PROSIMPLUS APPLICATION EXAMPLE

HYDROGEN PRODUCTION BY ELECTROLYSIS

EXAMPLE PURPOSE
This document showcases the use of the "electrolyzer" module that allows to produce hydrogen from the electrolysis of water. It also allows to discover some graphical features of ProSimPlus (change of modules visuals, display of tags on the flowsheet).

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1. PROCESS MODELLING

1.1. Process description

Hydrogen is the subject of growing interest in energy transition projects and should take an important place in the energy mix. Although it is essentially used today in the chemical and refining industries, it also represents an energy carrier that provides an interesting alternative to fossil fuels. It is an inexhaustible and non-polluting fuel that makes it possible to store the energy produced by the main sources of renewable energy (hydraulic, wind, photovoltaic) [AFH17], [CEA12], [DAM92].

Hydrogen being almost non-existent in nature, in the molecular state, it is mainly obtained from the following processes:

- The reforming or gasification of hydrocarbons;
- The thermochemical dissociation of water or biomass;
- The electrolysis of water.

The interest of hydrogen as a clean energy remains today limited by the fact that it is mainly produced from fossil fuels (reforming and gasification of hydrocarbons). Water electrolysis is the main alternative for carbon-free hydrogen production. It involves the application of an electric current in order to decompose water into oxygen and hydrogen:

$$H_2O \rightarrow H_2 + \frac{1}{2}O_2$$

An electrolysis cell is composed of two electrodes (the anode and the cathode) that are connected to a direct current generator and separated by an electrolyte. This electrolyte can be either liquid (acidic or basic aqueous solution) or solid (polymer or ceramic membrane). The electrolysis module consists of a stack of electrolysis cells that can be connected in parallel or in series.

*Note: with this in mind, a distinction is made in this example, between the quantities related to the electrolysis **cell** and those related to the **stack** itself.*

The Faraday law allows to compute the amount of hydrogen produced by an ideal electrolyzer composed of N electrolysis cells:

$$F_{H2,prod} = \frac{\eta_F . I_{cell} . N}{z\ F}$$

With:

$F_{H2,prod}$: the total molar flowrate of hydrogen produced by the electrolyzer (mol/s)

η_F : the Faraday efficiency (-)

I_{cell} : the cell electric current (A)

N : the number of cells (-)

z : the number of electrons exchanged per mol of hydrogen produced ($z = 2$ electrons/mol)

F: the Faraday constant (96485 C/mol)

The electrolysis module available in ProSimPlus enables to represent the three main electrolyzer technologies:

- The alkaline electrolyzer: the cells are separated by a diaphragm and immersed in an electrolytic solution.
- The PEM electrolyzer (Proton Exchange Membrane): the cells are separated by a solid electrolyte consisting of a polymer membrane ensuring the conduction of H^+ protons.
- The SOEC electrolyser (Solid Oxide Electrolysis Cell): the cells are separated by a solid electrolyte consisting of a ceramic membrane ensuring the conduction of O^{2-} ions.

In this context, this application example (inspired by the research work published in [SAN18]) presents the simulation of an overall process of hydrogen production by alkaline electrolysis. The material and energy balances are calculated for the following elements:

- The electrolysis module;
- The surrounding equipment (pumps, vapor-liquid separation drums);
- The utilities.

1.2. Simulation flowsheet

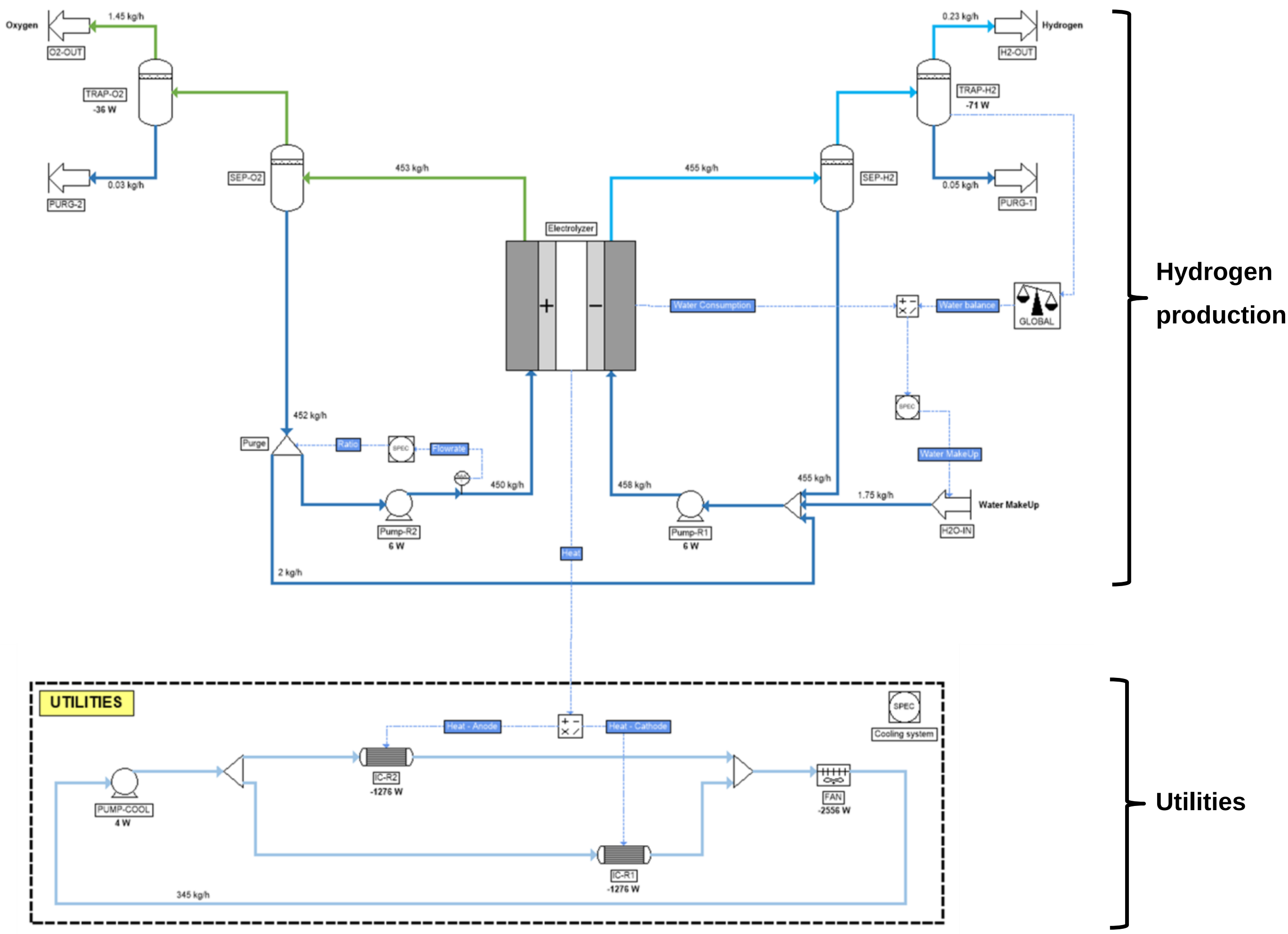
The simulation flowsheet is described below. It is divided into two sections:

1. Hydrogen production:

The central element of this section is the electrolysis module (“Electrolyzer”), allowing the production of vapor-liquid streams “H2-STACK” (essentially composed of hydrogen and water) and “O2-STACK” (essentially composed of oxygen and water). These steams, leaving the electrodes, are sent to separation drums (“SEP-O2” and “SEP-H2”). The electrolyte solution is recycled at the inlet of the electrolyzer using pumps (a make-up is necessary on the cathode side while a purge is necessary on the anode side). The gas streams leaving the separation drums are brought to atmospheric pressure and at a temperature of 25°C in order to reduce the water content.

2. Utilities:

This section allows to simulate the utilities used to cool the electrolyzer. The total amount of heat required is calculated by the “Electrolyzer” module. Half of this heat, corresponding to the anode side, is sent to the "IC-R2" heat exchanger while the other half, corresponding to the cathode side, is sent to the "IC-R1" heat exchanger. The utility fluid consists of pure water circulating in a closed loop and cooled by an air cooler (“FAN”).



1.3. Components

Components taken into account in the simulation, along with their chemical formula and CAS[1] number, are presented in the following table. Pure components physical properties are extracted from the ProSimPlus standard database [ROW22]. The electrolyte solution is represented by pure water in this example.

Component	Chemical formula	CAS number[(1)]
Water	H_2O	7732-18-5
Hydrogen	H_2	1333-74-0
Oxygen	O_2	7782-44-7

1.4. Thermodynamic model

Two "thermodynamic calculators" are defined in this example:

- "Process": this calculator includes all the components defined previously, and is used in the "Hydrogen production" section. The "PSRK" thermodynamic profile is selected.
- "Cooling water": this calculator is used in the "Utilities" section for the modelling of the electrolyzer cooling system. The "pure water" thermodynamic profile is selected.

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

1.5. Operating conditions

1.5.1. "Hydrogen production" section

✓ Electrolyzer module:

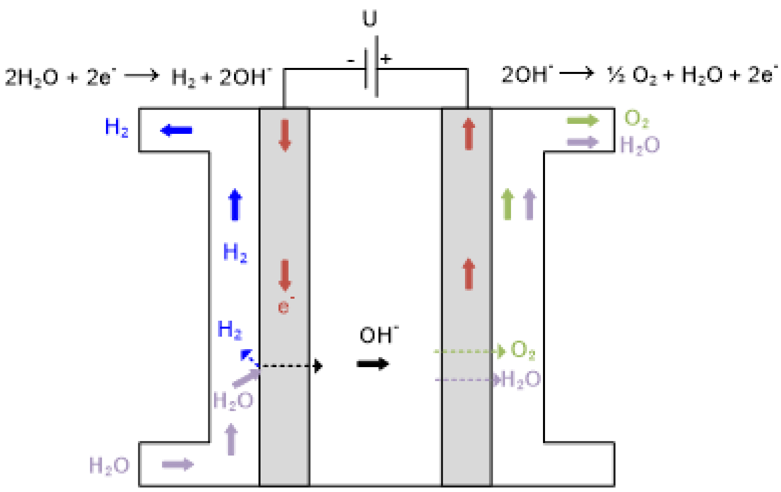
The electrolyzer module, based on the alkaline technology, is composed of 12 cells associated in series. The chemical reactions involved at the electrodes are the following:

- At the anode: oxygen production

$$2\,OH^- \rightarrow \frac{1}{2}O_2 + H_2O + 2\,e^-$$

- At the cathode: hydrogen production

$$2\,H_2O + 2\,e^- \rightarrow \,H_2 + 2\,OH^-$$



The operating conditions are provided in the following table:

Electrolyzer configuration	**Technology**	Alkaline
	Stack configuration	Serie
	Number of cells	12
	Active area per cell	0.1 m^2
Operating conditions	**Electric power**	10 kW
	Heat losses	266 W
	Temperature	75°C
	Anode pressure	Equal to the feed
	Cathode pressure	Equal to the feed

The electrical power being supplied, the cell voltage must be determined in order to deduce the current intensity, and access all the electrical characteristics of the stack and the electrolysis cells. There are three options to define the cell voltage: it can be either supplied, calculated by a correlation or defined by script (user model). In this example, it is calculated by a correlation, involving the following different contributions:

$$V_{cell} = V_{rev} + V_{ohm} + V_{act} + V_{con}$$

With:

V_{cell} : the cell voltage (V)

V_{rev} : the reversible voltage (V)

V_{ohm} : the ohmic overvoltage (V)

V_{act} : the activation overvoltage (V)

V_{con} : the concentration overvoltage (V)

The calculation conditions for each term are provided in the following table:

Term	Calculation mode	Correlation	Parameters
V_{rev}	Calculated by a correlation	$V_{rev} = \frac{\Delta G_r(T,P)}{z.F}$	-
V_{ohm}	Calculated by a correlation	$V_{ohm} = (A + B.T) . J_{cell}$	A = 4.26336.10^{-5} B = 6.88874.10^{-9}
V_{act}	Calculated by a correlation	$V_{act} = A \log\left[\left(B + \frac{C}{T+E} + \frac{D}{(T+E)^2}\right).J_{cell} + 1\right]$	A = 0.33824 B = -0.01539 C = 2.00181 D = 15.24178 E = -273.15
V_{con}	Neglected	$V_{con} = 0$	-

The “Efficiencies” tab allows to provide the following data:

- The transfer ratio of hydrogen and oxygen through the membrane, defined as follows:

$$Hydrogen\ transfer = \frac{(Hydrogen\ flowrate)_{anode}}{(Hydrogen\ flowrate)_{produced}}$$

$$Oxygen\ transfer = \frac{(Oxygen\ flowrate)_{cathode}}{(Oxygen\ flowrate)_{produced}}$$

- The Faraday efficiency, that can be defined from three different modes: it can be either supplied, calculated by a correlation or defined by script (user model).

The calculation conditions are provided in the following table:

Transfer through the membrane	**Hydrogen transfer**	0.8 %
	Oxygen transfer	0 %
Faraday efficiency	**Calculation mode**	Calculated by a correlation
	Correlation	$\eta_F = \frac{{J_{cell}}^2}{A + B.T + {J_{cell}}^2}(C + D.T)$
	Parameters	A = 1285298.66 B = -2953.15 C = 132.368 D = -0.104

Finally, in the “Options” tab, the printing of the “voltage – current density” curves is activated:

✓ <u>Vapor-liquid separators:</u>

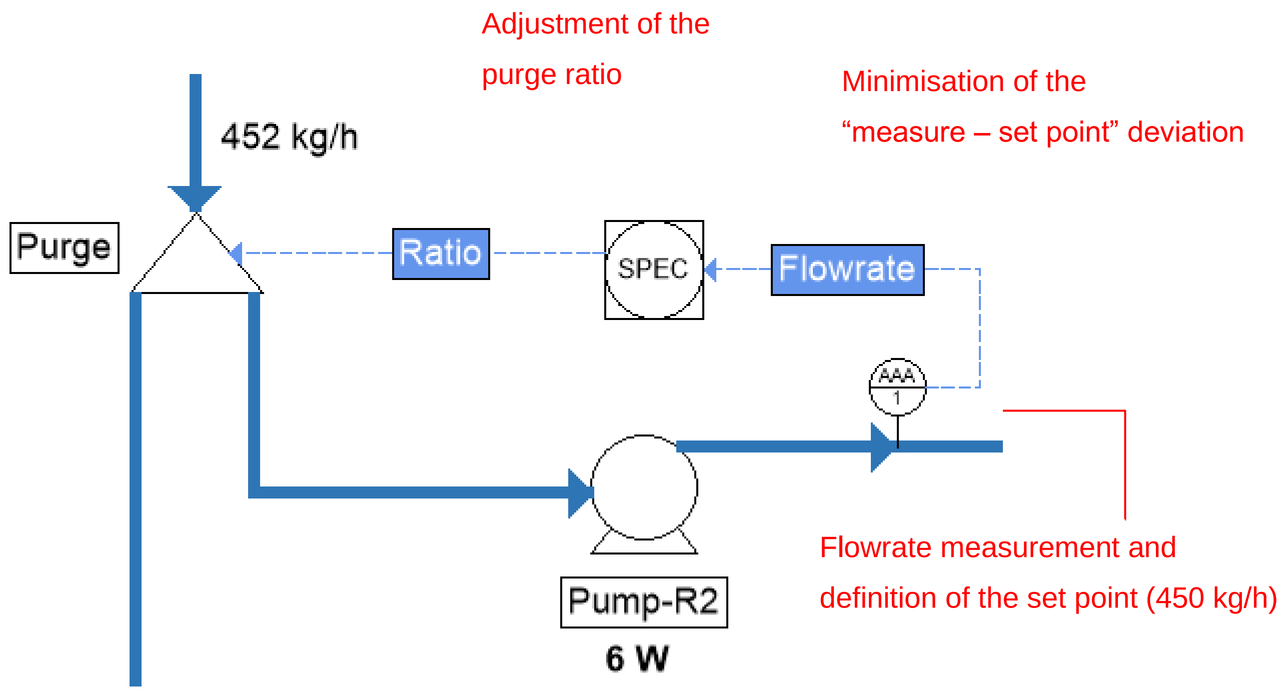
Name	Type	Operating conditions
SEP-O2	Constant pressure and enthalpy flash	Pressure drop = 0.3 bar Heat duty = adiabatic
SEP-H2	Constant pressure and enthalpy flash	Pressure drop = 0.3 bar Heat duty = adiabatic
TRAP-O2	Constant temperature and pressure flash	T = 25°C P = 1 bar
TRAP-H2	Constant temperature and pressure flash	T = 25°C P = 1 bar

✓ Pumps:

Name	Exhaust pressure	Efficiencies
Pump-R1	7 bar	Default values
Pump-R2	7 bar	Default values

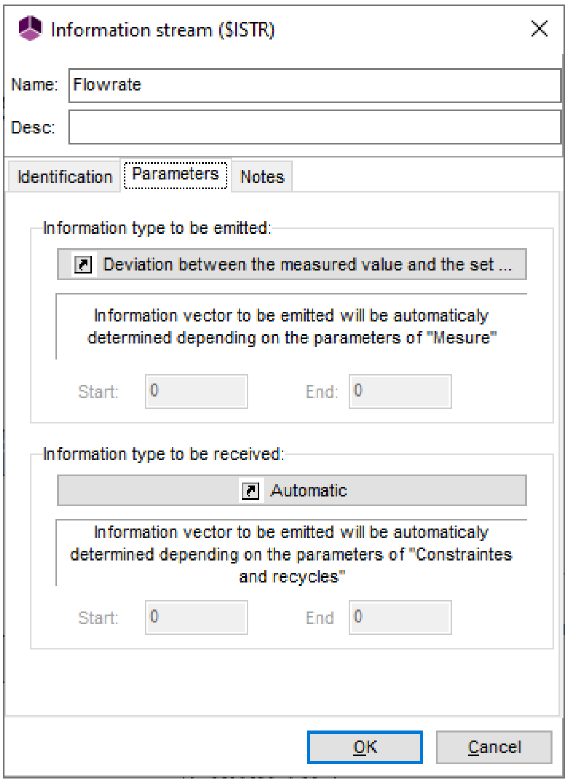
✓ Purge:

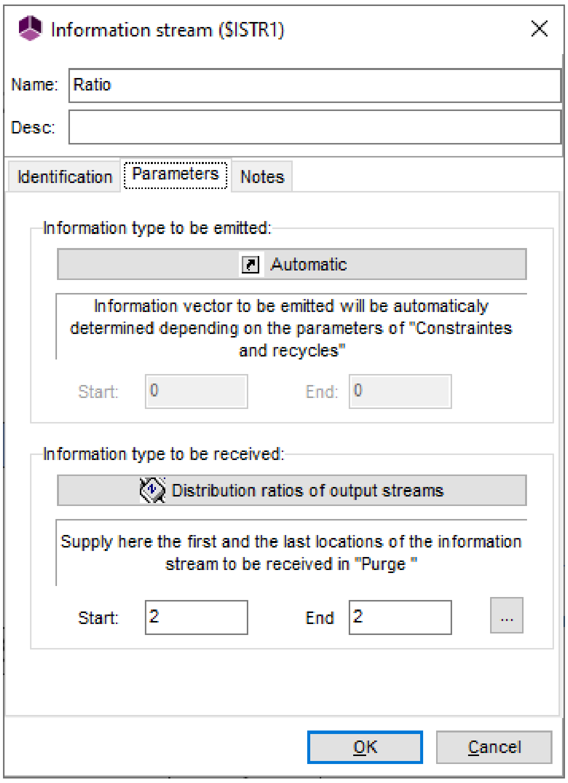
A purge is necessary, on the anode side, in order to eliminate excess water. Since the water is recycled at the electrolyzer inlet, the software automatically computes the flowrate of water circling in the system, in order to verify the mass balance. This water flowrate depends on the purge ratio. With this in mind, a specification is added so that the software automatically calculates the purge ratio leading to a desired flowrate of 450 kg/h at the electrolyzer inlet. This specification consists of the items below.



The default configuration is used for the "SPEC" module that manages the constraints and recycles.

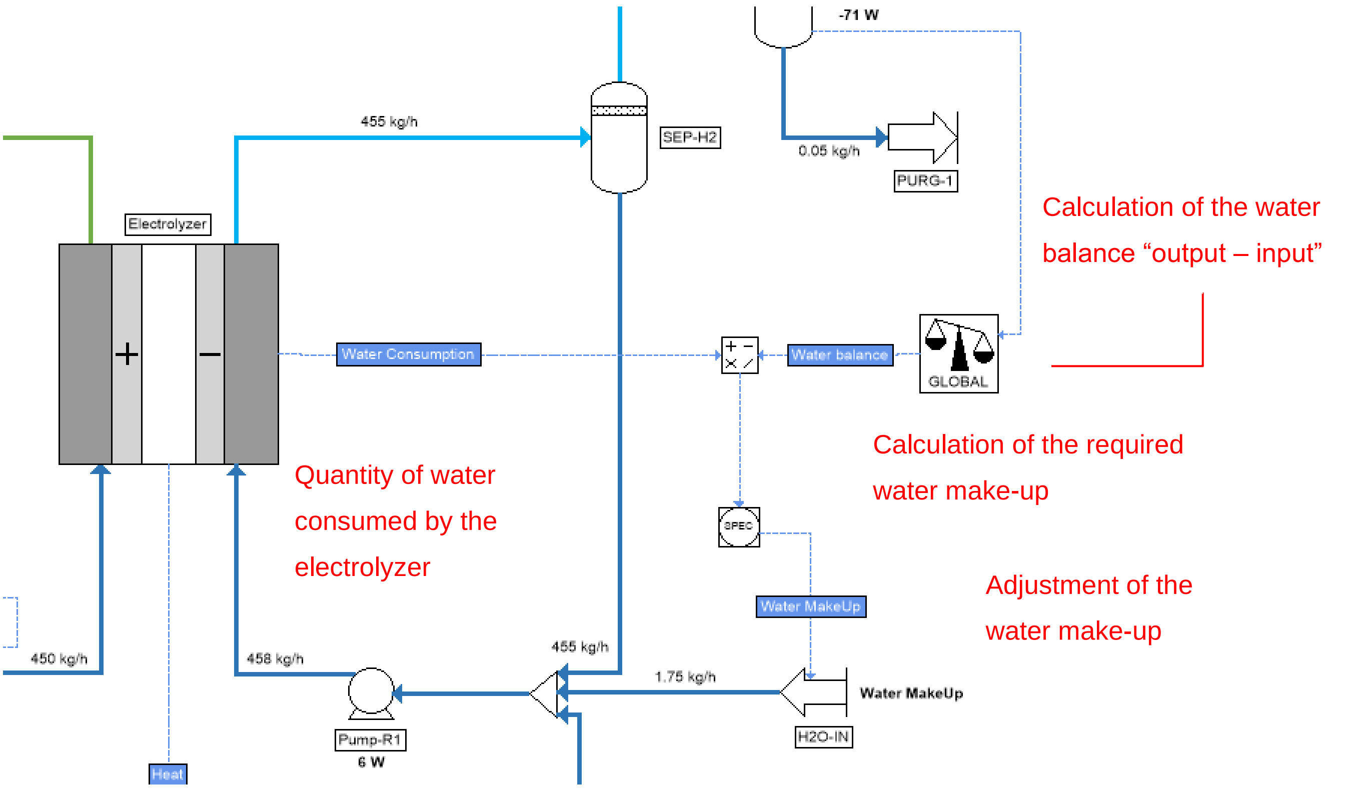
The information streams are defined as follows (with the configuration windows of the “Flowrate” stream on the left and the “Ratio” stream on the right):



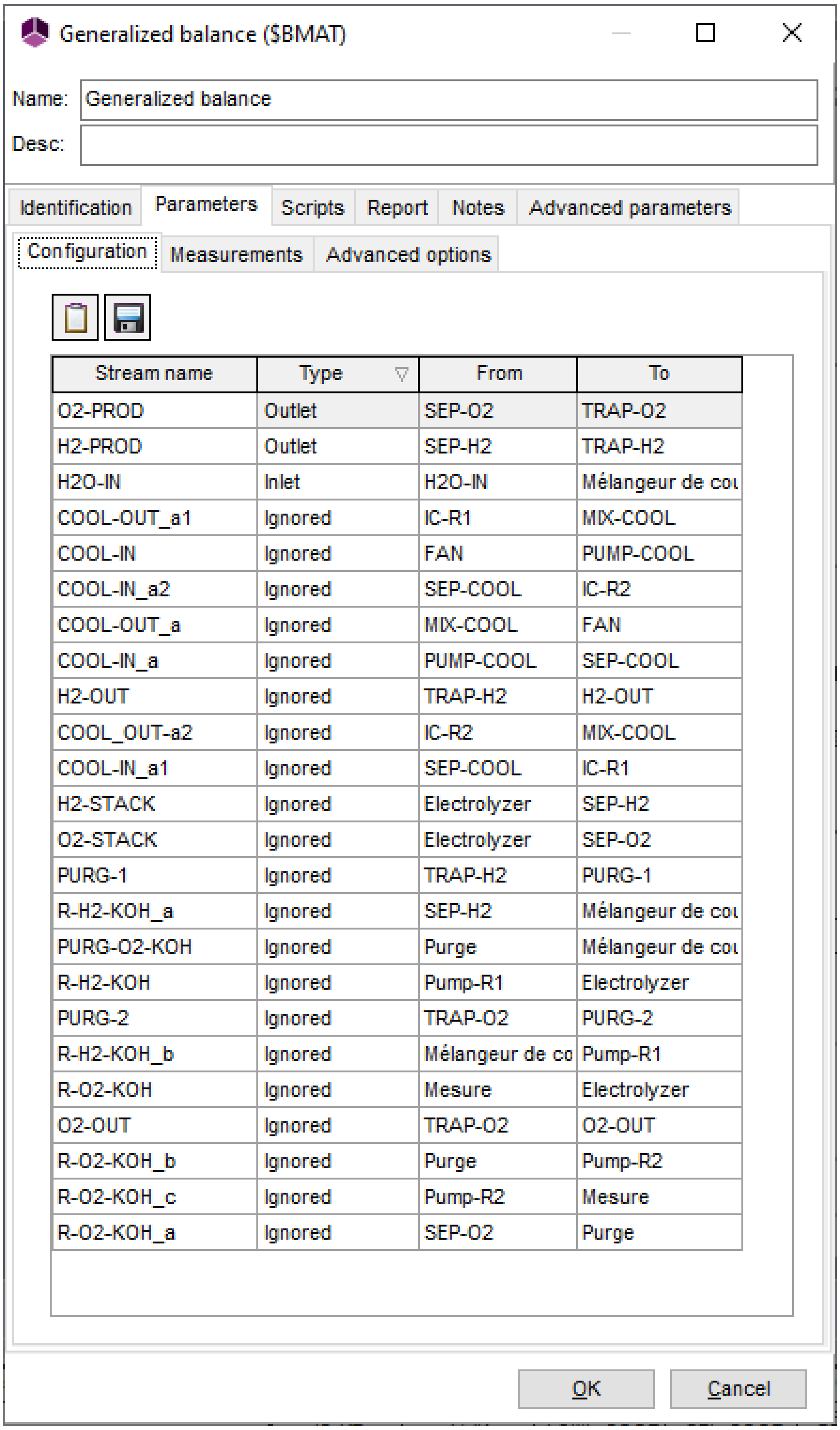


- ✓ <u>Water make-up:</u>

A water make-up is necessary, on the cathode side, in order to balance the quantity of water consumed in the electrolyzer and leaving with the vapor streams from the vapor-liquid separators. Here as well, a "SPEC" module is used to automatically adjust the flowrate of water supplied according to the operating conditions.



The "Generalized balance" module is used to calculate the water balance ("output - input"), taking into account the water leaving the process in the "O2-STACK" and "H2-STACK" streams from the electrolyser and the water entering the process in the "H2O-IN" stream. The configuration of this module is the following:

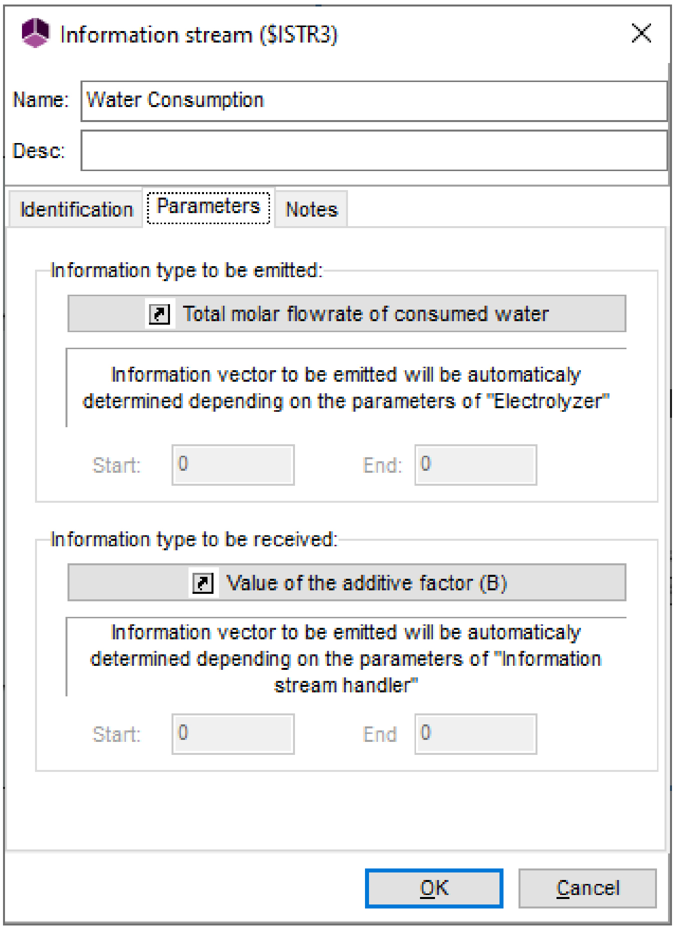


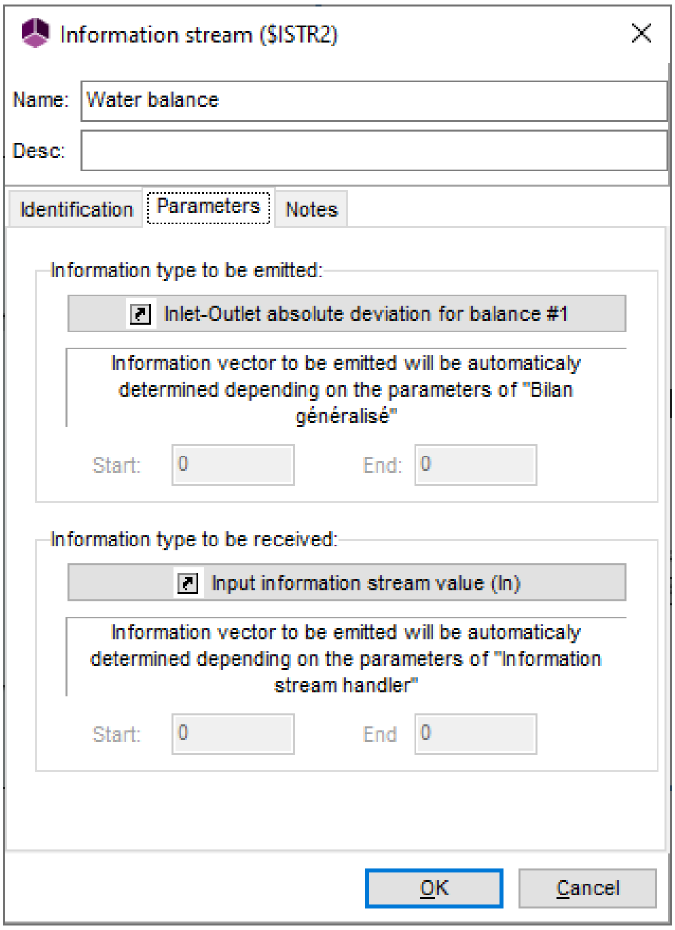
Stream name	Type	From	To
O2-PROD	Outlet	SEP-O2	TRAP-O2
H2-PROD	Outlet	SEP-H2	TRAP-H2
H2O-IN	Inlet	H2O-IN	Mélangeur de coι
COOL-OUT_a1	Ignored	IC-R1	MIX-COOL
COOL-IN	Ignored	FAN	PUMP-COOL
COOL-IN_a2	Ignored	SEP-COOL	IC-R2
COOL-OUT_a	Ignored	MIX-COOL	FAN
COOL-IN_a	Ignored	PUMP-COOL	SEP-COOL
H2-OUT	Ignored	TRAP-H2	H2-OUT
COOL_OUT-a2	Ignored	IC-R2	MIX-COOL
COOL-IN_a1	Ignored	SEP-COOL	IC-R1
H2-STACK	Ignored	Electrolyzer	SEP-H2
O2-STACK	Ignored	Electrolyzer	SEP-O2
PURG-1	Ignored	TRAP-H2	PURG-1
R-H2-KOH_a	Ignored	SEP-H2	Mélangeur de coι
PURG-O2-KOH	Ignored	Purge	Mélangeur de coι
R-H2-KOH	Ignored	Pump-R1	Electrolyzer
PURG-2	Ignored	TRAP-O2	PURG-2
R-H2-KOH_b	Ignored	Mélangeur de co	Pump-R1
R-O2-KOH	Ignored	Mesure	Electrolyzer
O2-OUT	Ignored	TRAP-O2	O2-OUT
R-O2-KOH_b	Ignored	Purge	Pump-R2
R-O2-KOH_c	Ignored	Pump-R2	Mesure
R-O2-KOH_a	Ignored	SEP-O2	Purge

An “information stream handler” module is then used to add, to the water balance, the quantity of water consumed by the electrolyzer:

$$\textbf{\textit{Total water balance}} = \underbrace{\textit{(Water leaving the process – Water entering the process)}}_{\text{Calculated by the « generalized module »}} + \underbrace{\textit{Water consumed}}_{\text{Calculated by the « electrolyzer » module}}$$

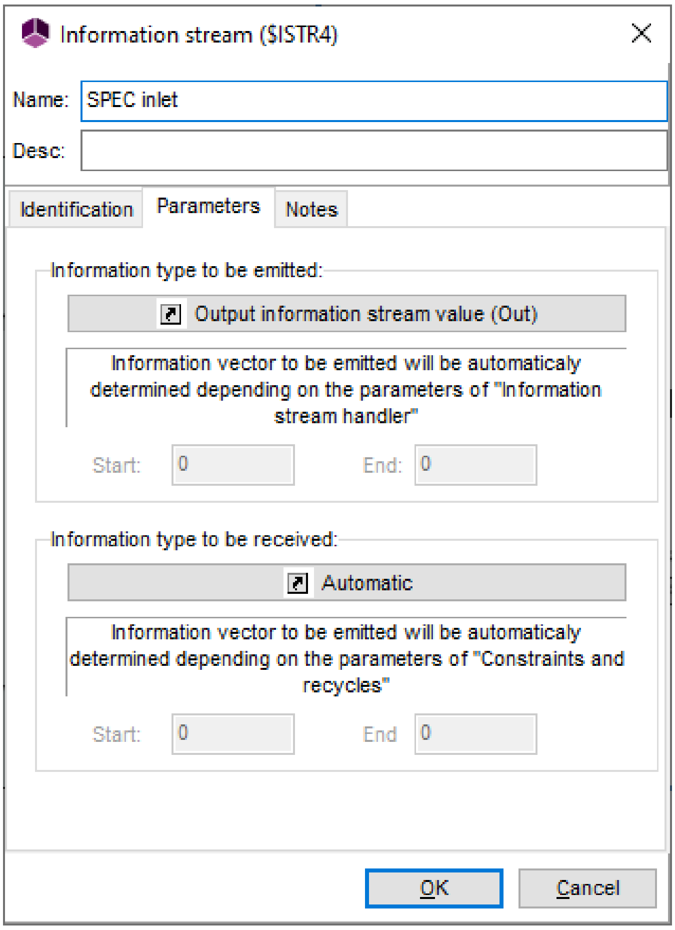
The equation involved in the “information stream handler” module is “Out = $A*In^P + B – C$”. Therefore, the coefficient A is set to 1 and the information streams named “water consumption” and “water balance” are configured as follows:

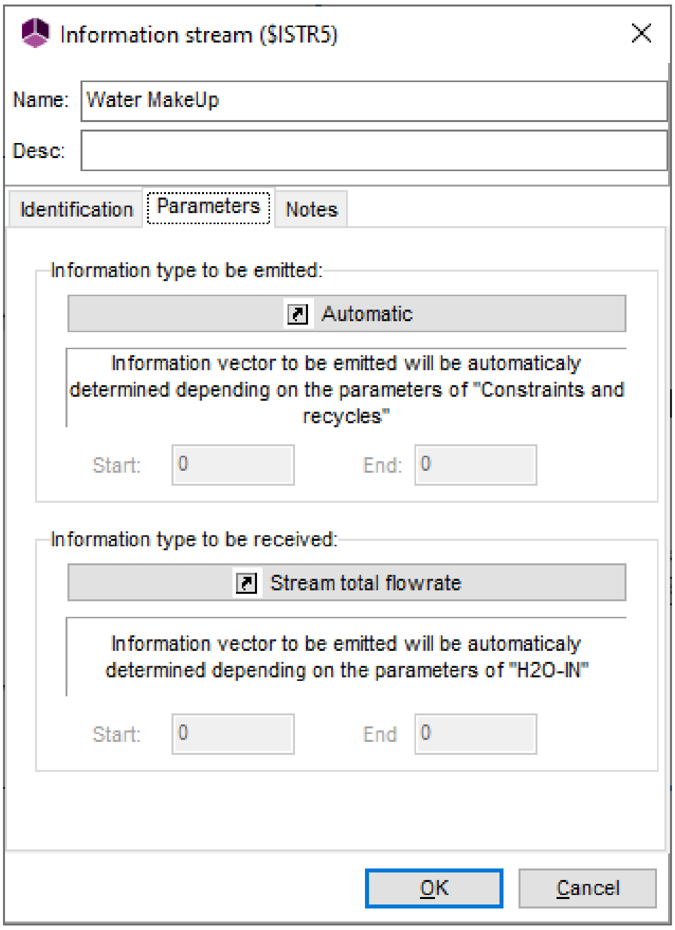




The "SPEC" module then makes it possible to minimize the value of the total water balance by adjusting the water flowrate defined in the "H2O-IN" supply. The “Newton–Raphson” numerical method is used (with default numerical parameters).

The information streams at the inlet and outlet of the "SPEC" module are defined as follows:





Note: an information stream is also defined between the “TRAP-H2” module and the “generalized balance” module. This stream is only used to impose the calculation sequence so that the “generalized balance” module is calculated at the end of the sequence. No information is transmitted.

1.5.2. “Utilities” section

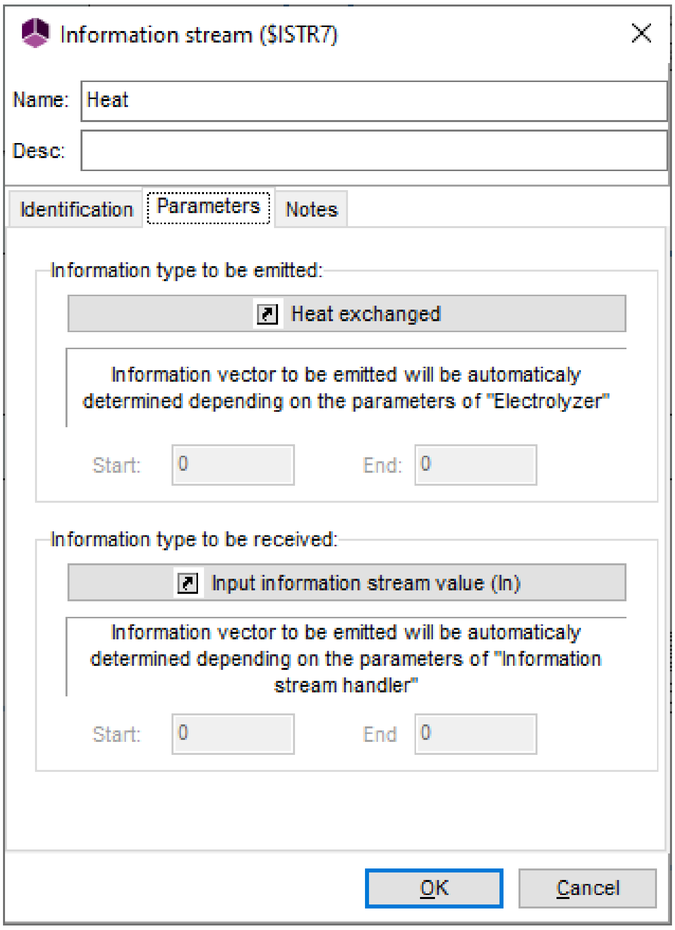
✓ <u>Heat exchangers:</u>

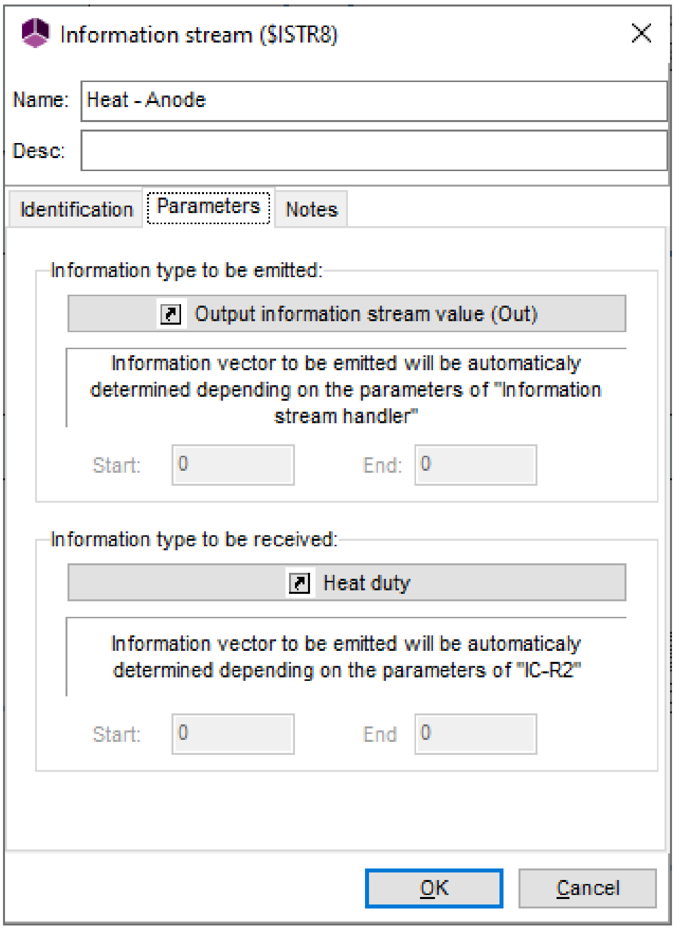
The heat exchangers "IC-R1" and "IC-R2", that allow to cool the electrodes, are represented by a “simple heat exchanger” module (the visual is changed in order to represent a “shell and tubes” heat exchanger, this functionality being described in the paragraph 1.7.1).

Name	Pressure drops	Heat duty
IC-R1	0.3 bar	0 (initialization value)
IC-R2	0.3 bar	0 (initialization value)

The required heat duty is calculated by the electrolysis module. Information streams, associated to an "information stream handler" module, allow to transfer half of this value to the "IC-R1" and "IC-R2" exchangers (total heat duty = heat duty at the anode + heat duty at the cathode).

The equation of the "information steam handler" is then defined by "A = 0.5" (*i.e.:* Out = 0.5*In), with the following configuration for the information stream at the input (on the left) and output (on the right) of the module:





The "FAN" heat exchanger is represented by a "cooler/heater" module (the visual corresponding to an "air-cooled" heat exchanger is selected, this functionality being described in the paragraph 1.7.1). The outlet temperature is set to 35°C.

- ✓ Pump:

Name	Exhaust pressure	Efficiencies
Pump-COOL	2.6 bar	Default values

- ✓ Stream splitter:

The “SEP-COOL” module is defined with a splitting ratio of 0.5.

- ✓ “SPEC” module:

Since this section involves a recycle, a “SPEC” module is necessary. The default configuration is used.

1.6. Initializations

1.6.1. “Hydrogen production” section

The calculation sequence is automatically determined by ProSimPlus. Two tear streams are identified: the streams “R-H2-KOH” and “R-O2-KOH” (the two inlets of the electrolyser). The following initialization is used:

Stream	Partial mass flowrate	Temperature	Pressure
R-O2-KOH	Water: 450 kg/h	75 °C	7 bar
R-H2-KOH	Water: 450 kg/h	75 °C	7 bar

1.6.2. “Utilities” section

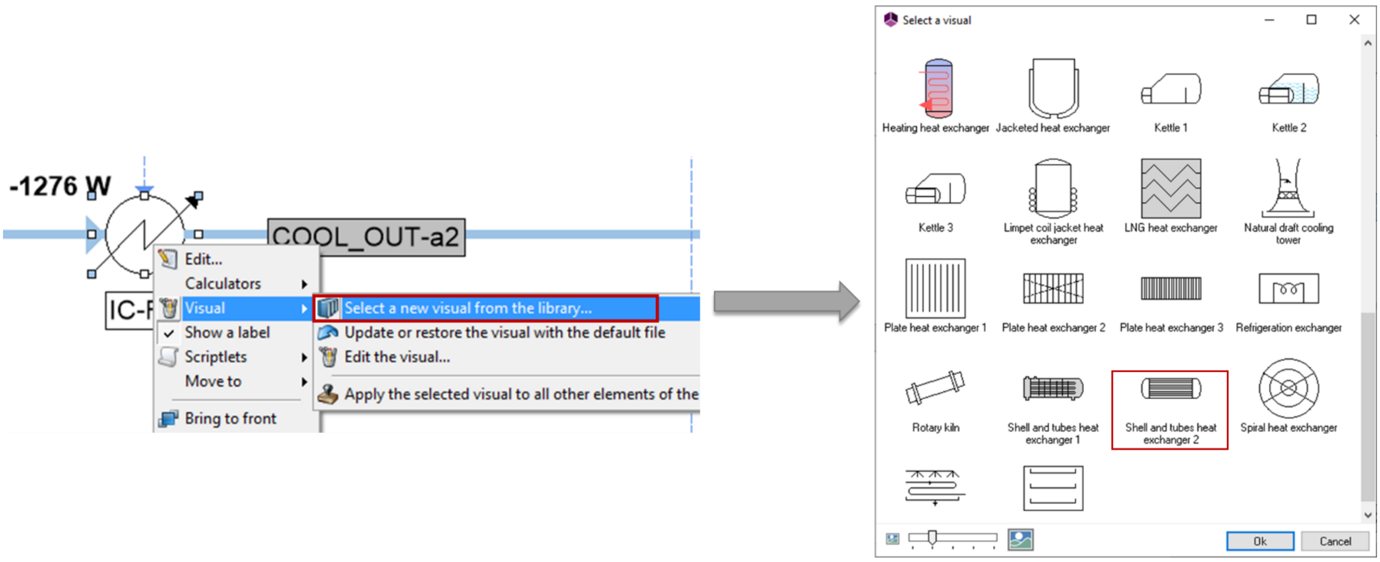
The calculation sequence is automatically determined by ProSimPlus. One tear stream is identified: the stream “COOL-IN” connected from the “FAN” heat exchanger to the pump. The following initialization is used:

Stream	Partial mass flowrate	Temperature	Pressure
COOL-IN	Water: 345.37 kg/h	35 °C	2.3 bar

1.7. Hints and tips

1.7.1. Change of module visuals

A default visual is provided for each of the modules available in the unit operations library. It is possible to change this visual and import an image from a library or provide a custom image. In order to import a visual from the library, do a right-click on the module and then click on “select a new visual from the library”, as illustrated below for the “IC-R2” heat exchanger which is a “shell and tubes” type:

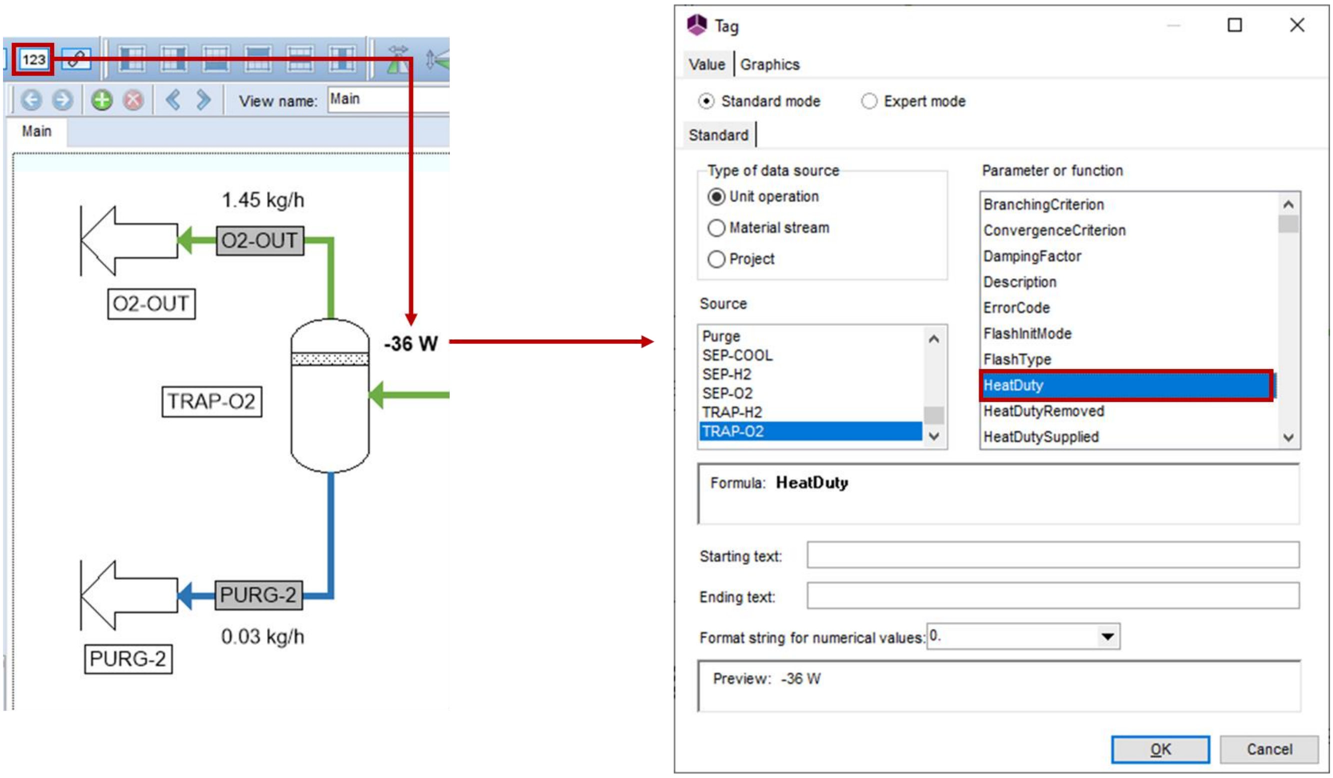


1.7.2. Display of “tags” on the flowsheet

“Tags” are added to the flowsheet in order to display the following results:

- The mass flow rates;
- The powers required for the pumps;
- The heat duties required for the heat exchangers;
- The key results.

For example, the heat duty involved in the "TRAP-O2" separator is displayed by configuring the tag as follows:



2. RESULTS

2.1. Hydrogen and oxygen production

	At the anode	At the cathode	TOTAL
Hydrogen production	0.02 Nm^3/h	1.97 Nm^3/h	1.99 Nm^3/h
Oxygen production	0.99 Nm^3/h	0 Nm^3/h	0.99 Nm^3/h

The molar compositions of the final products are provided in table below. Hydrogen is produced with a purity of **96.8%.**

	"H2-OUT" stream	"O2-OUT" stream
Water	3.2%	3.2%
Hydrogen	**96.8%**	1.5%
Oxygen	0%	**95.3%**

2.2. Electrolyzer characteristics

For the simulated operating conditions, the Faraday efficiency obtained is 94.7%. The electrical characteristics are displayed in the following table:

	Cell	Stack
Electric current	417 A	417 A
Current density	4175 A/m^2	4175 A/m^2
Voltage	2 V	24 V

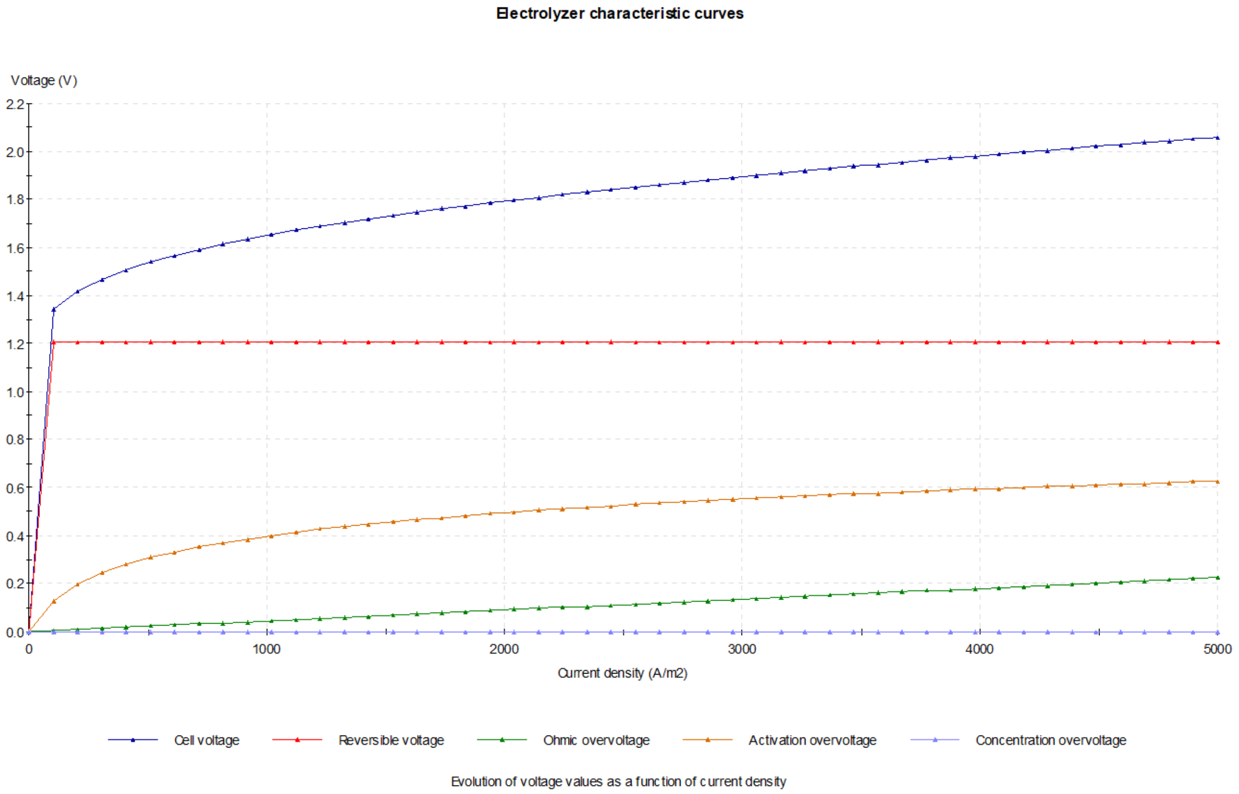
The reversible decomposition voltage for a cell, corresponding to the minimum voltage necessary for the electrolysis reaction to take place, is 1.2 V.

The reaction enthalpy, under these operating conditions, is 282 kJ/mol. Since the reaction is endothermic, it is necessary to apply a cell voltage higher than the reversible decomposition voltage in order to compensate for the reaction heat and maintain the electrolyser at a constant temperature. This corresponds to the thermo-neutral voltage of a cell and it is equal to 1.46 V.

The cell voltage applied in reality is higher and equals 2 V. This value is the sum of the following contributions ($V_{cell} = V_{rev} + V_{ohm} + V_{act} + V_{con}$):

Reversible voltage (V_{rev})	1.2 V
Ohmic overvoltage (V_{ohm})	0.2 V
Activation overvoltage (V_{act})	0.6 V
Concentration overvoltage (V_{con})	0 V
Cell voltage (V_{cell})	**2.0 V**

It is possible to access the electrolyzer “characteristic curves” (corresponding to the evolution of the different voltage contributions as a function of current density) from the “Profiles” tab:



2.3. Energy balance

The total required energy, corresponding to the sum of the reaction heat and the thermal energy (for an isothermal operation of the electrolyzer) equals 7.19 kW.

Heat of reaction	6.94 kW
Thermal energy	0.25 kW
Total energy required	**7.19 kW**

Since the applied cell voltage is higher than the thermo-neutral voltage, it is necessary to cool the electrolyser in order to maintain a constant operating temperature. The overall energy balance below is used to calculate the quantity of heat to be removed:

Heat to be removed = Electrical power - Total energy required - Heat losses

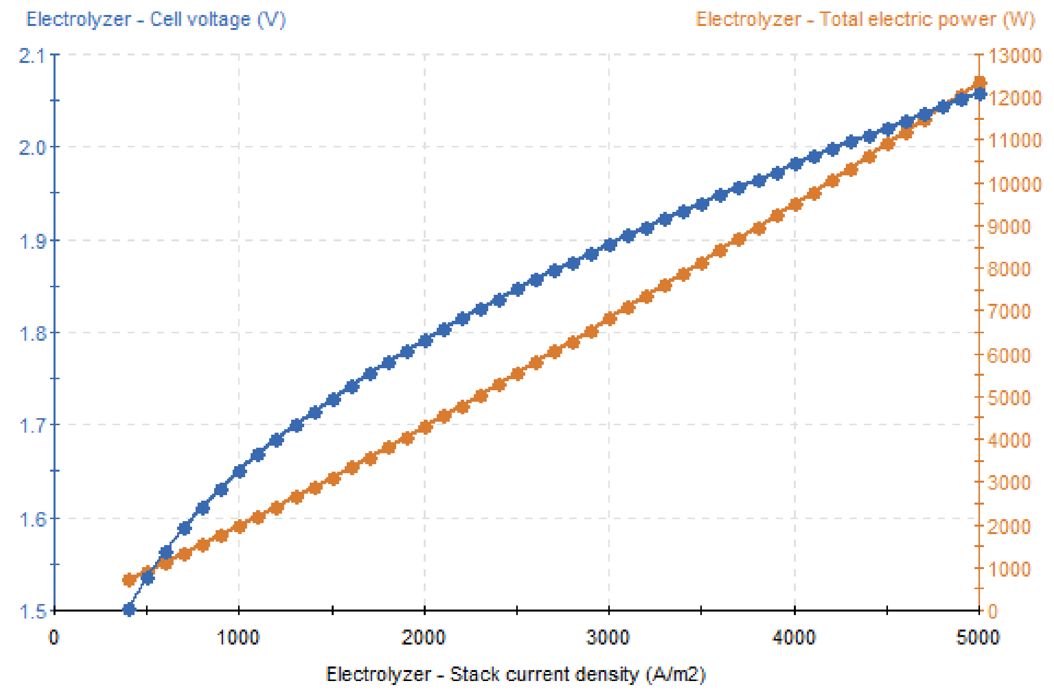
Total energy required	7.19 kW
Electric power	10 kW
Heat losses	0.27 kW
Heat to be removed	**2.56 kW**

It is necessary to cool the electrolyzer and remove a total heat of 2.56 kW, corresponding to 1.28 kW per electrode.

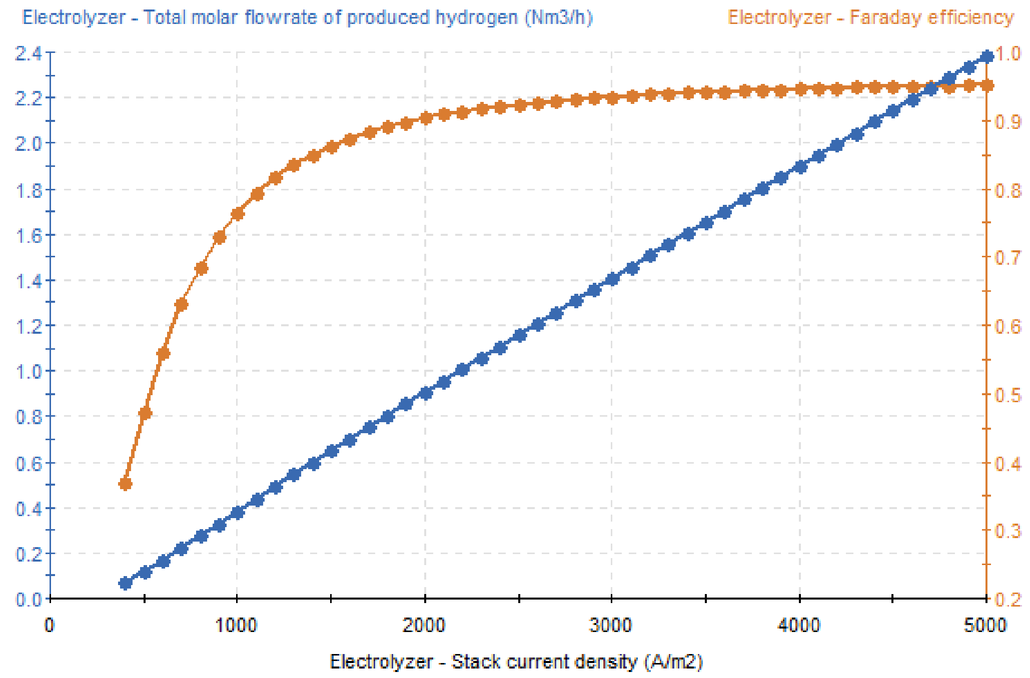
2.4. Case study

A case study analysis is performed and the current density is varied from 400 to 5000 A/m². It should be noted that to do this, the specification of the electric current must be changed to "Current density" in the "General" tab. The minimum value for the current density was selected to ensure that the electrolyser was operating above the thermo-neutral voltage. The results are displayed below:

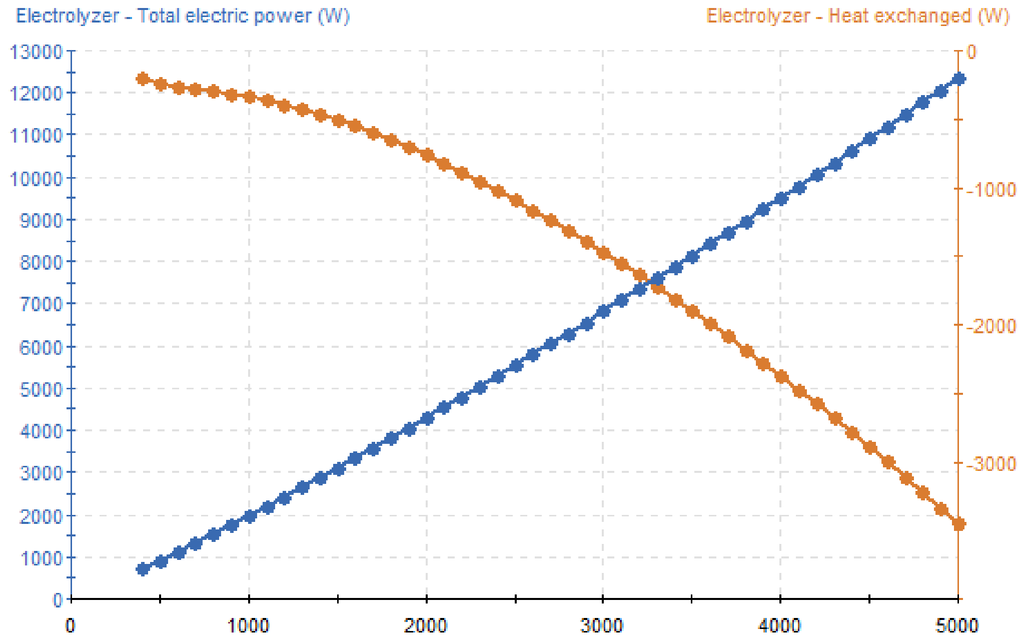
- ✓ Cell voltage and electric power as a function of current density:



- ✓ Total flowrate of produced hydrogen and Faraday efficiency as a function of current density:



✓ Total electric power and heat exchanged as a function of current density:



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