From Pyro to Bio: Applications of the Constrained Gibbs Energy Method

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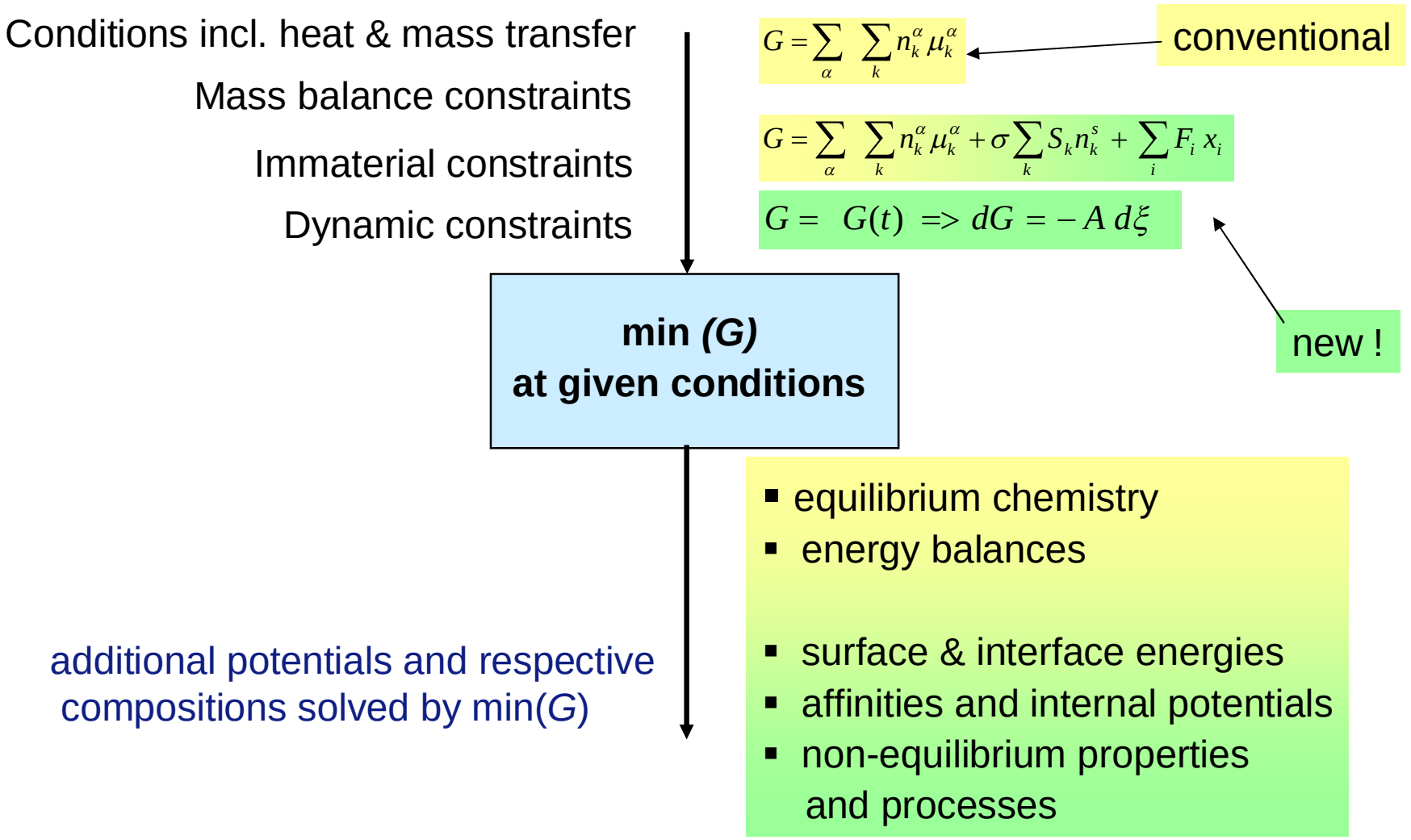
Outline of presentation

1. Motivation for min(G) in process modeling
2. The Constrained Free Energy (CFE) method
3. Applications
   - ❑ Phase diagrams with surface energy (for nano-particles)
   - ❑ CFE in high-temperature process simulation
   - ❑ A biochemical example
4. Summary

Why to use Gibbs free energy for process models ?

- Generic method with great versatility of applications
- Combined and interdependent chemistry and energy
- Whole chemistry: includes major & minor species
- Use of measurable well-defined properties – easy to validate
- Easy to combine with other (physical) models

Introducing New Constraints to min(*G*) Methods



Koukkari,P. and Pajarre, R, Calphad,´30 (2006), 18-26.

Constraints in Gibbs energy minimization

(Chemical) equilibrium principle $G = \sum_{\alpha}\sum_{k} n_k^{\alpha}\mu_k^{\alpha} + \sigma A + sE$

$\min G(\mathbf{n})$ s.t. $\mathbf{Cn}=\mathbf{b}$; $n_k \geq 0 \quad \forall k$

C-matrix (example):

	O	C
O2(g)	2	0
CO(g)	1	1
CO2(g)	2	1
C(s)	0	1

min(G) using the Lagrange method $G = \sum_{j=1}^{m} b_j \pi_j + \sum_{j=m+1}^{m^*} b_j \pi_j$

Constraints

$j = 1,\ldots m \qquad b_j - \sum_k c_{kj} n_k = 0$ (elemental abundances)

Smith & Missen: Chemical Equilibrium Analysis, J. Wiley&Sons 1991

Constraints in Gibbs energy minimization

(Chemical) equilibrium principle $G = \sum_{\alpha}\sum_{k} n_k^{\alpha}\mu_k^{\alpha} + \sigma A + sE$

$\min G(\mathbf{n})$ s.t. $\mathbf{Cn}=\mathbf{b}$; $n_k \geq 0 \;\; \forall k$

C-matrix (example):

	O	C	Immaterial constraint
O2(g)	2	0	
CO(g)	1	1	
CO2(g)	2	1	
C(s)	0	1	
Extent of rxn/phase restriction			

min(G) using the Lagrange method $G = \sum_{j=1}^{m} b_j \pi_j + \sum_{j=m+1}^{m^*} b_j \pi_j$

Constraints

$j = 1,\ldots m$ $\quad b_j - \sum_k c_{kj} n_k = 0$ (elemental abundances)

$j > m$ $\quad A - \sum_{k=1}^{N} A_k n_k^s = 0$ (surface area of an equilbrium system)

$V - \sum_{k=1}^{N} V_k n_k = 0$ (volume of an equilbrium system/subsystem)

$\sum_{k=1}^{N_\alpha} z_k n_k^{\alpha} = 0$ (electroneutrality of a given phase α)

$\int R \cdot dt - \sum_k a_{kr}\upsilon_{kr}\xi_r = 0$ (extent of reaction in terms of given reactant or product)

Koukkari & Pajarre, *Calphad* 2006 ; *Comp & Chem.Engng*, 2006; Koukkari, Pajarre & Hack, *Int.J.Mat 2007*

Lagrange Multipliers as Potentials of the Immaterial Components

$G(\mathbf{n})$ in terms of component potentials π_j

$$G = \sum_{j=1}^{m} b_j \pi_j + \sum_{j=m+1}^{m^*} b_j \pi_j$$

$$\pi_j = \frac{\partial G}{\partial b_j}$$

Chemical potentials of constituents for which $j \le m$:

$$\mu_k = \sum_{j=1}^{m} c_{kj} \pi_j$$

Potentials for additional components ($j > m$):

surface/interfacial tension	$b_j \pi_j = \sigma \cdot A$
electric/electrochemical potential difference	$b_j \pi_j = \Delta\varphi \cdot Q$
osmotic/swelling pressure	$b_j \pi_j = \Pi \cdot V$
affinity of a non-equilibrium reaction	$b_j \pi_j = Y_r \xi_r$
…	

Each Lagrange multiplier π_j represents a thermodynamic (equilibrium) potential of the constrained system

Calculation of Constrained and Partial Equilibria

Modification of the input data file for

- the use of ***immaterial attributes as additional components***
- introduction of ***virtual species***

Modeling tools:

- ***CSFAP*** (ChemSage File Administrator) program (to make the necessary modification to the ChemApp data-file)
- ***ChemSheet***
- Other ChemApp interfaces
- Coupled ChemApp and CFD

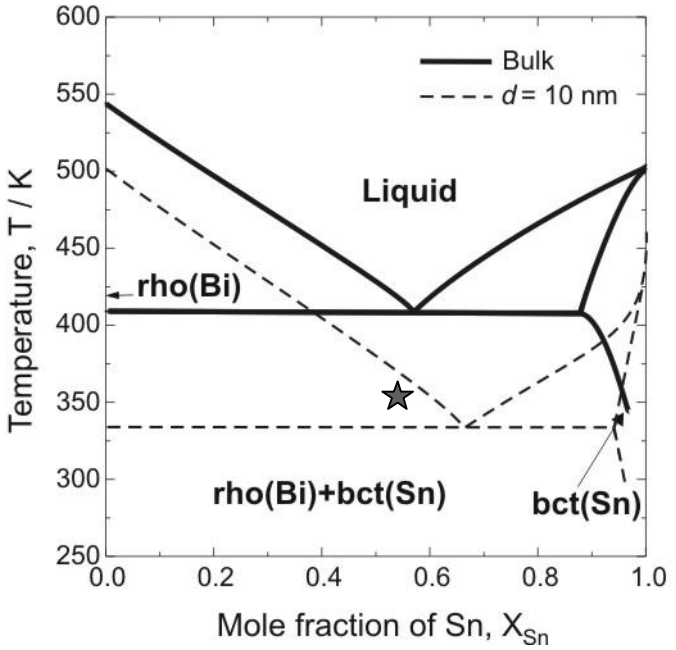
ChemSheet™

Effect of surface energy on the melting of nanoparticles

Surface Tension

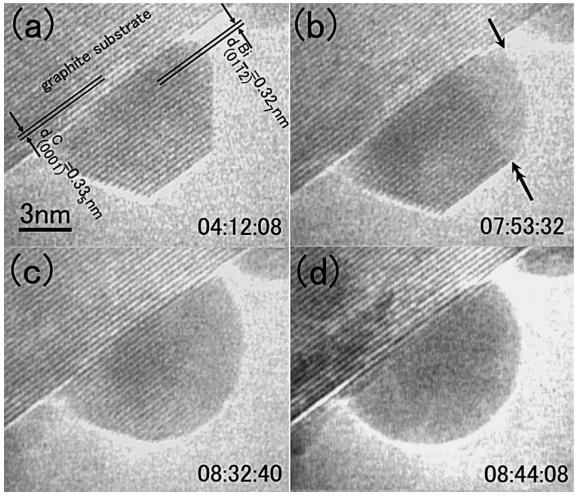
$$\Delta G^{Total} = \Delta G^{Bulk} + \frac{2\sigma V}{r}$$

Radius of a Particle



Validation by electron microscopy (J.J. Lee, Osaka University):

adding Sn to a Bi-nanoparticle causes melting at ca 80 C



Lee, J-H., Tanaka,T., Mori,H., Penttilä,K., JOM-J Min. Met. Mat. S. 57 (2005) 56-59.

Osaka University

Reactive Phase Diagrams from Multiphase Gibbs'ian Calculations

The reactive ethanol-acetic acid system:

$$A + B \rightarrow C + D$$

$$CH_3CH_2OH + CH_3COOH \rightarrow CH_3CH_2COOCH_3 + H_2O$$

Vapour phase (ideal gas):

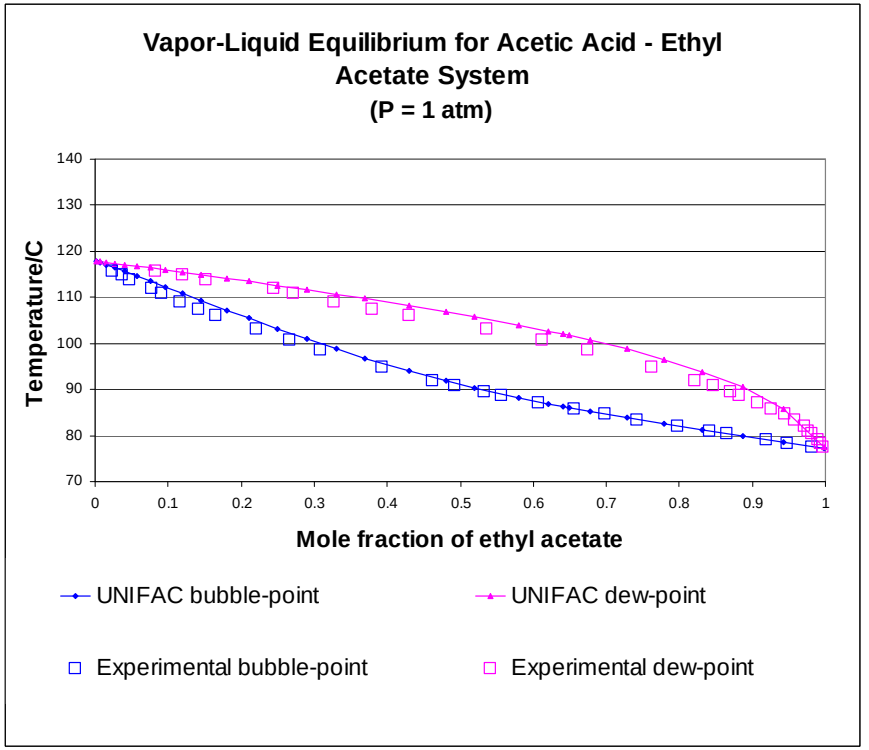
EtOH; AA; $(AA)_2$; EtOAc ; H_2O

Liquid mixture (G^E from UNIFAC):

EtOH; AA; EtOAc; H_2O

(A liquid-liquid equilibria is also possible, but not with the compositions used here)

Reaction may not proceed to equilibrium, but remains at a given extent of reaction, $\xi = \xi(t)$; phase eq. yet attained



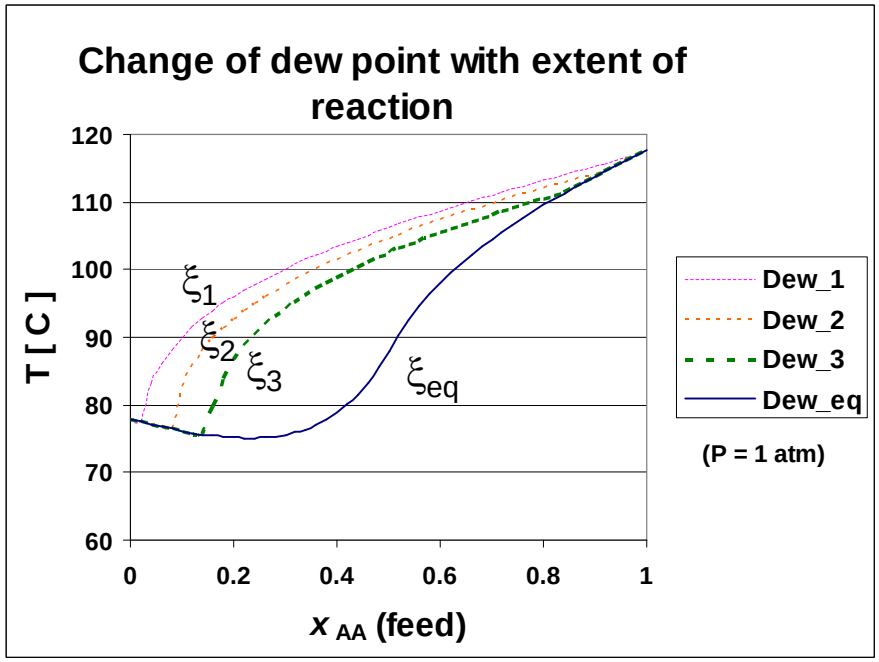
The Extent of Reaction–constraint for the Partial Equilibrium System

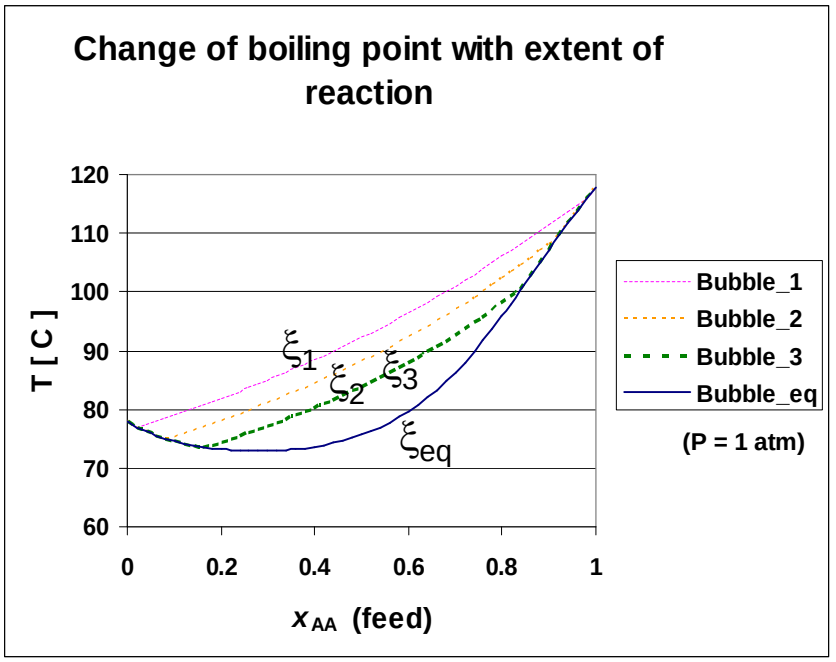
		H2O	EtOH	AA	R
vap	Ethanol		1		
	Acetic acid			1	
	Acid dimer			2	
	Water	1			
	Ethyl acetate	-1	1	1	1
liq	Ethanol		1		
	Acetic acid			1	
	Water	1			
	Ethyl acetate	-1	1	1	1
virtual	ξ+				1

$$G = \sum_{j=1}^{m} b_j \pi_j$$

- Immaterial virtual phase is used as input to 'freeze' the reaction at given ξ -value
- Standard potential of the 'virtual phase' by default zero $\mu^*_{\xi+} \equiv \mu^*_{\xi-} \equiv 0$
- For the non-equilibrium states the affinity of the constrained chemical reaction is $\Delta_r G = -\pi_R$

Bubble and Dew Points for the ξ-constrained System

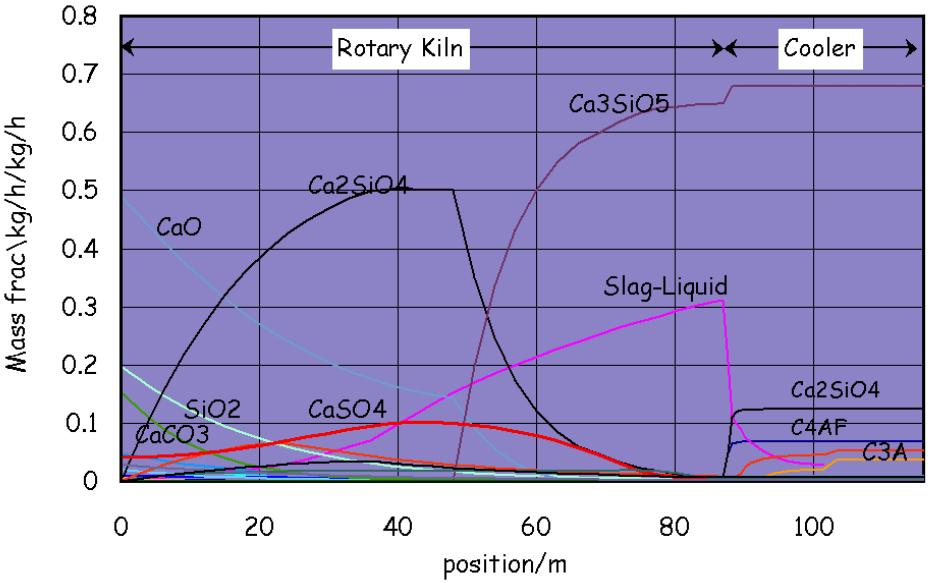




- gradual change in ξ allows for the analysis of the constrained VLE
- $0 < \xi < \xi(eq)$

  $\Rightarrow$ ξ(eq) controls the results at low & high values of x_{AA}

High-temperature process simulation: (looking beyond the steel cover of rotary kilns)



Chemical, temperature & heat profiles in:

- cement furnaces
- lime kilns for pulp mills etc.
- waste incineration
- other kilns
- use of ξ-constraint for non -equilibrium reactions

Yokota, M.: Application of KilnSimu in Industrial Scale Rotary Kiln Analysis in UBE, Presentation at VTT 19th June 2007.

Release of carbon dioxide from rotary kilns

Fuel burning (1200 C) $C + O_2 \rightarrow CO_2\uparrow$ (7.2 t/h)

Calcination reaction (890 C) $CaCO_3 \rightarrow CaO + CO_2\uparrow$ (4.2 t/h)

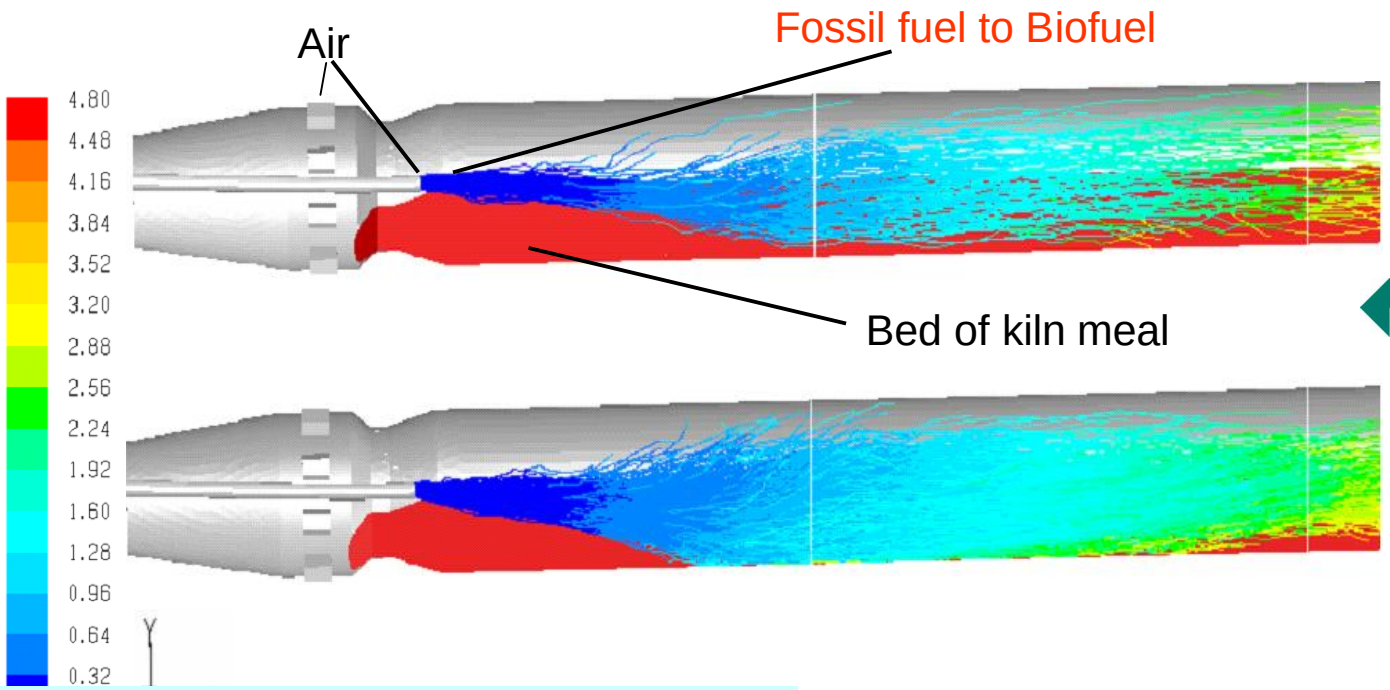
Typical lime kiln releases 170 TPD CO_2 from its fuel and 100 TPD CO_2 from the limestone calcination.

By 2013, the BAT (Best Available Technology) criteria for lime kilns will favour the use of biofuel instead of fossil carbon.

$\Rightarrow$ joint projects commencing to develope new burner technology for lime & cement* kilns

*) cement production accounts for about 5% of anthropogenic CO2 emissions worldwide.

Replacing burner coal and oil with biofuels

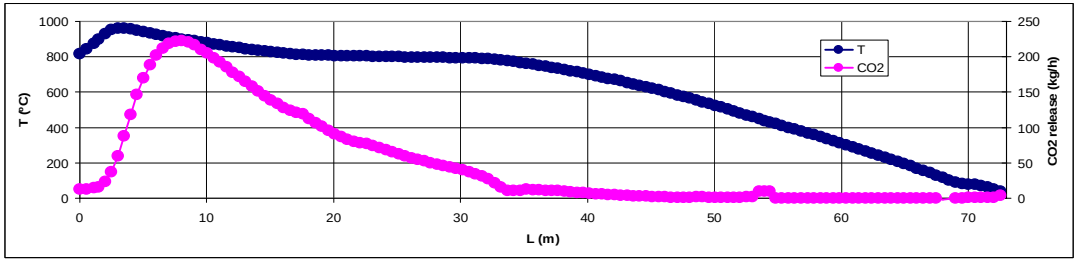


PROCESS FLOW

Nordkalk

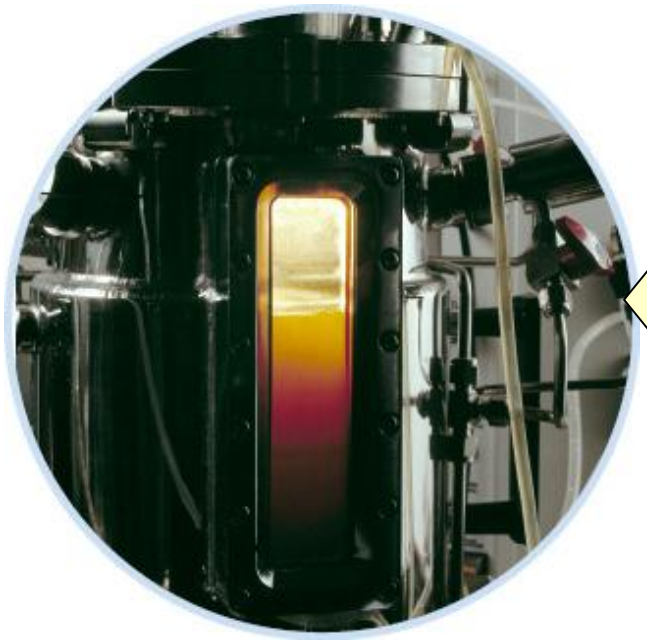
CLEEN
Cluster for Energy and Environment

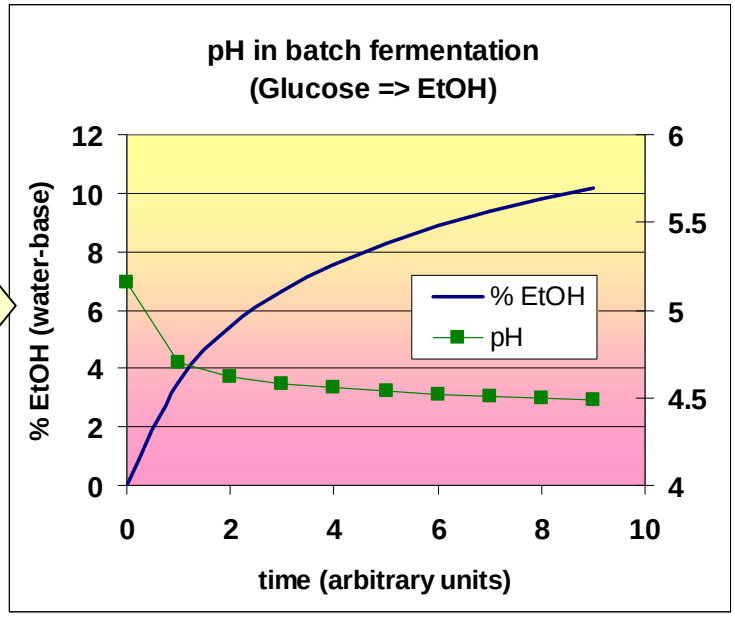
- advanced model by combining computational fluid dynamics with kiln thermochemistry
- target: biofuel usage with 'coal-compatible' profiles



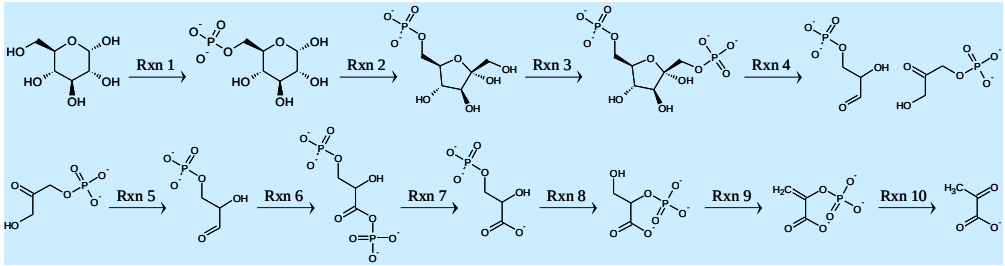
Eriksson, M. (Nordkalk Oy, Finland), Karema, H., Boström, S. (Process Flow Oy, Finland), Koukkari, P. and Penttilä, K. (VTT, Finland): Coupled Fluent-KilnSimu Simulation of a Rotary Lime Kiln, IFRF TOTeM 33 - Challenges in Rotary Kiln Combustion Processes, Pisa Italy, 11th-12th February, 2009.

New challenges: modeling bioreactors and biorefineries





Ref.
H. Akin, &al. :
Chemical Engineering & Processing, 2008



- Optimize & control fermentation conditions
- Guiding metabolic pathway modification with Gibbs free energy diagrams
- Support recovery and purification of biorefining products

Blomberg P. and Koukkari, P.: Combination of transformed and constrained Gibbs energies, Math.Biosci 220 (2009), 81-88.

VTT Research Notes 2506:
Advanced Gibbs Energy Methods for Functional Materials and Processes

http://www.vtt.fi/inf/pdf/tiedotteet/2009/T2506.pdf.'

- Surface and interface systems
- Donnan ion-exchange models for pulp and paper industries
- Multi-phase process simulation and industrial expert systems
- New applications for functional materials and bioprocessing