MODELING OF A HIGH TEMPERATURE ELECTROLYSER IN THERMOPTIM

A high-temperature electrolyzer receives a mixture of water vapor and hydrogen (typically with a molar composition of 80% - 20%) at 30 bar and 800 °C. It produces two fluids: oxygen and the initial mixture enriched with hydrogen. At the outlet of the electrolyzer, the hydrogen mixed with water vapor is collected. The separation does not pose any particular problem: it is sufficient to condense the water to obtain pure hydrogen.

The Thermoptim model includes a classic mixer upstream, used to create the mixture ([H2], [H2O]) at the entrance of the electrolyzer, and an external divider downstream, both connected by a process-point playing a passive role. A thermocoupler is used to provide heat to the component.

The structure of the model is shown in Figure 1 and the screen of the electrolyzer is shown in Figure 2.

The model we develop is very simple: it takes as parameters the molar fraction of hydrogen at the outlet α or the electricity supplied Pelec.

The balance of species is easy to establish. Electricity supplied electrolyzes water and produces hydrogen and oxygen, while heat provided by the high temperature thermocoupler raises the temperature of the device (Figure 3).

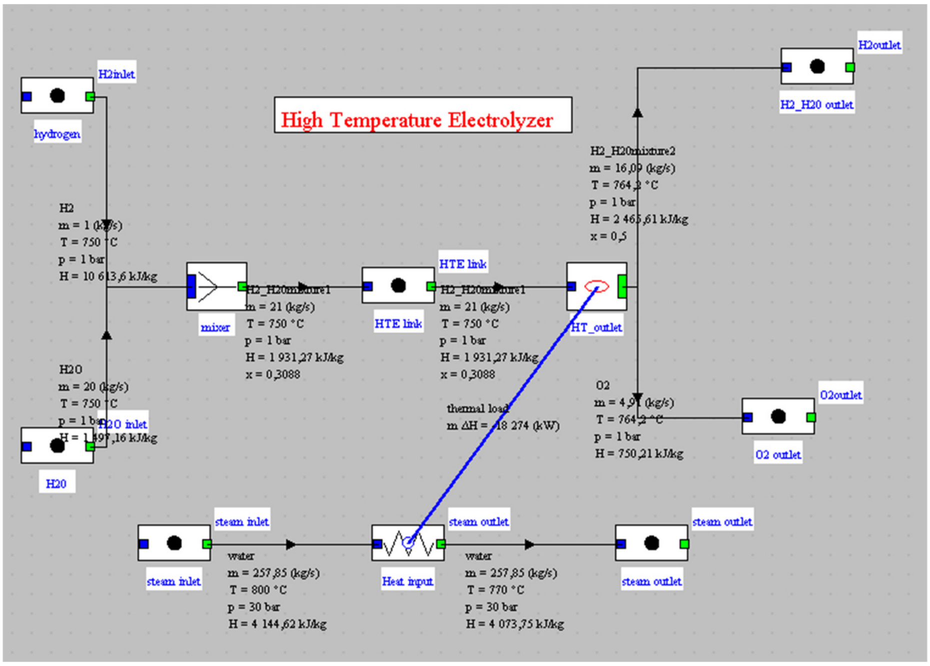
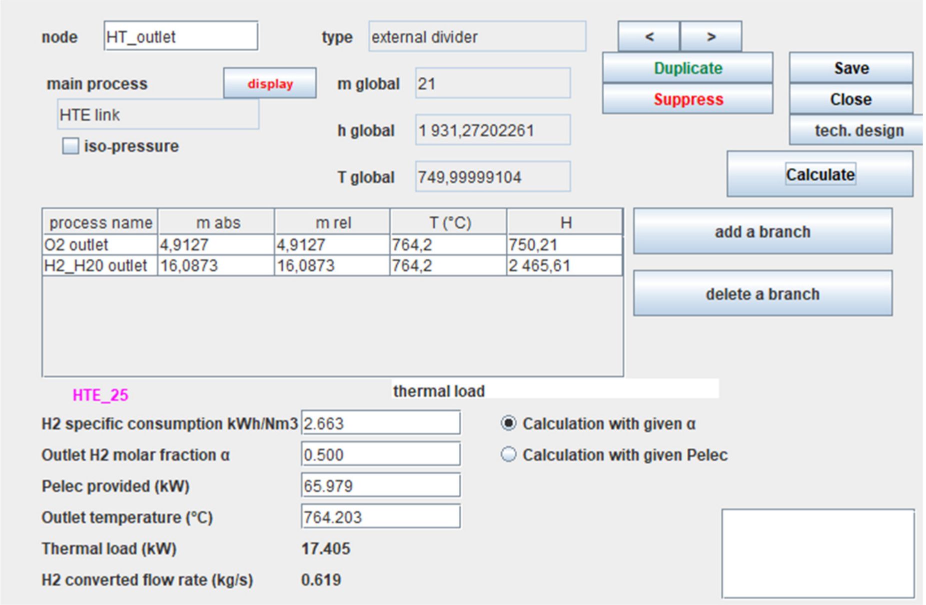


Figure 1: Diagram of HTE component with connections

Two calculation methods are possible:

- either determine Pelec knowing α;
- or determine α knowing Pelec.

In the first mode, the calculation is as follows: the model determines the inlet molar fraction and molar flow rate from the external divider main flow, deduces the molar flow of hydrogen electrolyzed, and establishes its balance.



node	HT_outlet	type	external divider
main process	HTE link	m global	21
☐ iso-pressure		h global	1 931,27202261
		T global	749,99999104

process name	m abs	m rel	T (°C)	H
O2 outlet	4,9127	4,9127	764,2	750,21
H2_H20 outlet	16,0873	16,0873	764,2	2 465,61

HTE_25

thermal load

H2 specific consumption kWh/Nm3	2.663
Outlet H2 molar fraction α	0.500
Pelec provided (kW)	65.979
Outlet temperature (°C)	764.203
Thermal load (kW)	17.405
H2 converted flow rate (kg/s)	0.619

● Calculation with given α
○ Calculation with given Pelec

Figure 2: Screen of HTE component

Molar flow balance

Let us call β the inlet mole fraction of hydrogen, and $\dot{n}_{mol}$ the inlet total molar flow rate.

The molar flow of hydrogen electrolyzed $\dot{m}_{H2}$ is:

$\dot{n}_{H2} = (\alpha - \beta)\, \dot{n}_{mol}$

The composition of the mixture $\frac{[H2]}{[H2O]}$ being known, its molecular weight can be determined. As its molar flow rate is equal to the inlet molar flow rate, the mass flow is known.

The molar flow-rate of oxygen is $\frac{\dot{n}H2}{2}$. Its mass flow rate is deduced directly.

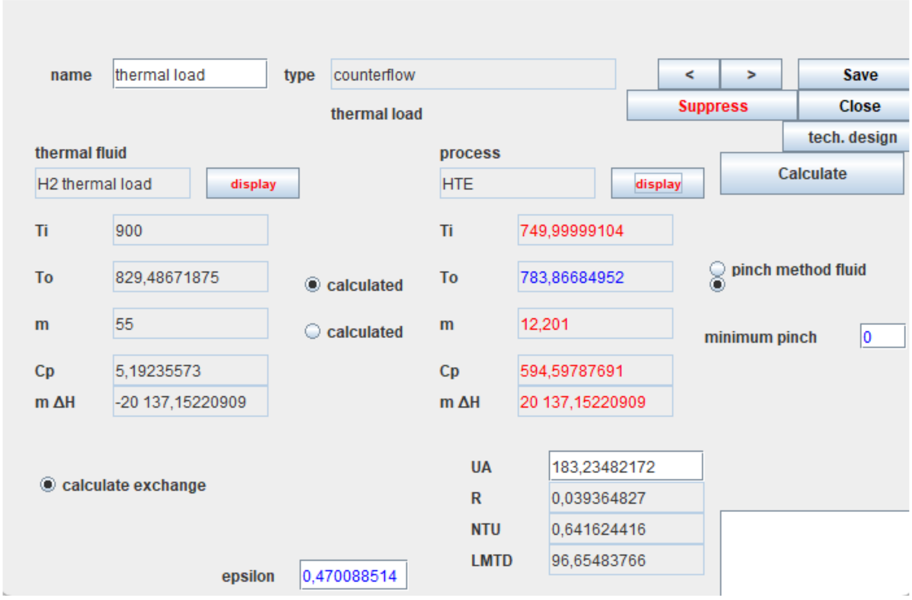
Energy balance

The overall energy balance of the water dissociation reaction is described by the First Law of thermodynamics, based on the relationship between enthalpy (ΔH), Gibbs energy (ΔG), and entropy (TΔS):

$\Delta H = \Delta G + T\Delta S$

Where:

- ΔH (Reaction Enthalpy) represents the total energy (electric + thermal) required for the reaction. It is the minimum total energy that must be provided.
- ΔG (Gibbs Energy) represents the part of the energy that must be provided in the form of electrical work. It is the minimum electric energy required.
- TΔS (Thermal Energy) represents the energy that can be provided in the form of heat. It is this component that makes the reaction endothermic.



name: thermal load
type: counterflow

thermal load

thermal fluid: H2 thermal load

process: HTE

	thermal fluid		process
Ti	900	Ti	749,99999104
To	829,48671875	To	783,86684952
m	55	m	12,201
Cp	5,19235573	Cp	594,59787691
m ΔH	-20 137,15220909	m ΔH	20 137,15220909

● calculated

○ calculated

○ pinch method fluid
●

minimum pinch: 0

● calculate exchange

UA: 183,23482172
R: 0,039364827
NTU: 0,641624416
LMTD: 96,65483766

epsilon: 0,470088514

Figure 3*:* High temperature electrolyzer thermocoupler screen

Regressions giving the theoretical values have been performed:

$T\Delta S_0$ = 61.491 * T/1000 - 6.2334;

ΔG_0 = -55.578 * T/1000 + 248.08;

Calculation of ΔG = Pelec

The cell voltage is a linear function of the HTE temperature:

U_cell = a T + b

The total current is given by Faraday's law:

$$I_{total} = \frac{\dot{n}_{H_2O} \times 2 \times F}{\eta_F}$$

The electric power is then given by:

Pelec = U_cell * I_total

An efficiency can be expressed as eta = ΔG_0/Pelec.

Calculation of TΔS = Q_abs

The heat provided by the thermocoupler is given by Q_abs = $\dot{n}$H2 $T\Delta S_0$
Where $T\Delta S_0$ is calculated by the regression given above.

In practice, we consider that the heat provided must slightly exceed this value, and we increase it by 5%.

The enthalpy balance is given by:

Calculation of ΔH

ΔH = Pelec + Q_abs

The "specific consumption" in kWh/Nm3 allows calculation of the amount of electricity to be supplied ΔH by:

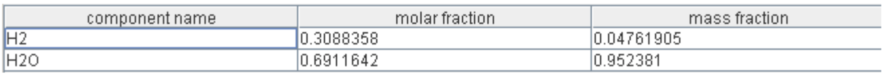
$$\Delta H = \dot{n}_{H2}\, M_{H2} \frac{3{,}600}{1{,}000 \,.\, 0.08988}$$

ΔH_0 being the theoretical heat of reaction (246 kJ/mol), the heat released is:

In the second mode, the sequence of calculations is slightly modified: knowing Pelec, $\dot{m}_{H2}$ can be determined, from which we deduce α. Q is determined in the same way.

RESULTS

With the settings above (1 kg/s hydrogen and 20 kg/s of water at the electrolyzer inlet), the gas compositions obtained are shown in Figures 4 and 5:

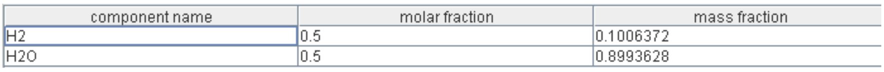


component name	molar fraction	mass fraction
H2	0.3088358	0.04761905
H2O	0.6911642	0.952381

Figure 4: Humidified hydrogen at inlet, flow rate 21 g/s, LHV: 5,712 kJ/kg

This model can be used to represent an electrolyzer integrated into a system, and particularly to study the thermal integration of the process in order to minimize the external heat input.

The external class is named HTE_25.java.



component name	molar fraction	mass fraction
H2	0.5	0.1006372
H2O	0.5	0.8993628

Figure 5: Humidified hydrogen at outlet, flow rate 16.09 g/s, LHV: 12,072 kJ/kg

An alternative model configuration without the thermocoupler could supplement this approach. Here, the inlet mixture would be preheated by the thermal energy (Qabs) accounting for the TΔS thermodynamic term in the electrolysis model, with the outlet temperature of the electrolyzer component being the same as the reference case.

This model has some limitations:

- Simplified linear voltage relationship (reality is more complex)
- No consideration of degradation
- Constant efficiency (actually varies with current)
- Ignores auxiliary consumption