

Convection of Chemicals and Other Substances with ThermoSysPro

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Abstract

Digital twins are a powerful support tool for plant operation: they provide further understanding on ongoing phenomena and allow realistic projection of the current plant state into the future. Among other twins, EDF is developing a digital twin of the chemistry of the secondary circuits of its nuclear plants. Such a tool will give access to the pH in any point of the circuit and in any operating condition (e.g. partial load, power transients...), outperforming the current, limited, monitoring techniques. It is expected to help operators and engineers to better monitor the circuit (e.g. for erosion corrosion) and anticipate the consequences on equipment of different operating strategies (e.g. for amines' injection pumps maintenance).

ThermoSysPro, the EDF R&D's thermal-hydraulic library, is the bedrock of the tool under development. To meet the needs of the target application, modeling of amines convection and some related chemistry, allowing the computation of pH , are introduced in a new version of the library. Moreover, the presented approach aims at proposing a general framework allowing the convection of custom substances (i.e. easily customized by the end user following its needs). This will open the door for a wide range of other applications: radioactive substances, pollution (e.g. salted water ingress coming from a heat-exchanger leak), just to cite a few, could be modeled in ThermoSysPro to augment the scope of the digital twins.

Keywords: Digital Twin, Secondary Chemistry, Substance Convection, Amines, ThermoSysPro

1 Introduction

Nowadays, a increasing number of Digital Twins, virtual copies of industrial units, are developed all over the world and in every industries including nuclear power plants. Physical and statistical models, fed by plant data in real time, allow, for example:

- to investigate otherwise inaccessible phenomena, in particular where no (or too few) measures are available;
- to diagnose safety or performance issues;
- to project the future plant state for decision making support.

In EDF R&D, our team and its partners have worked for several years on digital twins for thermal-hydraulic applications (see for example (Girard 2014; Corona Mesa-Moles et al. 2019; Schwartz 2023; Gerrer and Girard 2020)), mainly supported by our Modelica library: ThermoSysPro (El Hefni and Bouskela 2019). The application presented in this paper however, goes beyond the strict thermal-hydraulic domain and concerns secondary circuit chemistry of French nuclear power plants.

1.1 Industrial Application

The main objective of secondary chemistry is to limit various types of corrosion. By doing so, it ensures the integrity of the equipment (and boosts their lifetime) and reduces the corrosion product source term responsible for fouling - which leads to plant performances limitation - and tube support plates clogging of steam generators - which may lead to tube instability and vibration and its rupture; both these phenomena require expensive treatments or component replacements. Secondary chemistry mainly consists in implementing appropriate chemical conditioning and pollution monitoring. It is a compromise between safety, performance, environmental releases and wastes, and operating and maintenance costs.

To identify the best compromise, it is necessary to have an online, i.e. at different loads and during transients, view of the chemistry at each point of the circuit. However, currently, this is not possible by only using available measures, due to very limited measuring points or a too low sampling frequency.

1.2 Needs for a ThermoSysPro Evolution

To go beyond the current limitations, the idea is to develop a digital twin of the secondary chemistry, combining the few (both in space and in time) available measures with thermal-hydraulic and *simple* chemistry modeling. *Simple* since for our application the main phenomena of interest are:

- The convection, in the several components of the secondary circuit, of the conditioning amines, which are the chemicals used to control the pH .
- The evaluation of the pH (at the desired temperature, i.e. the fluid or the ambient one).

Such a digital twin will provide nuclear power plant chemical engineers with a complete view of the secondary circuit chemistry at any point and continuously. It will also allow to project the impact of a specific manoeuvre on the secondary chemistry to optimize the operation of the plant. This paper presents the recent developments of the ThermoSysPro library to make it able to deal with such phenomena. These developments are enough general to open the door for other application combining thermal-hydraulics and convection of whatever substances of interest (not just conditioning amines). The modeling approach will be detailed in chapter 2, while chapter 3 will present some simple application examples. The conclusions and perspectives will be discussed in chapter 4.

2 Modeling Approach

2.1 Main Modeled Phenomena

The present application concerns the convection of a few amines (bases) in a water biphasic circuit. However, it is quite easy and convenient to generalize the problem so that any kind and any number of substances can be convected in such a circuit. Specifically, the mass balance equation has to be respected for any substance i :

$$\frac{dMi}{dt} = Qi_{IN} - Qi_{OUT} \quad (1)$$

where Mi is the mass of the substance i in a control volume and Qi_{IN} (respectively Qi_{OUT}) the inlet (outlet) mass flow rate for that substance at the boundary of the volume.

Equation 1 supposes that there is no mass source S_{IN} or mass sink S_{OUT} inside the control volume. This is a normal assumption for thermal-hydraulic modeling where the fluid is considered as a unique media; however, this may not be the case when substances are taken individually: chemicals may react and *mutate*, i.e. a substance may disappear and another one appear; the same happens for radioactive substances that naturally disintegrate. Amines are chemicals and sources/sinks may exist in the circuit, depending on the nature of the amine and on the thermodynamic conditions. However, as a first modeling approach, their effect is neglected.

Assumption 1 *Inner sources and sinks of convected substances are out of the scope of the current work.*

Knowing that the global mass balance is already resolved, it is also possible to use the mass concentration of each substances $Ci = \frac{Mi}{M}$, where M is the total mass in the volume, instead of its mass Mi . The equation 1 becomes:

$$\frac{d(M * Ci)}{dt} = Ci_{IN} * Q_{IN} - Ci * Q_{OUT}$$

$$V * \rho * \frac{Ci}{dt} + Ci * \frac{dM}{dt} = Ci_{IN} * Q_{IN} - Ci * Q_{OUT}$$

$$V * \rho * \frac{Ci}{dt} + Ci * (Q_{IN} - Q_{OUT}) = Ci_{IN} * Q_{IN} - Ci * Q_{OUT} \quad (2)$$

where V is the constant volume of the control volume, ρ the fluid density, Q_{IN} and Q_{OUT} the inlet and outlet total mass flow and Ci_{IN} the mass concentration of the substance i in the inlet flow.

The equation 2 can easily be adapted in case of multiple inlets/outlets:

$$V * \rho * \frac{Ci}{dt} + Ci * (\sum Q_{IN_k} - \sum Q_{OUT_k}) = \sum (Ci_{IN_k} * Q_{IN_k}) - \sum (Ci * Q_{OUT_k}) \quad (3)$$

with obvious notation.

Equation 3 make the hypothesis that the concentration Ci is the same for all the outputs. This is generally the case when the convected substance is homogeneously dissolved in the fluid. While this is a quite common assumption for monophasic conditions, it is far from true in a component where liquid and gas phases are split. A steam dryer or a steam generator with blowdown are typical examples of component where this assumption is refuted.

In this case Ci should be split in Ci_{GAZ} and Ci_{LIQ} which are directed to the corresponding outlet(s). Additional equation should then be added to evaluate how the Ci entering a control volume is split in gaz and liquid phase. This depends on the nature of the substances. For amines, the equilibrium between gas and liquid concentrations is mainly controlled by:

- A *distribution coefficient* defined as the ratio of the concentrations (in molality, mol/kg) of the species in the vapor phase to the undissociated species in the aqueous phase.
- An *association constant* governing the equilibrium, in the aqueous phase, of the undissociated and the dissociated species.

Besides amines, some *generic* substances can be conceived, such as:

- A *homogeneous* substance who make no distinction between gas and liquid phases. In this case $Ci = Ci_{GAS} = Ci_{LIQ}$.
- A *non-volatile* substance who cannot pass to the gas phase. In this case $Ci_{GAS} = 0$ and $Ci = Ci_{LIQ} * (1 - x)$, where x is the vapor quality in the control volume.¹

¹It has to be noticed that, with this definition, the liquid concentration tends to infinite when the vapor quality tend to 1. It corresponds to the expected behaviour since the substance cannot migrate to the gas phase and accumulate in the liquid one; however, such a substance would probably crystallize, so *leaving* the liquid phase, above some threshold of liquid concentration; to take into account such a phenomena, a sink should be added to the model (out of the current scope, see Assumption 1).

These generic substances can be used to model the convection of several substances with similar behaviour (for example the 2.1 could be used to model salt in water). These generic substances will be used in chapter 3 for illustration purpose.

Within the framework of this work, the concentration of the transported substances is supposed to be low, of some *ppm* or even *ppb*. Such values does not impact the thermal-hydraulic properties of the fluid, such as the density or the viscosity.

Assumption 2 *The concentration of the transported substances does not impact the thermal-hydraulic properties of the fluid.*

Once the concentration of the substances (amines in this specific case) are defined, the *pH* can be computed. *pH* is the *potential of hydrogen* and it is defined as follows:

$$pH = -\log_{10}([H^+]) \quad (4)$$

$[H^+]$ being the equilibrium molar concentration in mol/L of hydrogen ions in the solution.

Equation 4 could be rewritten as a function of $[OH^-]$ (hydroxide ions concentration), to which the concentration of hydrogen ions is related via the self-ionization constant of water, *K_w*:

$$pOH + pH = -\log_{10}(K_w) \quad (5)$$

It is worth noticing that the value of *K_w* depends on water temperature and pressure (see for example Marshall and Franck (1981)).

The OH^- formulation is preferred since the hydroxide ions concentration also appears in the equations governing the biphasic equilibrium (see above).

2.2 Code Implementation: the `ConvectedQuantities` Package

One of the main objectives of this development is to ease the reuse of the substances' convection models: in the framework of the target application, 4 chemical species have to be convected (to compute the *pH*); more generally, *None* or other sets of substances may have to be convected in the future. For this reason, the proposed approach consists in developing two subpackages, `Components` and `Substances`.

2.2.1 The `Components` sub-Package

The `Components` package is dedicated to the modeling of the convection of the substances, following the equation 3 (module `MassBalance`) or its declination for heterogeneous liquid/gaseous outlet (module `MassBalance_HeterogeneousPhases`).

The equations in these modules are *vectorized* so that they can deal with any number of substances (general approach).

2.2.2 The `Substances` sub-Package

Substances have then to be *vectorised* too. The concentrations of a set of substances is store as an enumeration as suggested by Tiller (2023) for chemicals. The other information to be provided for each set is how the concentrations of each substance distribute in biphasic fluid. Here follow the example code for *None*, *Homogeneous* and *NonVolatile* substances:

Listing 1. *None* definition

```
package None
  replaceable type Concentrations =
    enumeration (:);

  replaceable block PhasesSeparation
    import ThermoSysPro.Units.SI;

    input SI.Temperature T "Fluid
      Temperature";
    input SI.Density rho_liquidPhase "
      Fluid Density";
    input Real x "Title";
    input Real SubC[None.Concentrations]
      "Total Species Concentrations";

    output Real Cl[None.Concentrations] "
      Species Concentration in the
      Liquid Phase";
    output Real Cg[None.Concentrations] "
      Species Concentration in the Gas
      Phase";

  equation
    Cl = fill(0, size(Cl, 1));
    Cg = fill(0, size(Cg, 1));

  end PhasesSeparation;
```

Listing 2. *Homogeneous* definition

```
package Homogeneous "Substance with
  homogeneous distribution in gas and
  liquid phases"
  extends None (
    redeclare type Concentrations =
      enumeration (substance "Gas/
        Liquid homogeneous substance"),
    redeclare block PhasesSeparation =
      PhasesSeparation_internal);

  block PhasesSeparation_internal

    import ThermoSysPro.Units.SI;

    input SI.Temperature T "Fluid
      Temperature";
    input SI.Density rho_liquidPhase "Fluid
      Density";
    input Real x "Title";
    input Real SubC[HomogeneousSubstance.
      Concentrations] "Total Species
      Concentrations";

    output Real Cl[HomogeneousSubstance.
      Concentrations] "Species
```

```

        Concentration in the Liquid Phase";
output Real Cg[HomogeneousSubstance.
Concentrations] "Species
Concentration in the Gas Phase";

equation
  Cl = SubC;
  Cl = Cg;

end Homogeneous;

```

Listing 3. *NonVolatile* definition

```

package NonVolatile "Substance tending to
remain in liquid phase"
extends None (
  redeclare type Concentrations =
    enumeration (substance "Gas/Liquid
homogeneous substance"),
  redeclare block PhasesSeparation =
    PhasesSeparation_internal
);

block PhasesSeparation_internal

import ThermoSysPro.Units.SI;

input SI.Temperature T "Fluid
Temperature";
input SI.Density rho_liquidPhase "Fluid
Density";
input Real x "Title";
input Real SubC[NonVolatile.
Concentrations] "Total Species
Concentrations";

output Real Cl[NonVolatile.
Concentrations]
"Species Concentration in the Liquid
Phase";
output Real Cg[NonVolatile.
Concentrations]
"Species Concentration in the Gas
Phase";

equation
  Cl * (1-x) = SubC;
  Cg = fill(0, size(Cl,1));

end PhasesSeparation_internal;

end NonVolatile;

```

As with *Homogeneous* and *NonVolatile* sets (of only one substance), any other set of substances can be defined by extending *None* and redeclaring the *Concentration* enumeration and *PhasesSeparation* according to the characteristic of the that specific set.

2.3 Application to waterSteam or Fluid Packages of ThermoSysPro

The code presented in the previous paragraph deals with the convection of generic substances, but still have to be "connected" with existing ThermoSysPro modules, which deal with "everything else" (i.e. fluid mass balance, energy

balance, fluid properties...). Since the target application concern chemical water conditioning, the connection have been done to the ThermoSysPro packages² *WaterSteam* and *Fluid*. However, the following fundamentals for linking *ConvectedQuantities* apply for other fluids/-packages.

The general required modifications are listed hereafter:

- The *replaceable* definition of the convected species (see Listing 4) is added. *None* is used as default so that nothing is convected if useless (no trailing equations/variables *polluting* or increasing the size of the system of equations). The size of *Concentration* is 0 in this case.
- Fluid connectors are replaced with new connectors which contains also a new *SubC* variable which is defined to host the convected *Species.Concentration*.

Listing 4. Definition of Convected *Species*

```

// In the declaration part
replaceable package Species = ThermoSysPro.
ConvectedQuantities.Substances.None ;

```

Subsequent modifications depend on the nature of module: *biports* (Singular and Pipe Pressure Losses, Stodola Turbines, Control Valves, Pumps...) or *volumes* (or junctions).

2.3.1 Biports

In this components, the convected substances concentration is transmitted from the inlet to the outlet: inlet and outlet concentration have to be equalized.

Listing 5. Connection of input and output concentration in a *biport*

```

// In the equation part
Cl.subC = C2.subC ;

```

2.3.2 Volumes

These components require the use of the additional modules developed in the *ConvectedQuantities* package. In particular the *MassBalance[...]* module (with specific binding equations) has to be used to calculate the distribution of the substances between the different outputs and to model their dynamic behaviour. An example is given in Listing 6.

Listing 6. Connection of *MassBalance* to a *volume*

²The ThermoSysPro library is composed by several packages, needed to model any type of power plant; for example: *InstrumentationAndControl*, *Combustion*, *ElectroMechanics* and some packages dedicated to different fluids (e.g. *WaterSteam*); since the version 4.0 of ThermoSysPro, the *Fluid* package merges them all (e.g. oils, flues gases, refrigerants...).

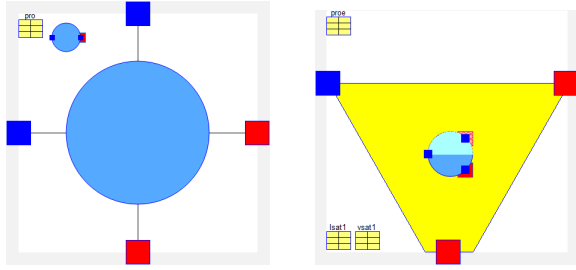


Figure 1. Modified Diagrams of *VolumeA* (left) and *SteamDryer* (right). The icons corresponding to the used `MassBalance[...]` components are visible.

```

ThermoSysPro.ConvectedQuantities.
Components.MassBalance
sub_massBalance(
  redeclare package Species = Species,
  n_in=2, n_out=2, #Number of inlets and
  of outlets
  dynamic_mass_balance=
    dynamic_mass_balance,
  V=V,
  Qin = {Ce1.Q,Ce2.Q}, #Binding the inlet
  mass flow rates
  Qout = {Cs1.Q,Cs2.Q}, #Binding the inlet
  mass flow rates
  rho = rho)

```

3 Examples

3.1 Homogeneous Substances

The first simple example concerns the mixing of two water flows with different concentrations of a single generic substance. Figure 3 shows the ThermoSysPro model, composed by:

- a main water line (the horizontal one at the bottom of the diagram, "Source A") with null concentration at the beginning of the simulation;
- a secondary line (on the top, "Source B") that injects water with 100 *ppm* of such a substance when a control valve is opened (from 5 to 11 *seconds*).

Figure 2 shows the resulting concentration of the water reaching the sink: as expected, once the valve is opened (@ 6 *seconds*) the concentration increases.

The increase does not end at 11 *seconds* (when the valve is fully opened) because of the *inertia* due to the mixing volume where a perfect mixing is assumed. For reproduction purpose: the volume is of 100 m^3 , to be compared to a mass flow rate of 5000 *kg/s* on the main line and 2716 *kg/s* on the secondary line.

3.2 Amines and pH

The second example is related to the target application: the convection of amines and the evaluation of *pH* in a secondary circuit. To focus on the heterogeneous behaviour of amines in biphasic conditions, in this example

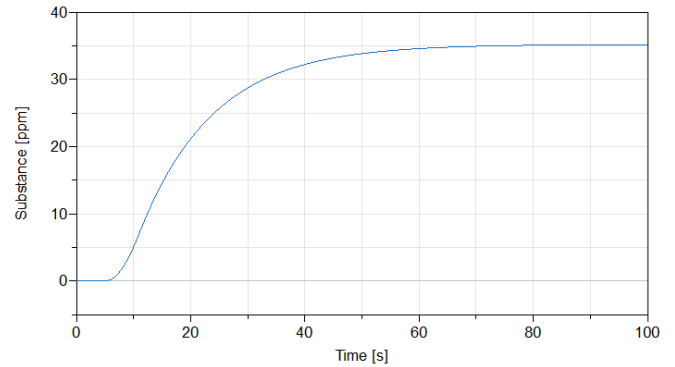


Figure 2. Evolution of the concentration of a generic convected substance: effect of the *inertia* due to a mixing volume.

a small portion of a classical secondary circuit is modeled (cf. Figure 4): the steam dryer following a high pressure turbine (not in the model's scope). The dryer module separates liquid flow (going down in the diagram), which feeds the preheaters (out of the scope of the example), from gaseous flow (going right in the diagram), which is reheated before feeding the low pressure turbine. It is then a relevant example to see test the `MassBalance_HeterogeneousPhases` module.

In this application, the `Concentration` array is of length 4, since 4 different amines are used:

- Ethanolamine
- Morpholine
- Ammonia
- Hydrazine

These amines are characterized by a very different behaviour in diphasic conditions: Ammonia concentrates in the gaseous phase, while Hydrazine and Ethanolamine concentrates in the liquid phase; as to Morpholine, it tends to slightly concentrates in diphasic conditions.

In the example, arbitrary but reasonable values are set for the concentration of the amines upstream and see how they split in the dryer: the results are illustrated by Table 1.

[ppm]	upstream	liquid	gas	liq/gas
Ethanolamine	4	11.3	0.891	12.6
Morpholine	8	11.3	6.58	1.72
Ammonia S.	3	0.398	4.12	0.097
Hydrazine	0.2	0.609	0.025	24.5

Table 1. Concentrations of amines *upstream* of the dryer and in its *liquid* or *gaseous* outlets.

Results show that Ethanolamine is almost 13 times more concentrated in the liquid phase than in the gaseous one; this ratio reaches 25 for Hydrazine. For Morpholine this effect (greater concentration in the liquid phase)

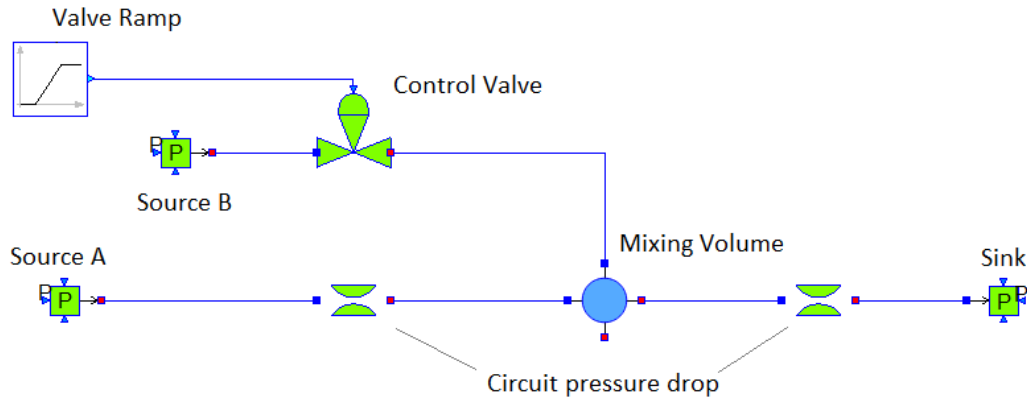


Figure 3. Simple Example for homogeneous substances (Volume)

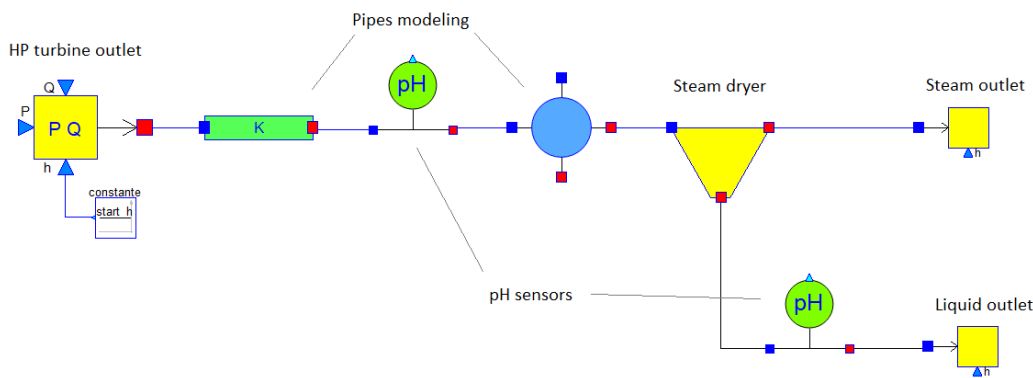


Figure 4. Simple Example for Amines (Steam Dryer)

is far lower while for Ammonia the opposite is true: this amine concentrates itself in the gaseous phase (about 10 times more than in the liquid phase). These results are consistent with the experts' expectation (historical measurements, cf. § 4) and some *back-of-the-envelope* verification (hand-calculations in simplified configurations).

Concerning pH , two *sensors* are included in the model, as shown in Figure 4. pH can be measured at fluid temperature or at ambient temperature (in the latter case the diphasic fluid is condensed). The results are displayed in Table 2.

pH	<i>upstream</i>	<i>liquid</i>
@ Fluid T	7.71	7.71
@ Ambient T	9.86	9.89

Table 2. pH upstream and in the *liquid* outlet. pH is provided at the fluid or at ambient Temperatures.

At fluid temperature, the pH upstream and in the liquid line are the same. This corresponds to the expected behaviour since the pH calculation are mainly based on the amines' concentrations in the liquid phase, which are the same in this two measurement points.

When the fluid is brought to ambient conditions (pres-

sure and temperature), the pH is significantly higher. In this case, the amines' concentrations are different in the two measurement points: while in the *liquid* one there only is liquid, in the *upstream* one gas is also present; it condensate in the cooling process and mixes with the previous liquid phase. As a result, the pH values are different.

Some more quantitative and extensive tests are ongoing (see the perspectives in the § 4) and the preliminary results confirm the consistency of the computed values.

4 Conclusions and Perspectives

In this paper are illustrated the fundamentals of an approach to implement the convection of substances in the thermal-hydraulic library ThermoSysPro. The target application for these recent developments is building a dynamic digital twin for our power plant, with a particular focus on the secondary chemistry. One of the main interests of using ThermoSysPro as the base thermal-hydraulic layer is the opportunity of being able to reuse already developed thermal-hydraulic models. Thanks to the Modelica language it was possible to develop a generic approach, with some basic substances *hard-coded* in ThermoSysPro and easy customization for the end user: amines in the target application; but the user can easily develop specific set of substances (any number of simultaneous substances)

by defining specific biphasic equilibrium. The developed modules allow for taking into account dynamic evolution (dilution/concentration) of substances concentration and heterogeneous biphasic behaviour.

The next steps includes the continuation of the verification and validation phase: in particular, the model output will be compared to experimental data (*pH* values and amines' concentrations) coming from several EDF nuclear power plants. In fact, some experimental campaigns have been realized in the last decades and provide a pertinent database for the validation of our models (data is not public). The comparison between computed and measured values will provide an estimation of the accuracy of the digital twin.

Moreover, the modifications listed in paragraph 2.3 still need to be applied to all the `Fluid` and/or `WaterSteam` packages of ThermoSysPro. The developments have been realized on Dymola (Dymola 2023); tests on other softwares, OpenModelica in particular (Fritzson et al. 2020), have still to be performed. All this work will hopefully lead to a new major ThermoSysPro version which will be made available in the GitHub repository of ThermoSysPro (ThermoSysPro 2023). Currently, the v4.0, which does not include the features presented in this paper, is publicly available.

Then, further studies will be dedicated to overcome some current limitations:

- ThermoSysPro deals with flow reversal without using the *stream* concept (El Hefni and Bouskela 2019). The ThermoSysPro's way of dealing with flow reversal still has to be applied to substance convection.
- As per Assumption 1, current developments do not take into account the possible creation or destruction of convected substances. However, such phenomena may be of interest, for example for chemical species who would react and mutates in other species: it is the case of some amines in particular conditions. Radioactive disintegration is another relevant application.

Finally, a comparison with other solutions devoted to substance convection, such as the Modelica Standard Library, should be performed to identify potential improvements for our developments.

Acknowledgements

The authors would like to thank Daniel Bouskela for his last teachings and for his legacy.

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