ProSim

07 AIChE
Annual Meeting. Salt Lake City. Utah

2007 AIChE Annual Meeting
Salt Lake City, Utah

#457a Benchmarking of Thermochemical Cycles for Advanced Hydrogen Manufacturing Processes (TG009)

S-I Cycle Simulation Using ProSimPlus

ProSim: Olivier Baudouin, Stéphane Dechelotte, Philippe Guittard
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OUTLINE

- HYTHEC project overview
- Thermodynamic models used in HYTHEC
- Some ProSimPlus features valued in HYTHEC
- Examples of use of ProSimPlus by the partners
  - CEA / ProSim
  - USFD
  - DIMI
  - DLR
- Concluding Remarks

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THE HYTHEC PROJECT

See paper #89a: Ray ALLEN et al.

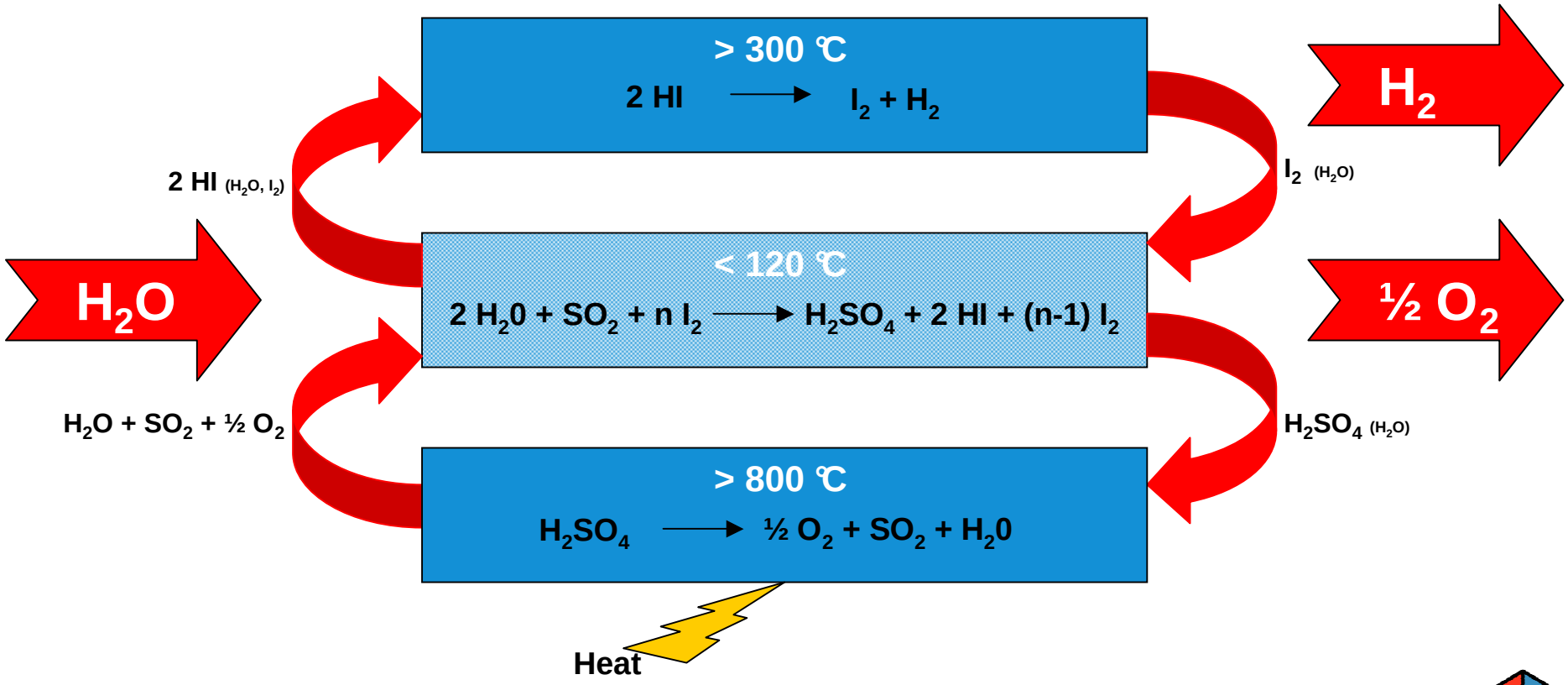
- **HYTHEC (HYdrogen THErmochemical Cycles): the search for a long term massive hydrogen production route**
- **EC funded project within its 6th framework program**

SIXTH FRAMEWORK PROGRAMME

- **Partners:**
  - Commissariat à l'Energie Atomique (CEA – F)
  - University of Sheffield (USFD – UK)
  - Università degli studi – Roma tre (DIMI – I)
  - Deutsches Zentrum für Luft und Raumfahrt (DLR – D)
  - Empresarios Agrupados (EA – SP)
  - ProSim (F)
- **Schedule:** April 2004 to December 2007 (45 months)
- **Resources:** 230 man.months (~ 3 M€)

HYTHEC OBJECTIVE

Assessment and improvement of the Iodine-Sulfur cycle for massive hydrogen production



ROLE OF PROSIM WITHIN HYTHEC

HYTHEC

Simulation tools provider

- Support on simulation when required: complex parts of the flowsheets, reactive distillation,…
- Improvement of the codes when appropriate
- Implementation of the thermodynamic models selected by CEA and some advice on thermodynamic modeling
- Proposition of improvement of the flowsheet developed by CEA (process expertise, heat integration,…)

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H_2SO_4 SECTION: THERMODYNAMICS

- **Involved components: H_2SO_4, H_2O, SO_2, SO_3, O_2 ➔ ENGELS model**
  (H. ENGELS "Phase equilibria and phase diagrams of electrolytes"-Chemistry Data Series, Vol. XI, Part 1)

- **ENGELS: thermodynamic model dedicated to strong acids:**
  - ✓ **Acid dissociation in liquid phase**
  - ✓ **Several azeotropes**
  - ✓ **Significant, even very important, heat of dilution**
  - ✓ **ENGELS assumed that dissociation of electrolyte gave rise to the formation of a complex**

$$m\,L + E \Leftrightarrow \nu\,C$$

$$4\,H_20 + H_2SO_4 \Leftrightarrow 3\,C$$

$$K = \frac{(x_C \gamma_C)^{\nu}}{(x_L \gamma_L)^{m} x_E \gamma_E}$$

$$x_L = x_L^0 + x_C\left[x_L^0(m+1-\nu) - m\right]$$

$$x_E = x_E^0 + x_C\left[x_E^0(m+1-\nu) - 1\right]$$

  - ✓ **Activity coefficients are calculated using so-called local composition models: NRTL (Engels) has been used in HYTHEC**

HI_x SECTION: THERMODYNAMICS

- **H_2O - HI - I_2 - H_2 reactive liquid-liquid-vapour system ➔ Neumann's model**
  (Neumann, Diplomaufgabe, RWTH Aachen – 1987)

$$y_i \bullet \Phi_i^V \bullet P_{tot} = x_i \bullet \gamma_i \bullet \Phi_i^0 \bullet P_i^0 \bullet \exp\left[\int_{P_i^0}^{P_{tot}} \frac{v_i}{R \bullet T} dp\right]$$

$$m\,L + E \Leftrightarrow \nu\,C \qquad K_a = \frac{(x_C \gamma_C)^\nu}{(x_L \gamma_L)^m x_E \gamma_E}$$

$$x_L = x_L^0 + x_C\left|x_L^0(m+1-\nu) - m\right|$$

$$x_E = x_E^0 + x_C\left|x_E^0(m+1-\nu) - 1\right|$$

- **Main model assumptions:**
  - ✓ **The vapour phase is ideal** $\quad y_i \bullet P_{tot} = x_i \bullet \gamma_i \bullet P_i^0$
  - ✓ **The following solvation equation is taken into account in the liquid phase:**

$$5\ H_2O + HI \Leftrightarrow 2\ \{(5H_2O,H+) + I-\}$$

HI_x SECTION: THERMODYNAMICS

➢ Activity coefficient model: modified NRTL

$$\ln(\gamma_i) = \frac{\sum_{j=1}^{N} \Lambda_{ji} \bullet G_{ji} \bullet x_j}{\sum_{j=1}^{N} G_{ji} \bullet x_j} + \sum_{k=1}^{N} \frac{x_k \bullet G_{ik}}{\sum_{j=1}^{N} G_{jk} \bullet x_j} \bullet \left\{ \Lambda_{ik} - \frac{\sum_{n=1}^{N} \Lambda_{nk} \bullet G_{nk} \bullet x_n}{\sum_{j=1}^{N} G_{jk} \bullet x_j} \right\}$$

With:

$$G_{ij} = \exp\left(-\alpha_{ij}\Lambda_{ij}\right)$$

$$\Lambda_{ij} = a_{ij} + b_{ij} / T$$

$$\alpha_{ij} = 1{,}2^{(c_{ij}+d_{ij}/T)}$$

$$\alpha_{ji} = -\alpha_{ij}$$

➢ Enthalpy and entropy calculations:

$$h = \sum_{i=1}^{N} x_i \bullet h_i^0 + h^E \quad \Longrightarrow \quad h = x_L \bullet h_L^0 + x_E \bullet h_E^0 + \upsilon \bullet x_C \bullet h_C^0 + h^E$$

$$\upsilon \bullet h_C^0 = R \bullet T^2 \bullet \frac{\partial \ln(K_a)}{\partial T} + m \bullet h_L^0 + h_E^0 \qquad h^E = -R \bullet T^2 \bullet \sum_{i=1}^{N} x_i \bullet \frac{\partial \ln(\gamma_i)}{\partial T} \qquad g = h - Ts$$

Interesting results have been obtained within HYTHEC, however thermodynamic modeling of HI section requires further improvements to cover the process operating conditions:

⇨Higher pressure: EOS approach with complex mixing rules such as MHV2, PSRK,…

⇨Wider concentration range: new experimental data are needed

HI_x Section: Experimental Measurements

- **Neumann's data**
- **H2O-HI and H2O-HI-I2 systems have been investigated**
  - ✓ **Temperature and liquid composition are fixed**
  - ✓ **Measured data are: total pressure and partial pressures**

Mixture	H_2O –HI	H_2O – HI – I_2
Temperature range [K]	351.45 - 554.05	373.35 - 557.95
HI liquid mole fraction range [-]	0.017 - 0.1744	0.0171 - 0.159
I_2 liquid mole fraction range [-]	-	0.0033 - 0.7525
Pressure range [bar]	0.22 - 53.8	0.4599 - 64.02

- **Measurements in progress at CEA** *See: "Status of Sulfur-Iodine Cycle Assessment at CEA" (Philippe CARLES et al. # 89b)*

Mixture	H_2O – HI	H_2O – HI – I_2
Temperature range [K]	356.15 - 386.15	390.15 - 406.15
HI liquid mole fraction range [-]	0.15 - 0.21	0.0963 - 0.1323
I_2 liquid mole fraction range [-]	-	0.3902 - 0.4036
Pressure range [bar]	0.6 - 1.892	0.51 - 2.15

⇨ ***When all the measurements will be available, the thermodynamic model will be adjusted and new parameters will be regressed***

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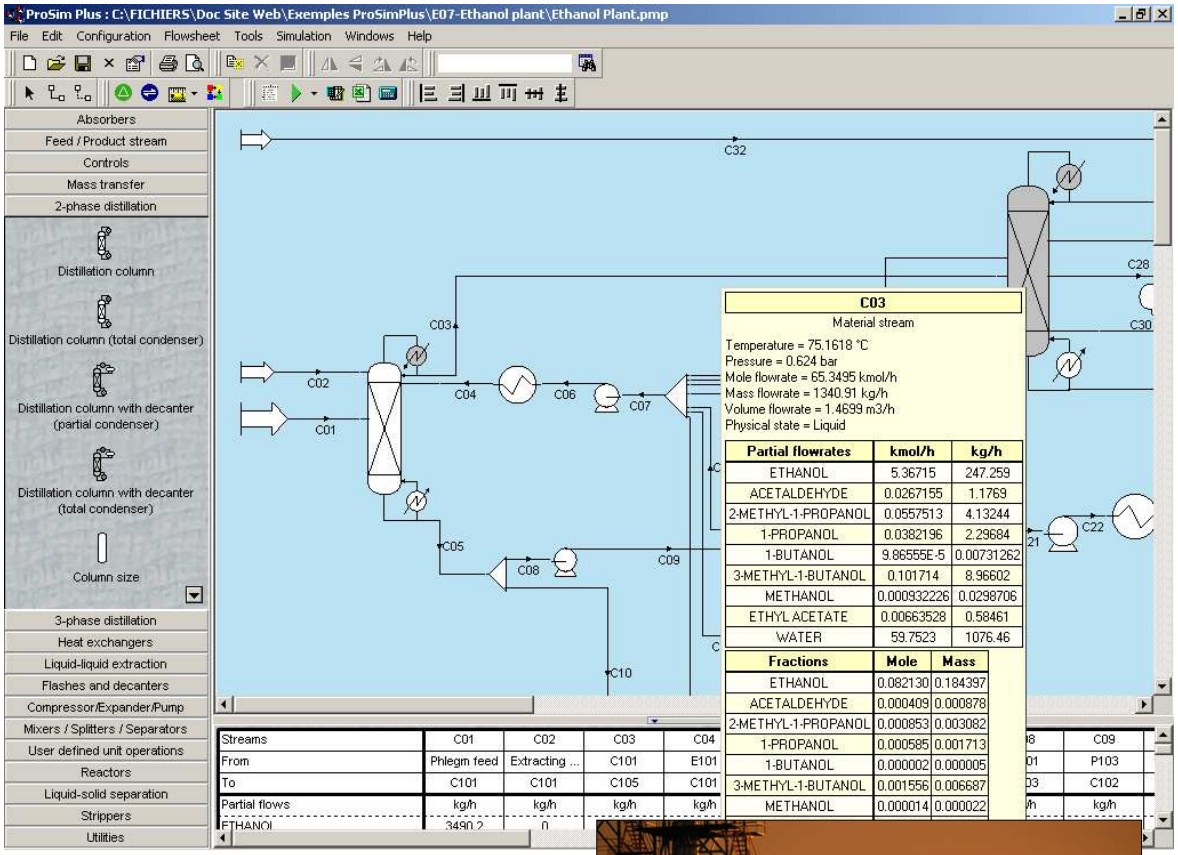
OVERVIEW OF PROSIMPLUS



Steady-state process simulation software

- **Capability to model highly non-ideal systems: strong thermo package**
- **Extensive unit operations library including complex models: "Rate-Based" approach, plate-fin heat exchangers, three-phase and reactive distillation…**
- **Efficient convergence methods**
- **Easy-to-use**
- **Solution widely used by oil, chemicals and engineering companies**
- **Open software**

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The SW Component Architecture of ProSimPlus

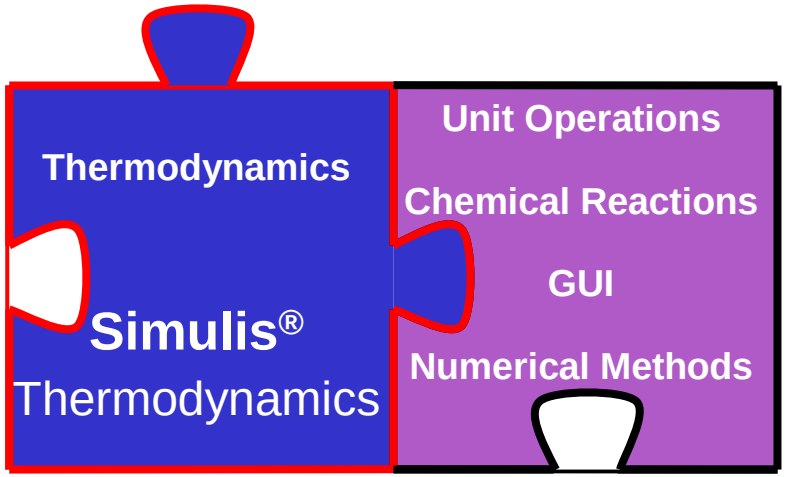
Thermodynamics
Chemical Reactions
Unit Operations
Numerical Methods
GUI

Conventional simulator

Monolithic program (generally divided into several source files and DLLs)

ProSimPlus

- **Thermodynamic calculations are performed within a component (Simulis® Thermodynamics)**
- **This component implements CAPE-OPEN standardized interfaces (Plug & Socket)**
- **ProSimPlus also implements CO "Unit Socket" standardized interface**



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CAPE-OPEN THERMODYNAMIC "SOCKET"

Ability to use an external thermodynamic model *(CAPE-OPEN "Property Package")*

- Successfully tested with
  - ⇨Multiflash (Infochem)
  - ⇨PPDS (TUV-NEL)
  - ⇨Aspen Properties (AspenTech)
  - ⇨COCO TEA (AmsterCHEM)
  - ⇨COM Thermo (AspenTech)
  - ⇨IVCSEPThermoSystem (IVC-SEP)
  - ⇨etc…

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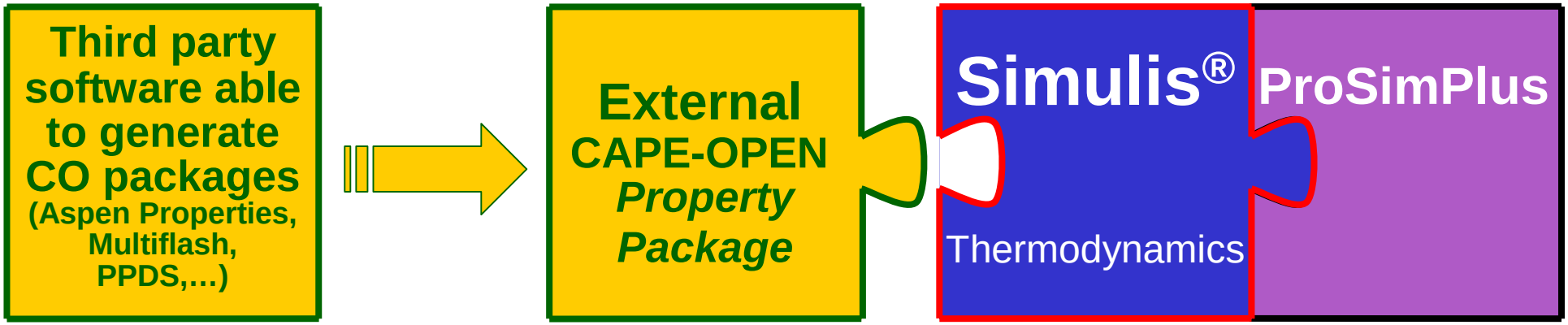

⇨***If required, a third party thermo package can be used within ProSimPlus***

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CAPE-OPEN THERMODYNAMIC "PLUG"

Ability to generate CAPE-OPEN "Property Packages" to be used within CO compliant modeling tools

- Successfully tested in
  - ⇨Aspen Plus (2004 and v12.1)
  - ⇨Aspen Hysys (2004 and v3.2)
  - ⇨PRO/II (v7.1)
  - ⇨gPROMS®
  - ⇨Xist (HTRI)
  - ⇨UNISIM Design
  - ⇨etc…

CO LaN
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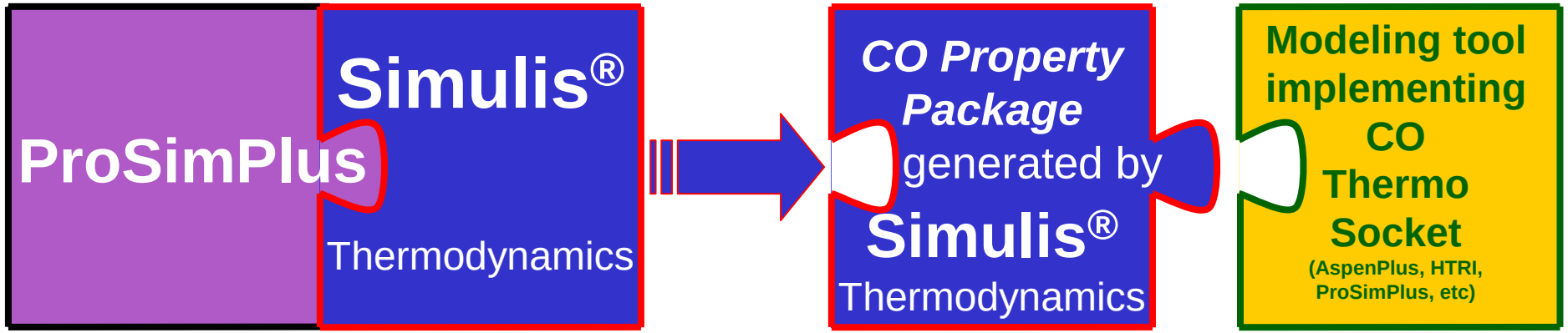

⇨ ***When available, a fully satisfactory thermodynamic model will be usable in several simulation packages***

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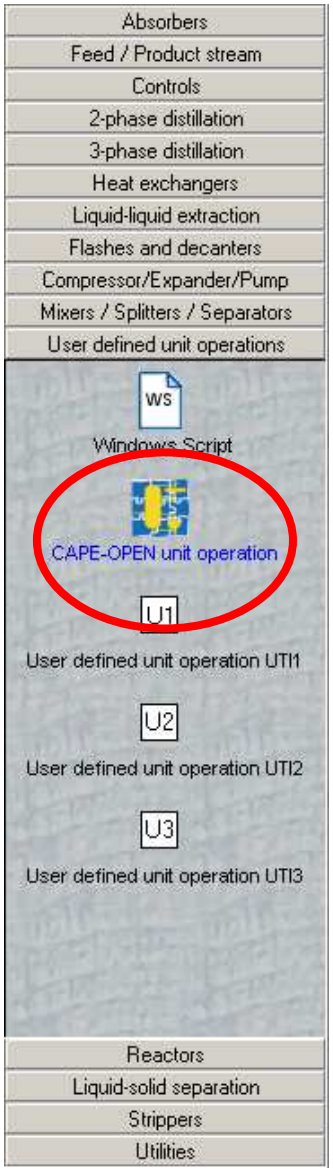
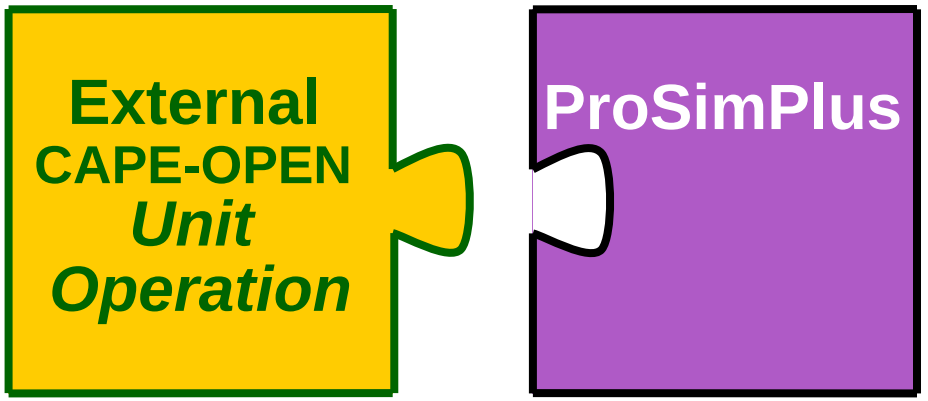
CAPE-OPEN UNIT SOCKET



Ability to use a third party unit operation

(CAPE-OPEN compliant UO)



- Examples of application:
  - ⇨Fuel cell model:

    See paper # 344d (Rafiqul GANI et al.): "Application of CAPE-OPEN standards for the interoperability between Computer Aided Modeling Tool MoT and Process Simulator ProSimPlus"
  - ⇨Membrane model
  - ⇨Electrolyser model

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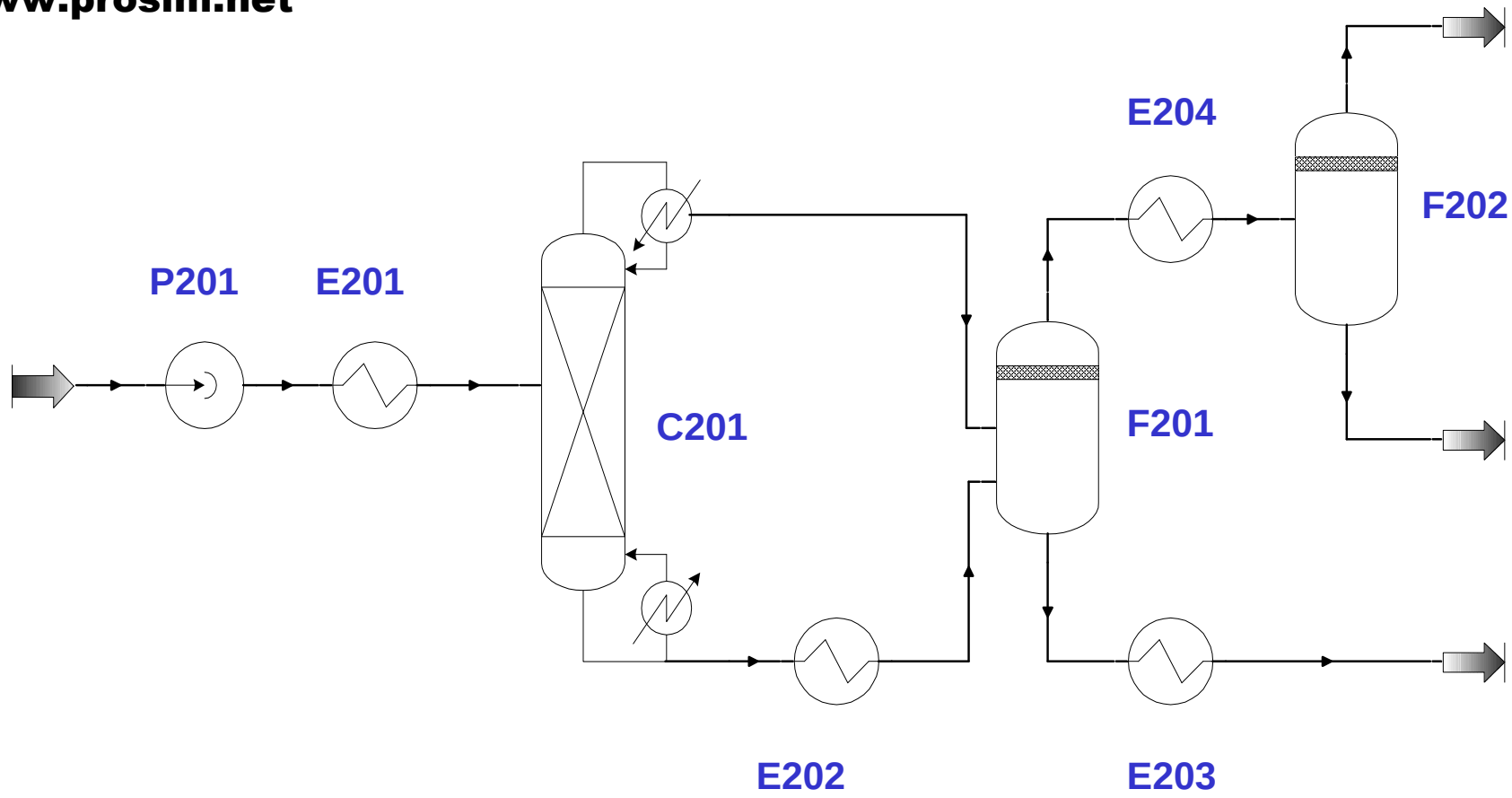
HI_x Section: Hythec Process Diagram



- **Specificity of HIx section: reactive distillation**

$$2HI_{(g)} \Leftrightarrow H_{2(g)} + I_{2(g)} \qquad Ln(K) = 2.6981 - \frac{90.48}{T} - 1.5959 * Ln(T) + 0.005545 * T$$

HI_x SECTION: SIMULATION

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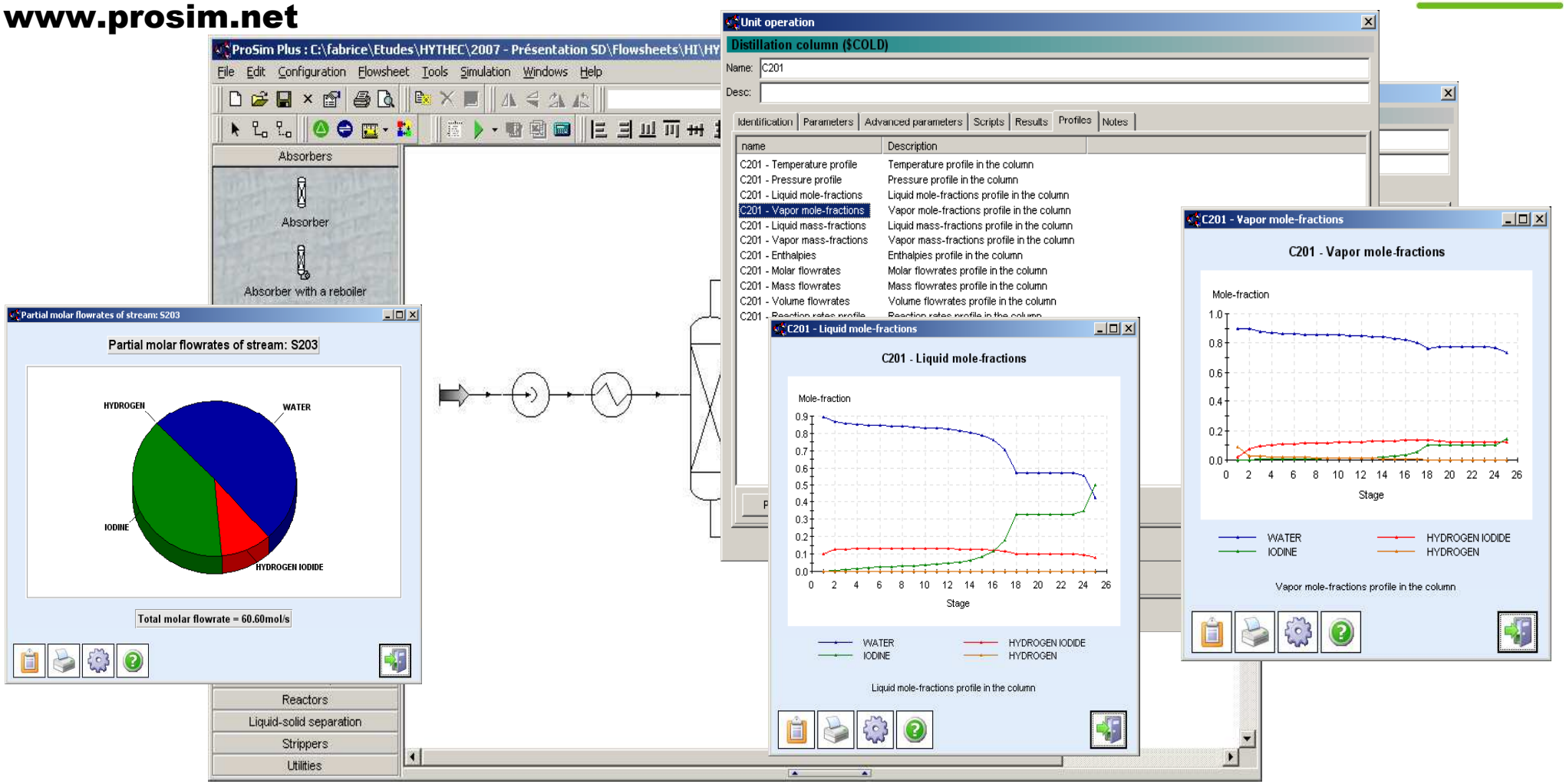
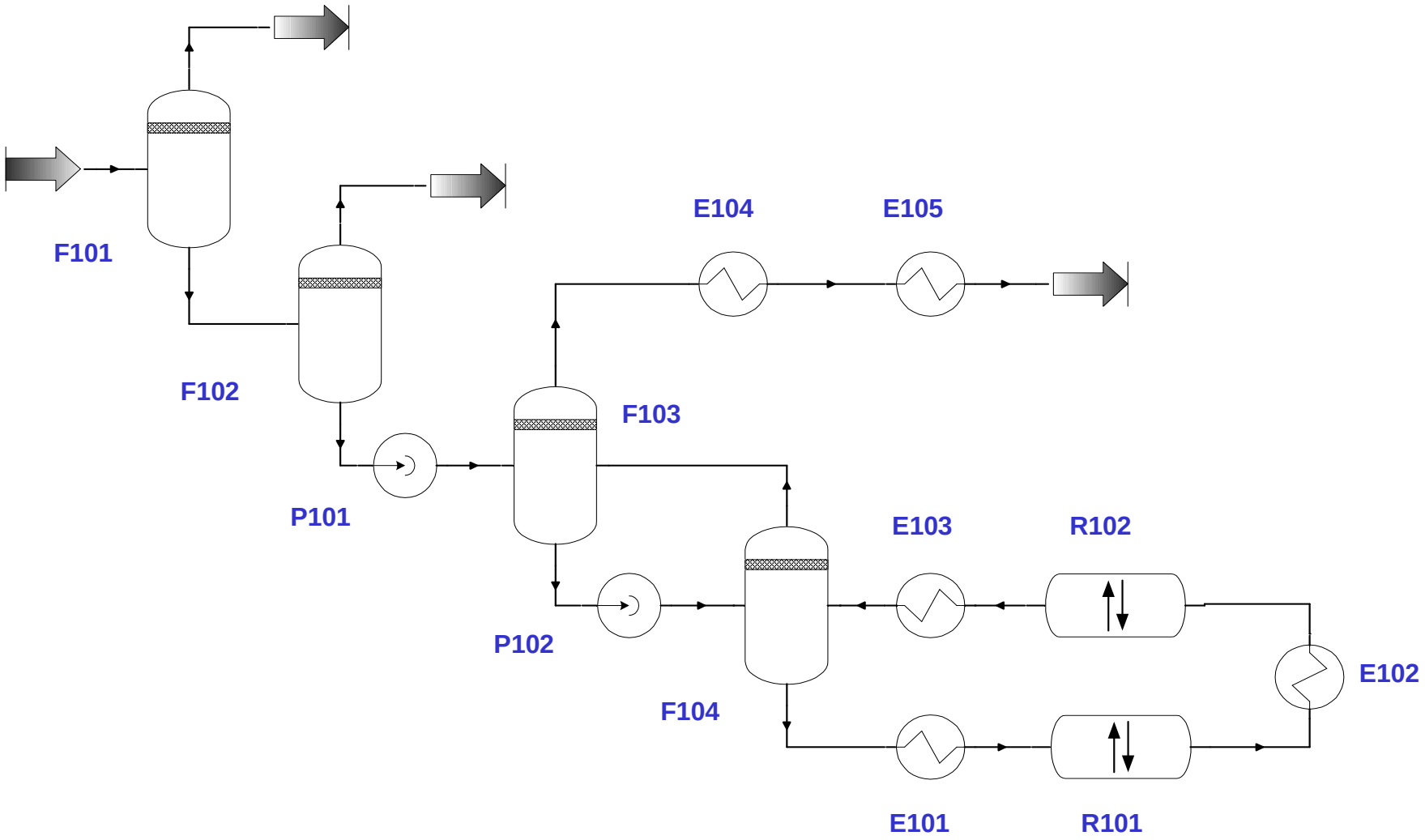


⇨***Simulation of the HI section without time-consuming convergence tests***

⇨***Easy and powerful exploitation of results***

H_2SO_4 Section: Hythec Process Diagram



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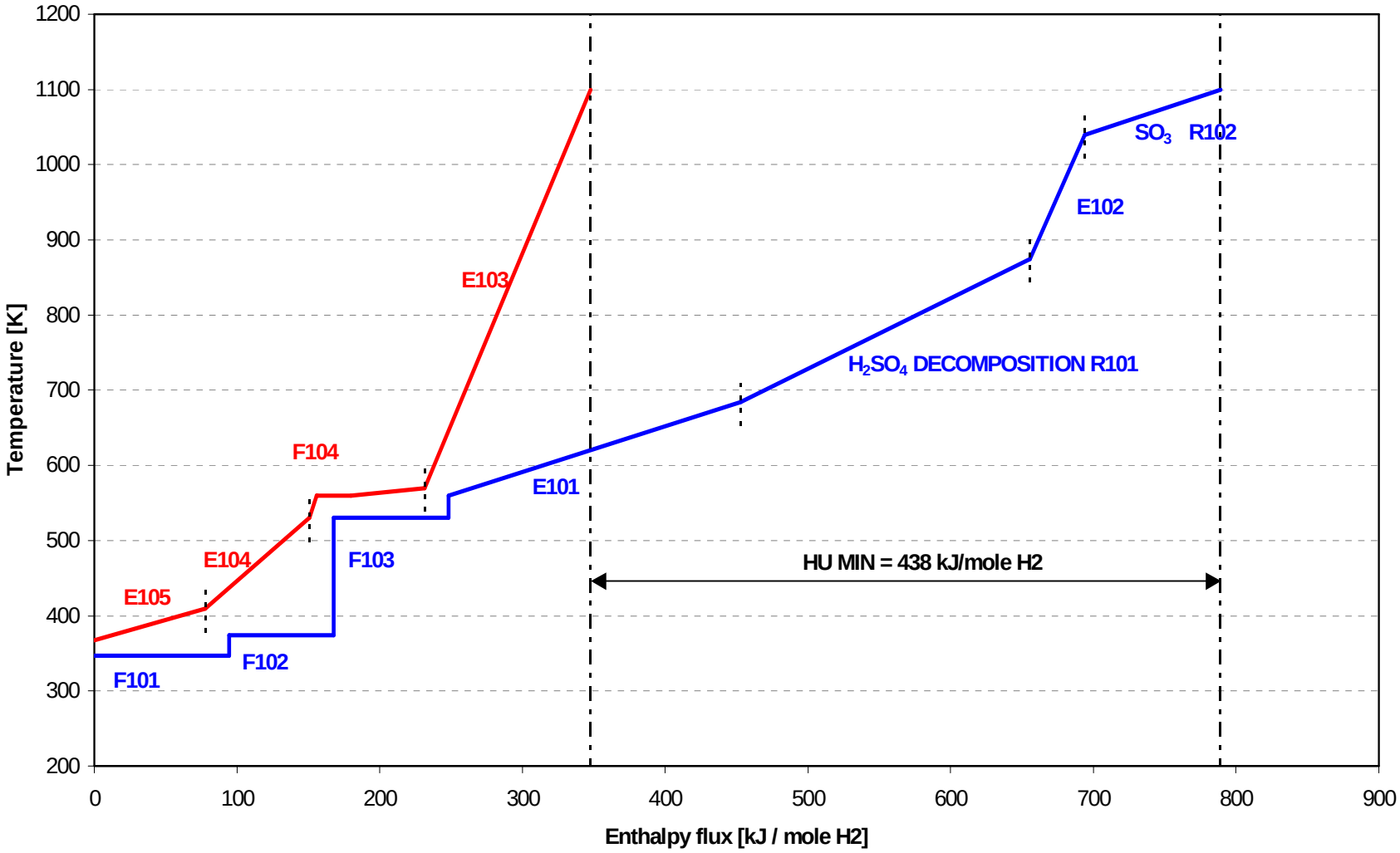
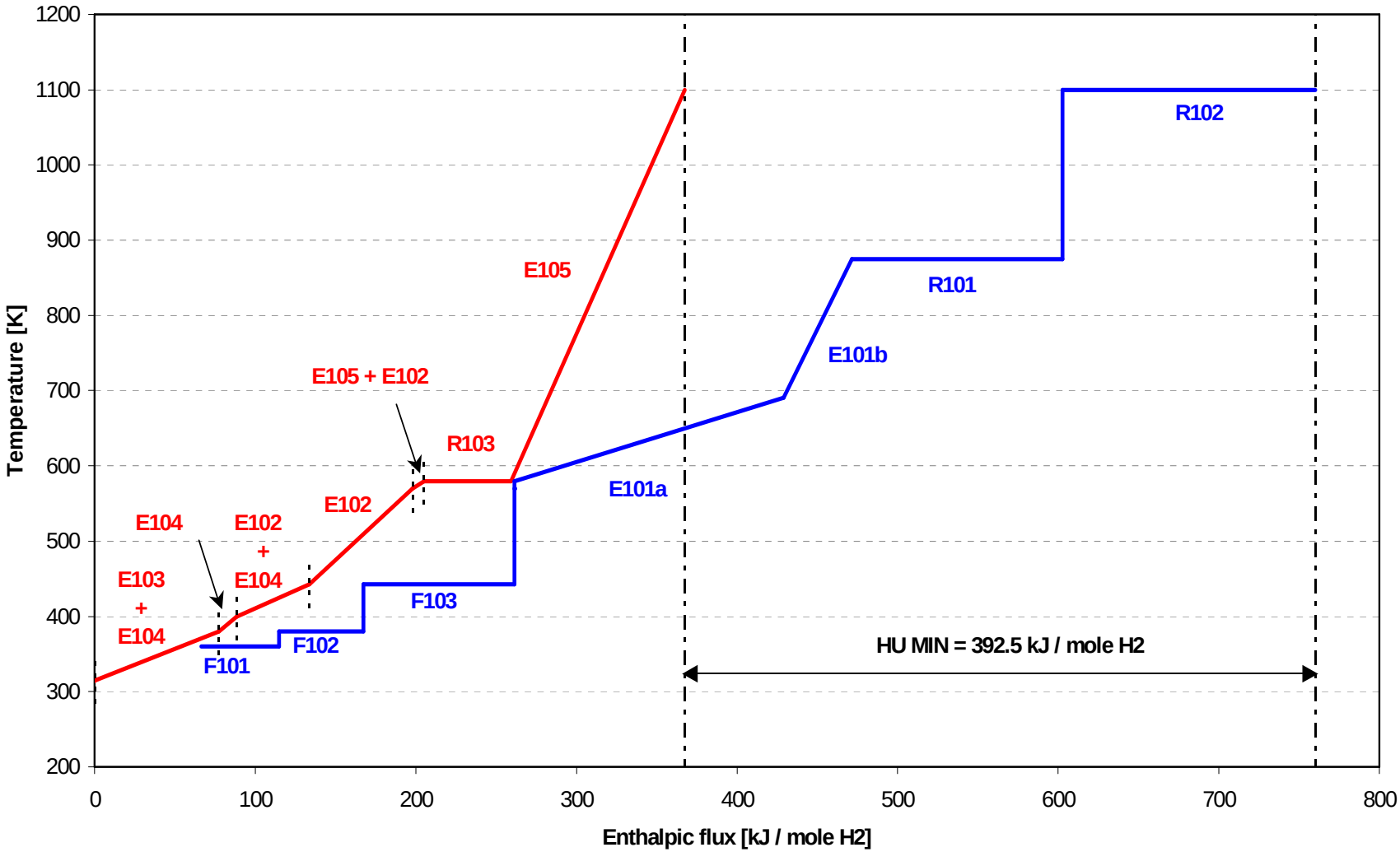
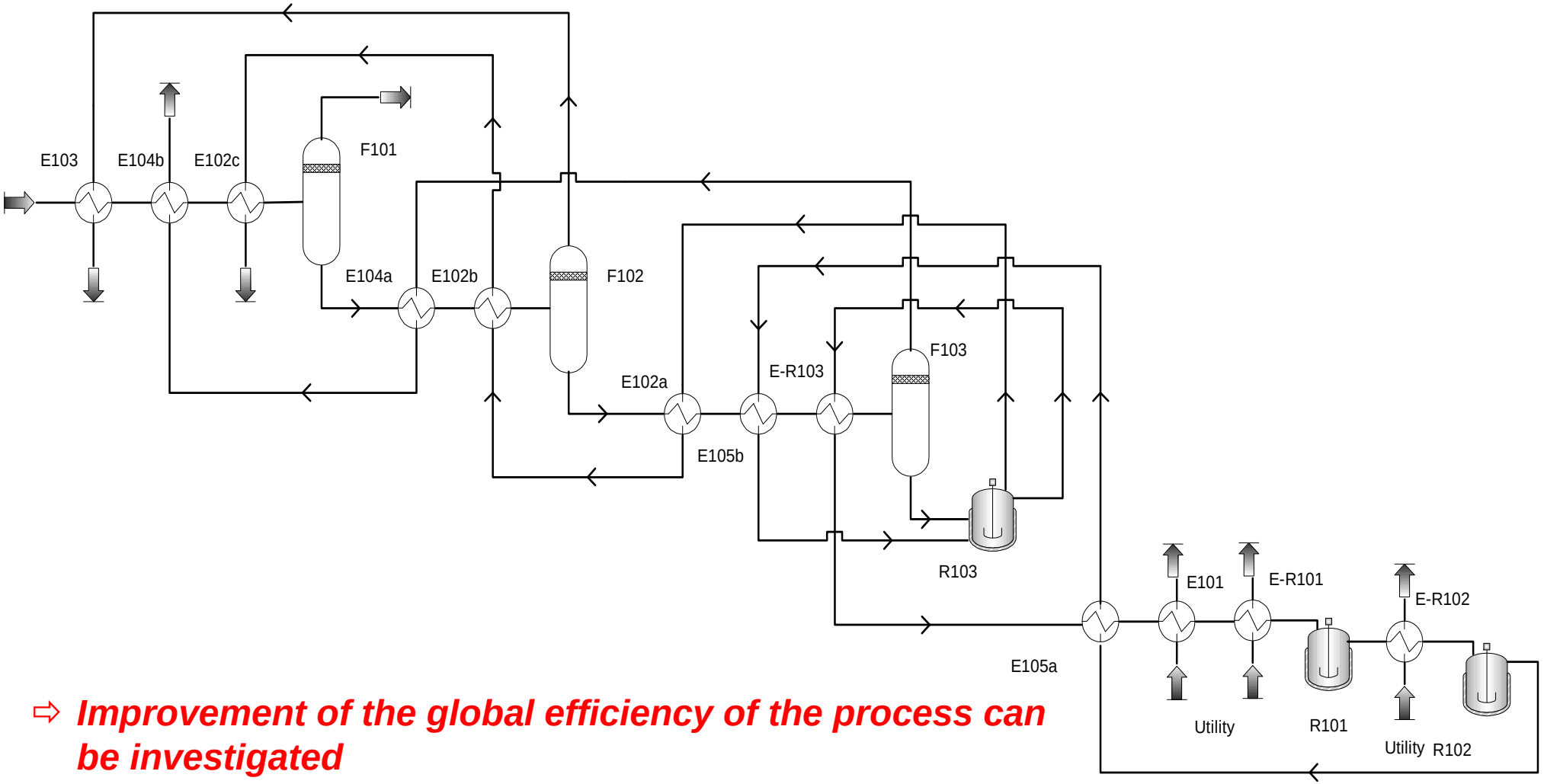
H_2SO_4 Section: Heat Integration



H_2SO_4 Section: Improved Process Diagram
Heat Integration



H_2SO_4 Section: Improved Process Diagram



- ***Improvement of the global efficiency of the process can be investigated***
- ***Full benefit of this analysis will came when taking into account the 3 sections of the process***

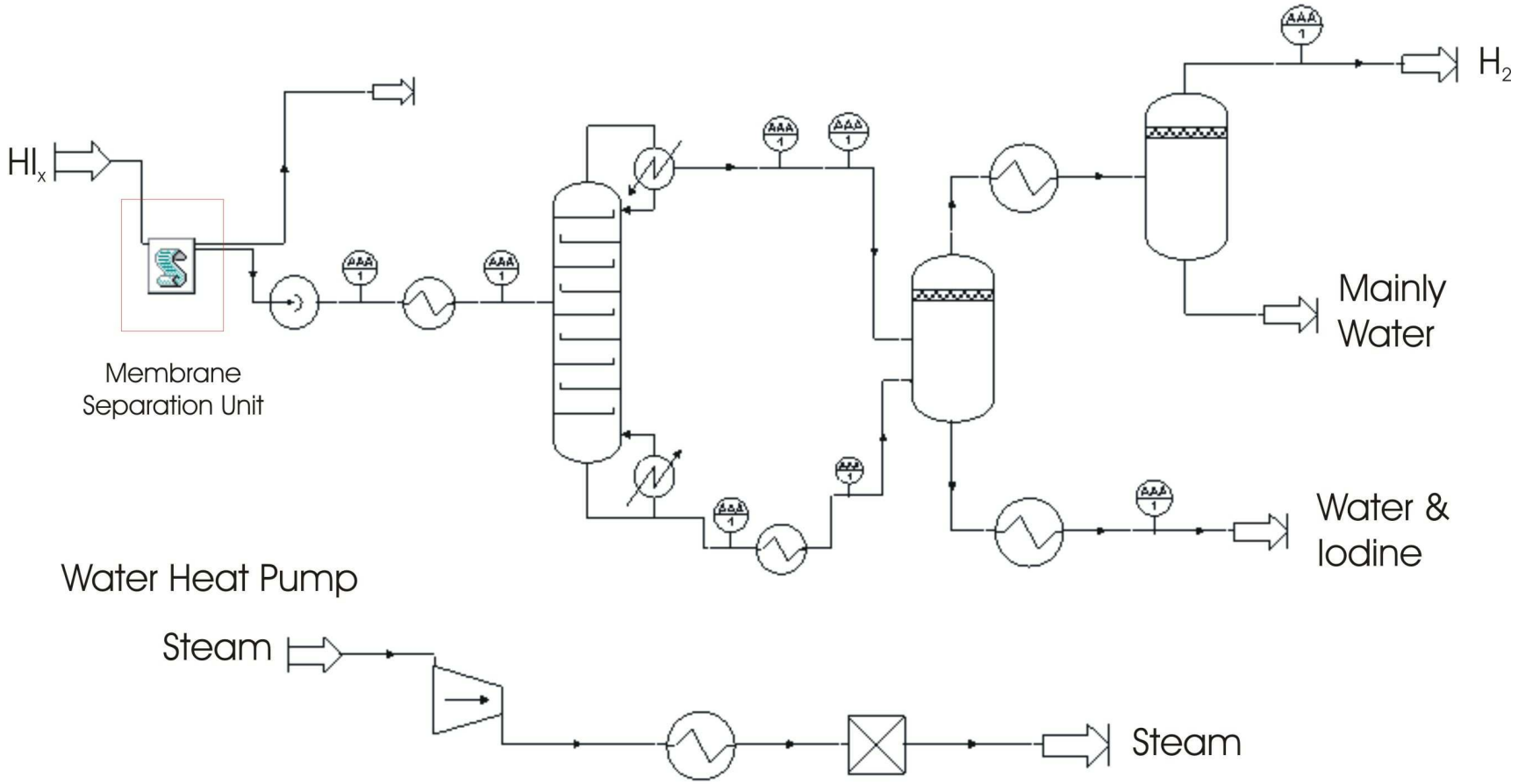
EXAMPLE OF USE OF PROSIMPLUS BY USFD

Membrane modeling for HIx separation (See paper # 299f, Elder et al.)

- ✓ **The application of a membrane separation unit to the HIx processing section of the Sulphur Iodine cycle has been investigated by process flowsheet modeling using ProSimPlus** (only membrane separating liquid phases are considered in this work)
- ✓ **The application of a membrane unit has been investigated in 3 process locations: on the column feed, at the column reboiler and on a column sidestream**
- ✓ **Two potential advantages have been demonstrated: an increase in the global process efficiency and the option of less extreme operating conditions**

⇨ ***USFD developed their own code for membrane separation modeling and implemented it in ProSimPlus using a "Script module". This module was further used as a built-in module to simulate the whole flowsheet***

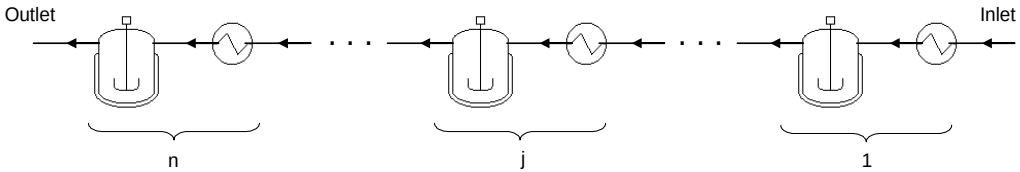
Membrane modeling for HIx Separation



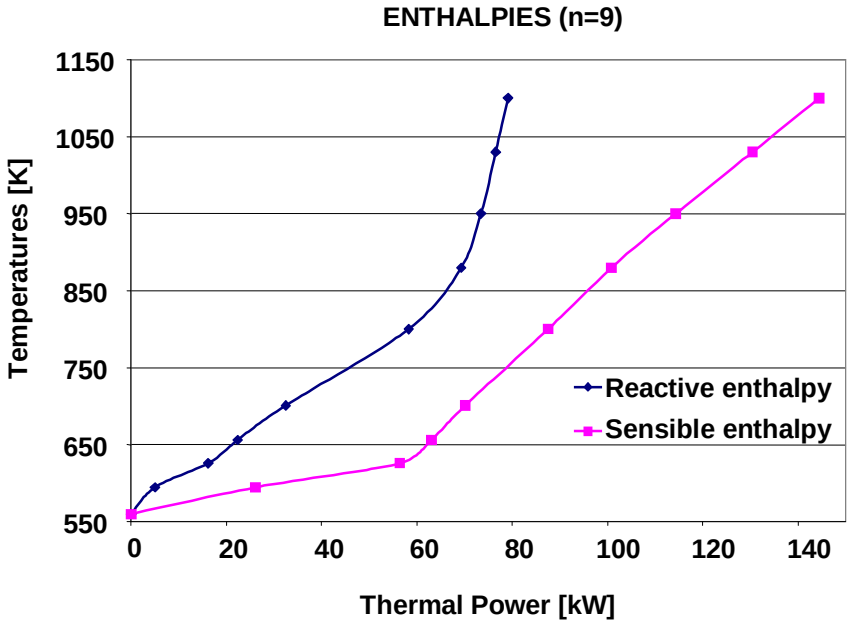
➪ ***This work takes advantage of the openness of the software***

Modeling of the SO3 and H2O recombination process (Cerri et al.)

- ✓ **Objective: to get data suitable to perform sizing of the reactive heat exchanging equipment (i.e. temperature vs enthalpy)**



The recombination process is modeled by a series of chemically inert heat transfer unit and equilibrium non adiabatic CSTR



⇨ **According to DIMI: *"ProSimPlus has shown robustness, reliability and relatively reduced computing efforts"***

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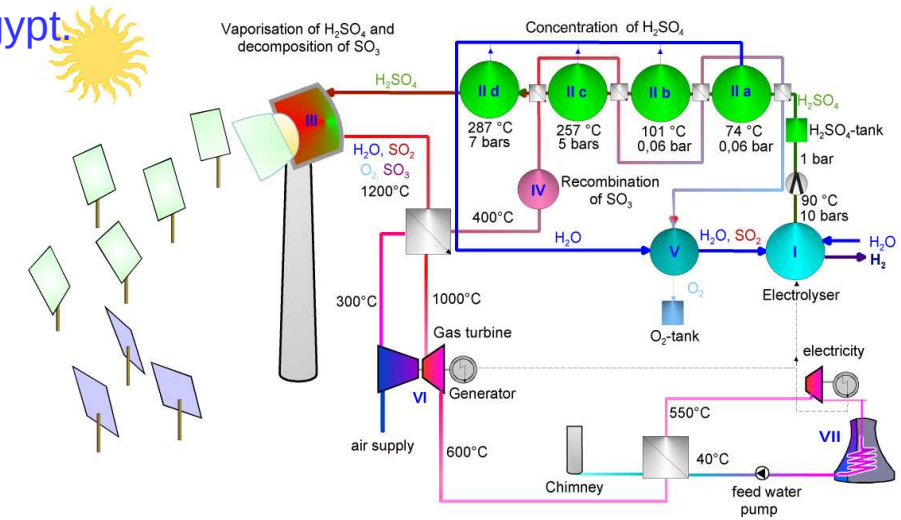
EXAMPLE OF USE OF PROSIMPLUS BY DLR

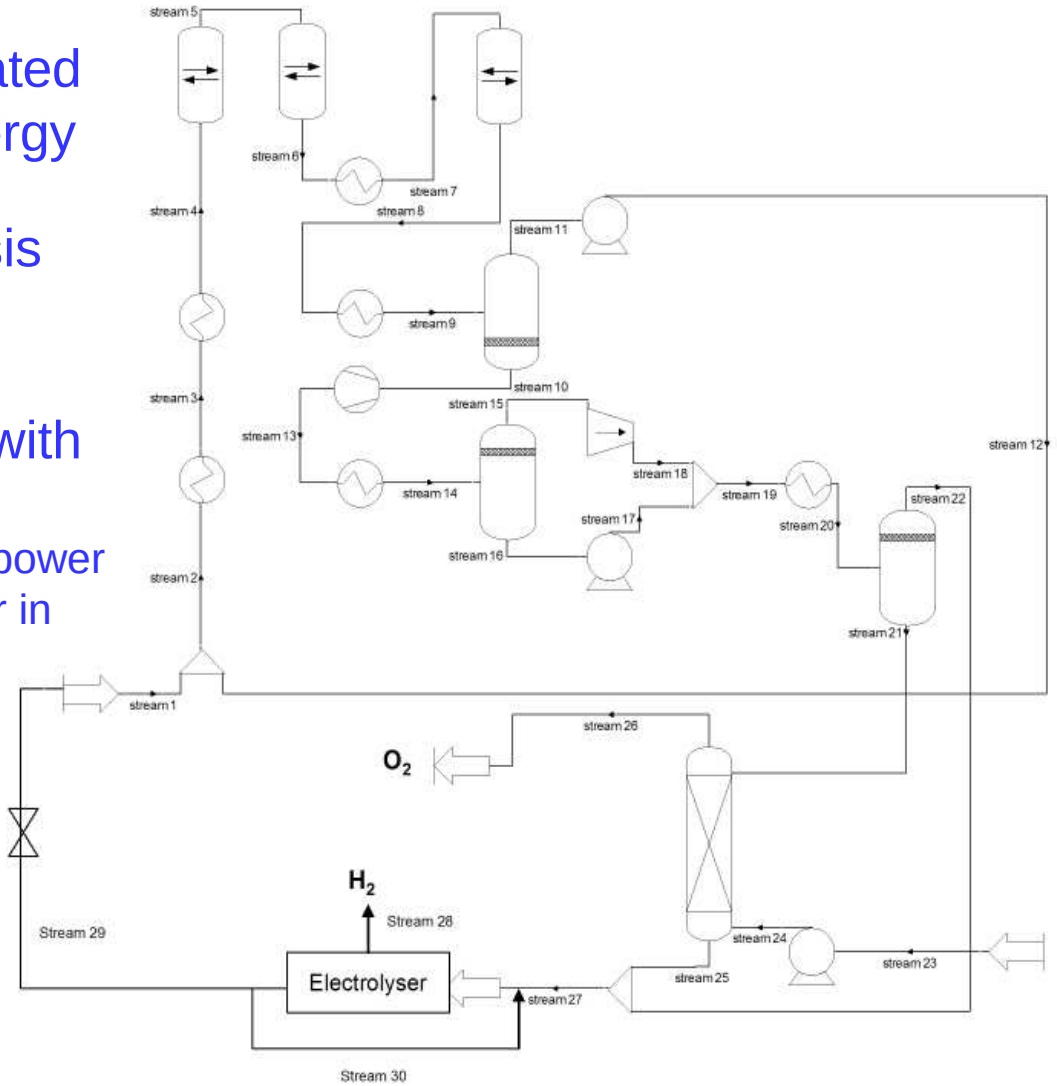
DLR

Evaluation of the Hybrid Cycle

- 3 different cases have been investigated
- For one process using only solar energy (for sulfuric acid decomposition and electricity required for electrolyser) a detailed analysis and component sizing have been performed
- Heat and mass balances performed with ProSimPlus

Example of a plant with an annual average thermal power of 50 MW located in the region close to Lake Nasser in Egypt.





CONCLUDING REMARKS

- **ProSim Plus has been successfully used in HYTHEC**
- **It demonstrates interesting capabilities:**
  - **Easy simulation of HI section (reactive distillation)**
  - **Very diverse uses**
  - **Openness**
  - **Ease of use: rapid adoption by the partners without specific training**
- **The key point remains thermodynamic modeling**
  - **Further experimental data is needed**
  - **When available, the model will be usable in several environments thanks to CAPE-OPEN compliance of ProSim tools**

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