

PROSIMPLUS APPLICATION EXAMPLE

**SIMULATION OF A REACTIVE BRAZED
PLATE AND FIN HEAT EXCHANGER
(BPFHE) FOR ORTHO-PARA HYDROGEN
CONVERSION WITH THE CAPE-OPEN
PROSEC REACTION UNIT OPERATION**

EXAMPLE PURPOSE

This example deals with a hydrogen liquefaction heat exchanger-reactor with simultaneous consideration of the ortho-para hydrogen conversion reaction. Since the formalism of this reaction is not available in CO-ProSec Reaction, it has been described via an external DLL. Tags are used to display results on the simulation scheme. Some of these tags involve the use of the advanced mode.

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CORRESPONDING PROSIMPLUS FILES

COPROSEC_EX_EN-ortho-para-hydrogen-conversion.pmp3

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1. PROCESS MODELING

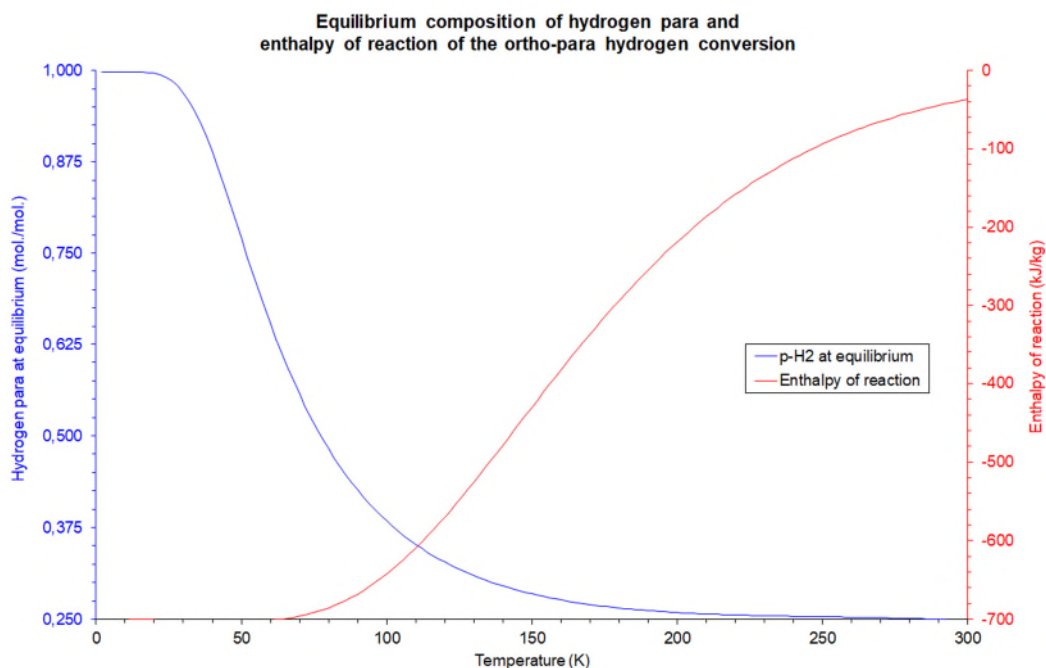
1.1. Process description

Hydrogen represents a zero-emission fuel when used, for example, in fuel cells for mobility or electricity production. The only emissions emitted by fuel cells are heat and water [VOL16]. Hydrogen is obtained by the following main production methods:

- ✓ Reforming or gasification of hydrocarbons, cf. “PSPS_EX_EN-Ammonia-Synthesis-Process” and “PSPS_EX_EN-Three-cycle-combined-electricity-generation-plan”;
- ✓ Thermochemical dissociation of water or biomass, cf. “PSPS_EX_EN-IGCC-Plant”;
- ✓ Water electrolysis, cf. “PSPS_EX_EN-Hydrogen-Production-Electrolysis”.

One of the technological challenges of using hydrogen is associated with its transport and storage. It can be either liquefied (e.g. at 1.3 bar and 21 K) or compressed (usually between 200 and 700 bar and close to ambient temperature). Cryo-compression is another possible process in which compression is done while remaining at cryogenic temperature and which allows to have densities around 80-85 kg/m³ rather than 70 kg/m³ at pressure close to ambient pressure [CRY23]. The choice of the transport mode depends on different parameters such as the amount of hydrogen, the transport distance and the desired physical state for distribution and end use. The advantage of liquefied hydrogen (LH2) is that the energy density is almost 4.5 times higher than that of hydrogen compressed to 200 bar. This reduces the volume and weight required for storage facilities, which becomes particularly attractive if large quantities of hydrogen need to be transported from remote locations and distributed to filling stations in cities [GOD12].

A major challenge in hydrogen liquefaction lies in its nature, which is composed of two spin isomers: ortho hydrogen and para hydrogen. As shown in the figure below, the equilibrium ratio between the two isomers is about 3:1 at ambient temperature. This mixture is called n-H2 normal hydrogen. The ortho hydrogen content decreases more drastically as temperatures become cryogenic [DON19].



The ortho-para conversion of hydrogen is exothermic with an enthalpy of reaction exceeding the heat of evaporation [BAK78]. In addition, the natural ortho-para conversion is inherently slow [MIL97], which gradually results in the vaporization of liquefied hydrogen in uncooled storages. The coupling of liquefaction and simultaneous ortho-para conversion (catalytically induced) allows the management of reaction heat within the exchanger itself, thus reducing reliquefaction expenses or product losses [SCH64], [HAU13].

[HUT65], [HUT66] and [HUT70] present both experimental data and models (but do not provide associated parameters) of the reaction rate of ortho-para hydrogen conversion in the presence of a catalyst. [WEI60a] and [WEI60b] also published experimental measurements under different conditions. [WIL18], [DON19] and [ONE23] used these experimental data to derive 1st-order kinetics ([WIL18], [DON19], [ONE23]) or Langmuir-Hinshelwood kinetics ([DON19]). The 1st-order kinetic models allow a better representation of the ortho-para conversion kinetics of hydrogen over a wide range of para hydrogen content [ONE23]. The model of [WIL18] has been used in this example. It has been encoded as a DLL with the use of analytic derivatives to reduce computation time. An Intel Fortran project template can be provided for users who want to develop their own kinetic model.

The catalyst used industrially is iron oxide Fe_2O_3 (oxide/hydroxide mixture). The supplier, Molecular Products, guarantees a conversion of 46.5% for a flow rate of 1200 SCCM of normal hydrogen at 77 K and 1.36 bar [DON19] after a regeneration process where the catalyst is heated to 160°C for 16 h under a flow of H_2 at 1.36 bar.

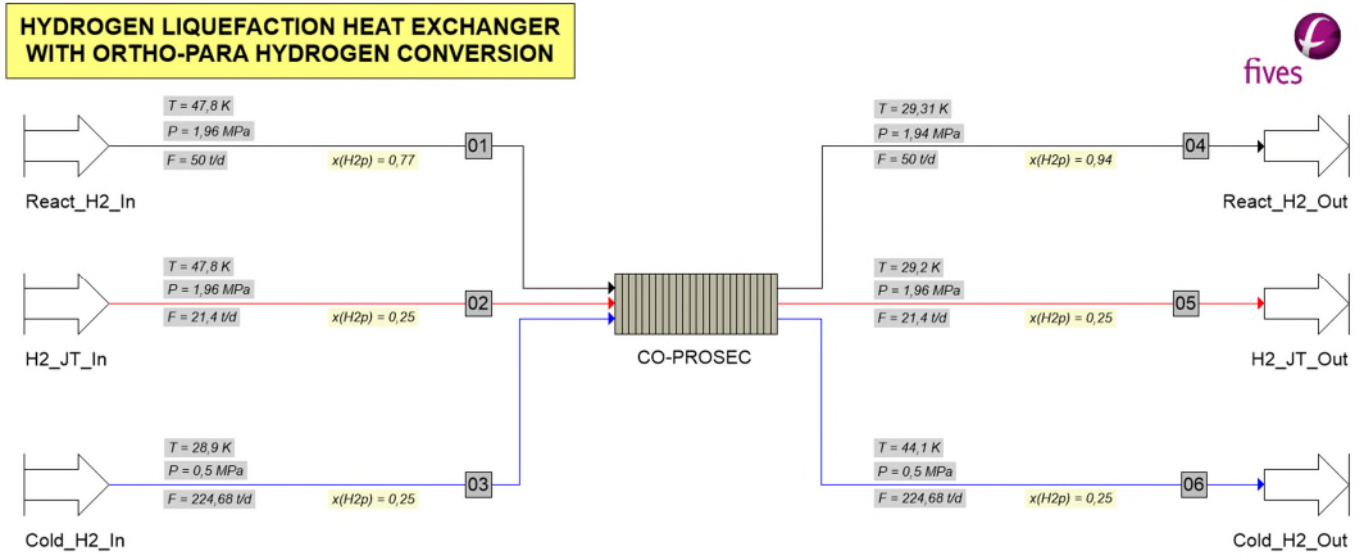
A conventional hydrogen liquefaction process consists of four consecutive steps [OHL14]:

1. Pre-compression of hydrogen feed gas, if necessary.
2. Pre-cooling of hydrogen gas up to approximately 80 K.
3. Cryogenic cooling of hydrogen gas up to 20-30 K, including ortho-para hydrogen conversion.
4. Final expansion and liquefaction of hydrogen.

The processes presented in the literature differ most significantly in the pre-cooling and cryogenic cooling steps (steps 2 and 3). Most current hydrogen liquefaction technologies are characterized by the nature of the refrigeration cycle used in the cryogenic refrigeration section, *e.g.* using a Claude cycle or an inverted Brayton cycle [OHL14]. This example focuses only on the heat exchanger of the stage 3. However, the other steps can be simulated with the ProSimPlus simulation environment.

This example is based on the reference case of [WIL18]. It is a heat exchanger-reactor that involves three hydrogen fluids: two hot and one cold. Its purpose is to cool and liquefy the reactive hydrogen flux and the non-reactive hydrogen flux from a temperature of 47.8 K to of 29.3 K. The non-reactive flow represents the Joule-Thomson branch of a Claude-type hydrogen liquefaction process. The cold fluid is a 28.9 K hydrogen stream. It is assumed that normal hydrogen corresponds to a mixture of 25% molar para hydrogen and 75% molar ortho hydrogen. The reactive hydrogen flux corresponds to a mixture of normal hydrogen and para hydrogen, allowing to have an overall para hydrogen composition of 77% molar at the inlet [WIL18]. The streams of non-reactive and cold hydrogen are assumed to be normal hydrogen.

1.2. Process flowsheet



Process flowsheet of a heat exchanger-reactor for the ortho-para hydrogen conversion

1.3. Compounds

The compounds considered in the simulation, along with their chemical formulae and CAS numbers, are shown in the table below. They are imported from the "H2" database, which was developed mainly for this application, and from the standard ProSimPlus database [WIL21].

Compound	Chemical formula	Notation	CAS number ⁽¹⁾
HYDROGEN (normal, isomers model)	H ₂	n-H ₂	1333-74-0
HYDROGEN (para, isomers model)	H ₂	p-H ₂	55000-01-6

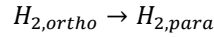
To correspond to the publication of [WIL18], it was decided to work with normal hydrogen and para hydrogen. Ortho hydrogen is also available in the "H2" database. It is therefore possible to set up the same simulation and obtain similar results by using a mixture of ortho hydrogen and para hydrogen instead of the mixture of normal hydrogen and para hydrogen.

1.4. Thermodynamic model

The thermodynamic profile "Hydrogen (isomers)" is used in this example. This model allows to represent the energy and transport properties of mixtures containing n-H₂, p-H₂ and o-H₂ for temperatures between 20 K and 400 K and pressures between 0.1 bar and 100 bar. The Redlich-Kwong equation of state [RED49] was selected as well as the generalized Twu-Nancy alpha function [LEG16]. For a good representation of the transport properties (vapor and liquid dynamic viscosity, and vapor and liquid thermal conductivity) the parameters of the models of [ASS11], [MUZ13], [REI77] were adjusted using experimental data.

1.5. Chemical reactions

The reactive model used in this example is provided by [WIL18]. The rate is expressed in m^3 of free volume. This model is therefore not able to model the impact of the porosity of the catalyst bed on the ortho-para conversion kinetics of hydrogen. This kinetics is established for a specific ortho-para conversion. A correction is made in the calculation DLL to account for the fact that the model is based on normal hydrogen.



$$r = KLn \left(\left(\frac{x_p}{x_p^{eq}} \right)^n \left(\frac{1 - x_p^{eq}}{1 - x_p} \right) \right)$$

$$K = b + c \frac{T}{T_c} + d \frac{P}{P_c}$$

$$a = 1.0924$$

$$b = 0.0597 \text{ kmol/m}^3 \cdot s$$

$$T_c = 32.937 \text{ K}$$

$$c = -0.2539 \text{ kmol/m}^3 \cdot s$$

$$P_c = 1.28377 \text{ MPa}$$

$$d = -0.0116 \text{ kmol/m}^3 \cdot s$$

$$n = a$$

The critical temperature and pressure of [WIL18] were used, rather than those of the pure compounds coming from the "H2" database (see section 1.3), in order to remain consistent with the publication of [WIL18].

The molar fraction of hydrogen para at equilibrium is:

$$x_p^{eq} = \frac{a_1}{\exp\left(\frac{a_2}{T/T_c}\right) + a_1} + a_3 \left(\frac{T}{T_c}\right)^3 + a_4 \left(\frac{T}{T_c}\right)^2 + a_5 \frac{T}{T_c} + a_6$$

$$a_1 = 0.1$$

$$a_2 = -5.313$$

$$a_3 = -2.52 \times 10^{-4}$$

$$a_4 = 3.71 \times 10^{-3}$$

$$a_5 = -2.04 \times 10^{-3}$$

$$a_6 = -0.00227$$

It is assumed that normal hydrogen, n-H₂, is a mixture of 25% molar of para hydrogen, p-H₂, and 75% molar of ortho hydrogen, o-H₂. Thus, the overall molar fraction of para hydrogen will be:

$$x_{H_2p} = 0.25x_{n-H_2} + x_{p-H_2}$$

1.6. Operating conditions

1.6.1. Process feeds

The "React_H2_In" feed corresponds to the supply of hydrogen that will be liquefied and converted as much as possible into para hydrogen. It is a hot fluid. The second hot fluid is the "H2_JT_In" fluid. The cold fluid is the "Cold_H2_In" fluid. The latter two streams are non-reactive. The composition of the "React_H2_In" feed was calculated to have an overall para hydrogen composition of 0.77 as the reference case mentioned in [WIL18].

	React_H2_In	H2_JT_In	Cold_H2_In
Molar fraction			
n-H ₂	0.31	1	1
p-H ₂	0.69	0	0
Flow rate (t/d)	50	21.4	224.682
Temperature (K)	47.8	47.8	28.9
Pressure (MPa)	1.96	1.96	0.5

1.6.2. Heat exchanger

✓ Global parameters

Parameters	Values
Heat exchanger type	CO-ProSec
Number of bodies	1
Orientation	Horizontal
Fin database	2015 -> Now
Material	Aluminum SASSENAGE
Used width (mm)	1500
Thickness of side bars (mm)	27
Thickness of end bars (mm)	27
Thickness of separation plates (mm)	1.5
Thickness of closing plates (mm)	1.5

✓ Catalysts

Due to the lack of information on the actual geometry of the catalyst particles, they will be assumed to be spherical in this example.

[DON19] mentions very low bed porosities of less than 20%. A more classic value is used for this example. As mentioned in the section 1.5, this parameter has no influence on the ortho-para conversion kinetics (limitation of the [WIL18] model). In addition, [WIL18] does not estimate pressure drops in its publication. In this case, the impact on the results is limited.

Parameters	Values
Name	IONEX
Particles diameter(mm)	0.446
Particles shape factor	1
Bed porosity	0.48
K1 parameter of Ergun's equation	150
K2 parameter of Ergun's equation	1.75

✓ Streams parameters

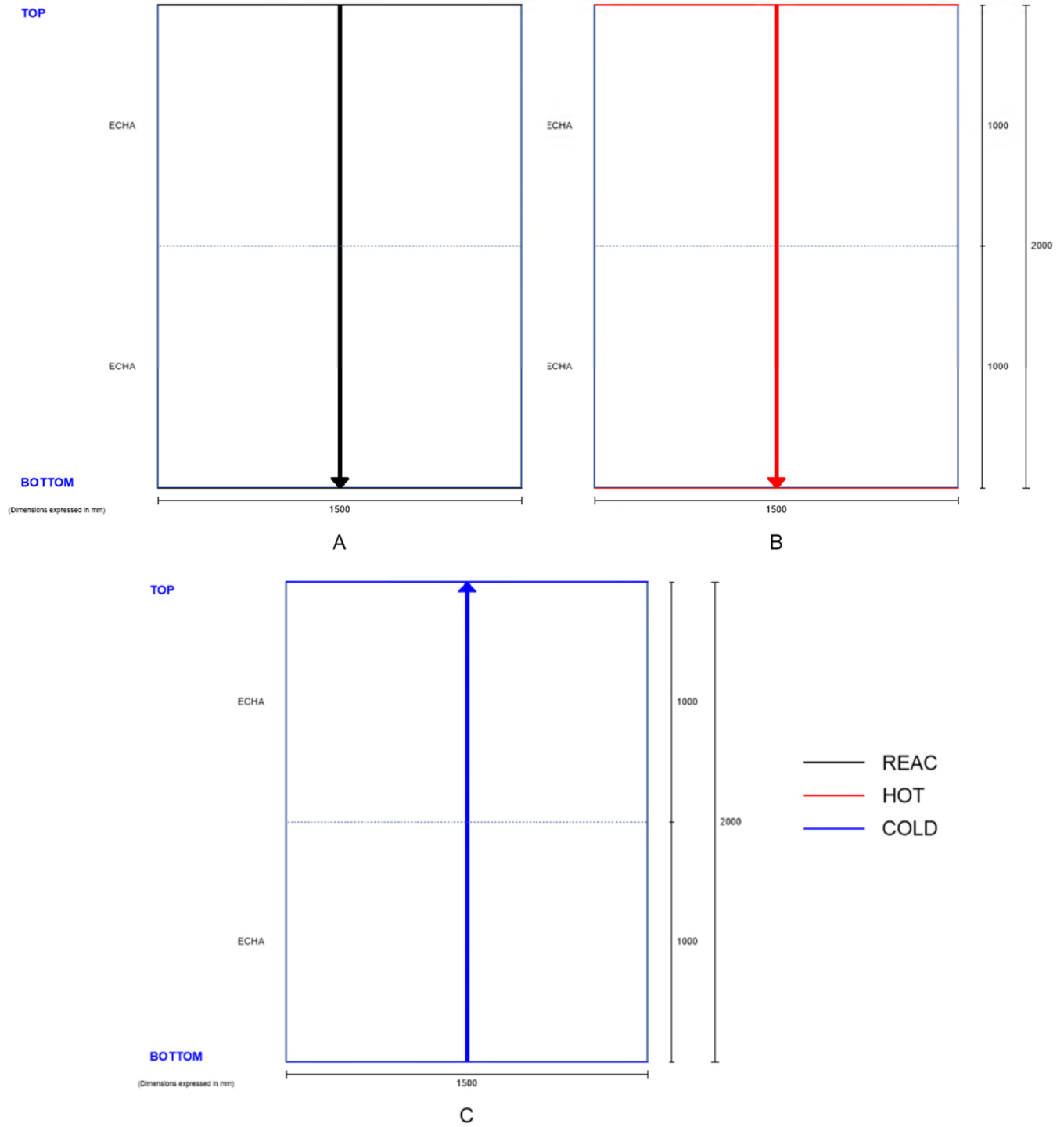
Parameters	Streams		
	React_H2_In	H2_JT_In	Cold_H2_In
Name	REAC	HOT	COLD
Continuous thermodynamic	Yes		
Reactive	Yes	No	
Catalyst considered	Yes IONEX	No	
Direction of circulation	From top to bottom		From bottom to top
Heat exchange coefficient correlation	HTFS85		
Other parameters	Default value		

✓ Fins characteristics

Parameters	Values
Name	Fin #1
Origin	User
Reference	1001
Calculation mode	From geometry
Type	Right fin
Height (mm)	4
Thickness (mm)	0.35
Fins number per meter	909.9
Other parameters	Default value

✓ Reference layers

The figures below show the three reference layers of this heat exchanger.

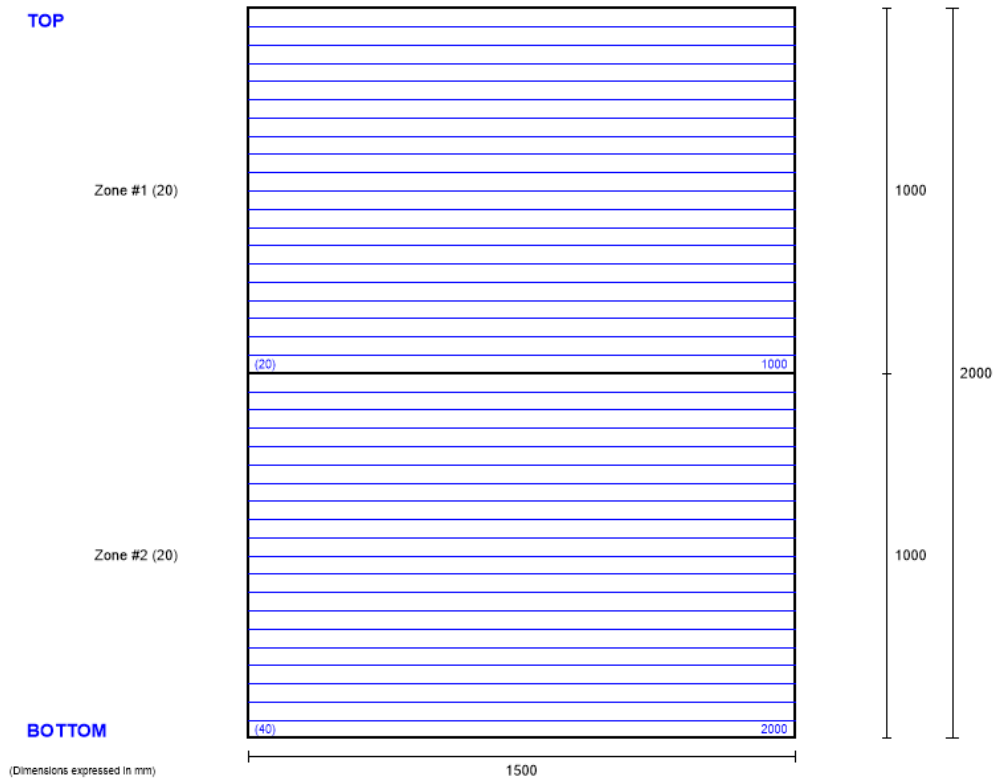


✓ Stacking

For a heat exchanger-reactor, the resolution is made according to the CWT (Common Wall Temperature) assumption. Thus, only the number of passes for each reference layer needs to be defined.

Parameters	Values
Sequence 1	
Number of repetitions of the sequence	48
Layer 1	A
Layer 2	B
Sequence 2	
Number of repetitions of the sequence	48
Layer 1	C

✓ Number of mesh for each elementary zone (dimensions are expressed in millimeters)



✓ Numerical parameters

Parameters	Values
Only CWT (Common Wall Temperature) execution	Yes
Value of the convergence criterion	0.001
Non evolution criterion	0.01
Safety margin on the bounds of fluid enthalpies	500%
Bed porosity fraction taken into account	1
Other parameters	Default values

Safety margin on the bounds of fluid enthalpies

For each stream, the bounds on enthalpies are calculated using the thermodynamic model of the stream for the minimum and the maximum inlet temperatures. A safety margin is then applied to not prevent the convergence. The default value is increased to take into account the enthalpy of reaction.

Bed porosity fraction taken into account

If a fixed bed of catalyst is specified for a reactive stream, it is possible to indicate the fraction of the porosity of the bed taken into account in the calculation of the reaction volume. A value of 0 implies that the reaction volume is the geometric volume multiplied by the bed porosity defined for each catalyst in the Catalyst tab. A value of 1 induces that the reaction volume corresponds to the geometric volume. For a value between 0 and 1, the reaction volume is the geometric volume multiplied by this value. Since the kinetic model of [WIL18] does not take into account the porosity of the bed (see section 1.5), the value of 1 was specified so that the reaction volume is equal to the geometric volume.

1.7. “Tips and tricks”

“Tags” are used to display, on the process diagram, the temperatures, pressures, mass flow rates and molar fractions of para hydrogen for each stream. Temperatures, pressures, and mass flow rates are part of the quantities that are directly available. To display the actual content of para hydrogen, the following relationship has to be used (see section 1.5):

$$x_{H_2p} = 0.25x_{n-H_2} + x_{p-H_2}$$

The tag expert mode allows to code this equation in VBS.

Tag

Value | Graphics

Standard mode Expert mode

Expert

Parameters of the unit operation usable in the script

Unit operation:

Parameter:

Syntax:

Paste Info More

```
1 (0.25*Project.Streams("01").PartialMolarFlowRate(1) + Project.Streams("01").PartialMolarFlowRate(2))/Project.Streams("01").MolarFlowRate
```

Starting text: x(H2p) =

Ending text:

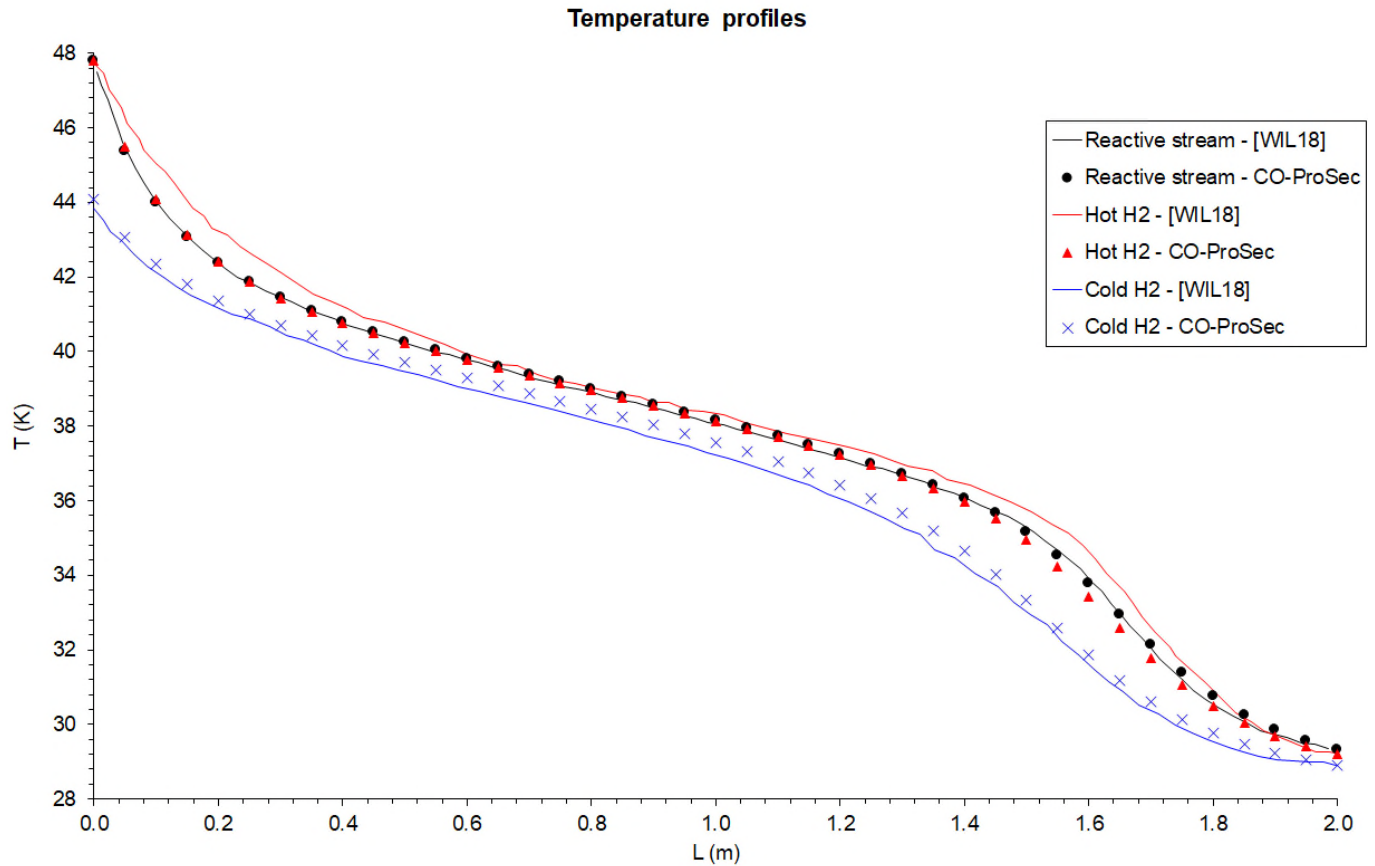
Format string for numerical values: 0.##

Preview: x(H2p) = 0,77

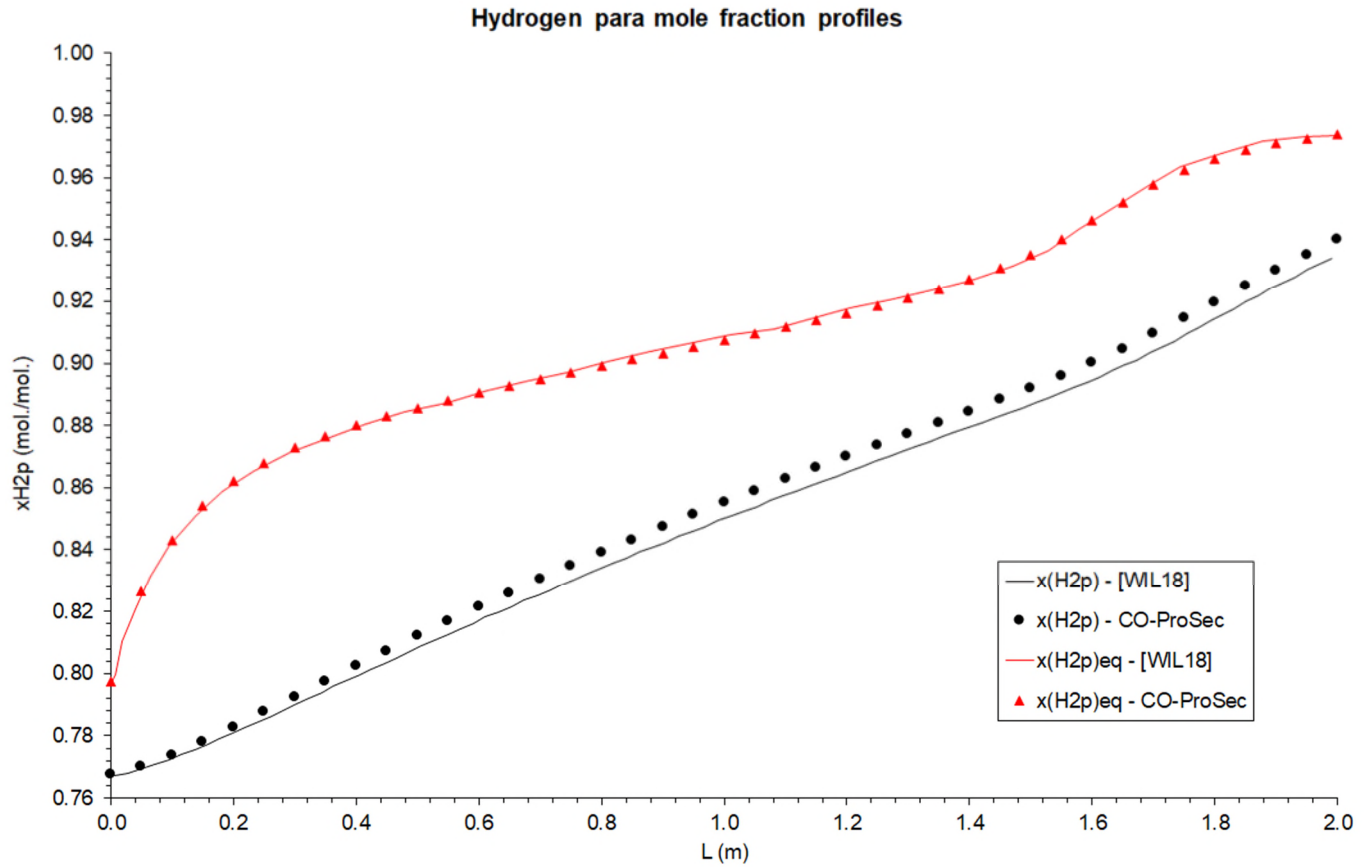
OK Cancel

2. RESULTS OF THE SIMULATION

The following figure compares the temperature profiles of each fluid obtained with CO-ProSec and those of [WIL18]. The profiles obtained using CO-ProSec are similar to those of [WIL18]. The discrepancies can be explained by differences in thermal modelling.



The following figure compares the equilibrium and real para hydrogen molar fraction profiles obtained with CO-ProSec and those of [WIL18]. The profiles obtained using CO-ProSec are similar to those of [WIL18]. The small differences can be explained by differences in temperature profiles.



Many other profiles are available in CO-ProSec.

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