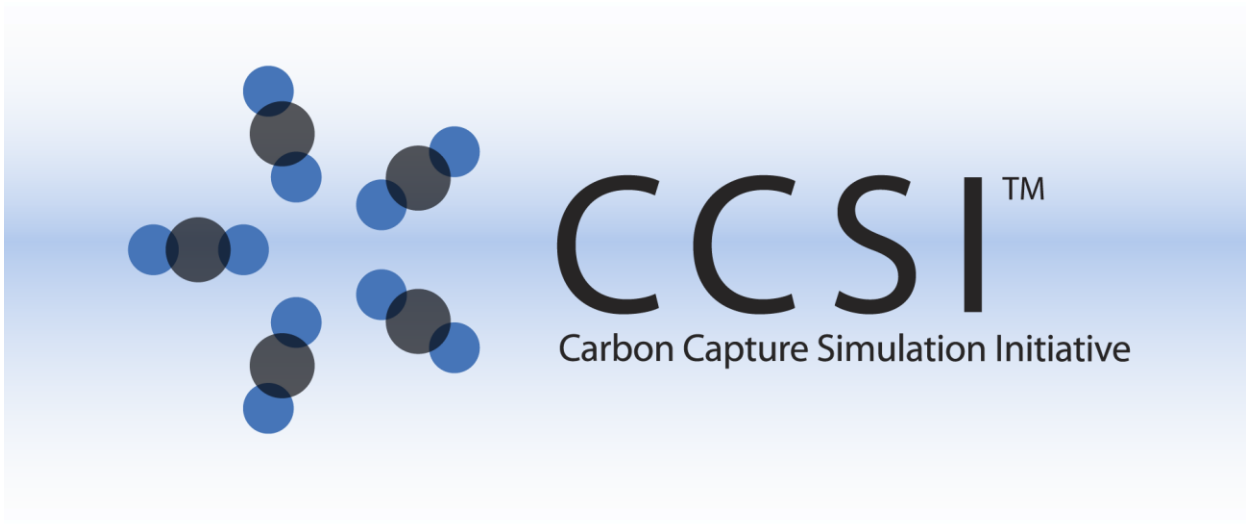


# CCSI Steady State MEA Model (MEA ssm)

# User Manual

**Version 2.0.0**

**March 2018**






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# 1.0 REPORTING ISSUES

To report an issue, please send an e-mail to ccsi-support@acceleratecarboncapture.org.

# 2.0 VERSION LOG

| Product | Version Number | Release Date | Description |
|---|---|---|---|
| Steady State MEA Model | 2.0.0 | 3/31/2018 | Initial Open Source release |
| Steady State MEA Model | 2015.10.0 | 10/16/2015 | |

# MEA Steady State Model

## 1.0 MODEL DEVELOPMENT

### 1.1 Model Background

This document describes a solvent-based $CO_2$ capture system using aqueous monoethanolamine (MEA). The model consists of the "CCSI_MEAModel.bkp" file with supporting files "gold.opt" and "gold.dll," which contain FORTRAN user models associated with the simulation. This model was developed with Aspen Plus® V8.4 and is compatible with V8.4 and higher.

This model represents the first version of the "gold standard" model for the MEA capture system. It is composed of individually developed submodels for physical properties of $CO_2$-loaded aqueous MEA solutions and hydraulic and mass transfer models for the system of interest. Each submodel is developed and calibrated with relevant data over the full range of process conditions of interest (e.g., temperature, composition). For each submodel, existing models are considered as candidates and are modified to better fit experimental data over the conditions of interest.

### 1.2 Physical Property Models

Physical property models developed in this work include standalone models and an integrated thermodynamic framework. Standalone models for viscosity, density, and surface tension of the system have been developed, with uncertainty quantification, as described in Morgan et al.,[1] and are implemented as FORTRAN user models. The thermodynamic framework of this system is developed using UT Austin's Phoenix model[2] thermodynamic framework as a precursor. Here, the solution thermodynamics are represented by the ELECNRTL method in Aspen Plus, which uses the Redlich-Kwong equation of state to calculate the vapor phase fugacity coefficients and the electrolyte non-random two liquid (e-NRTL) model to calculate the activity coefficients in the liquid phase. Model parameters are calibrated by fitting data for VLE, heat capacity, and heat of absorption for the ternary MEA-$H_2O$-$CO_2$ system and VLE data for the binary MEA-$H_2O$ system. The kinetic model used in this work is taken from the Phoenix model, in which the overall ionic speciation of the system is simplified into two equilibrium reactions:

$$2MEA + CO_2 \leftrightarrow MEA^+ + MEACOO^- \quad (1)$$

$$MEA + CO_2 + H_2O \leftrightarrow MEA^+ + HCO_3^- \quad (2)$$

The forward reaction rate constants are taken from the Phoenix model, and the overall reaction rate is written in terms of the equilibrium constants which are also calculated as part of the thermodynamic framework of the system. This follows the methodology presented in Mathias and Gilmartin[3], and is implemented to ensure that the reaction kinetics are consistent with the thermodynamic framework.

## 1.3 Mass Transfer and Hydraulic Models

The hydrodynamic models developed in this work include models for pressure drop and hold-up. The Billet and Schultes[4] correlation is regressed with data from Tsai[5] for MellapakPlus™ 250Y packing, which is similar to MellapakPlus 252Y packing, which is considered in this work. In this work, a novel and integrated methodology to obtain the mass transfer model is proposed. In this integrated mass transfer model, parameters of the interfacial area, mass transfer coefficients, and diffusivity models are regressed using wetted wall column data from Dugas[6] and pilot plant data from Tobiesen et al.[7] This required simultaneous regression of process model and property parameters, which was accomplished using the CCSI software Framework for Optimization and Quantification of Uncertainty and Sensitivity (FOQUS).

## 1.4 Development of Process Model

The aforementioned submodels are integrated into this steady state process model, which is representative of the configuration of the National Carbon Capture Center (NCCC) in Wilsonville, Alabama, for which data have been obtained for validation of this model. No parameters are tuned to improve the fit to the fit to the pilot plant data. The model includes both the absorber and stripper columns, although the recycle of the lean solvent from the regenerator outlet to the absorber inlet is not modeled. The columns are modeled as rate based columns using RateSep™.

The various submodels are implemented in Aspen Plus either as built-in models (e.g., ELECNRTL thermodynamic framework) or FORTRAN user models, in cases where built-in models with the appropriate model form are not available. The user models are combined into a dynamic library ("gold.dll" for this model) and a dynamic linking options (DLOPT) file ("gold.opt") is also provided, which has already been specified in the Aspen Plus file for this model. The various user models contained in the linked library include physical property models for viscosity, density, surface tension, and diffusivity, the hydraulics model, the interfacial area model, and the reaction kinetics model.

## 1.5 Model Features

The "CCSI_MEAModel.bkp" file included is representative of a typical operating case at NCCC and some adjustment of operating variables is possible. Table 14 includes some of these variables and suggested ranges for which the model is expected to work, based on the ranges considered in the testing at NCCC.

**Table 1: Suggested Ranges for Variables in Simulation**

| Variable | Range |
|---|---|
| Lean Solvent Amine Concentration (g MEA/g MEA+$H_2O$) | 0.25 – 0.35 |
| Lean Solvent $CO_2$ Loading (mol $CO_2$/mol MEA) | 0.05 – 0.50 |
| Lean Solvent Flowrate (kg/hr) | 3000 – 12000 |
| Flue Gas Flowrate (kg/hr) | 1250 – 3000 |
| Regenerator Reboiler Duty (kW) | 150 – 700 |

Table 14 includes the major variables that dictate the performance of the process, although the list is not exhaustive. Other variables, including operating temperature and pressure of the equipment, are set at typical values for the MEA-based $CO_2$ capture process, and slight variation of these variables is allowable. As the lean solvent flowrate is decreased, the intercooler flow rates should be adjusted accordingly. **Note:** The apparent mole fractions of molecular species may be calculated from the amine concentration ($\gamma$) and $CO_2$ loading ($\alpha$) using the equations:

$$X_{MEA} = \left(1 + \alpha + \left(\frac{MW_{MEA}}{MW_{H_2O}}\right)\left(\frac{1}{\gamma} - 1\right)\right)^{-1} \quad (3)$$

$$X_{CO_2} = \alpha X_{MEA} \quad (4)$$

$$X_{H_2O} = 1 - X_{MEA} - X_{CO_2} \quad (5)$$

# 2.0 TUTORIAL

## 2.1 Predicting System VLE

1. Place the "CCSI_MEAModel.bkp" file and the supporting files "gold.opt" and "gold.dll" in the same directory. Open the "CCSI_MEAModel.bkp" file. If the Model Palette is not visible, it may be selected from the "View" tab at the top of the window. In the Model Palette, navigate to the "Manipulators" tab and then select "Mult" to create a multiplier block, which will be referred to by its default name "B1." Double-click "B1" and then set the multiplication factor to "1." Add an inlet stream to the block by clicking "Material" in the Model Palette, the red arrow on the inlet of B1, and then elsewhere in the flowsheet. Repeat the procedure for the outlet stream of B1. Name the inlet and outlet streams as "IN" and "OUT," respectively. **Note:** The streams may be renamed by double clicking the default name and typing the new name.
2. Double-click "IN" and configure it as follows:
    a. Select "Temperature" and "Vapor Fraction" as the "Flash Type" specifications.
    b. Temperature: 40°C.
    c. Vapor Fraction: 0.0001.
    d. Select "Mass-flow" in "gm/hr" as the composition basis. Set the values for "$H_2O$" and "MEA" as "7" and "3," respectively.
3. In the left navigation pane, navigate to "Model Analysis Tools" → "Sensitivity," and then click "New." The new sensitivity block may be named "PCO2." Under "Manipulated variable" in the "Vary" tab, select "New," select "Mole Flow" as "type," "IN" as "stream," "CO2" as "component," and "mol/hr" as the "units." Under "Manipulated variable limits," specify "0.0005" and "0.03" as the "lower" and "upper limits," respectively, and "10" as the "number of points." Navigate to the "Define" tab and then create a new measured variable named "PCO2." Under "Edit selected variable," select "Streams" as the "category," "Stream-Prop" as the "type," "IN" as the "stream," and "PPCO2" as the "prop set." Navigate to the "Tabulate" tab and then click "Fill Variables." Navigate to the "Options" tab and select the "Do not execute base case," option under "Execution options."
4. Run the simulation by clicking the "Run" arrow or pressing "F5." The results of the "PCO2" sensitivity block should be consistent with what is shown in Table 15. **Note:** All of the warnings that appear in the "Control Panel" while running the simulation may be ignored.

**Table 2: Results of $PCO_2$ Sensitivity Block**

| Row/ Case | Status | CO2 MOLEFLOW (MOL/HR) | PCO2 (KPA) |
|---|---|---|---|
| 1 | OK | 0.0005 | 1.50E-05 |
| 2 | OK | 0.003778 | 0.000778 |
| 3 | OK | 0.007056 | 0.003344 |
| 4 | OK | 0.010333 | 0.009855 |
| 5 | OK | 0.013611 | 0.026325 |
| 6 | OK | 0.016889 | 0.07395 |
| 7 | OK | 0.020167 | 0.261753 |
| 8 | OK | 0.023444 | 1.626653 |
| 9 | OK | 0.026722 | 15.53083 |
| 10 | OK | 0.03 | 81.84875 |

5. From this example, the vapor-liquid equilibrium (VLE) of the ternary MEA-$H_2O$-$CO_2$ system as a function of temperature and $CO_2$ loading may be determined for 30 wt% MEA. The $CO_2$ loading (mol $CO_2$/mol MEA) may be calculated by multiplying the $CO_2$ molar flow by the molecular weight of MEA and dividing by the mass flow of MEA. For example,

$$\frac{\mathbf{0.0005\ mol\ CO_2}}{\mathbf{hr}} \times \frac{\mathbf{61.08308\ g\ MEA}}{\mathbf{mol\ MEA}} \times \frac{\mathbf{hr}}{\mathbf{3\ g\ MEA}} \approx \mathbf{0.0102\ mol\ CO_2/mol\ MEA} \quad (6)$$

Following this procedure and evaluating the sensitivity block for temperatures of 80 and 120°C, by changing the temperature of the stream "IN" and re-running the simulation, a plot similar to Figure 34 may be generated.

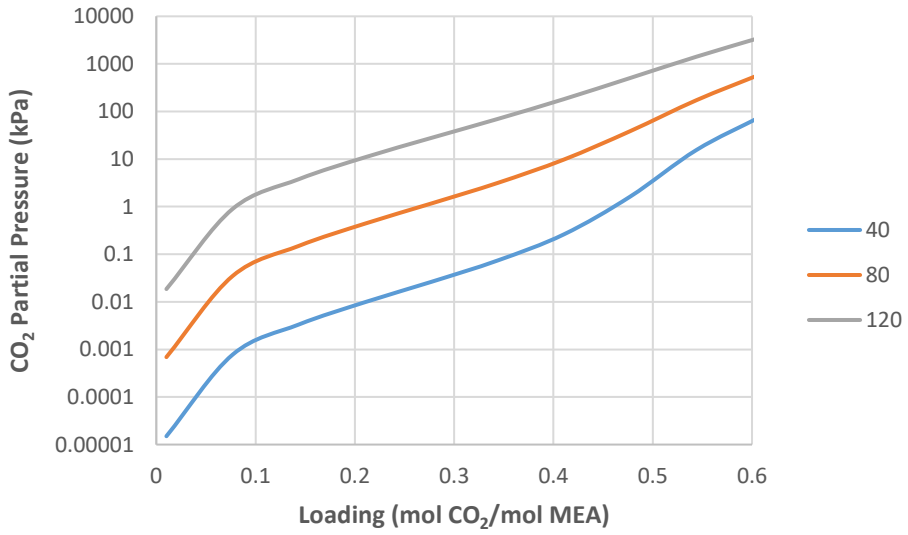



**Figure 1: $CO_2$ partial pressure as a function of loading and temperature (30 wt% MEA).**

## 2.2 $CO_2$ Capture Process Simulation Base Case Setup

The base case model that is set up in the file "CCSI_MEAModel.bkp" has operating variables and equipment configurations as specified in Table 16.

**Table 3: Variables for Base Case Simulation**

| Variable | Value |
|---|---|
| **ABSLEAN Stream (Absorber Solvent Inlet)** | |
| Temperature (°C) | 40.97 |
| Pressure (kPa) | 245.94 |
| Mass Flow (kg/hr) | 6803.7 |
| **Component Mole Fractions** | |
| $H_2O$ | 0.87457 |
| $CO_2$ | 0.01585 |
| MEA | 0.10958 |
| **GASIN Stream (Absorber Gas Inlet)** | |
| Temperature (°C) | 42.48 |
| Pressure (kPa) | 108.82 |
| Mass Flow (kg/hr) | 2266.1 |
| **Component Mass Fractions** | |
| $H_2O$ | 0.04623 |
| $CO_2$ | 0.17314 |
| $N_2$ | 0.71165 |
| $O_2$ | 0.06898 |
| **Absorber** | |
| Intercooler #1 Flowrate (kg/hr) | 7364.83 |
| Intercooler #1 Return Temperature (°C) | 40.13 |
| Intercooler #2 Flowrate (kg/hr) | 7421.57 |
| Intercooler #2 Flowrate (°C) | 43.32 |
| Absorber Top Pressure (kPa) | 108.82 |
| Absorber Packing Diameter (m) | 0.64135 |
| Absorber Packing Height (ft) | 60.7184 |
| **Regenerator** | |
| Inlet Temperature (°C) | 104.81 |
| Inlet Pressure (kPa) | 183.87 |
| Top Pressure (kPa) | 183.7 |
| Reboiler Duty (kW) | 430.61 |
| Packing Diameter (in) | 23.25 |
| Packing Height (ft) | 39.6837 |

The variables described in Table 16 may be varied within reason, although abrupt changes in certain variables may results in failure of the simulation to converge. In the simulation provided in the example file, the variables for the "ABSLEAN" and "GASIN" streams can be located by double-clicking the respective streams. The variables for the absorber intercoolers can be located from the navigation pane by selecting "Blocks" → "ABSORBER" → "Configuration" → "Pumparounds," and the first and second intercoolers are referred to as "P-1" and "P-2," respectively. The top pressure of the absorber and regenerator can be located by double-clicking the "ABSORBER" and "REGEN" blocks and selecting the "Pressure" tab. Moreover, the reboiler duty for "REGEN" is located under the "Configuration" tab. The column packing diameters and height can be located by selecting "Blocks" → "ABOSRBER" or "REGEN" → "Sizing and Rating" → "Packing Rating" → "1" → "Setup." The values of the regenerator inlet pressure and temperature are specified in the "PUMP" and "EXCHANGE" blocks, respectively. **Note:** A sensitivity block, referred to as "FLOW" in the simulation, is used to set the flowrate of the inlet solvent stream, as the simulation will not automatically converge for such a low flow rate.

## 2.3 $CO_2$ Capture Process Simulation Example

In this example, the $CO_2$ capture process, which includes the absorber and regenerator columns, is evaluated for two sets of operating conditions.

1. Open the "CCSI_MEAModel.bkp" file. In the navigation pane, right-click "Blocks," select "Activate," right-click "Streams," and then select "Activate." Run the simulation. **Note:** All streams and blocks have been deactivated to reduce the time required to obtain the results for the test in Section 2.1 Predicting System VLE. If block "B1" and streams "IN" and "OUT" have already been created in the same file, they need to be deactivated by right-clicking them and selecting "Deactivate" before activating all streams with the aforementioned procedure.
2. In the flowsheet, right-click stream "ABSRICH," select "Results," and then select "STRIPOUT" from the drop-down arrow at the top of the right column. Ensure that the results obtained match those given in Table 17, noting that only selected rows are included in the table.

**Table 4: Selected Stream Table Results**

| Mole Flow mol/hr | ABSRICH | STRIPOUT |
|---|---|---|
| H2O | 257894 | 246184 |
| CO2 | 0.903922 | 9.918261 |
| MEA | 5802.829 | 21569.32 |
| MEA+ | 13570.85 | 5500.753 |
| MEACOO- | 12831.36 | 5118.272 |
| HCO3- | 739.4945 | 382.4814 |
| N2 | 35.44019 | 1.53E-16 |
| O2 | 5.791765 | 5.50E-20 |
| Temperature C | 51.06899 | 120.2257 |
| Pressure kPa | 108.82 | 183.7 |
| Enthalpy J/kmol | -304340000 | -285550000 |

3. Reinitialize the simulation by clicking “Reset” or pressing “Shift+F5,” and then selecting “OK.” In the navigation pane, navigate to “Blocks” → “Absorber” → “Configuration” → “Pumparounds” → “P-1,” and then change the “flow rate” to “3000 kg/hr.” Navigate to “P-2” and then change the “flow rate” to the same value.
4. Navigate to “Model Analysis Tools” → “Sensitivity” → “FLOW” → “Input.” This sensitivity block is used to report the $CO_2$ capture percentage in the absorber and the lean solvent loading in the regenerator exit as a function of the flow rate of the lean solvent into the absorber. Modify the “Cases” by adding additional rows as shown in Figure 35. **Note:** The $CO_2$ capture percentage and lean solvent loading are calculated in calculator blocks “CAPP” and “LLDG,” respectively, which can be located by navigating to “Flowsheeting Options” → “Calculator.”

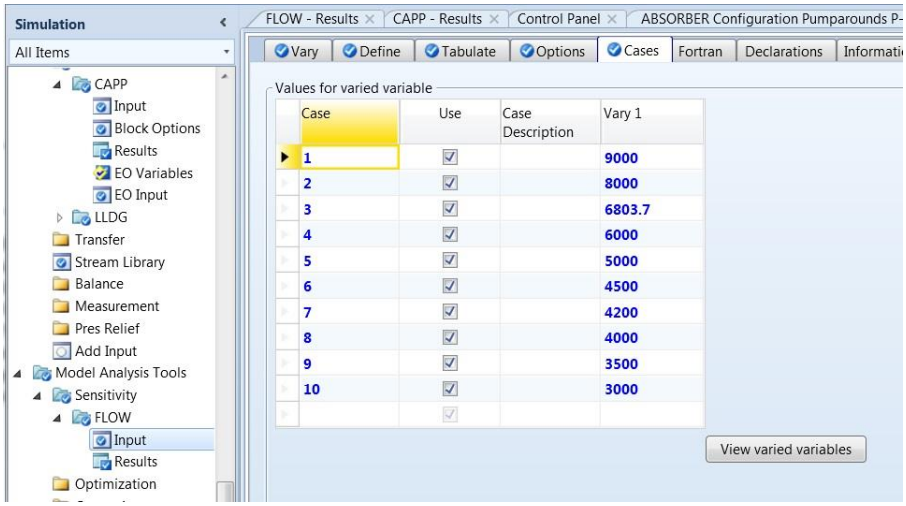
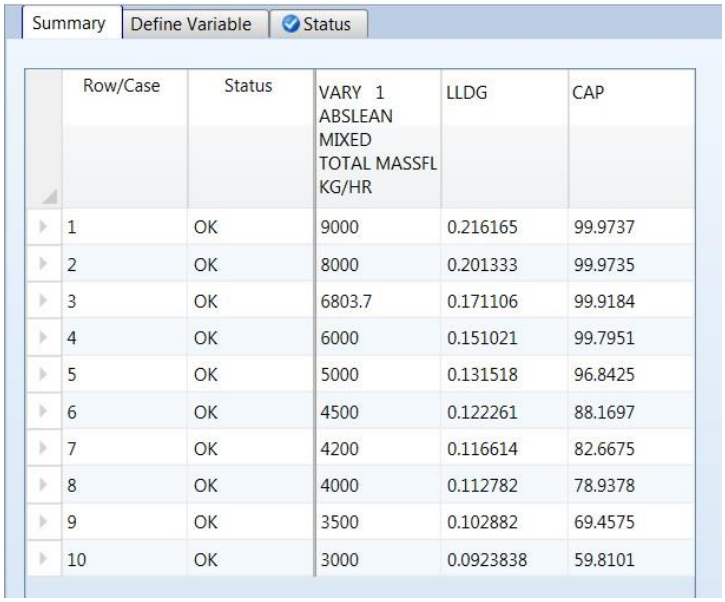



**Figure 2: Setup of the “FLOW” sensitivity block for the case study.**

5. Run the simulation. Navigate to “Results” under the Sensitivity block “FLOW” and then verify that the results are similar to those shown in Figure 36.




| Row/Case | Status | VARY 1 ABSLEAN MIXED TOTAL MASSFL KG/HR | LLDG | CAP |
|---|---|---|---|---|
| 1 | OK | 9000 | 0.216165 | 99.9737 |
| 2 | OK | 8000 | 0.201333 | 99.9735 |
| 3 | OK | 6803.7 | 0.171106 | 99.9184 |
| 4 | OK | 6000 | 0.151021 | 99.7951 |
| 5 | OK | 5000 | 0.131518 | 96.8425 |
| 6 | OK | 4500 | 0.122261 | 88.1697 |
| 7 | OK | 4200 | 0.116614 | 82.6675 |
| 8 | OK | 4000 | 0.112782 | 78.9378 |
| 9 | OK | 3500 | 0.102882 | 69.4575 |
| 10 | OK | 3000 | 0.0923838 | 59.8101 |

**Figure 3: Results of the "FLOW" sensitivity block for the case study.**

6. Navigate to “Blocks” → “Absorber” → “Profiles” and then highlight the columns labeled “Vapor Temperature” and “Liquid Temperature.” Under “Plot” on the “Home” tab, select “Custom,” and then verify that the resulting plot resembles Figure 37. **Note:** These temperature profiles correspond to the last simulation executed (Case 10 as defined in Figures 35–36).

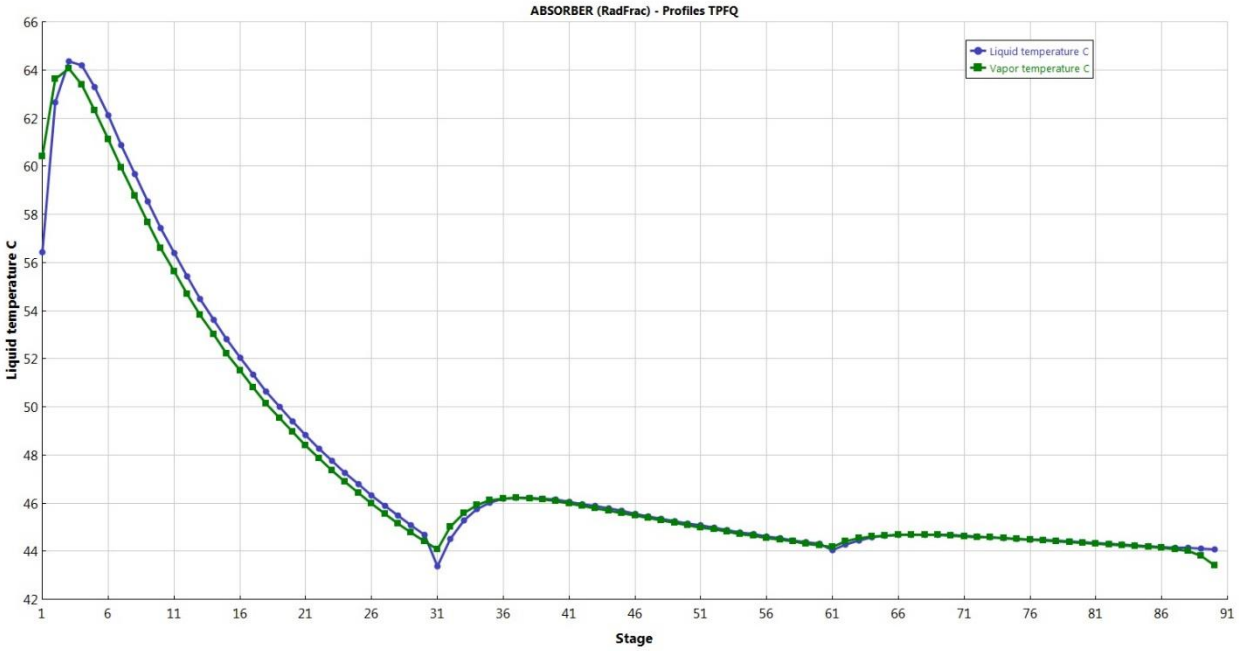



**Figure 4: Absorber temperature profile for the case study.**

7. Navigate to “Blocks” → “Regen” → “Profiles” and then repeat the procedure described in Step 6. Verify that the temperature profile resembles what is shown in Figure 38.

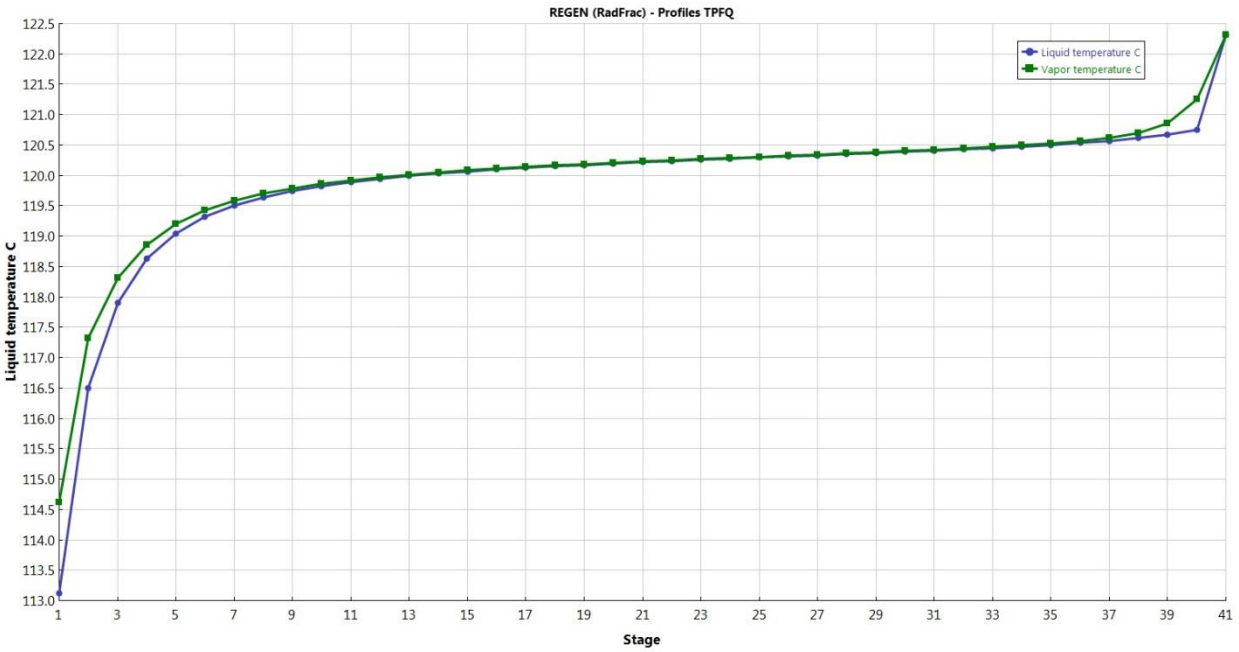



**Figure 5: Regenerator temperature profile for the case study.**

# 3.0 USAGE INFORMATION

## 3.1 Environment/Prerequisites

This product requires Aspen Plus V8.4 or newer with an Aspen Rate-Based Distillation license. As such, the supported environments are limited to:

- Windows® XP SP3
- Windows Vista® Business SP2
- Windows Vista Ultimate SP2
- Windows 7 Ultimate (32- and 64-Bit)
- Windows 7 Professional (32- and 64-Bit)

## 3.2 Support

Support can be obtained from ccsi-support@acceleratecarboncapture.org or by filling out the "Submit Feedback/Request Support" form available on the product distribution page.

# 4.0 REFERENCES

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