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PROSIM DAC APPLICATION EXAMPLE

VTSA PROCESS

DICHLOROMETHANE ADSORPTION ON ACTIVATED CARBON

EXAMPLE PURPOSE
This example deals with a VTSA process (Vacuum Thermal Swing Adsorption) in which dichloromethane is adsorbed on an activated carbon. The regeneration of the activated carbon is done in two steps: 1. Thermally by a hot nitrogen stream, 2. In vacuum by a low-pressure nitrogen stream This process is modeled within ProSim DAC, ProSim's dynamic simulation software dedicated to gas adsorption columns.

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1. PROCESS MODELING

1.1. Process description

ProSim DAC is a dynamic simulation software based on mass and enthalpy balances dedicated to gas-solid adsorption columns. The adsorption and the regeneration steps can be modeled. The available types of regeneration are: thermal regeneration (co- or counter-current), steam regeneration (co- or counter-current) and pressure regeneration. The TSA (Thermal Swing Adsorption), PSA (Pressure Swing Adsorption) or VTSA (Vacuum Thermal Swing Adsorption) processes can be represented. A management system of events allows going from one step to another depending on criterions specified by the user (duration, breakthrough ratio, concentration…). An end simulation time or a number of cycles can be defined. The characteristics (temperature, pressure, flow rate, compositions) of the feeds (flow to be purified, regenerating flows…) can be constant or time dependent. The main models of adsorption isotherm (Langmuir, Toth, Dubinin-Radushkevich, Langmuir extended, Sips...) are available. The mass and heat transfer coefficients can be specified by the user or calculated by ProSim DAC. A data base of activated carbons and of adsorption isotherms of VOCs on activated carbons is available. An economical balance of the regeneration steps can be performed to compare different solutions.

In this example, dichloromethane is adsorbed on an activated carbon. The regeneration of the adsorbent is done in two steps (VTSA process):

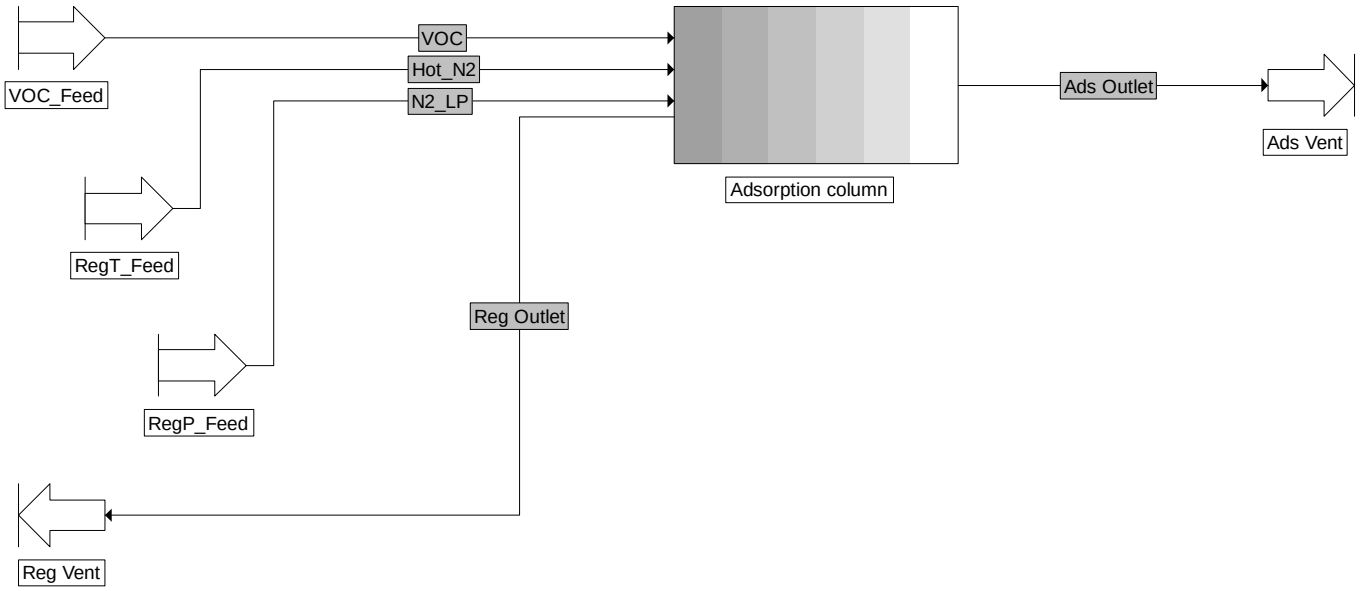
1. Thermally by a hot pure nitrogen stream,
2. In vacuum by a low-pressure flow of nitrogen.

Three inlet streams are used in this example: the “VOC” stream, the “Hot_N2” stream and the “N2_LP” stream. During the adsorption step only the “VOC” stream is used. This stream is the gas stream to be purified (i.e. in which the dichloromethane must be removed). During the thermal regeneration step only the “Hot_N2” stream is used. This stream is the hot nitrogen stream used to regenerate the bed of adsorbent. During the pressure regeneration step only the “N2_LP” stream is used. This stream is a low-pressure nitrogen stream. It’s used to go further in the regeneration of the adsorbent bed. The sequence of the steps is done automatically thanks to the definition of events ending the different steps.

The parameters of the column (size, thermal behavior…), the adsorption isotherms, the type of the cycle (TSA, VTSA, PSA), the step events (breakthrough level, temperature, concentration…) are defined within the “Adsorption column” unit operation module.

This example is adapted from [RAM11].

1.2. Process flowsheet



1.3. Compounds

The compounds used in the simulation, their chemical formula, and CAS Registry Numbers® [1] are shown in the following table. Their pure component properties are extracted from the standard data base provided with ProSim DAC [ROW11].

Compound	Chemical formula	CAS number®
Dichloromethane	CH_2Cl_2	75-09-2
Nitrogen	N_2	7727-37-9

1.4. Thermodynamic model

The adsorption and the regeneration are done close to the atmospheric pressure (maximum pressure around 1.5 atm) and at temperature below 100°C. Thus the “Ideal” thermodynamic profile is selected in the Simulis Thermodynamics calculator.

[1] *CAS Registry Numbers® are the intellectual property of the American Chemical Society and are used by Fives ProSim SAS with the express permission of ACS. CAS Registry Numbers® have not been verified by ACS and may be inaccurate.*

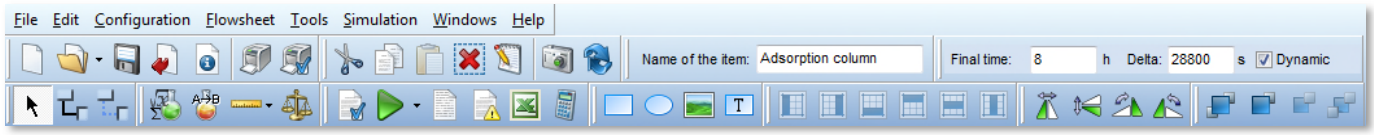
1.5. Operating parameters

1.5.1. Process feeds

	VOC stream	Hot nitrogen stream	Low pressure nitrogen stream
Temperature (°C)	24	95	24
Pressure (atm)	1	1	0,04
Total flow rate (kmol/h)	0,08399	0,022308	0,002612
Mole fractions			
Dichloromethane	0,0141	0	0
Nitrogen	0,9859	1	1

1.5.2. Simulation time

The “Final time” is the real working duration of the process (adsorption + thermal regeneration in this example). The “Delta” is the duration during which the “Adsorption column” module is working. As only one module is present, the “Final time” and the “Delta” should be identical. These two values are specified in the icon bar of ProSim DAC:



Simulation time	Value
Final	8 h
Delta	28 800 s

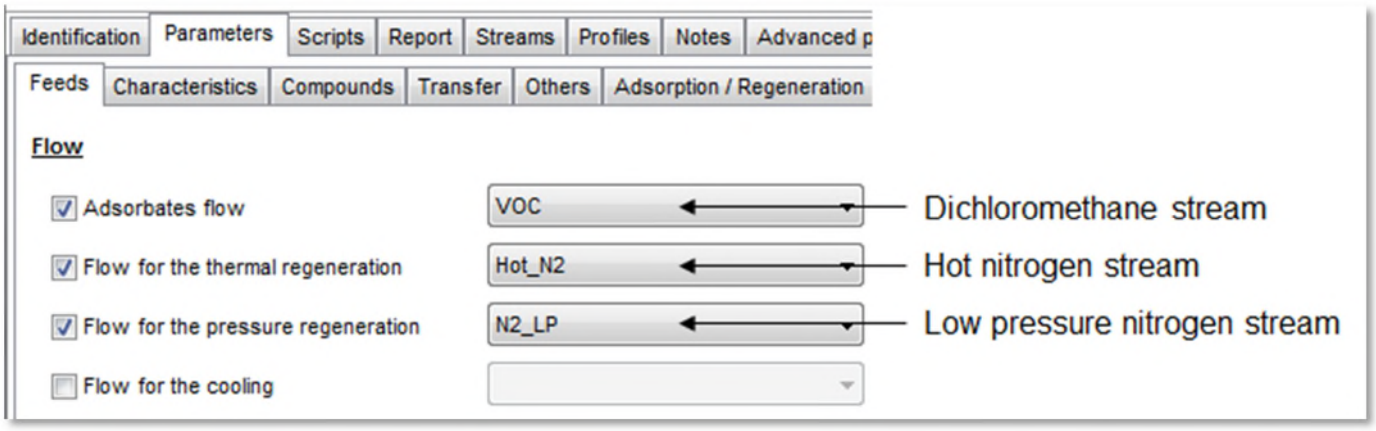
1.5.3. Adsorption column

1.5.3.1. Feeds

Four feeds can be used in ProSim DAC:

- ✓ Adsorbates flow: Flow to be purified during the adsorption step.
- ✓ Flow for the thermal regeneration: Flow used during the thermal regeneration (hot nitrogen, steam…).
- ✓ Flow for the pressure regeneration: Flow used during the pressure regeneration (low pressure nitrogen…).
- ✓ Flow for the cooling: Flow used to cool the column at the end of the thermal regeneration step.

Only the three first feeds are used in this example as shown on the screen shot below.

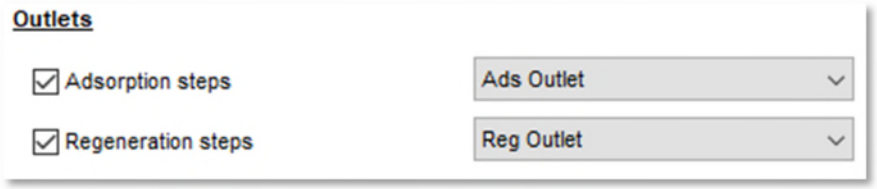


1.5.3.2. Outlets

Two outlets can be used in ProSim DAC:

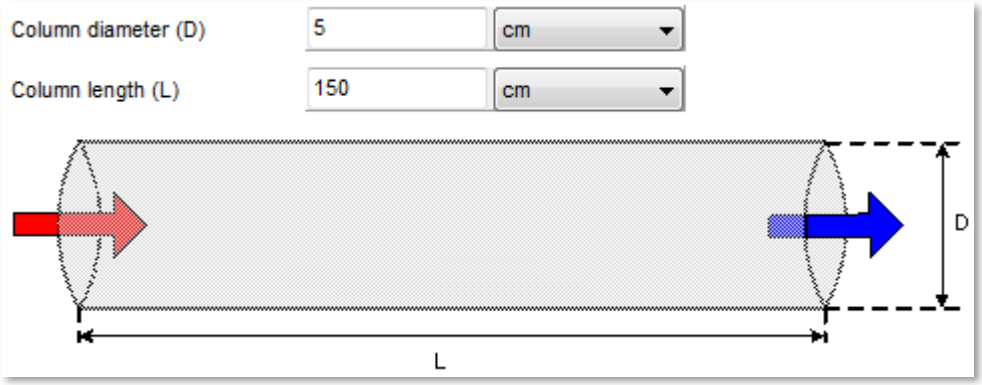
- ✓ Adsorption steps: Output stream during the adsorption steps
- ✓ Regeneration steps: Output stream during the regeneration steps

The output stream during the adsorption steps corresponds to “Ads Outlet” and the output stream during the regeneration steps corresponds to “Reg Outlet”, as shown on the screen shot below.



1.5.3.3. Column characteristics

The column used is a lengthwise flow column which characteristics are shown on the following screen shot. The dimensions to be specified are the ones of the adsorbent bed.



Transvers flow columns can also be modeled in ProSim DAC.

1.5.3.4. Thermal behavior

The following thermal heat exchanges can be modeled in ProSim DAC:

- ✓ Heat exchange in the bed: “Given heat duty without wall transfer”.
  This possibility allows to model an adiabatic working or a given heat duty for each step working (heat exchanger in the adsorbent bed).
- ✓ Wall heat transfer + thermal heat exchange in the bed: “Given heat duty and wall transfer”.
  The heat exchange is done by the wall of the column. By default, the wall temperature is constant during the time and along the length of the column. To go beyond this assumption, the option “take into account thermal inertia of the column wall” must be activated. It is possible to add a given heat duty (by default zero) in the adsorbent bed for each step.

In this example, the thermal transfer is done by the wall without any direct heating/cooling in the bed of adsorbent:

Thermal behavior	
Heat transfer	Given heat duty and wall transfer
Wall temperature	90°C

1.5.3.5. Adsorbent bed characteristics

Bed characteristics	
Void ratio	0.3556

1.5.3.6. Adsorbent characteristics

The density of the particles takes into account of the intra-particulate porosity.

Particles characteristics	
Diameter	4 mm
Density	550 kg/m^3
Specific heat	1050 J/kg/K
Surface/Volume ratio	1500 m^2/m^3

1.5.3.7. Measures conditions for concentration results

The user can specify the temperature and pressure conditions he wants to calculate the volumetric concentrations in the gas phase. Indeed, the density is then necessary and this one, particularly in the case of a gas, is sensitive to the temperature and the pressure. In this example, the volumetric concentrations in the gas phase are evaluated at 295 K and 1 atm.

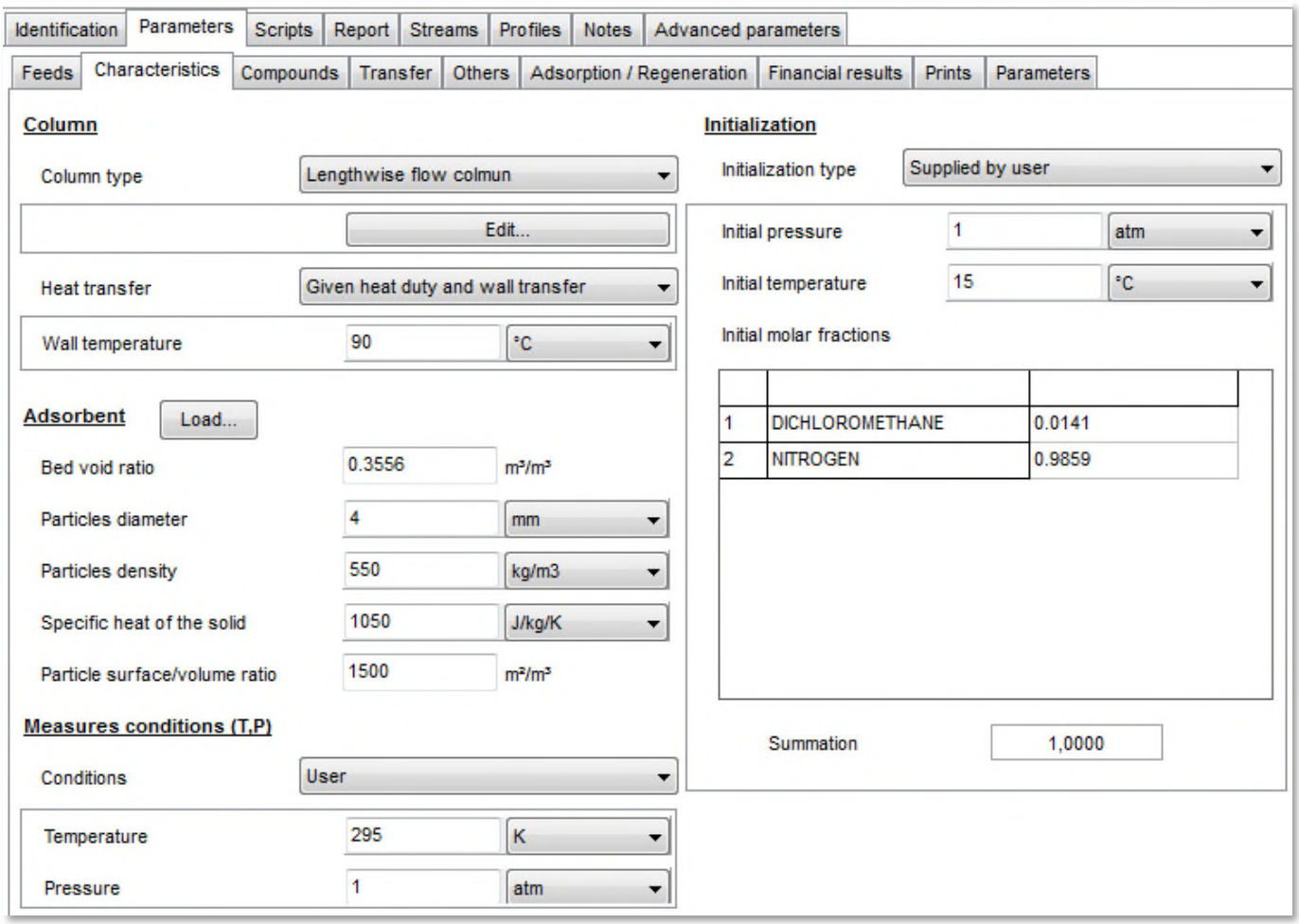
Measures conditions	**Value**
Conditions	User
Temperature	295K
Pressure	1 atm

1.5.3.8. Initialization

It's necessary to define the state of the column before its first use. In this example, it's assumed that the column is loaded with a gas flow identical to the VOC stream. ProSim DAC will automatically compute the adsorbed amounts at the initial time.

Initialization	Value
Type	Supplied by the user
Pressure	1 atm
Temperature	15°C
Mole-fractions Dichloromethane Nitrogen	 0,0141 0,9859

The screen shot below shows the information of the previous paragraphs (from paragraph 1.5.3.3 to paragraph 1.5.3.8 included) specified in the module interface: "Parameters" tab, "Characteristics" sub-tab.



1.5.3.9. Adsorption isotherms and enthalpies

The Langmuir model is selected for the adsorption isotherm of dichloromethane and nitrogen:

$$q_i = \frac{\left[q_{m0}\exp\left(\frac{q_{m1}}{T}\right)\right]\left[K_0\exp\left(\frac{K_1}{T}\right)\right]P_i}{1+\left[K_0\exp\left(\frac{K_1}{T}\right)\right]P_i}$$

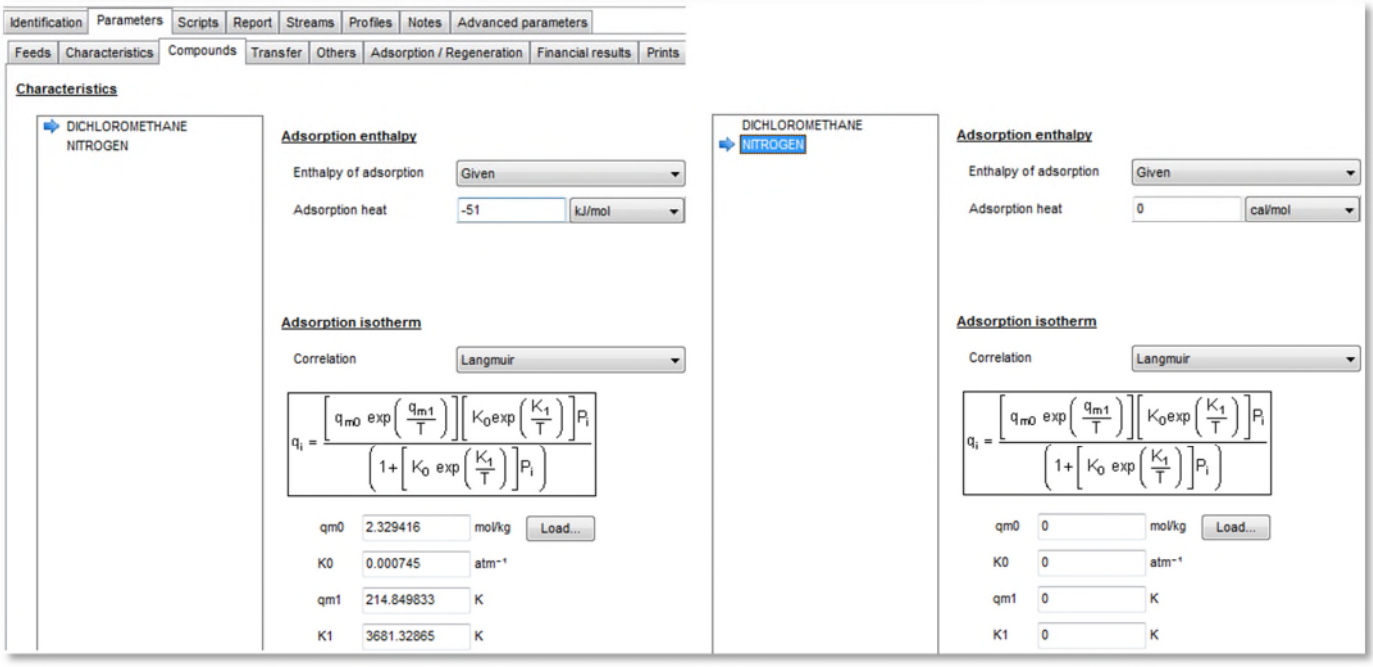
It's assumed that nitrogen is not adsorbed. The values of the parameters with the corresponding units are displayed in the table below.

Dichloromethane		**Nitrogen**	
Isotherm	Langmuir	**Isotherm**	Langmuir
q_{m0} (mol/kg)	2,329416	**q_{m0} (mol/kg)**	0
K_0 (atm^{-1})	0,000745	**K_0 (atm^{-1})**	0
q_{m1} (K)	214,849833	**q_{m1} (K)**	0
K_1 (K)	3681,32865	**K_1 (K)**	0

The adsorption phenomenon being exothermic, the values of the enthalpies of adsorption are negatives. As the nitrogen is assumed not to be adsorbed, its adsorption enthalpy is set to zero.

Adsorption enthalpy	**Dichloromethane**	**Nitrogen**
Type	Given	
ΔH_{ads} (kJ/mol)	-51	0

This information has to be specified in the "Parameters" tab, "Compounds" sub-tab:



1.5.3.10. Mass transfer

The following options are available for the mass transfer:

- ✓ Transfer coupled in gas and solid phase.
- ✓ Mass transfer resistance (“linear driving force” mode in gas phase and/or in solid phase, the mass transfer coefficient needed could be specified by the user or calculated by ProSim DAC. It’s also possible to neglect the mass transfer resistance.

In this example, the mass transfer resistance has been taken into account in the two phases. The necessary coefficients are calculated by ProSim DAC for the gas phase and specified for the solid phase. In this case they are obtained by comparisons with experimental results.

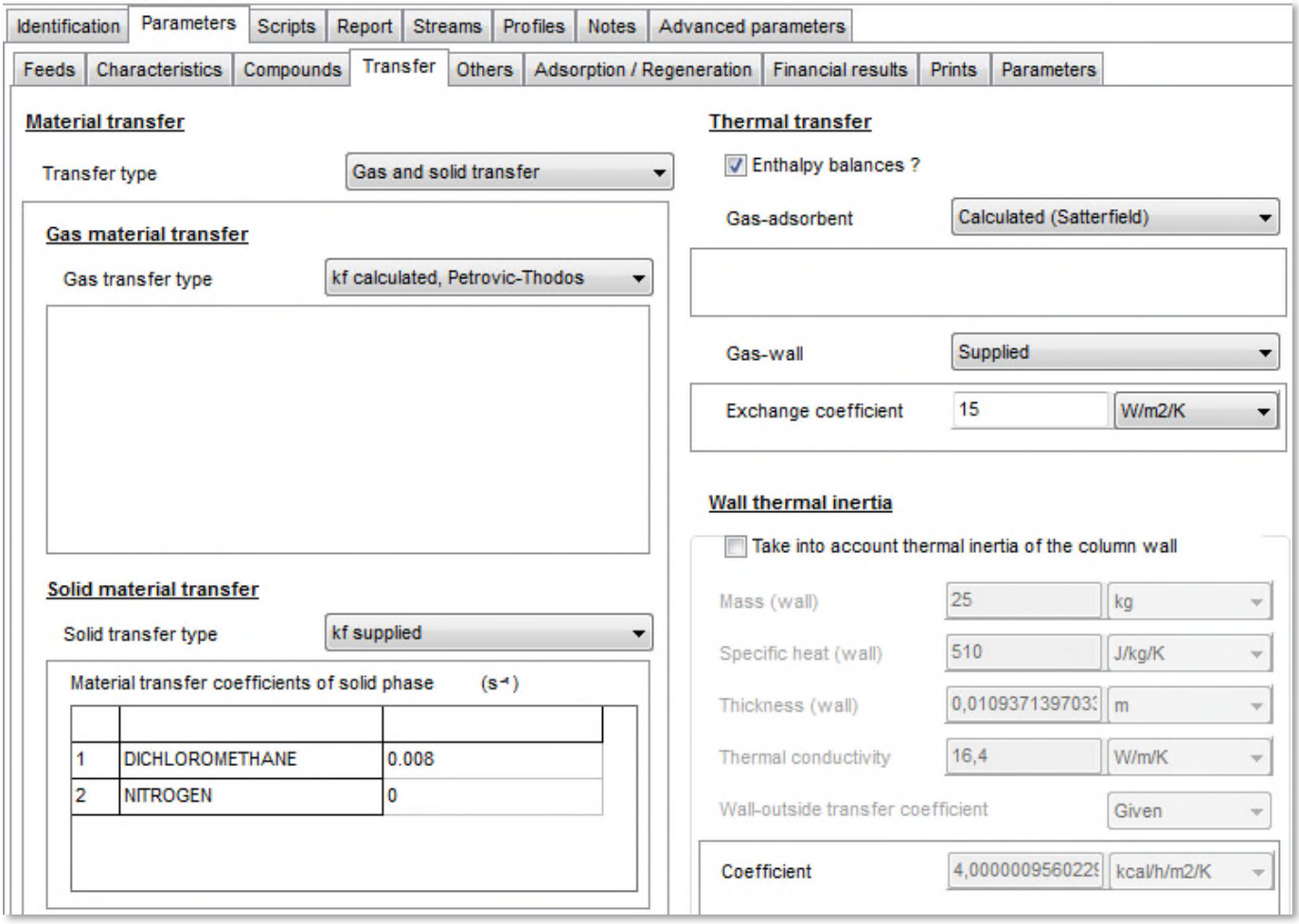
	Value
Mass transfer	
Type	Gas and solid transfer
Gas mass transfer	
Type	kf calculated, Petrovic-Thodos
Solid mass transfer	
Type	kf supplied
Dichloromethane	0,008 s^{-1}
Nitrogen	0 s^{-1}

1.5.3.11. Thermal transfer

It’s possible to take into account the enthalpy balance in ProSim DAC or to ignore it. An isothermal working can be modeled if the enthalpy balance is not taken into account. If the enthalpy balance is taken into account, the gas-adsorbent and the gas-wall heat transfer coefficients are necessary. They can be calculated, as the gas – adsorbent coefficient in this example, or specified as the gas – wall coefficient in this example. In this case it has been obtained by comparisons with experimental results.

Thermal transfer	**Value**
Enthalpy balances	Taken into account
Gas – Adsorbent	Calculated (Satterfield)
Gas – Wall Type Exchange coefficient	 Supplied 15 $W/m^2/K$

The screen shot below shows the information of the previous paragraphs 1.5.3.10 and 1.5.3.11 specified in the module interface: “Parameters” tab, “Transfer” sub-tab.



1.5.3.12. Adsorption thermodynamics

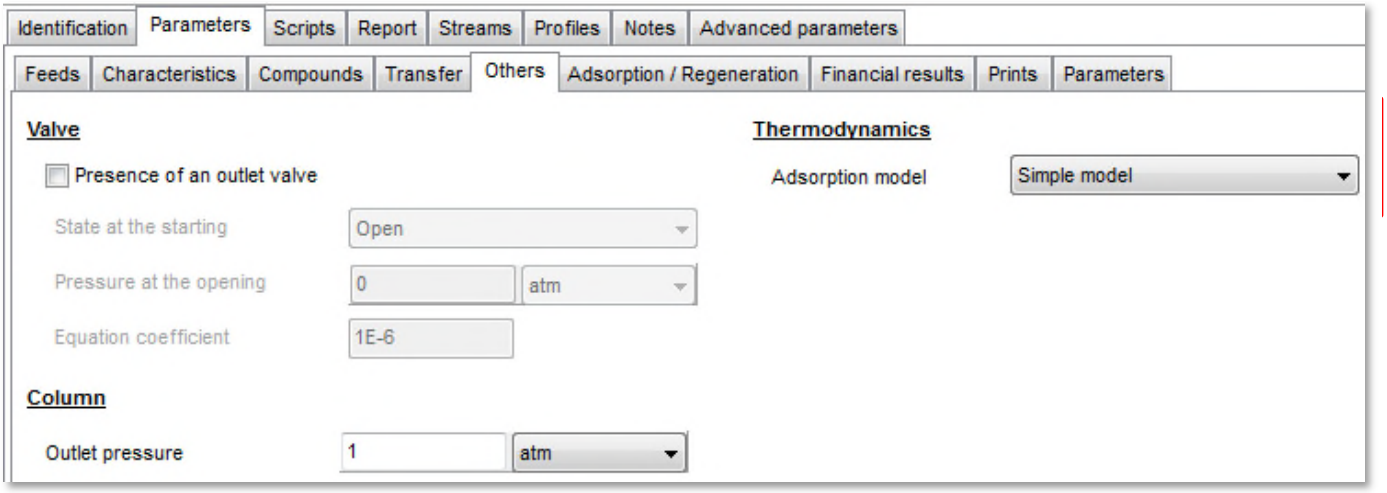
The adsorption thermodynamic models available are:

- ✓ Simple model: This model doesn't take into account the influence of the compounds on each other's. The adsorbed quantity of a given compound is directly given by its adsorption isotherm specified by the user.
- ✓ IAS or RAS: This model takes into account the influence of the compounds on each other's. The IAS model assumes an ideal adsorbed phase. The RAS model is used if an activity coefficient model is selected in the thermodynamic profile of the Simulis Thermodynamics calculator[2].
- ✓ Langmuir extended: This model takes into account the influence of the compounds on each other's. It must be used with pure compound adsorption isotherms of the type "Langmuir extended".

In this example, the simple model is selected.

Adsorption thermodynamics	Value
Adsorption model	Simple model

The adsorption thermodynamic model is specified in the “Parameters” tab, “Others” sub-tab. The left part of this sub-tab is used to specify an optional valve at the column outlet during the adsorption step.

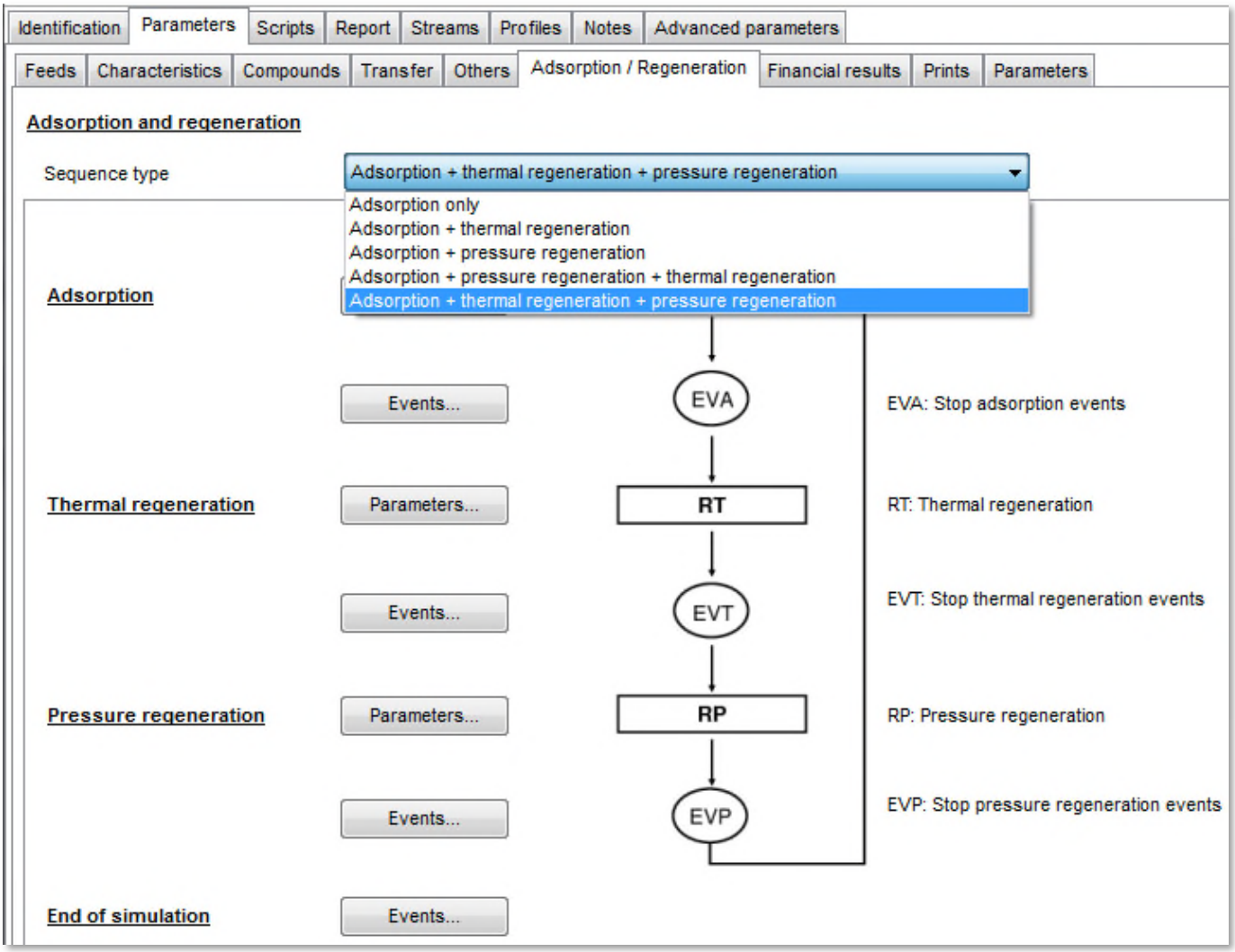


1.5.3.13. Sequence

The “Adsorption/Regeneration” sub-tab of the “Parameters” tab allows to select the type of the cycle to simulate between the five available:

1. Adsorption only
2. Adsorption + thermal regeneration
3. Adsorption + pressure regeneration
4. Adsorption + pressure regeneration + thermal regeneration
5. Adsorption + thermal regeneration + pressure regeneration

The cycle “Adsorption + thermal regeneration + pressure regeneration” is used in this example to model a VTSA (Vacuum Thermal Swing Adsorption) process as shown in the following figure.



Optional parameters can be defined for each step (“Parameters…” buttons):

- ✓ Adsorption:
  - o Wall temperature specific to this step.
  - o Heat duty exchanged in the bed.
- ✓ Thermal regeneration:
  - o Co- or counter-current regeneration.
  - o Bed and/or wall preheating of the column.
  - o Cooling of the column at the end of the step.
  - o Temporization of the column at the end of the step.
  - o Heat duty exchanged in the bed.
- ✓ Pressure regeneration:
  - o Pressure to reach.
  - o Pressure down duration.
  - o Pressure up duration.
  - o Vale coefficient.
  - o Warning if pressure not reached.

- Heat duty exchanged in the bed.

Each step is ended by an event. The first event reached starts the next step. The available events are the following ones (“Events…” buttons):

- ✓ Adsorption
  - Step duration.
  - Breakthrough rate of a compound at a given position in the column.
  - Gas phase concentration of a compound at a given position in the column.
  - Solid phase concentration of a compound at a given position in the column.
  - Maximal temperature reached at a given position in the column.
  - Maximal pressure reached at a given position in the column.
- ✓ Thermal or pressure regeneration
  - Step duration.
  - Gas phase concentration of a compound at a given position in the column.
  - Solid phase concentration of a compound at a given position in the column.
  - Maximal temperature reached at a given position in the column.
  - Maximal pressure reached at a given position in the column.
  - Amount produced of a compound at a given position in the column.
- ✓ Simulation end
  - End simulation time (§ 1.5.2) or number of cycles.
  - Total amount produced of a compound at a given position in the column.
  - Maximal temperature reached at a given position in the column.
  - Maximal pressure reached at a given position in the column.
  - Total amount treated of a compound.

In this example, the regeneration of the bed of adsorbent is a thermal regeneration done by a hot nitrogen stream following by a pressure regeneration done by a low-pressure nitrogen stream. These streams flow counter-currently compared to the adsorption flow.

Sequence	
Type	Adsorption + Thermal regeneration + Pressure regeneration

The option « Column cooling” is activated for the adsorption step. In this case, the wall temperature defined at the paragraph 1.5.3.4 is used only for the regeneration step. The wall temperature used for the adsorption step is defined at the sequence optional parameters level (see the table above).

Adsorption	
Parameters Column cooling Wall temperature Exchanged heat duty	 Activated 22°C 0 kcal/h
Events	Duration = 18 000 s

At the end of the adsorption step and before the start of the thermal regeneration step, the column is isolated (i.e. no feed and no production) and the bed is preheated uniformly during 2 400 s with a duty of 45 W.

Thermal regeneration	
Parameters	
Regeneration type	Counter-current
Column preheating	Activated
Heating type	Bed heating
Preheating power	45 W
Preheating duration	2400 s
Column cooling	Not activated
Column temporisation	Not activated
Exchanged heat duty	0 kcal/h
Events	Duration = 8 400 s

The parameters of the pressure regeneration step are specific to this example.

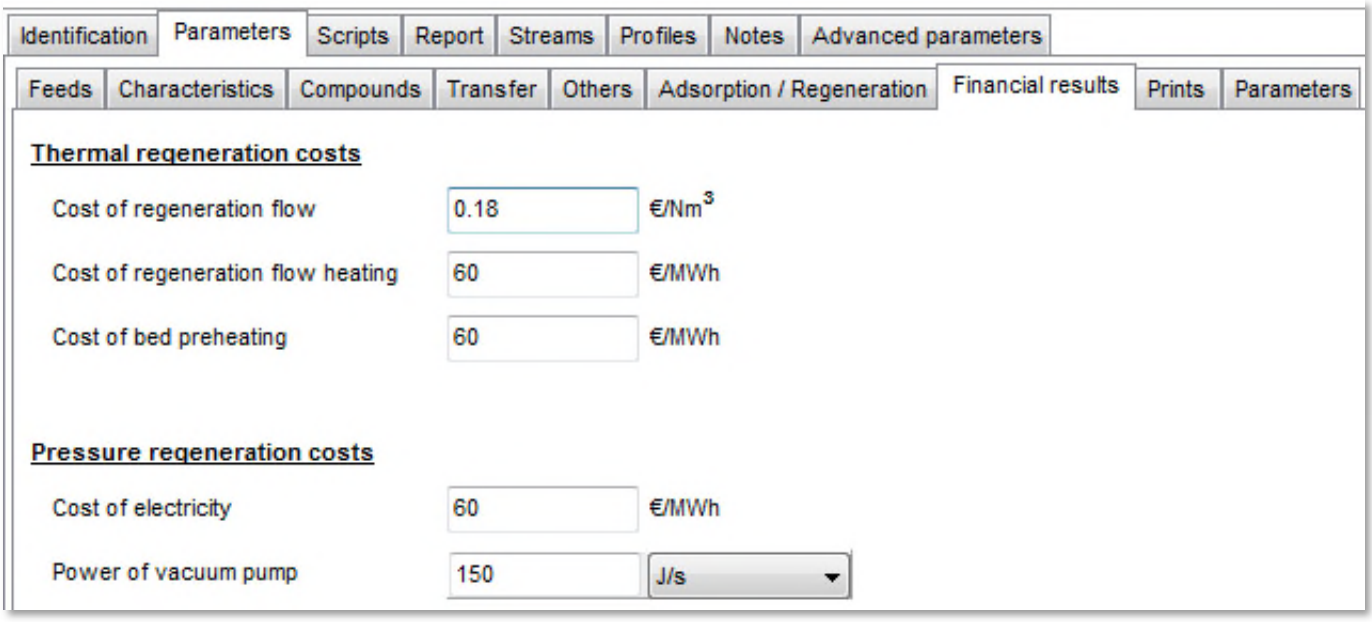
Pressure regeneration	
Parameters	
Pressure to reach	0.039 atm
Pressure down duration	100 s
Pressure up duration	60 s
Valve coefficient	0.0001
Warning if pressure is not reached	Not activated
Exchanged heat duty	0 kcal/h
Events	Duration = 2 400 s

The different steps and the simulation are stopped by a duration.

End of simulation	
Events	End simulation time

1.5.3.14. Financial balance

ProSim DAC performs a financial balance on the regeneration steps. If the user is interested, it’s possible to modify the parameters default values in the “Financial results” sub-tab of the “Parameters” tab.

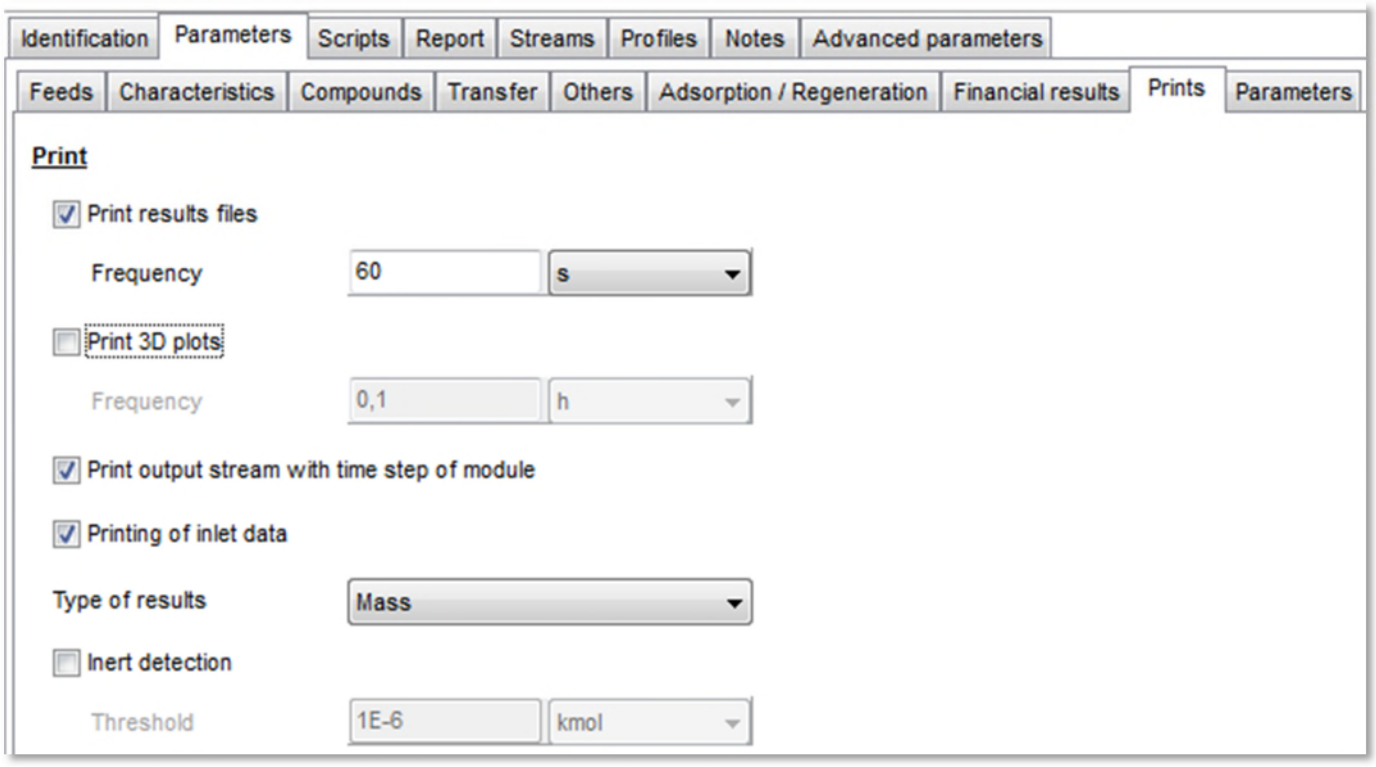


1.5.3.15. Prints

ProSim DAC offers different options for the printing of the calculation results. The parameters specified for this example are listed in the table below.

Parameters	Value
Print results files	Frequency = 60 s
Print 3D plots	Not activated
Print output stream with time step of module	Activated
Printing of inlet data	Activated
Type of results	Mass
Inert detection	Not activated

The following screen shot shows this information specified in the “Prints” sub-tab of the “Parameters” tab.

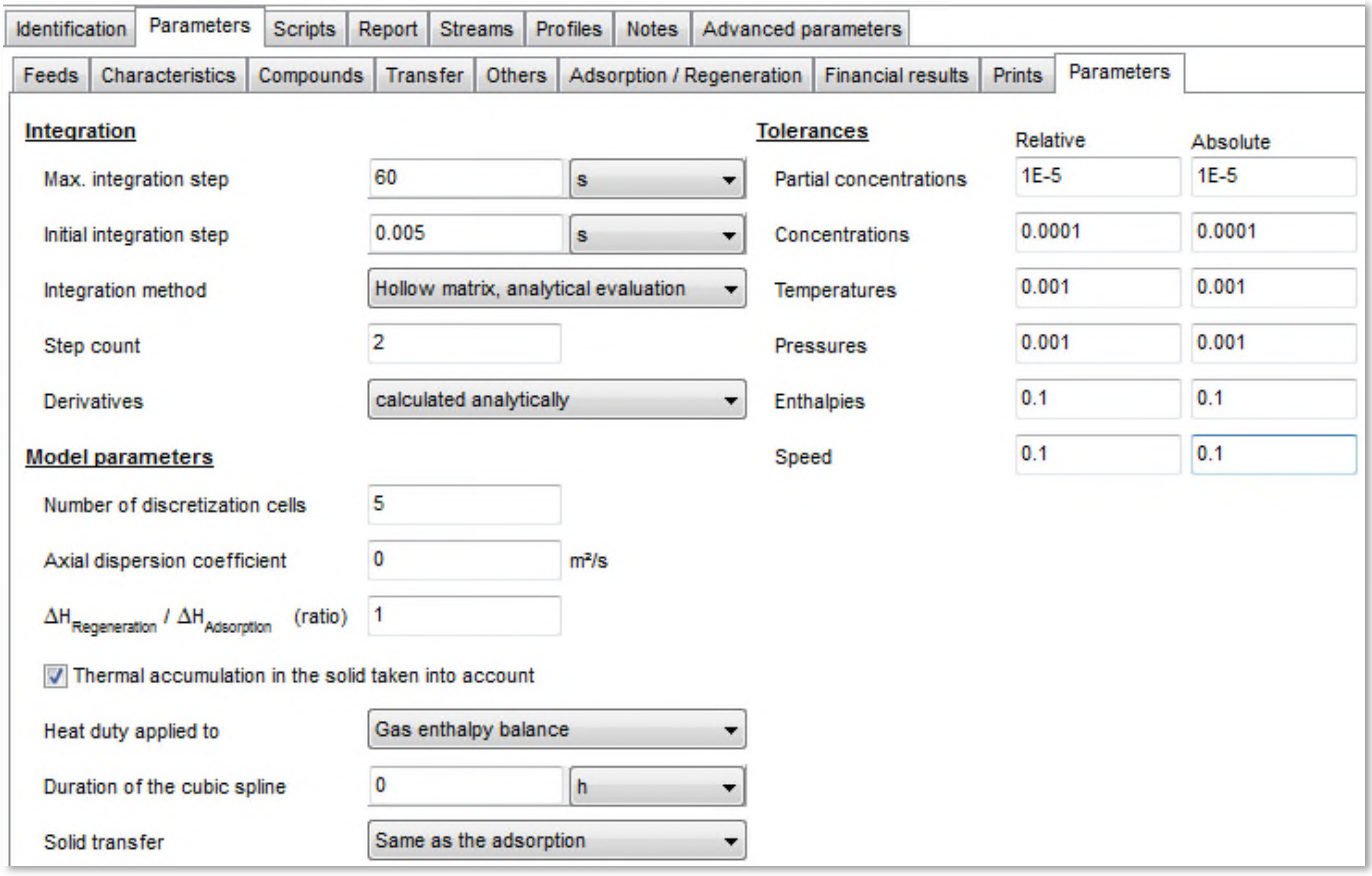


1.5.3.16. Integration, tolerances, and model parameters

In ProSim DAC, the user has access to a set of integration, tolerances, and model parameters. Only the parameters shown in the table below are modified compared to the default values. The use of the analytical calculation of the derivatives speeds up the solving of the problem. The model consists in a numerical time integration and on a spatial discretization. In this example, the column is discretized in 5 cells.

Parameters	Value
Maximum integration step	60 s
Derivatives	Calculated analytically
Number of discretization cells	5
Other parameters	Default values

The following screen shot shows this information specified in the “Parameters” sub-tab of the “Parameters” tab.



2. RESULTS

2.1. Simulation report of the adsorption column

The simulation report of the adsorption column (“Report”) presents global results (integrated during the time): initial characteristics of the column, adsorbed quantities, quantities recovered during the regeneration…

The mass of adsorbent is not directly specified in the input data. This value is calculated by ProSim DAC depending on the geometrical characteristics of the bed and the adsorbent characteristics. It’s then interesting to verify in the simulation report the mass of adsorbent calculated corresponds to the end wished. For this example, the mass of adsorbent is about 1 044 g.

COLUMN GENERAL CHARACTERISTICS

Adsorbent mass in the column:		1043.85	(G)
Column volume	:	2.94524	(L)
Solid volume	:	1.89791	(L)
Void volume	:	1.04733	(L)

With the operating parameters specified (see § 1.5.3.13 among others), the bed of adsorbent is not completely regenerated: 311 g of dichloromethane adsorbed, and 289 g recovered during the regenerations (223 g during the thermal regeneration and 66 g during the pressure regeneration).

AMOUNT ADSORBED (G)

COMPONENT	Cycle N° 1
DICHLOROMETHANE	310.724
NITROGEN	-5.882695E-02

AMOUNT RECOVERED DURING THERMAL REGENERATION (G)

COMPONENT	Cycle N° 1
DICHLOROMETHANE	222.834
NITROGEN	1041.75

AMOUNT RECOVERED DURING PRESSURE REGENERATION (G)

COMPONENT	Cycle N° 1
DICHLOROMETHANE	65.8272
NITROGEN	45.8530

TOTAL RECOVERED AMOUNT (G)

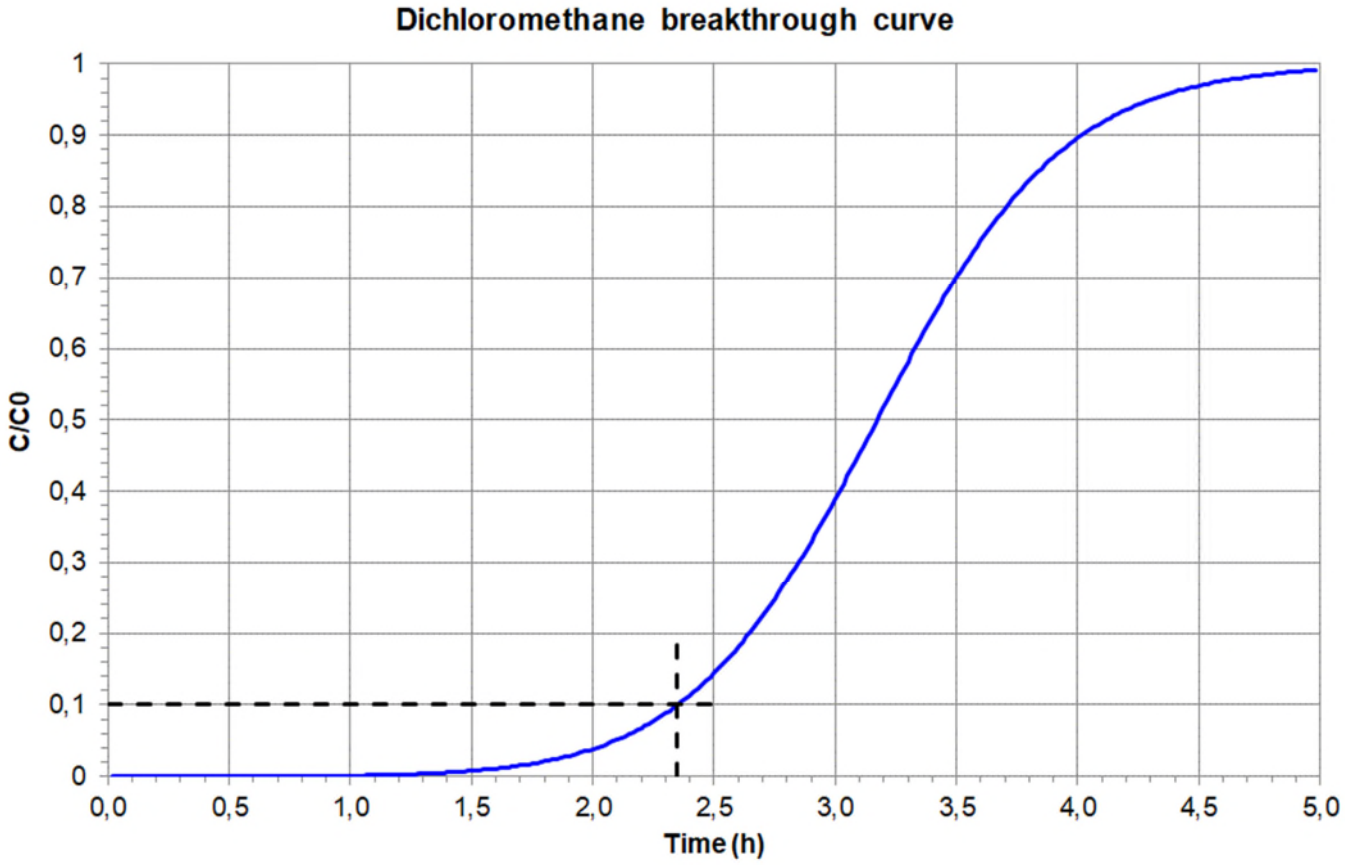
COMPONENT	QUANTITY
DICHLOROMETHANE	288.661
NITROGEN	1087.60

The negative value of the amount of nitrogen adsorbed corresponds to the mas balance deviation.

2.2. Profiles of the adsorption column

Several profiles (temperatures, pressures, velocities, concentrations, compositions, and breakthrough curves) in the adsorption column are available after the simulation from the module edition window (“Profiles” tab).

The following figure shows the breakthrough curve of dichloromethane. The breakthrough is assumed to be reached when the concentration at the column outlet is equal to 10% of the inlet concentration. The breakthrough is reached after 2h21min. The bed of adsorbent is saturated when the outlet concentration is equal to the inlet one. This is the case after 5 h.



The figure below presents the temperature profile in the first and the last discretization cell. In the case of the adsorption:

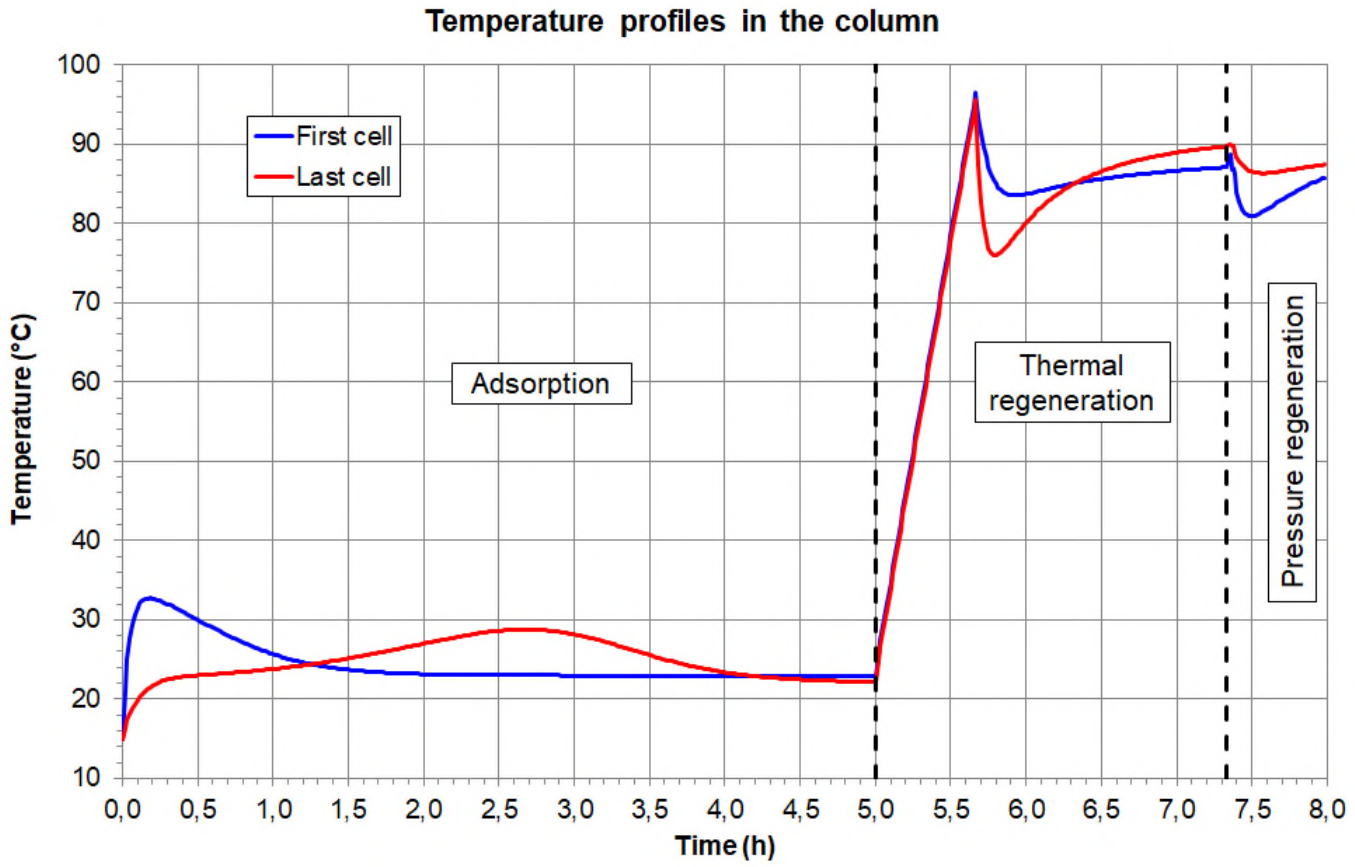
- ✓ First cell: Inlet cell of the column
- ✓ Last cell: Outlet cell of the column

As the regeneration is done counter-currently:

- ✓ First cell: Outlet cell of the column
- ✓ Last cell: Inlet cell of the column

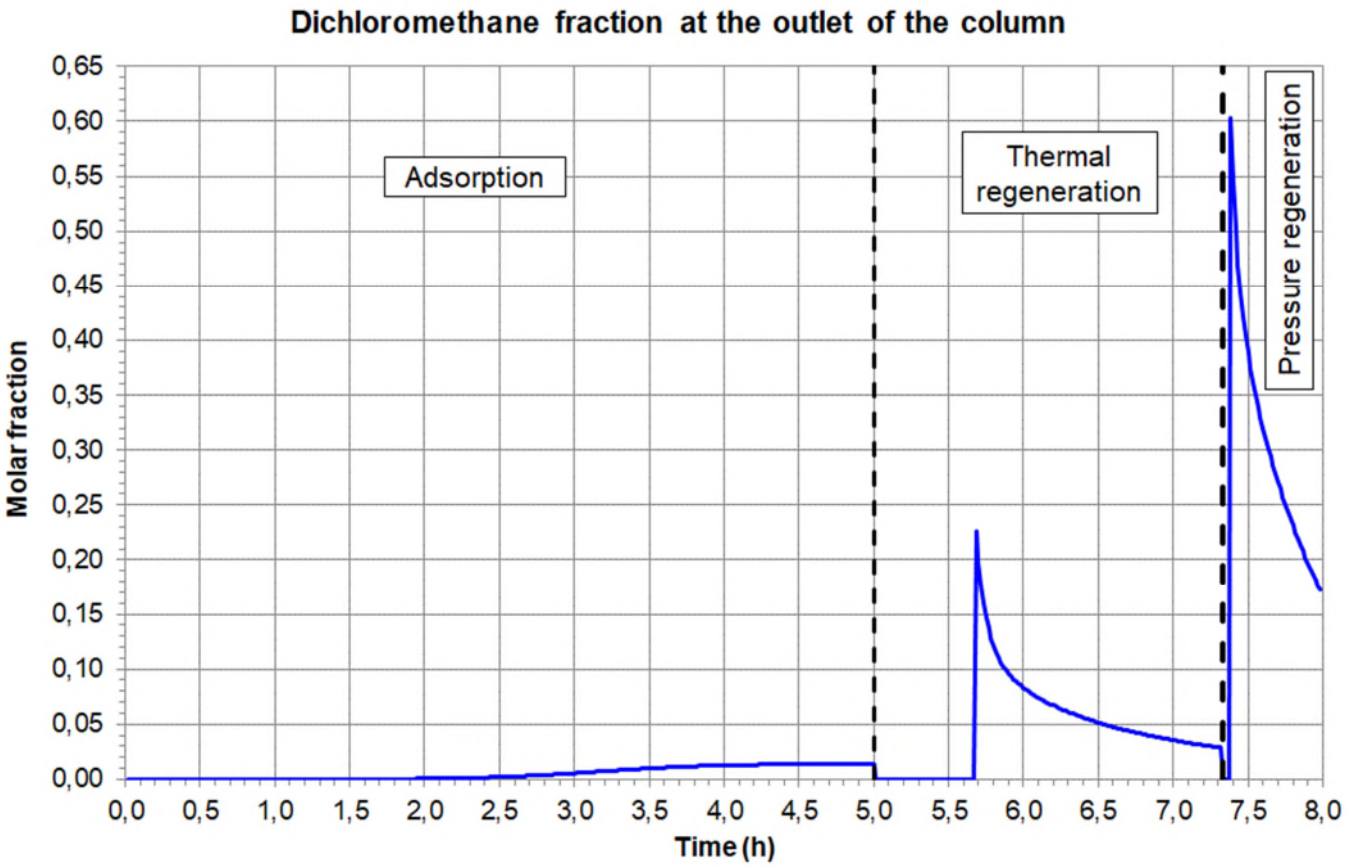
The temperature profiles during the adsorption step show the corresponding temperature peak. The linear increase of the temperature at the start of the thermal regeneration step corresponds to the bed preheating without feeds or productions.

During the two regeneration steps (thermal and then pressure), the temperature profiles first show a decrease due to desorption of dichloromethane (endothermic phenomenon). Then, the temperature increases to tend to the thermal equilibrium between the wall temperature and the gas flow temperature.



2.3. Profiles of the outlet stream

The following figure shows the evolution of the molar fraction of dichloromethane at the column outlet. Once the breakthrough is not reached, the adsorbent plays its role and the dichloromethane amount at the column outlet is null. When the breakthrough time is reached, the outlet stream is charged progressively in dichloromethane. In this example, the adsorption step is ended at the time corresponding to the saturation of the bed. The bed no more retained the dichloromethane, and its outlet concentration is equal to its inlet concentration. The counter-current thermal regeneration by a hot nitrogen stream allows to desorb the dichloromethane retained in the adsorbent. After a peak corresponding to the dichloromethane accumulated in the bed, the dichloromethane amount decreases because of the bed regeneration. The same phenomenon is observed for the pressure regeneration step. This second regeneration step allows to go further in the bed regeneration. However, in this example, the simulation is ended before a complete regeneration of the bed.



3. REFERENCES

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