Equations-of-State models in ChemApp/ChemSheet, a Fluent-KilnSimu link, and a metallurgical process simulation tool based on SimuSage

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3 topics

- EOS/GCM models with ChemSheet
  Karri Penttilä, VTT Process Chemistry
- FKS - Fluent-KilnSimu
  Karri Penttilä, VTT Process Chemistry
  Eero Immonen, ProcessFlow
- A metallurgical process simulation tool based on SimuSage
  Stephan Petersen, GTT-Technologies

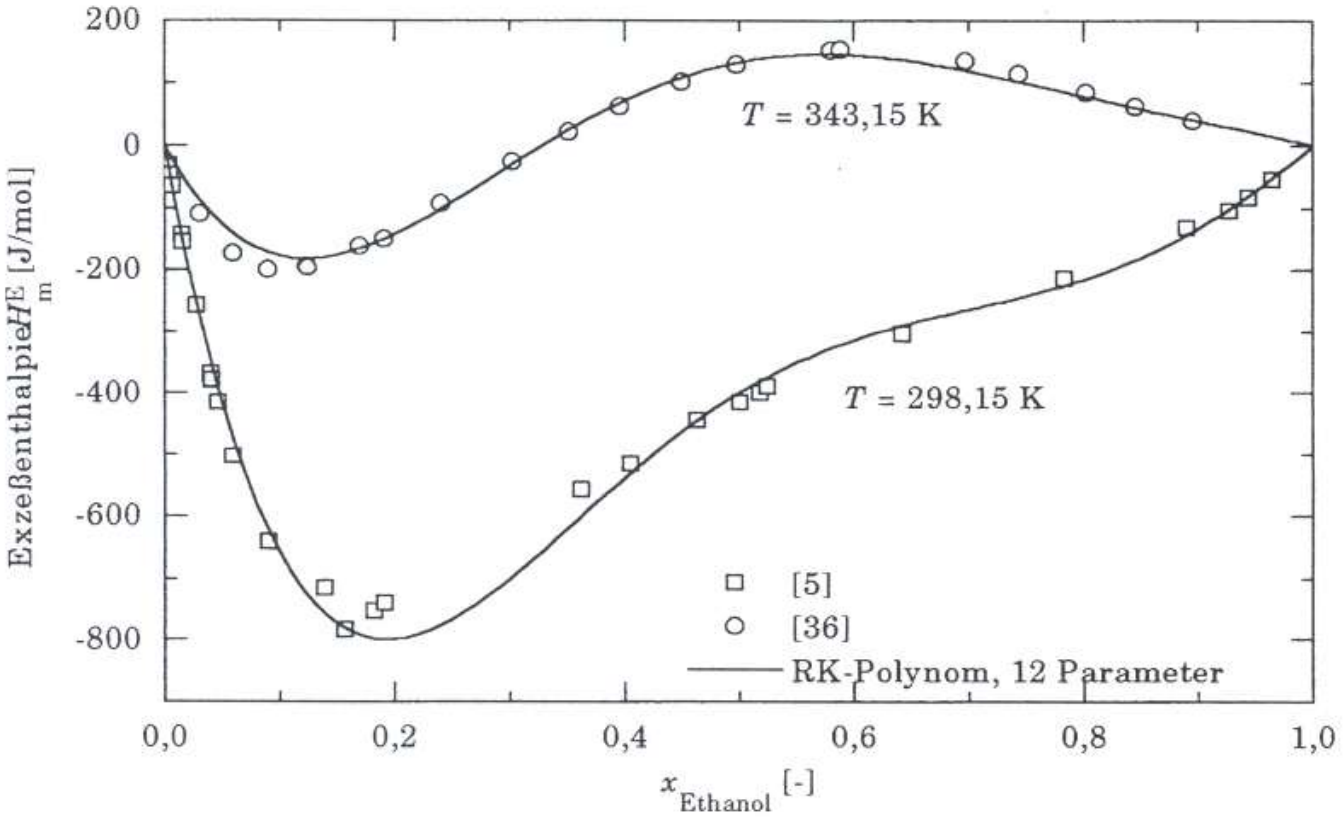
EOS/GCM Models With ChemSheet

Karri Penttilä, VTT Process Chemistry

Organic systems with ChemApp

- There is a demand from users of ChemApp and other programs built on it (such as ChemSheet) to use data for organic systems on their calculations.
- Enough data is available, but for use with a variety of equation of state (EOS) models.
- Both the EOS models (primarily used for gaseous substances) and the models for activity/fugacity coefficients used for condensed phases have not really been available in ChemApp.
- Work has been done to make such data available to ChemApp, first as “user defined models”.

Modelling the Excess Enthalpy for Ethanol-Water with Redlich-Kister



Excess enthalpy of the system ethanol-water at 298,15 and 343.15 K

M. Hack: „Simultane Modellierung thermodynamischer Eigenschaften wäßriger Systeme mit weiten Mischungslücken“, Dissertation, RWTH Aachen, Fakultät für Maschinenwesen,1998

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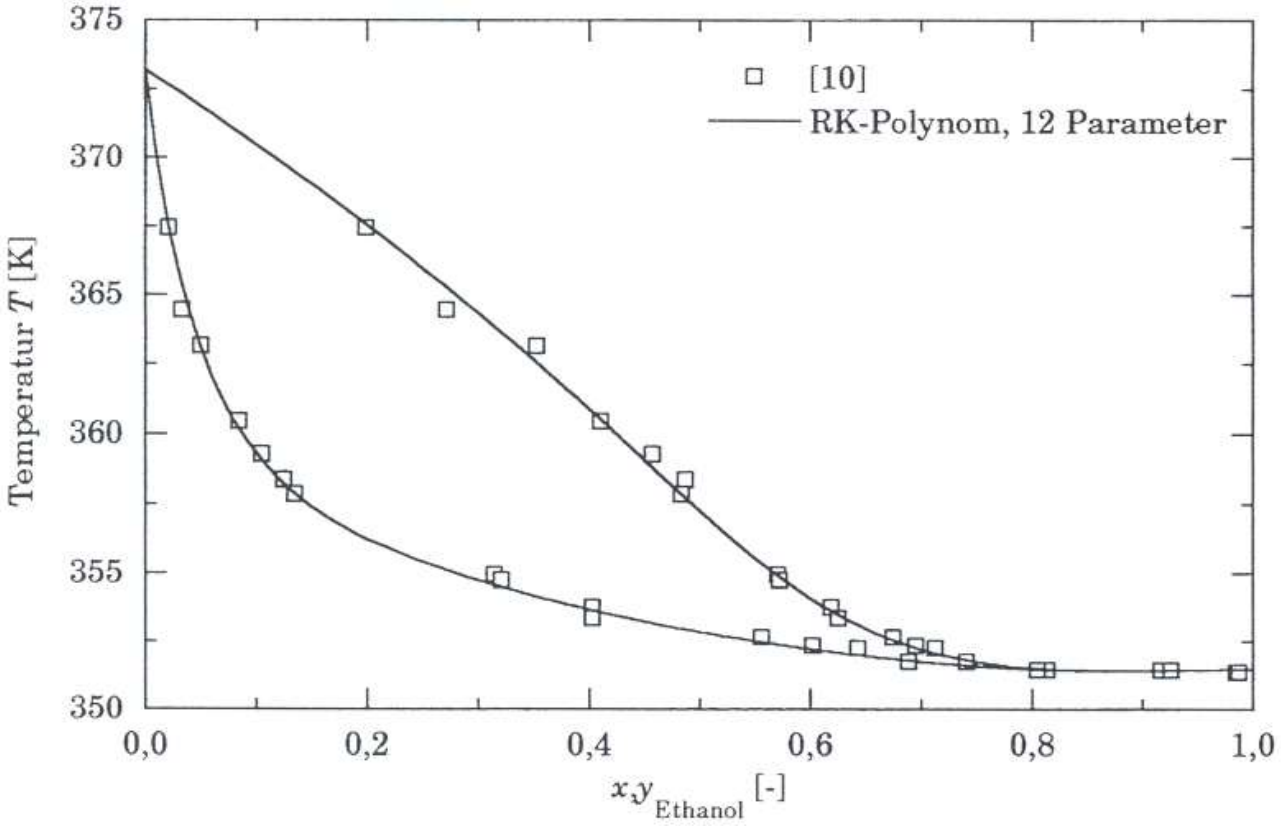
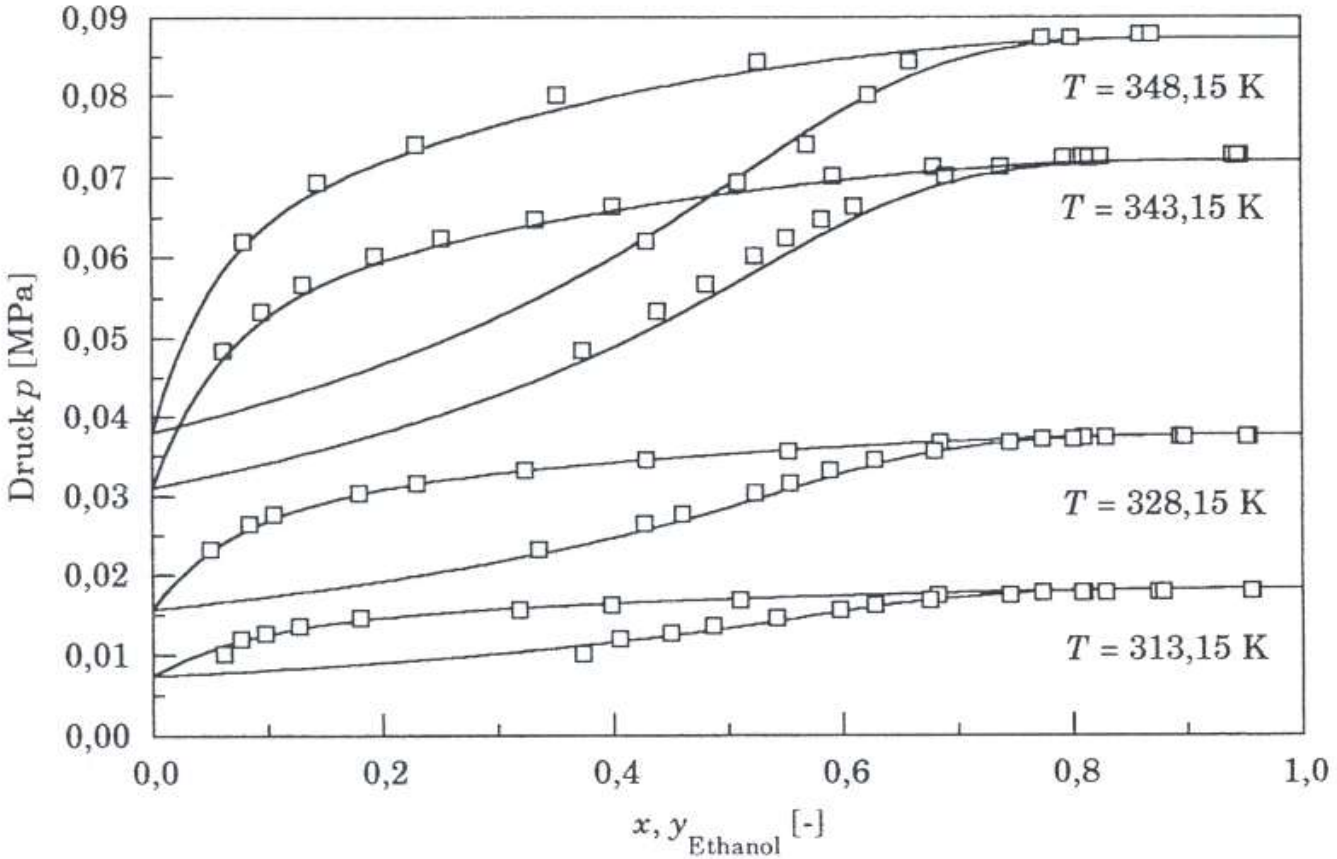


Boiling point diagram of the system ethanol-water at 0.1013 MPa

M. Hack: „Simultane Modellierung thermodynamischer Eigenschaften wäßriger Systeme mit weiten Mischungslücken“, Dissertation, RWTH Aachen, Fakultät für Maschinenwesen,1998

Modelling the Excess Enthalpy for Ethanol-Water with Redlich-Kister



Calculated boiling point diagrams of the system ethanol-water at 4 temperatures

M. Hack: „Simultane Modellierung thermodynamischer Eigenschaften wäßriger Systeme mit weiten Mischungslücken“, Dissertation, RWTH Aachen, Fakultät für Maschinenwesen,1998

Generalized Cubic EOS

The model for generalized two parameter cubic EOS is given as:

$$P = \frac{RT}{v - b_m} - \frac{a_m}{(v + c_1 b_m)(v + c_2 b_m)}$$

P pressure [Pa]
R gas constant [J/mol-K]
T temperature [K]
v molar volume [m^3/mol]
a attraction parameter [Pa-m^6/mol^2]
b covolume parameter [m^3/mol]

The classical mixing rules for a_m and b_m parameters are given as:

$$a_m = \sum_i \sum_j x_i x_j \sqrt{a_i a_j}\,(1 - k_{ij}) \qquad b_m = \sum_i x_i b_i$$

P_c critical pressure [Pa]
T_c critical temperature [K]

$$a_i = \Omega_a \frac{R^2 T_{ci}^2}{P_{ci}} \alpha_i(T_{ri}, \omega_i) \qquad b_i = \Omega_b \frac{RT_{ci}}{P_{ci}} \qquad \text{from: } \left(\frac{\partial P}{\partial v_i}\right)_T = \left(\frac{\partial^2 P}{\partial v_i^2}\right)_T = 0$$

where k_{ij} is emperical interaction parameter ($k_{ii} = 0$).

SRK	: $c_1 = 0$	$c_2 = 1$	$\Omega_a = 0.42748$	$\Omega_b = 0.08664$
PR	: $c_1 = 1 - \sqrt{2}$	$c_2 = 1 + \sqrt{2}$	$\Omega_a = 0.45724$	$\Omega_b = 0.07780$

GCM Activity Models

In Unifac group contribution model (**GCM**) the species are represented with molecular groups. The activity coefficient is a sum of the contributions of the groups in each molecular species in the mixture:

$$\ln \gamma_i = \underbrace{\ln \gamma_i^C}_{\text{combinatorial}} + \underbrace{\ln \gamma_i^R}_{\text{residual}}$$

Combinatorial contribution depends on the sizes and shapes of the molecules. It is given as:

$$\ln \gamma_i^C = 1 - V_i + \ln V_i - 5q_i\left(1 - \frac{V_i}{F_i} + \ln \frac{V_i}{F_i}\right)$$

Residual contribution depends on the group areas and group interactions. It is given as:

$$\ln \gamma_i^R = \sum_k \upsilon_k^{(i)}\left(\ln \Gamma_k - \ln \Gamma_k^{(i)}\right)$$

User Defined Model for ChemApp

•ChemSheet uses ChemApp library for Gibbs energy minimization.

•A special version of ChemApp calls a specific routine in usermod.dll file when it encounters a certain phase model name in ChemSage data-file (USX?). User calculates $\ln g_i$ (partial excess Gibbs energies) for each species in phase at given temperature, pressure and composition.

SUBROUTINE USERGX[DLLEXPORT](NTXX, ITXX1, ITXX2, ITXX3, ITXX4,

WTXX, PXX, TXX, G0XX, V0XX, XXX, MDLXX, NCXX, GINT, GXX)

...

XXX = MOLE FRACTIONS OF ALL PHASE CONSTITUENTS

MDLXX = MODEL NAME FOR THE PHASE

GXX = PARTIAL DERIVATIVE OF EXCESS INTEGRAL GIBBS ENERGY WITH RESPECT TO THE MOLE FRACTIONS OF ALL PHASE CONSTITUENTS

User Defined Model for ChemApp


```
PSRK Ethanol-Water
  3   3   0   2   2   0
C                        H                          O
     12.0110        1.0080       15.9990
  6   1   2   3   4   5   6
  1   1
GAS
USXG
ethanol
 4 2   2.0   6.0   1.0
 1500.0000     -256924.78      31.301527     -39.120400     -.74642560E-01
 .70514347E-05  288696.00
3  .00000000       .00  .00000000       .00  .00000000       .00
 1501.0000     -328906.32      922.89779     -167.59709      .00000000
 .00000000      .00000000
3  .00000000       .00  .00000000       .00  .00000000       .00
water
 4 4   0.0   2.0   1.0
 1100.0000     -255475.81     -15.282587     -25.781640     -.74748581E-02
 .92059316E-07  13999.660
3  1107.2718     99.00  .00000000       .00  .00000000       .00
 4000.0000      152152.28      164.70757     -53.145789     -.80540038E-04
 .00000000     -12075583.
3 -83128.276     99.00  5947.3700       .50  .00000000       .00
 6000.0000     -4469439.5      1472.4424     -155.19083      .00000000
 .00000000      .29826420E+09
3  778290.99     99.00 -64372.340       .50  .00000000       .00
 6001.0000     -302989.76      260.62247     -60.574924      .00000000
 .00000000      .00000000
3  .00000000       .00  .00000000       .00  .00000000       .00
```

User Defined Model for ChemApp


```
2
  1    1    3    0            INIT
  2
  1    0   41    0.6350       Ethanol Acentric factor       []
  2
  1    0   42    63.835       Ethanol Critical pressure     [bar]
  2
  1    0   43    516.20       Ethanol Critical temperature  [K]
  2
  1    0   44    167.00       Ethanol Critical volume       [cm3/mol]
  2
  2    0   41    0.344861     Water   Acentric factor       []
  2
  2    0   42    220.55       Water   Critical pressure     [bar]
  2
  2    0   43    645.15       Water   Critical temperature  [K]
  2
  2    0   44    55.838       Water   Critical volume       [cm3/mol]
  2
  1    0   49    4            Ethanol Alfa Mathias&Copeman
  2
  1    1   49    1.3327       Ethanol MC1
  2
[...]
 2O     = H2O
  2
  0    0   21    0            CALC
  0                           END
```

Supported User Models

- Unifac (for only liquid phase)
  - Original VLE
  - Original LLE
  - Dortmund modified
  - Lyngby modified
  - Dortmund PSRK (used with PSRK only)
  - Dortmund VTPR (used with VTPR only)

- SRK (for only vapour phase or vapour+liquid phases)
  Soave modification of Redlich-Kwong
- PR (for only vapour phase or vapour+liquid phases)
  Peng–Robinson
- PSRK (for vapour+liquid phases using PSRK Unifac)
  Predictive SRK
- VTPR (for vapour+liquid phases using VTPR Unifac)
  Volume-translated PR

FKS - Fluent-KilnSimu

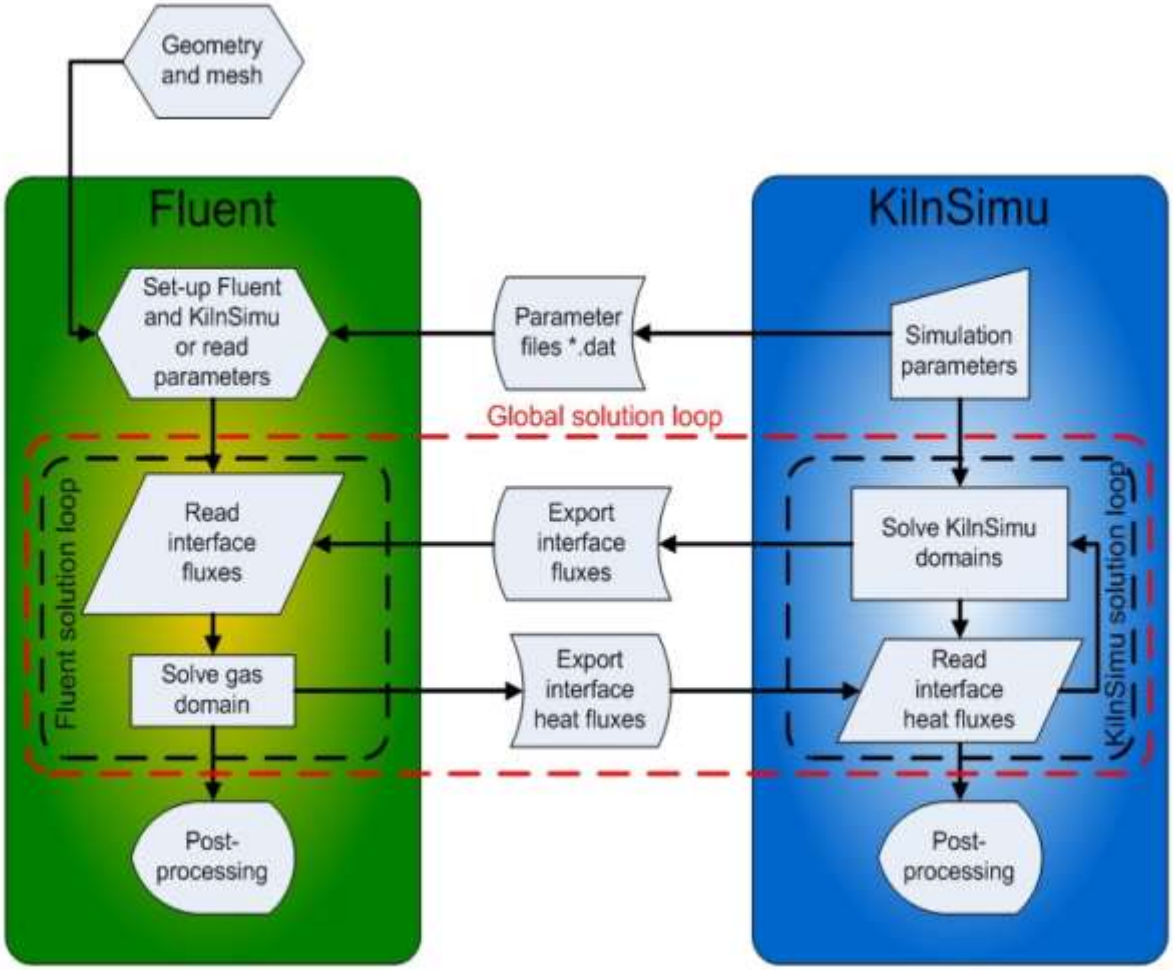
Karri Penttilä, VTT Process Chemistry

Eero Immonen, ProcessFlow

Fluent-Kilnsimu Coupling

- **KilnSimu** contains 1D geometry for the kiln and it calculates 1D-axial temperatures and composition for the bed and the gas sides and temperatures for the kiln inner and outer wall surfaces.
- **Fluent** contains 3D geometry for kiln where the kiln inner wall and the bed surface are the boundaries. **Fluent** calculates the gas side (burner, combustion and gas flow).
- After the first **KilnSimu** calculation **Fluent** calculates the gas side by using the temperatures for the bed and the inner wall calculated by **KilnSimu**. Also any volatiles formed in the bed (surface) are passed to **Fluent**.
- Data is passed from **KilnSimu** to **Fluent** by using text files. Data in the files is processed automatically by macros in **Fluent** and mapped from 1D nodes (Kilnsimu) to 3D nodes on the boundary surfaces and then saved into **Fluent** user defined memory.
- **Fluent** can use also parallel processing.

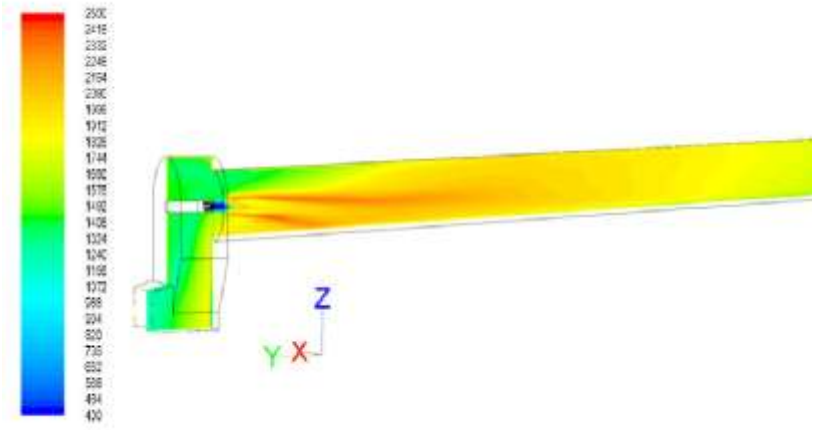
Fluent-Kilnsimu Coupling

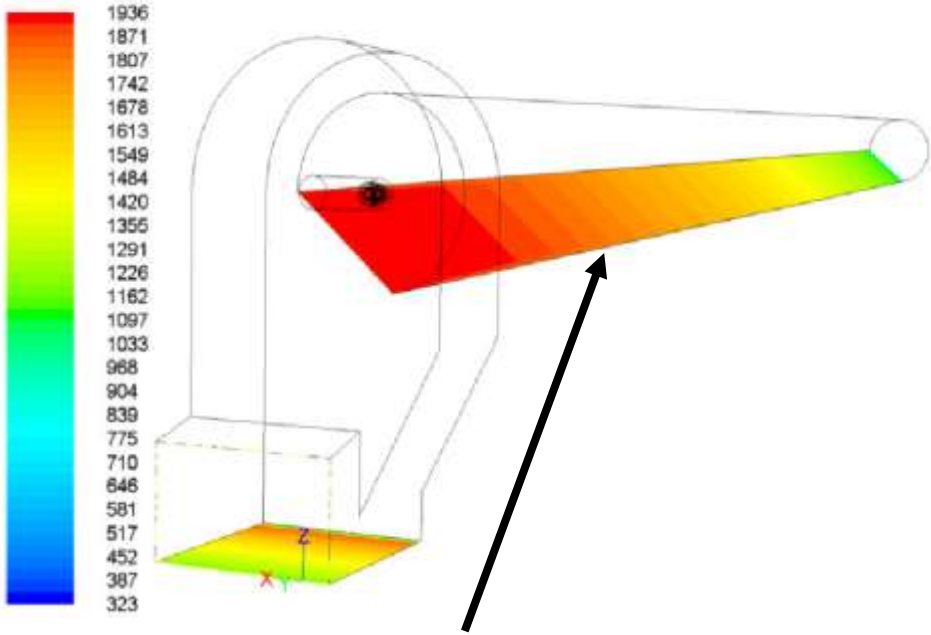


•In *two way coupling* **KilnSimu** uses average gas temperatures calculated by **Fluent** (as **Fluent** is able to calculate flame/gas more accurate) and then **KilnSimu** calculates the bed and the wall temperatures again (without changing the gas temperatures). And after this second **KilnSimu** calculation the gas side can be calculated again in **Fluent.**

Fluent-KilnSimu – Example results

- 3D gas flow temperatures calculated by **Fluent**
- Kiln inner wall and bed temperatures and formation of volatiles from bed calculuted by **KilnSimu** (as boundary conditions in **Fluent**).





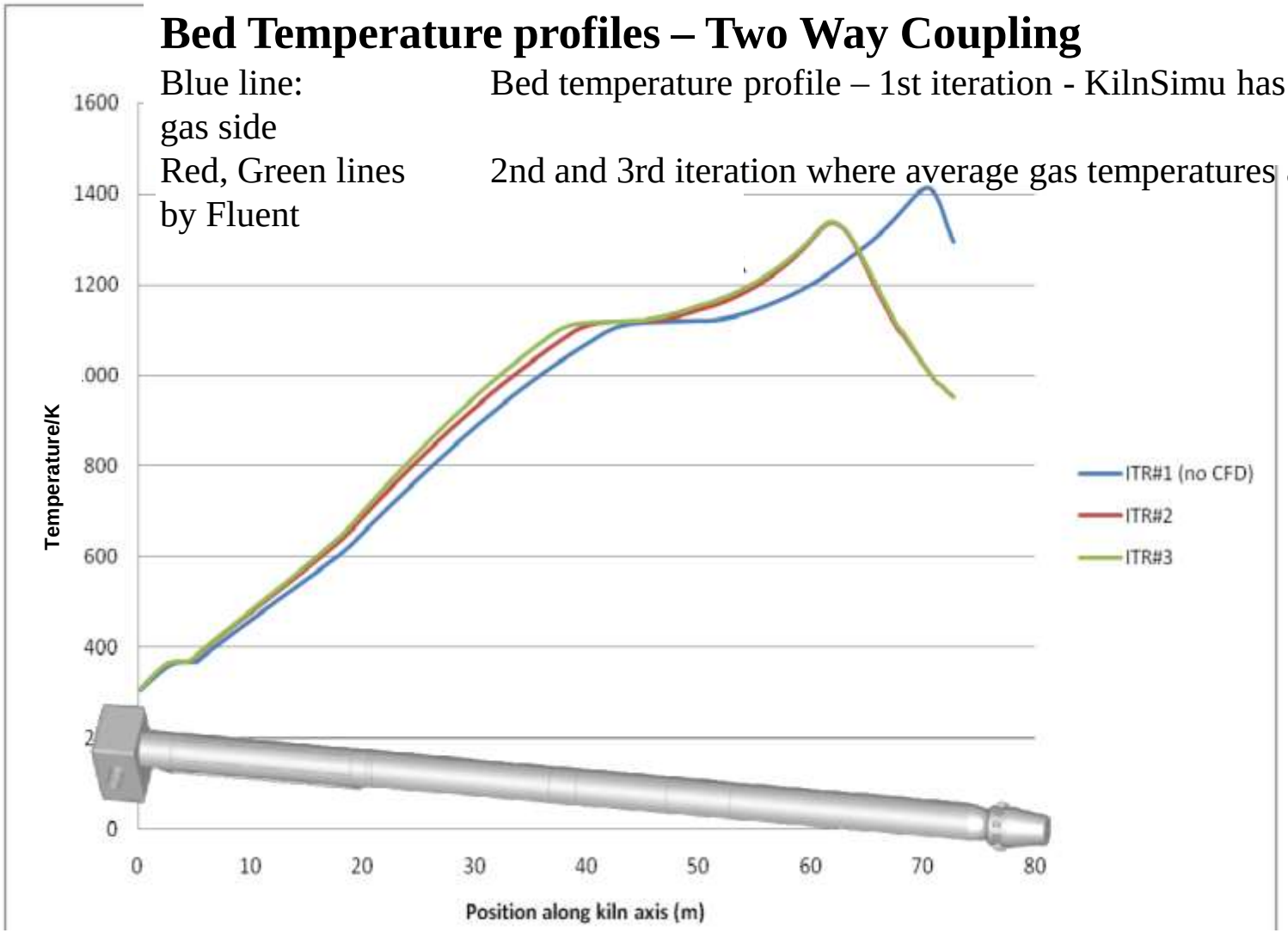
Bed temperatures calculated by KilnSimu and used as boundary condition in Fluent

Fluent-KilnSimu – Two way coupling in Lime kiln

Bed Temperature profiles – Two Way Coupling

Blue line: Bed temperature profile – 1st iteration - KilnSimu has calculated also gas side

Red, Green lines 2nd and 3rd iteration where average gas temperatures are calculated by Fluent



•*In Two way coupling* there might be differences in calculated temperatures (between Fluent and KilnSimu) due to using different model parameters like emissivities – so one must be careful.

A metallurgical process simulation tool based on SimuSage

- SimuSage is a flowsheeting tool, used primarily to model processes as networks of interconnected unit operations and streams.
- A number of processes would benefit from a different approach: processes with a single main reactor space submitted to a user-defined, flexible sequence of treatment steps (recipe).

A metallurgical process simulation tool based on SimuSage

- A program was developed which
  - consists of a simple flowsheet (1 reactor plus number of input streams and recycle streams) that is dynamically modified at run-time
  - implements a number of basic treatment steps together with relevant parameters as subroutines/methods
  - provides a GUI that allows the user to flexibly arrange these treatment steps in an arbitrary sequence and set their associated parameters
  - enables the user to store these “recipes” on disk; load, modify, and run them, and view and store results for post-processing

Thank you for your attention!