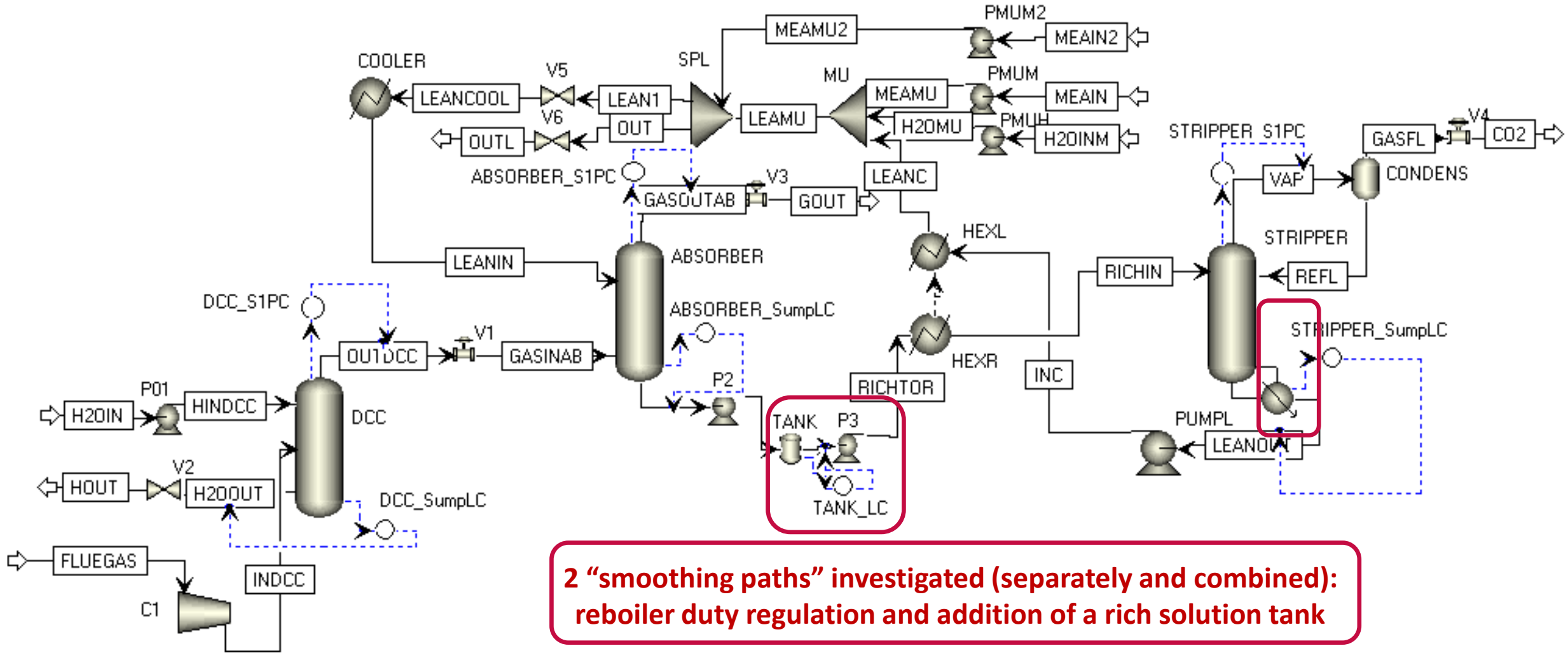
Nominal reboiler heating power (“P_{boiler-fix}”)

Dynamic calculation step

Dynamic simulations conditions

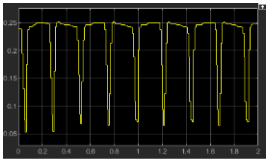
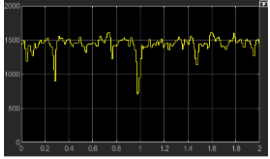
| | |
|---|--|
| Lime kiln flue gas flow rate (temporal variations) | 15000 m ³ /h to 34000 m ³ /h (at 110°C and 1 atm) |
| Flue gas composition (temporal variations) | N ₂ : 55 vol.% to 84 vol.% / CO ₂ : 5 vol.% to 25 vol.% O ₂ : 8 vol.% to 15 vol.% / H ₂ O: 2 vol.% to 5 vol.% |
| Targeted recovered CO ₂ flow rate | ~12600 kg _{CO2} /h (~ 90% of inlet CO ₂ on average) |
| Recovered CO ₂ purity | 99.0 wt.% |
| Solvent | Monoethanolamine (MEA) 30 wt.% in aqueous solution |
| Columns height | DCC: 8 m (8 stages x 1m) / Absorber: 17 m (17 stages x 1 m) Stripper: 10 m (10 stages x 1 m) |
| Columns (and sumps) diameter | DCC: 3 m / Absorber: 3.4 m / Stripper: 4.2 m |
| Columns sump height | ≈25% of columns height (DCC: 2 m / Absorber: 4 m / Stripper: 2.5 m) |
| Columns packing | Random metal packing IMTP 50 |
| Inlet liquid temperature | DCC: 30°C / Absorber: 40°C / Stripper: 110°C |
| Columns bottom pressure | DCC: 1.2 bar / Absorber: 1.2 bar / Stripper: 2 bar |
| Liquid flow rate (absorber inlet) | 192 m ³ /h (value minimizing E _{regen} in steady state mode) |
| Nominal reboiler heating power ("P _{boiler-fix} ") | 42.54 GJ/h → E _{regen} = 3.38 GJ/t _{CO2} |
| Dynamic calculation step | 0.01 h |

Aspen Dynamics® flow sheet

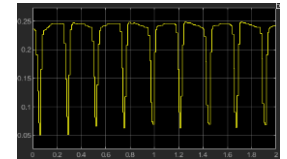
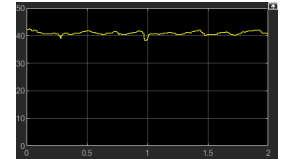
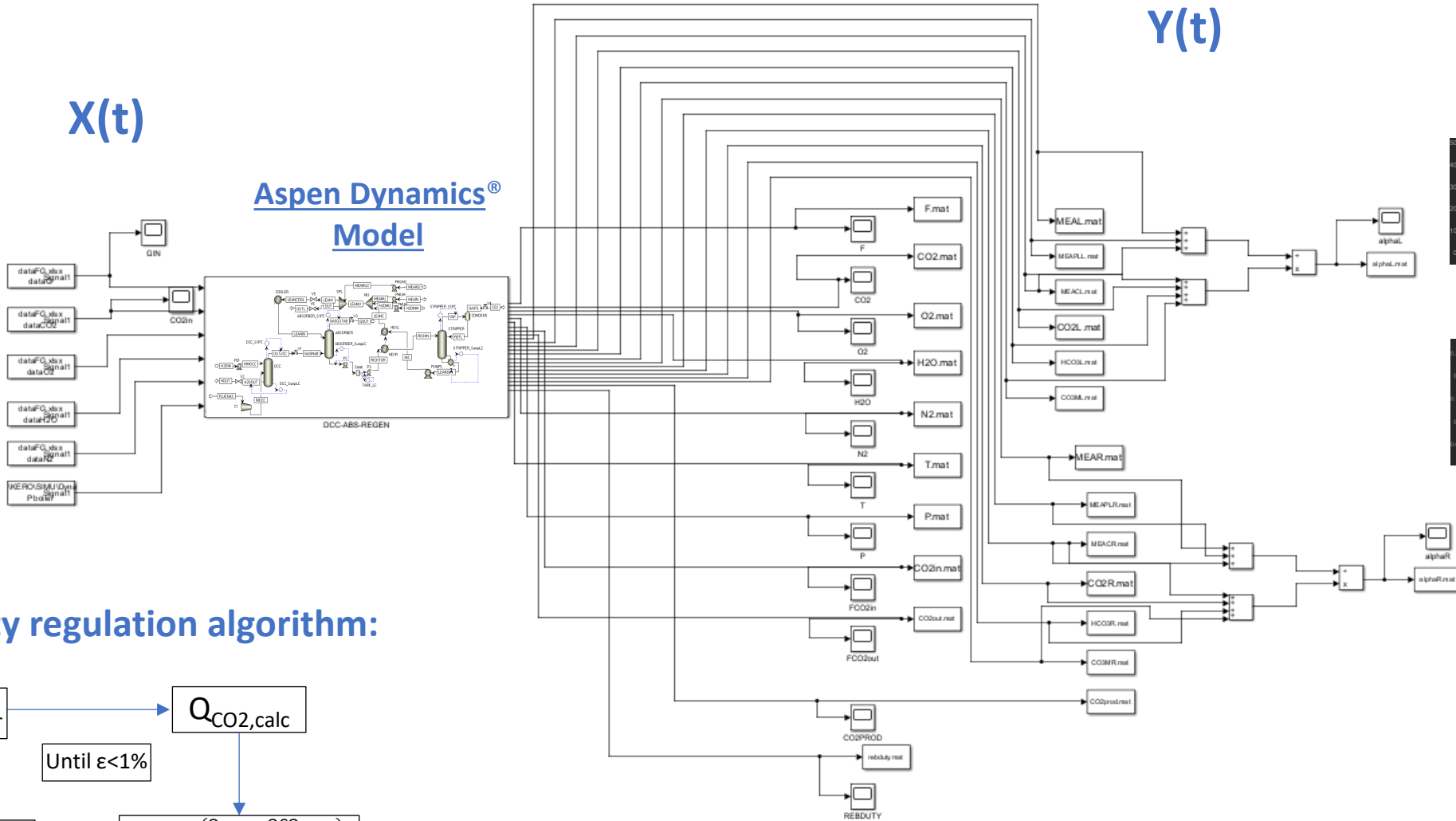


Note: gas holder not considered as option (expensive and needs a lot of space available)

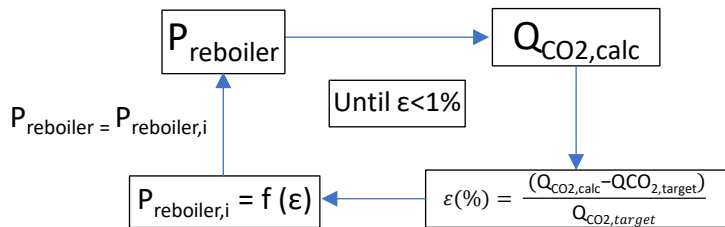
Integration with Matlab/Simulink®



Excel spreadsheets

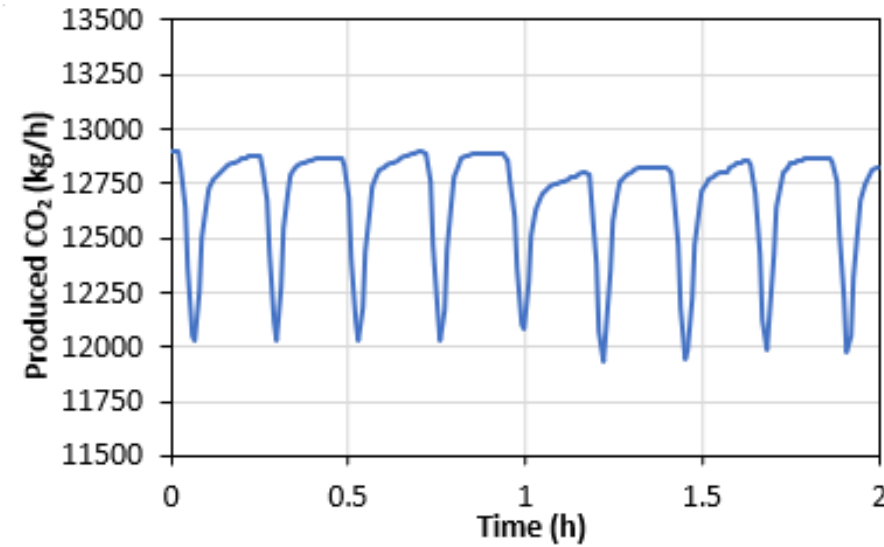
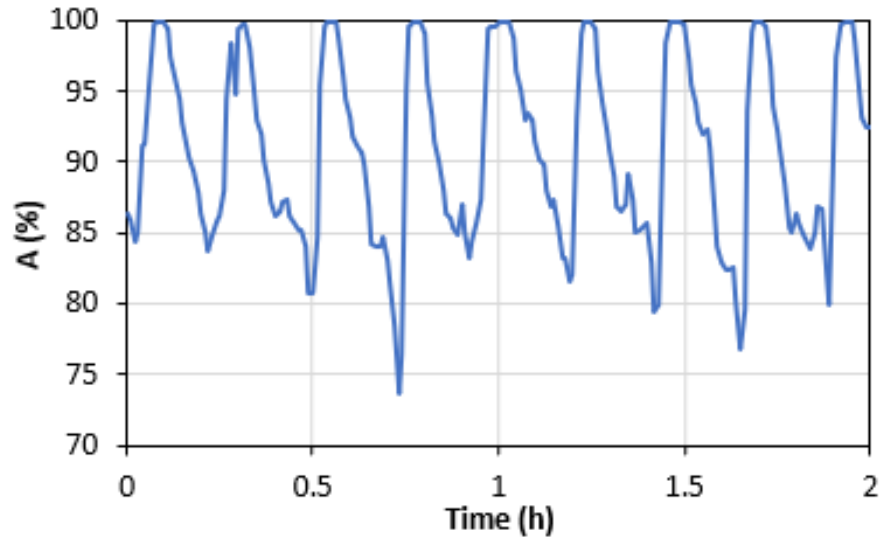


Reboiler duty regulation algorithm:



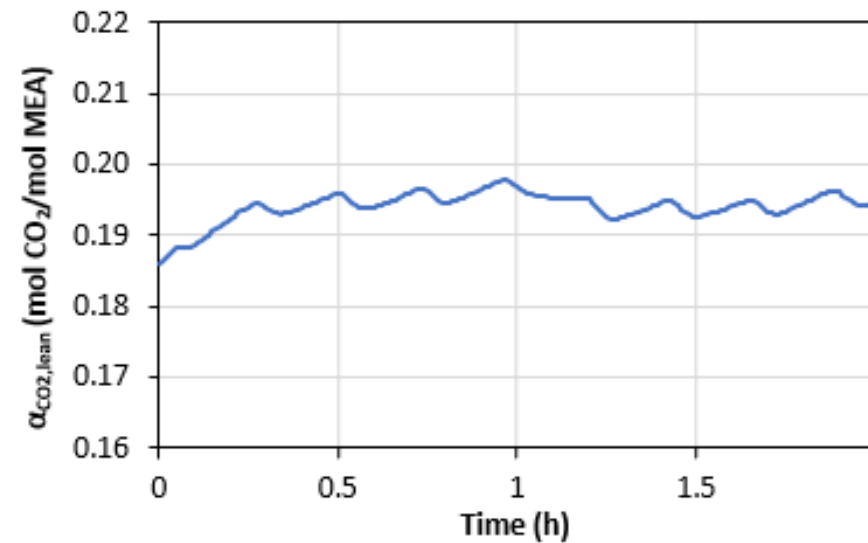
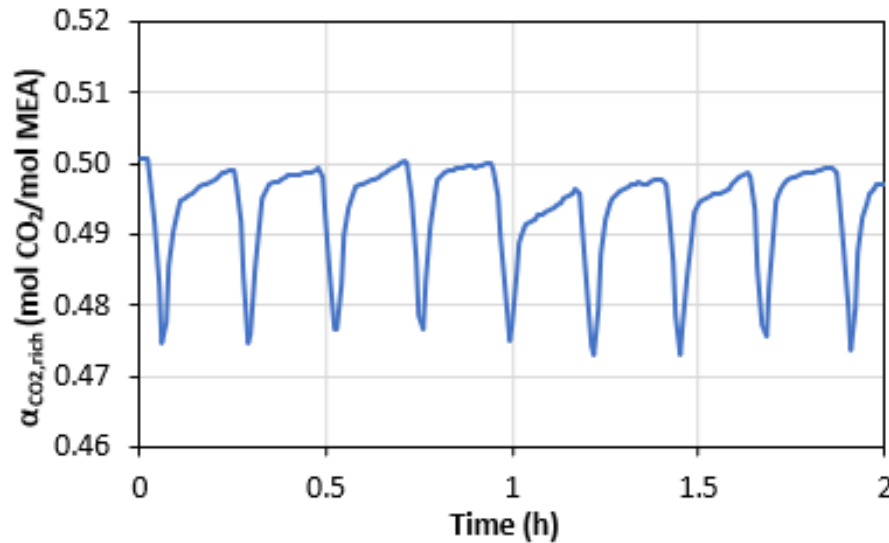
Base case results

As G & y_{CO_2} ↓
 A ↑ ↓



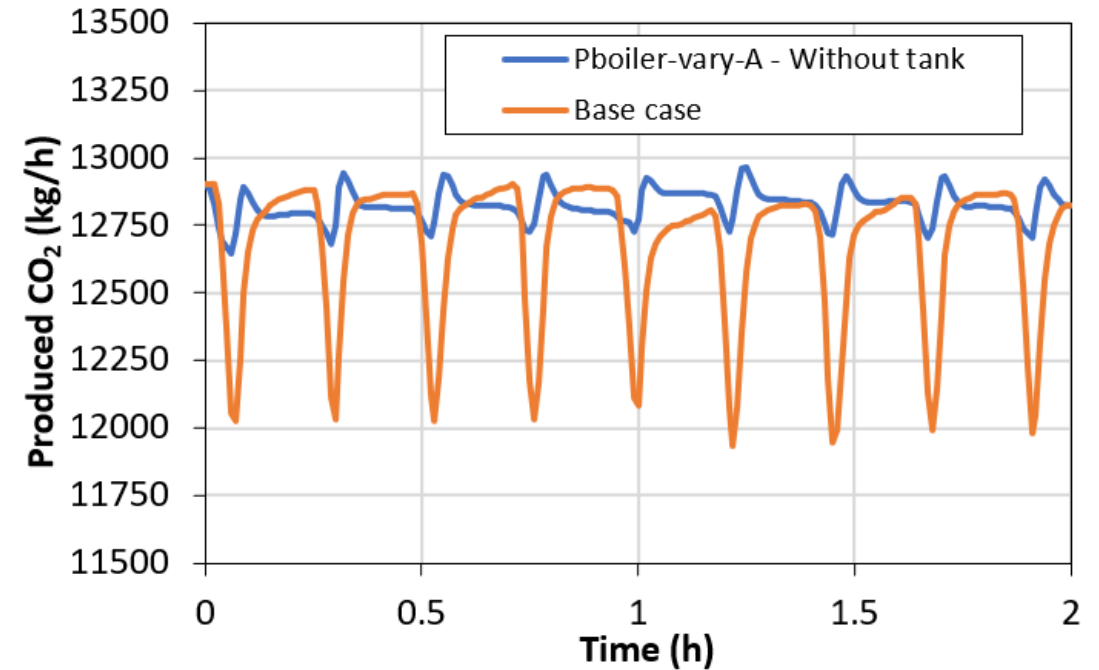
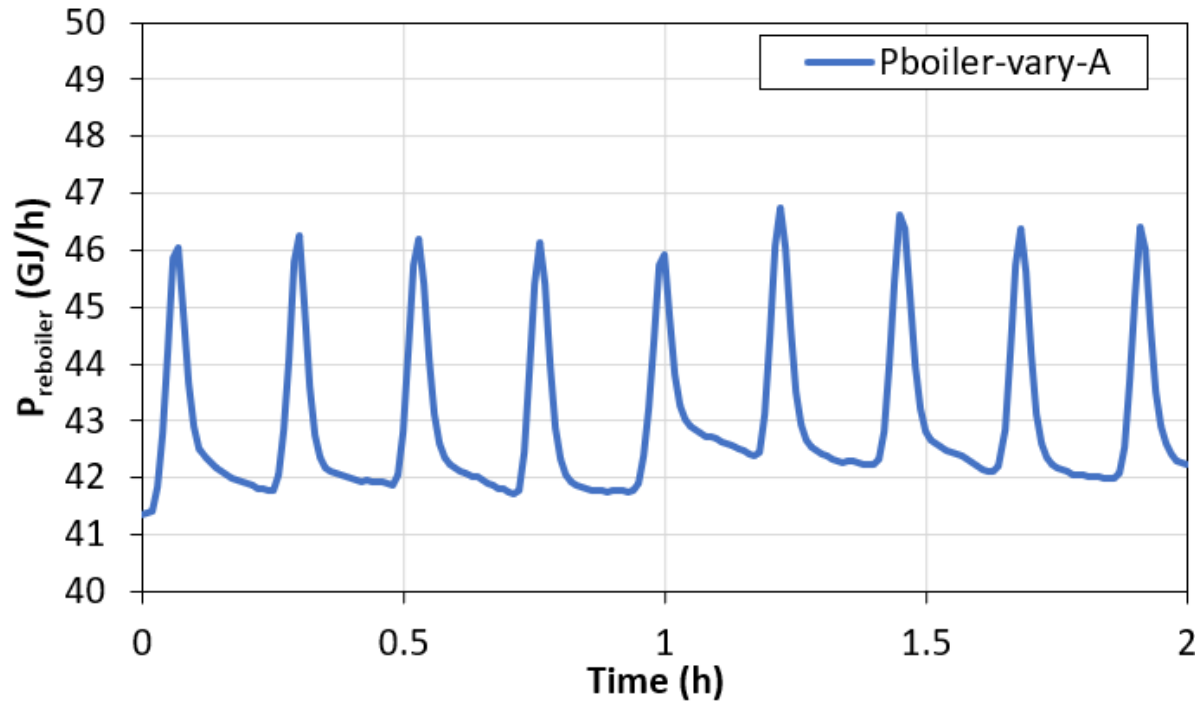
CO_2 production ↓
during 4 min

$\alpha_{CO_2,rich}$ ↓
during 4 min



$\alpha_{CO_2,lean}$
less impacted

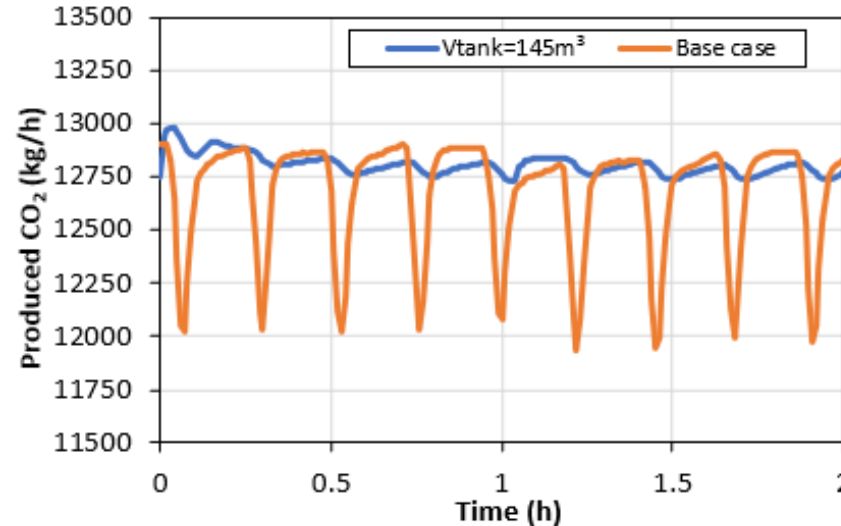
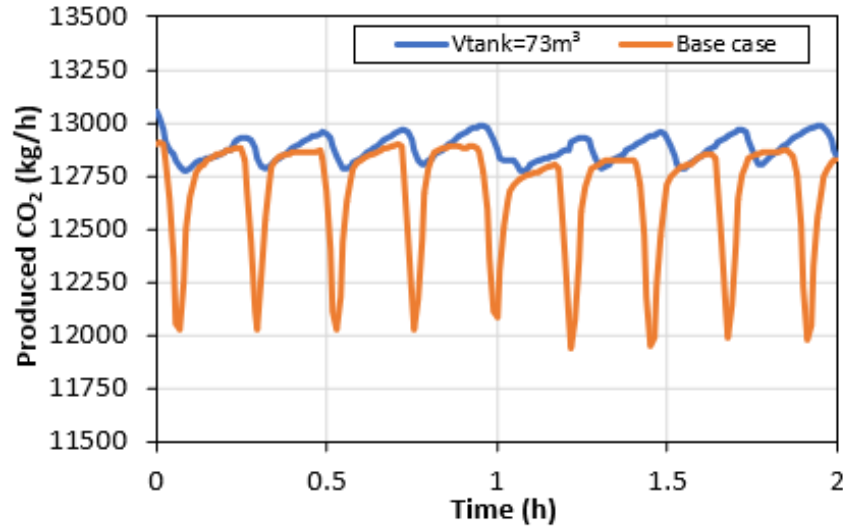
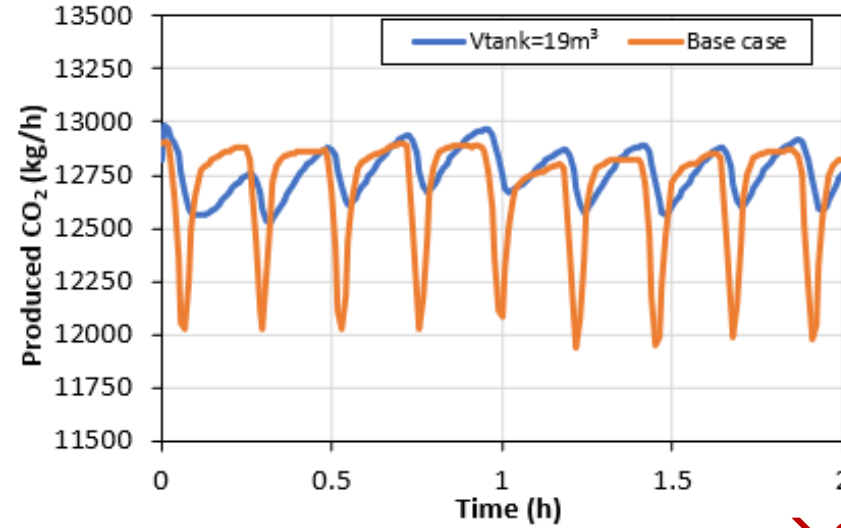
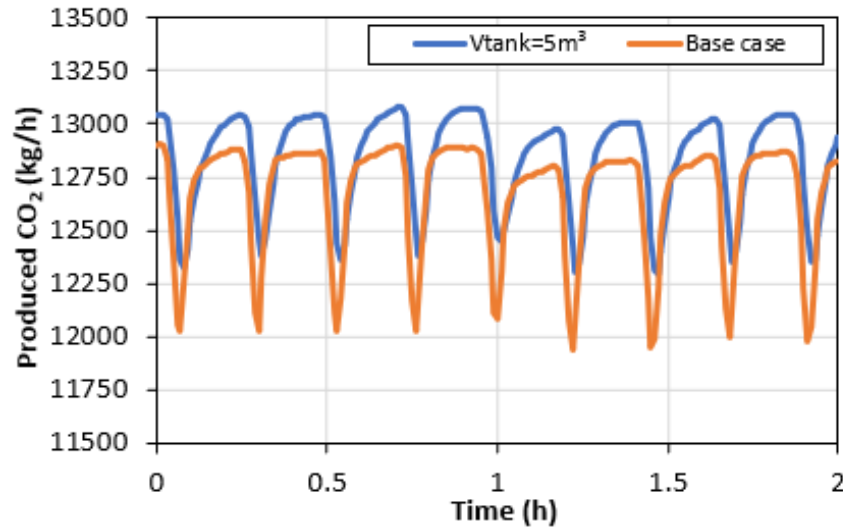
Reboiler duty regulation



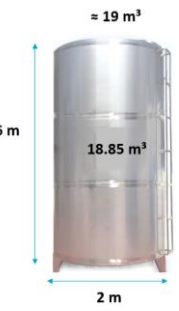
Thanks to reboiler heating regulation:

maximum **9.5%** temporary increases of the nominal heating power,
maximum **1.5%** of variation of the CO_2 production flow

Rich solution buffer tank

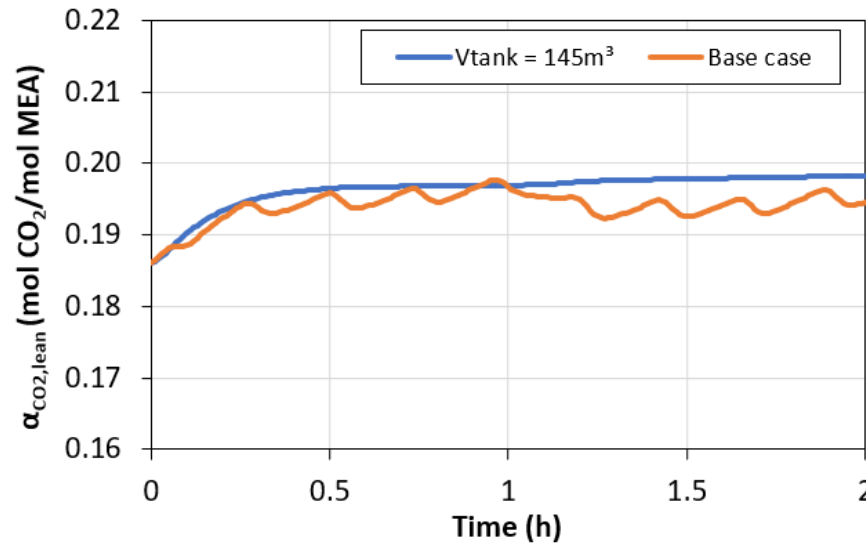
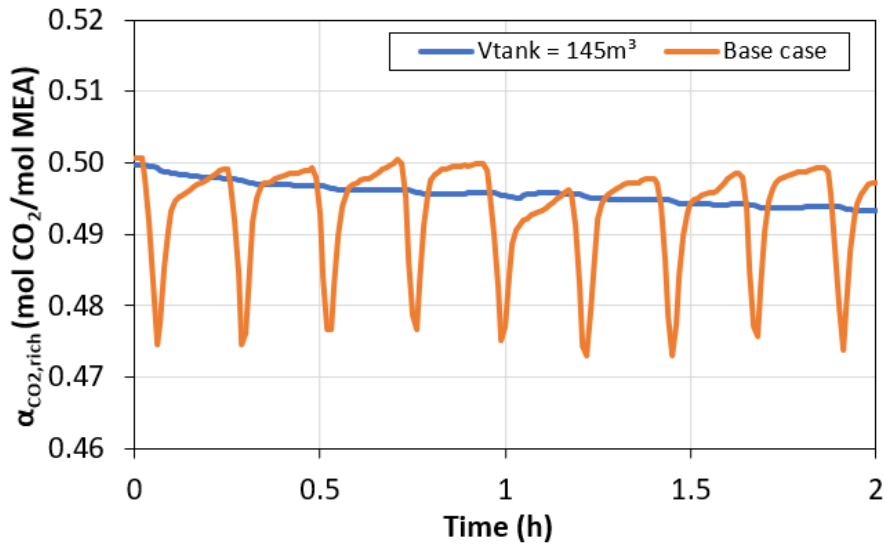


$V_{\text{tank}} \uparrow$
 $\rightarrow \text{CO}_2$ production more stable



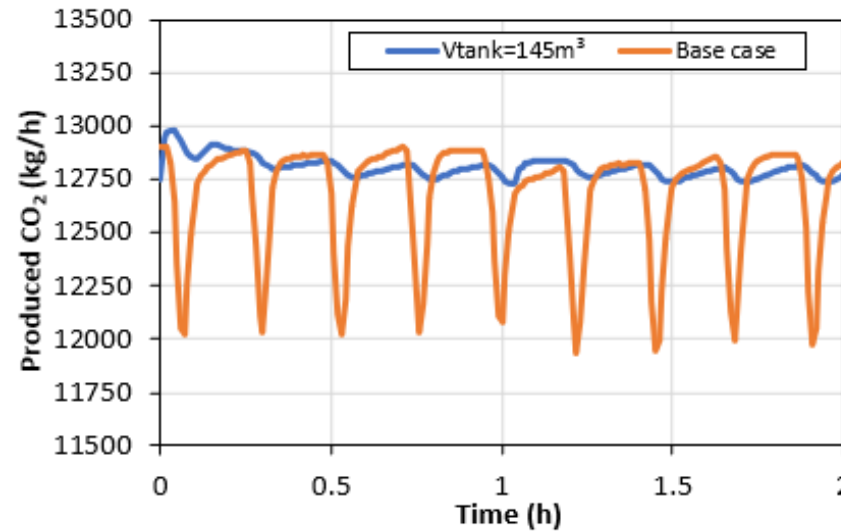
- $(D_{\text{tank}} \times H_{\text{tank}})$:
- $V_{\text{tank}} = 5 \text{ m}^3$
(2 m x 1.6 m)
- $V_{\text{tank}} = 19 \text{ m}^3$
(2 m x 6 m)
- $V_{\text{tank}} = 73 \text{ m}^3$
(3.4 m x 8 m)
- $V_{\text{tank}} = 145 \text{ m}^3$
(6.4 m x 4.5 m)

Rich solution buffer tank

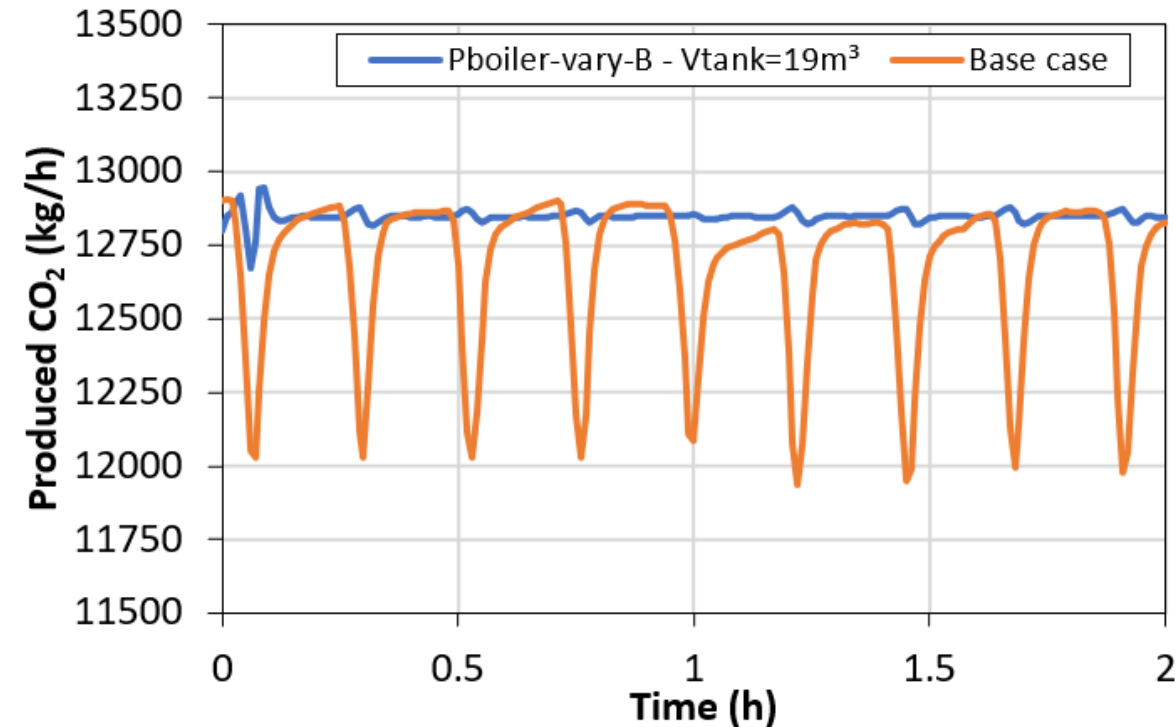
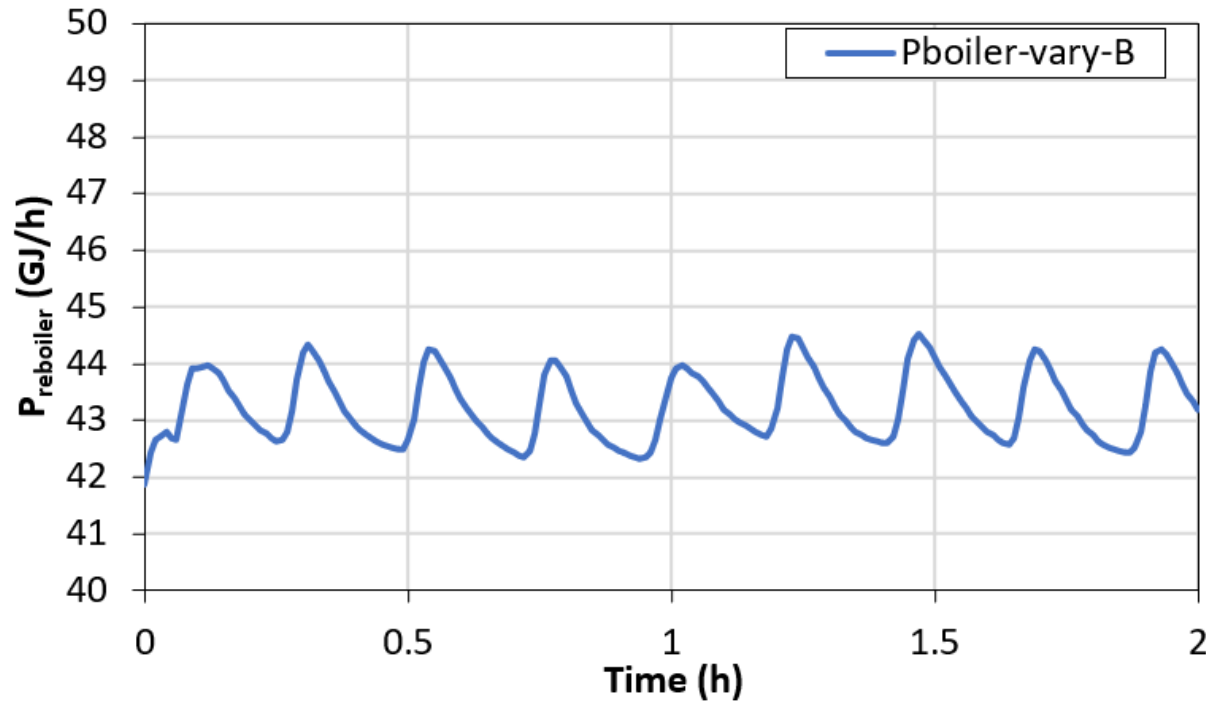


→ CO₂ production more stable

→ Both rich and lean CO₂ loadings more stable



Reboiler duty regulation & tank

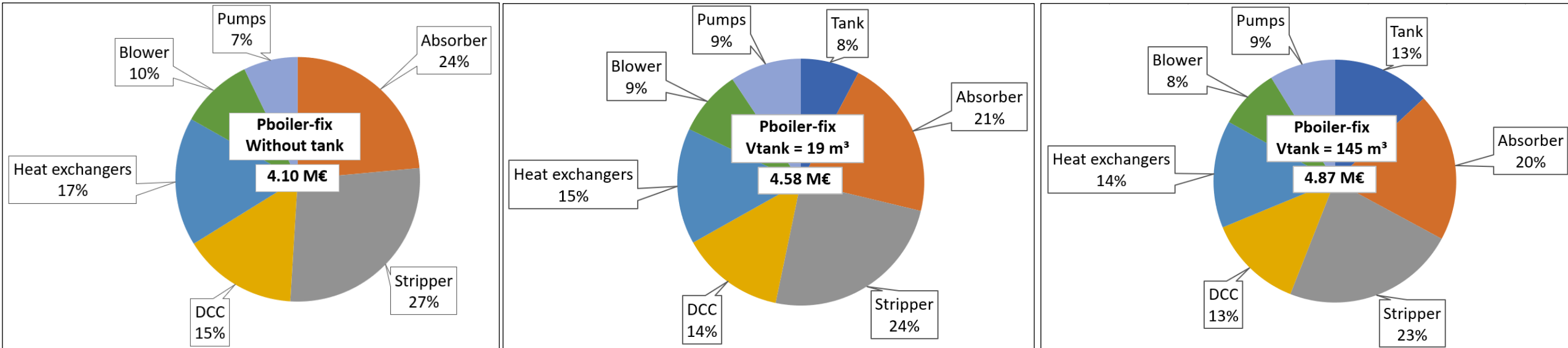


Thanks to reboiler heating regulation and rich solution tank (19 m^3) implementation:

maximum **5%** temporary increases of the nominal heating power,
maximum **0.3%** of variation of the CO_2 production flow

Equipment costs

Base case



CEPCI₂₀₂₃ = 797.9

8%

13%

Rich solution tank contribution to equipment costs from 8% to 13%

CAPEX

| Cost item / Process | Base case (no tank) | V _{tank} = 19 m ³ | V _{tank} = 145 m ³ |
|---|------------------------|--|---|
| Direct costs items | | | |
| Purchased Equipment | 1.73 | 1.94 | 2.06 |
| Equipment Setting | 0.03 | 0.03 | 0.03 |
| Piping | 0.68 | 0.76 | 0.81 |
| Civil | 0.13 | 0.15 | 0.16 |
| Steel | 0.07 | 0.08 | 0.09 |
| Others ⁽¹⁾ | 1.45 | 1.62 | 1.72 |
| Total direct costs (M€) | 4.10 | 4.58 | 4.87 |
| Indirect costs (M€)⁽²⁾ | 5.90 | 6.60 | 7.01 |
| Fixed Capital Investment (M€) ⁽³⁾ | 10.00 | 11.19 | 11.88 |
| Working capital (M€) ⁽⁴⁾ | 1.50 | 1.68 | 1.78 |
| CAPEX (M€) | 11.50 | 12.86 | 13.66 |
| /Conventional MEA process | | +12% | +19% |

(1) Instrumentation, electrical, insulation, and paint categories.

(2) Cost of engineering and supervision, legal expenses, construction expenses, contractors fees and contingency.

A ratio factor of 1.44 is applied across the direct purchased equipment cost for the indirect costs.

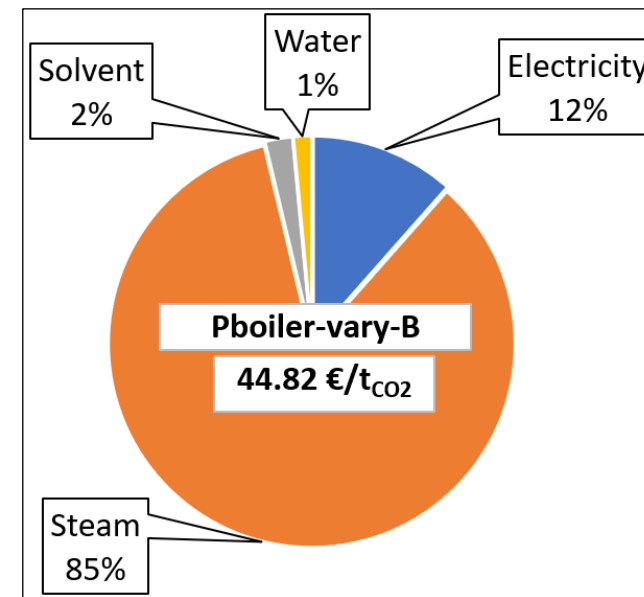
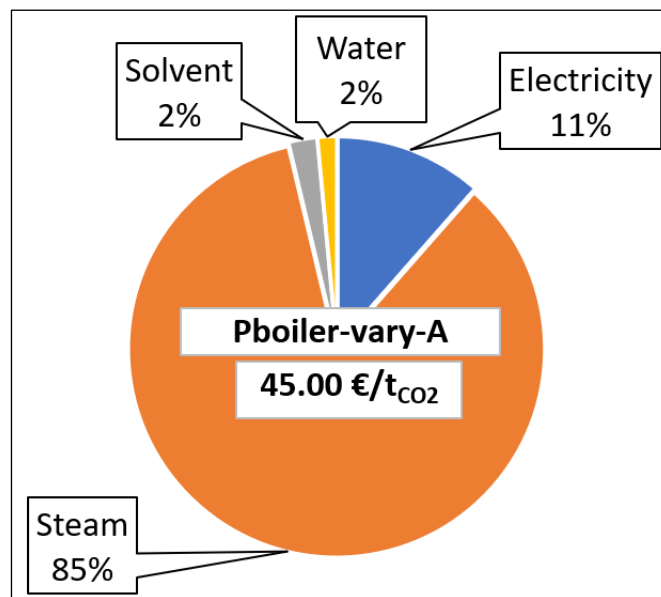
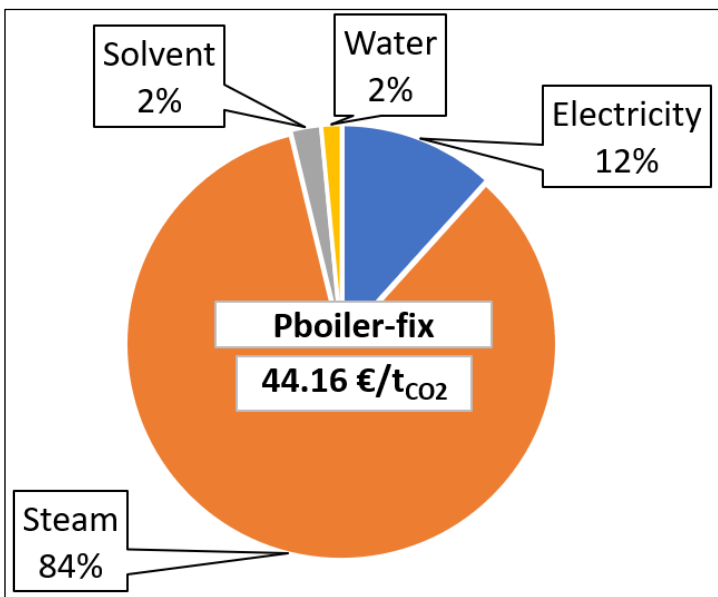
(3) Sum of the direct and indirect costs.

(4) Working capital = 15 % of the FCI.

Rich solution tank leads to a CAPEX increase from 12% to 19%

Variable costs

Base case



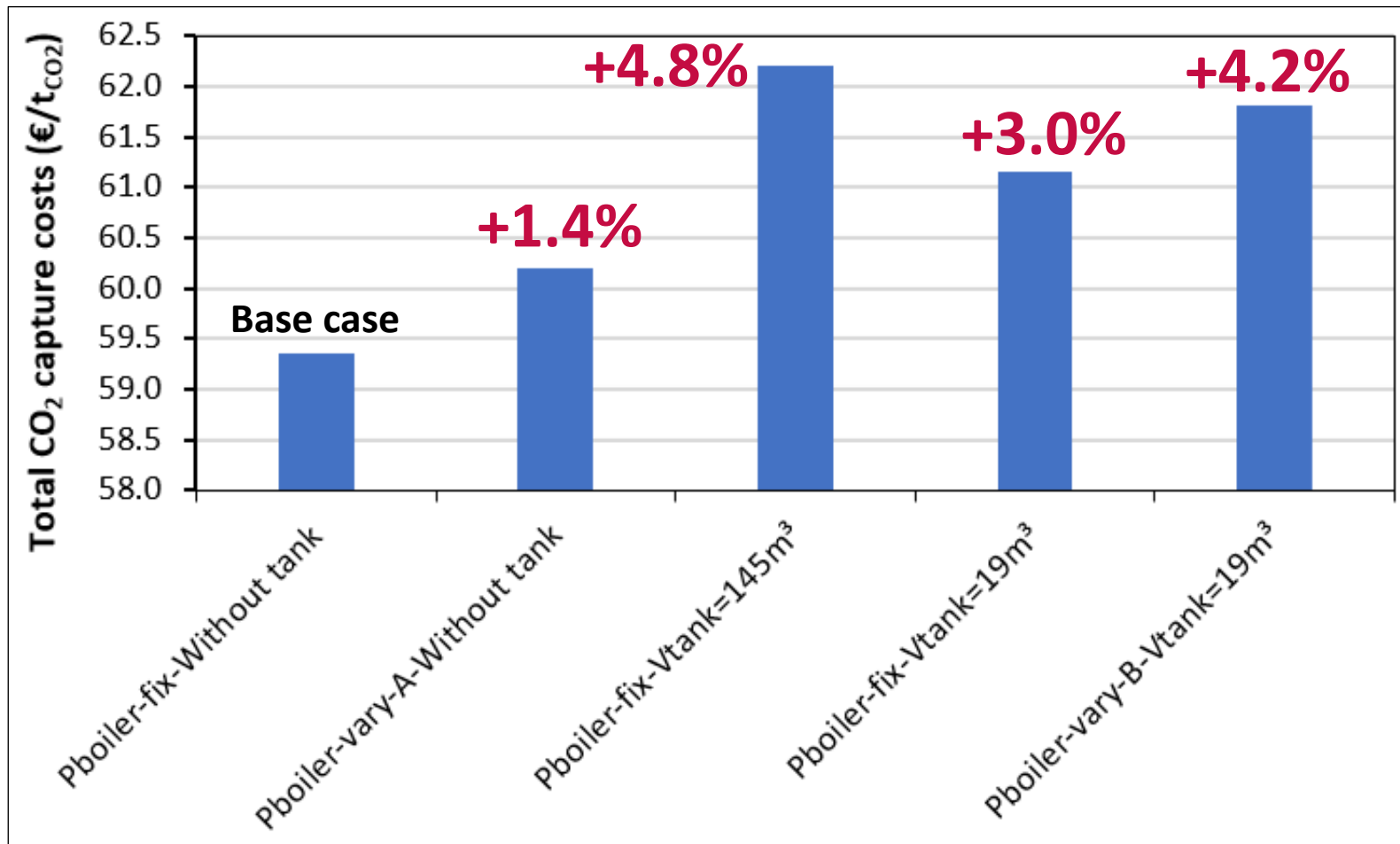
+1.9%

+1.5%

Electricity: 100 €/MWh
 Steam: 22.5 €/t_{steam}
 Cooling water: 0.1165 €/t_{water}
 Process water: 0.4241 €/t_{water}
 Solvent costs: 1 €/kg

Limited variable costs increase in both cases

Total CO₂ capture costs



Limited increase of the total CO₂ capture costs

Fixed costs included:
corresponding to operation and
maintenance expenses, fixed to
7% of the CAPEX.

Annualized CAPEX included:
lifetime of 25 years, 8232 hours of
annual effective operations,
interest rate corresponding to a
straight-line depreciation of 6.5%.

Conclusions

- **Management of lime plant flue gas fluctuations** is a challenge for carbon capture application.
- **Reboiler duty regulation** and/or **implementation of a rich solution buffer tank** are good solutions to “smooth” the recovered CO₂ flow with limited cost increase (<5%).
- The **combination** of the 2 solutions **limits the CAPEX increase** and offers **more flexibility**.
- Key aspects are the **costs (and availability)** of the **steam** and the **electricity** for such industrial plants.
- Future steps: **other solvents**, process **configurations**, comparison with **other CO₂ capture technologies**.

THANKS VERY MUCH FOR YOUR ATTENTION

QUESTIONS?



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