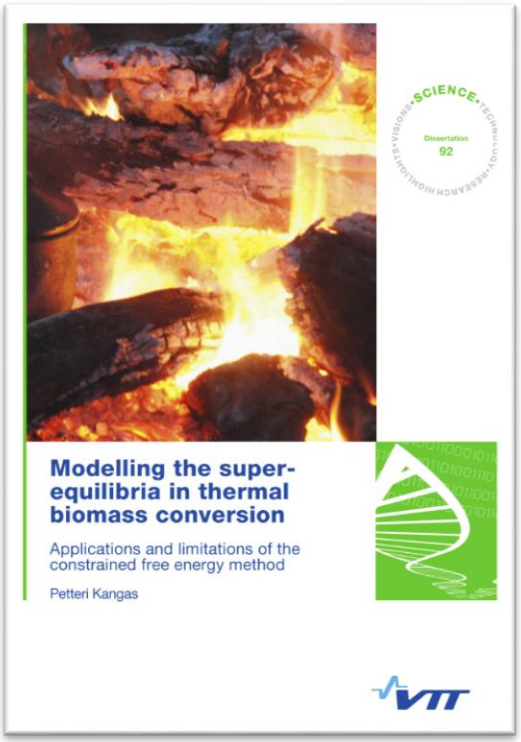


Applications of the constrained Gibbs energy method in modelling thermal biomass conversion.

GTT-Technologies' 17th Annual Users' Meeting, Herzogenrath, Germany, July 1-3, 2015

Petteri Kangas and Pertti Koukkari
VTT Technical Research Centre of Finland

In 2013: CFE for in the kraft recovery boiler modelling presented in GTT Annual Users' meeting

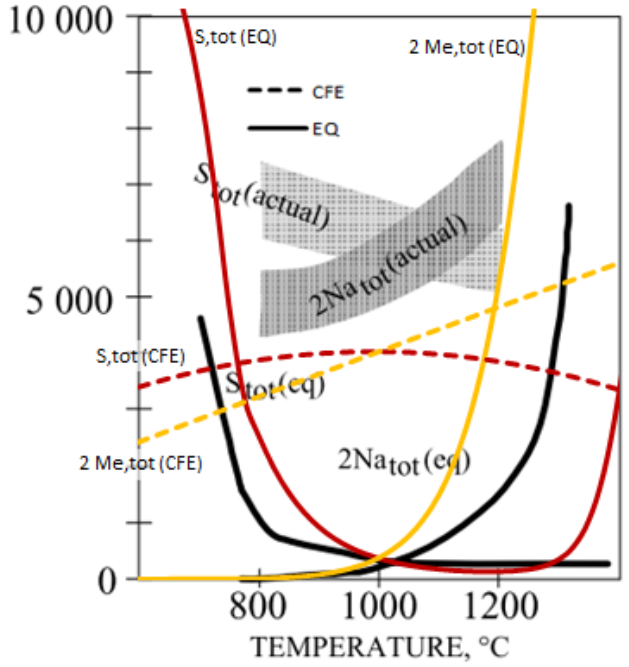


Figure 4. Equilbrium concentrations of S and 2 Me (2 Na + 2 K) in the fume of recovery boiler as a function of temperature. $\lambda_{furnace}$ = 0.7. Volatility: x_{Na} = 10 %, x_S = 30 % at 1000 C. EF_K = 1.4 and EF_{Cl} = 2.5. Reference figure from [1].

Methodology

Methodology – Constrained Free Energy (CFE) method

- CFE is an extension to Gibbs' free energy method where additional immaterial constraints are incorporated to chemical system
- Chemical system can be constrained by extent of reaction, electrochemical potential, surface area or volume
- The distinct benefit of this method lies in the calculation of constrained chemical reactions, enthalpic effects and state properties simultaneously and interdependently
- **ChemSheet** is applied as modelling tool, as it allows extending chemical system with virtual constraints

Table 1. Applications of constrained thermodynamic equilibrium.

Constraint	Application area	Details
Extent of reaction	Combustion	Benzene combustion
	Inorganic chemistry	Anatase-rutile transformation
	Inorganic chemistry	combustion of $TiCl_4$
	Inorganic chemistry	Mercury-chlorine system
	Biochemistry	Reaction pathways
	Papermaking	Calcium chemistry
	Metallic alloys	Para-equilibriums in steel making
	Internal combustion	NO freezing
	Internal combustion	CO freezing
	Internal combustion	Hydrogen combustion
	Internal combustion	Methane combustion
	Internal combustion	Methanol combustion
	Internal combustion	Formaldehyde
	Internal combustion	Ethanol combustion
	Biomass combustion	Black liquor combustion
	Biomass combustion	Biomass gasification
	Biomass combustion	Char gasification
	Biomass combustion	Biomass pyrolysis
	Biomass combustion	Biomass torrefaction
	Combustion	Thermal-NO
	Combustion	Fuel-NO
Electrochemical potential	Papermaking	Aqueous ion exchange
Surface area	Metal alloys	Surface tension
	Metal alloys	Nano-particles
Volume	Papermaking	Fibre - Water -phases

Kangas, P. 2015., Dissertation, Åbo Akademi University

Methodology – Constrained Free Energy (CFE) method

- Non-stoichiometric chemical system is solved by minimising the Gibbs energy with Lagrange method of undetermined multipliers

$$L = G - \pi\Psi = \sum_{k=1}^{K} n_k \mu_k - \sum_{l=1}^{L} \pi_l \left(\sum_{k=1}^{K} \nu_{kl} n_k - b_l \right) \qquad \left(\frac{\partial L}{\partial n_k} \right)_{n_{n \neq k}} = \mu_k - \sum_{l=1}^{L} \pi_l \nu_{kl} = 0 \qquad \left(\frac{\partial L}{\partial \pi_l} \right)_{\pi_{n \neq l}} = \sum_{k=1}^{K} \nu_{kl} n_k - b_l = 0$$

- Additional immaterial components and constituents are implemented into system for applying chemical kinetics

$$\mathrm{N} = \begin{bmatrix} \nu_{1,1} & \cdot & \nu_{1,L} & \nu_{1,L+1} & \cdot & \nu_{1,L+Y} \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \nu_{K,1} & \cdot & \nu_{K,L} & \cdot & \cdot & \cdot \\ 0 & \cdot & 0 & \nu_{K+1,L+1} & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ 0 & \cdot & 0 & \cdot & \cdot & \nu_{K+X,L+Y} \end{bmatrix}$$

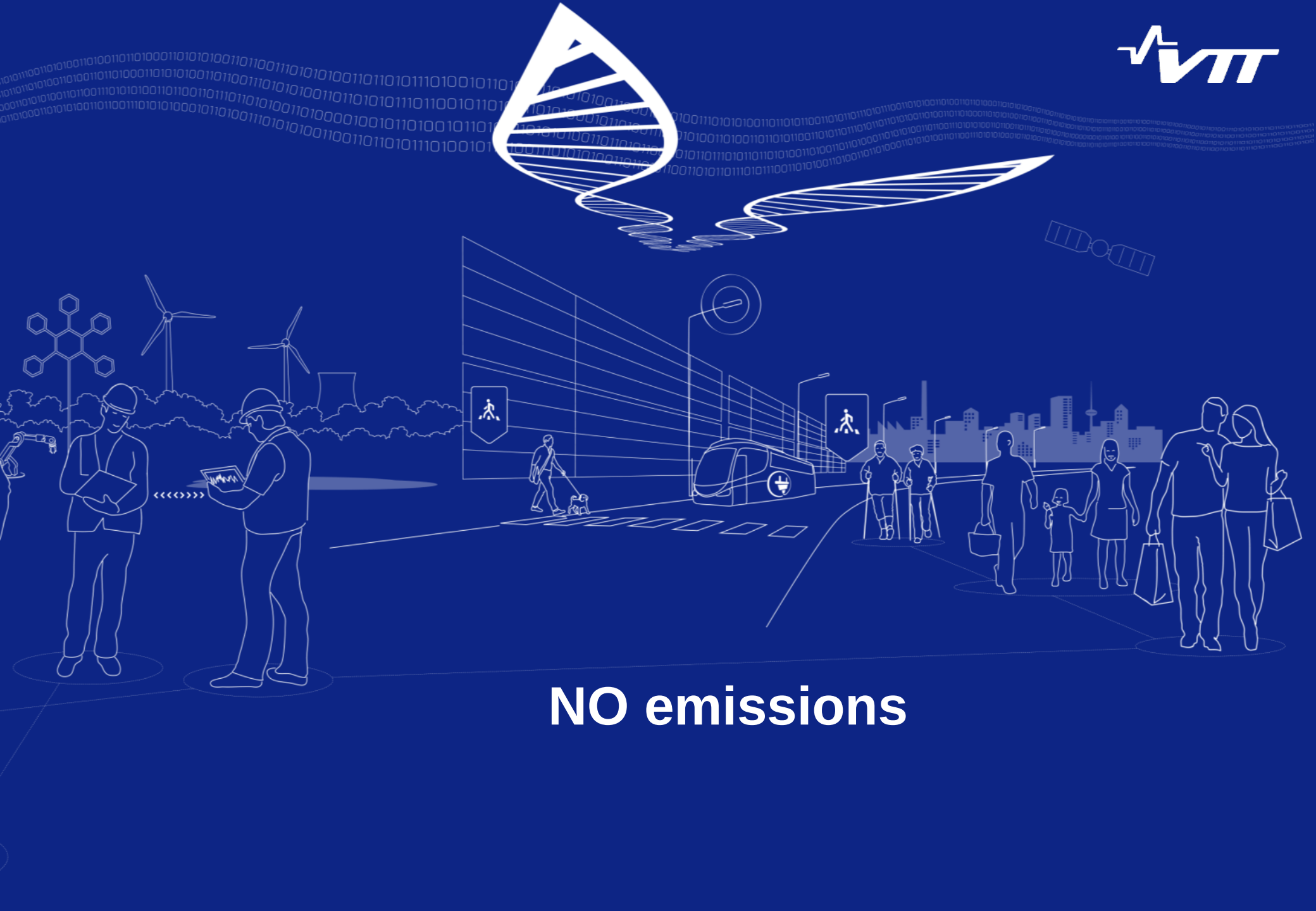
- Chemical system is constrained by defining immaterial constraints based on the extent of reactions.

$\xi_x = C_x$ (constant value)

$\xi_x = f_x(T)$ (temperature dependent model)

$\xi_x = \int_0^t r_x dt$ (global and elementary kinetic reactions)

$$r_x = r_{xf} - r_{xr} \qquad r = k \prod_b [j]^{a_b} \qquad k = AT^B \exp^{(-E/RT)}$$


NO emissions

Modelling NO emissions with CFE

Aim:

- Evaluate how reaction kinetic models could be implemented into CFE methodology
- Model thermal and fuel NO emissions

CFE method

- Constrained thermodynamic equilibrium with major kinetic reactions implemented [2,3]
- ChemSheet [15] applied as modelling tool

Reference and validation

- Pure kinetic model of combustion and NO formation ÅA mechanism
- 371 kinetic reactions applied
- ChemKin applied as modelling tool

(i) NO emissions - Dry air
Extended stoichiometric matrix for CFE

Table - Extended stoichiometric matrix; Total 60 gaseous species and 2 immaterial constraints; r_1: $N_2 + O \leftrightarrow NO + N$; r_2: $N + O_2 \leftrightarrow NO + O$

Phase	Constituent	O	N	N*	NO*
Gas	O	1			
	O_2	2			
	N		1	1	
	N_2		2		
	NO	1	1		1
	NO_2	2	1		
Constraints	r_1: $N_2 + O \leftrightarrow NO + N$			1	1
	r_2: $N + O_2 \leftrightarrow NO + O$			-1	1

(i) NO emissions - Dry air

- 'Synthetic' air: 21 v-% of O_2 and 79 v-% of N_2.
- No moisture.
- Heating air (no combustion here)
- Temperature range: 1200-2200°C
- Pressure 1 bar
- Zeldovich mechanism applied
  - 2 reaction limiting NO formation
    - r_1: $N_2 + O \leftrightarrow NO + N$
    - r_2: $N + O_2 \leftrightarrow NO + O$
  - Local equilibrium considered otherwise (e.g. amount of radical O)

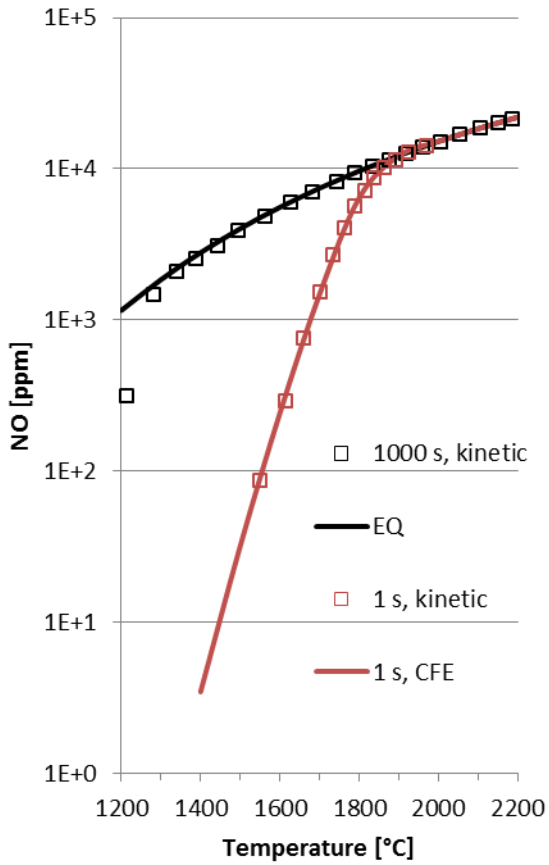


Figure 6. NO formation in dry air.

=> **CFE model agrees with kinetic model when dry air is considered**

(ii) NO emissions - Combustion of CO
Extending stoichiometric matrix

Table 3. Extended stoichiometric matrix; Total 60 gaseous species and 3 immaterial constraints;
r_1: $N_2 + O \leftrightarrow NO + N$; r_2: $CO + O_2 \leftrightarrow CO_2 + O$; r_3: $CO + O + M \leftrightarrow CO_2 + M$

Phase	Constituent	O	C	N	Ar	NO*	O*	CO*
Gas	CO	1	1					
	CO_2	2	1					
	O	1					1	
	N			1		2		
	N_2			2				
	NO	1		1				1
	Ar				1			
	…							
Constraints	r_1: $N_2 + O \leftrightarrow NO + N$					1		
	r_2: $CO + O_2 \leftrightarrow CO_2 + O$						1	-1
	r_3: $CO + O + M \leftrightarrow CO_2 + M$						1	-1

(ii) NO emissions - Combustion of CO; Dry air

- Combustion of carbon monoxide
- Excess air: $\lambda = 1.2$
- Dry air: 21 v-% of O_2 and 79 v-% of N_2
- Two additional constraints for CO + O:
  - r_2: $CO + O_2 \leftrightarrow CO_2 + O$
  - r_3: $CO + O + M \leftrightarrow CO_2 + M$
- Simplified Zeldovich mechanism for N:
  - r_1: $N_2 + O \leftrightarrow NO + N$

$\Rightarrow$NO formation during combustion (CFE) agrees with reference model (pure kinetics) when dry air is considered

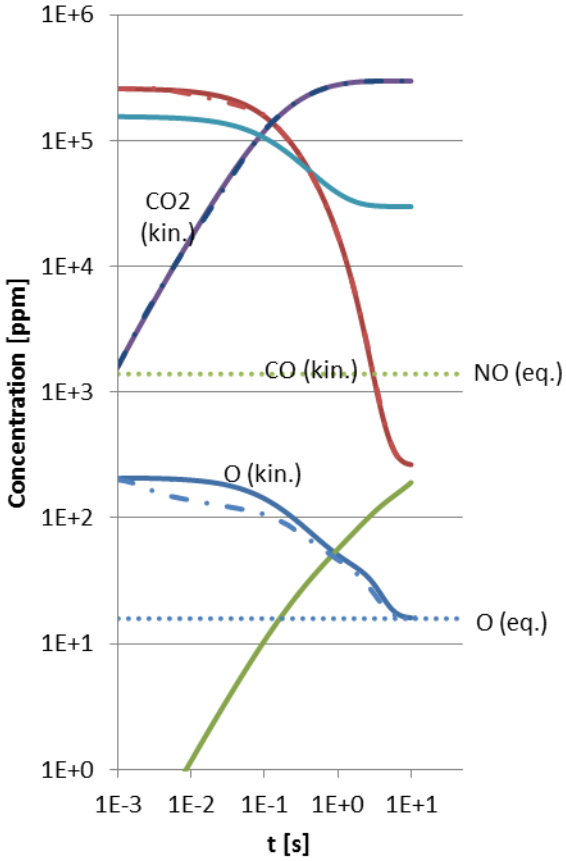


Figure 13. NO formation; CO combustion; 1500°C; Dry air;

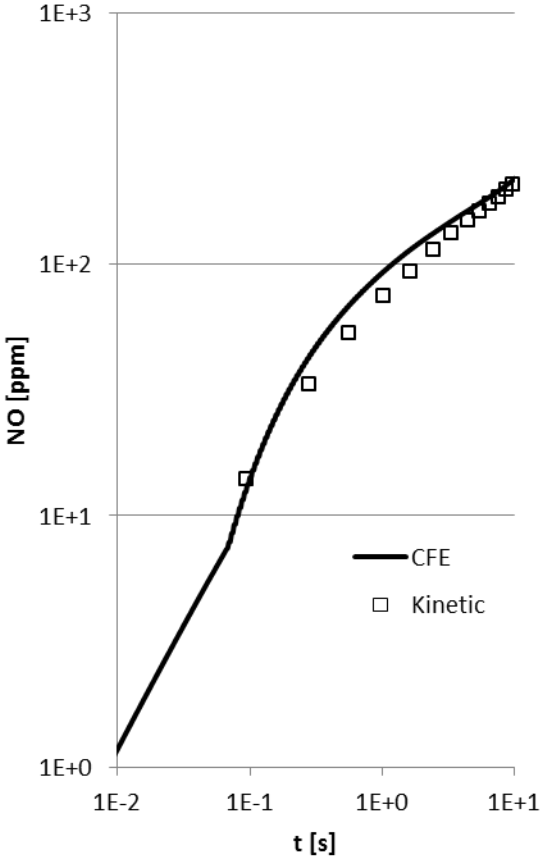


Figure 14. NO formation; CO combustion; 1500°C; Dry air;

(iii) NO emissions - Combustion of CO; Wet air

- Rapid combustion if moisture present
- Super-equilibrium of O-, H-, and OH-radicals formed

⇒Additional elementary reactions needed (O-, H- and OH- radicals)

⇒Additional constraints implemented to calculation and stoichiometric matrix is extended again.

Table 4. Elementary reactions for CO, wet air.

Constituent	Reaction
CO	$CO+OH \leftrightarrow CO_2+H$
	$CO+O+M \leftrightarrow CO_2+M$
H	$CO+OH \leftrightarrow CO_2+H$
	$O+OH \leftrightarrow H+O_2$
OH	$CO+OH \leftrightarrow CO_2+H$
	$O+OH \leftrightarrow H+O_2$
	$OH+OH \leftrightarrow H_2O+O$
O	$O+OH \leftrightarrow H+O_2$
	$CO+O+M \leftrightarrow CO_2+M$
	$OH+OH \leftrightarrow H_2O+O$

(iii) NO emissions - Combustion of CO; wet air
Extending stoichiometric matrix

Table 5. Extended stoichiometric matrix; Total 60 gaseous species and 5 immaterial constraints;

Phase	Constituent	O	H	C	N	Ar	CO*	NO*	O*	H*	OH*
Gas	CO	1		1			1				
	CO_2	2		1							
	H_2		2								
	H_2O	1	2								
	O	1							1		
	H				1					1	
	OH				2						1
	NO	1			1			1			
	Ar					1					
Constraints	r_1: $\Sigma\Delta r_{CO}$						1				
	r_2: $\Sigma\Delta r_{NO}$							1			
	r_3: $\Sigma\Delta r_{O}$								1		
	r_4: $\Sigma\Delta r_{H}$									1	
	r_5: $\Sigma\Delta r_{OH}$										1

(iii) NO emissions - Combustion of CO; Quasi steady-state assumption

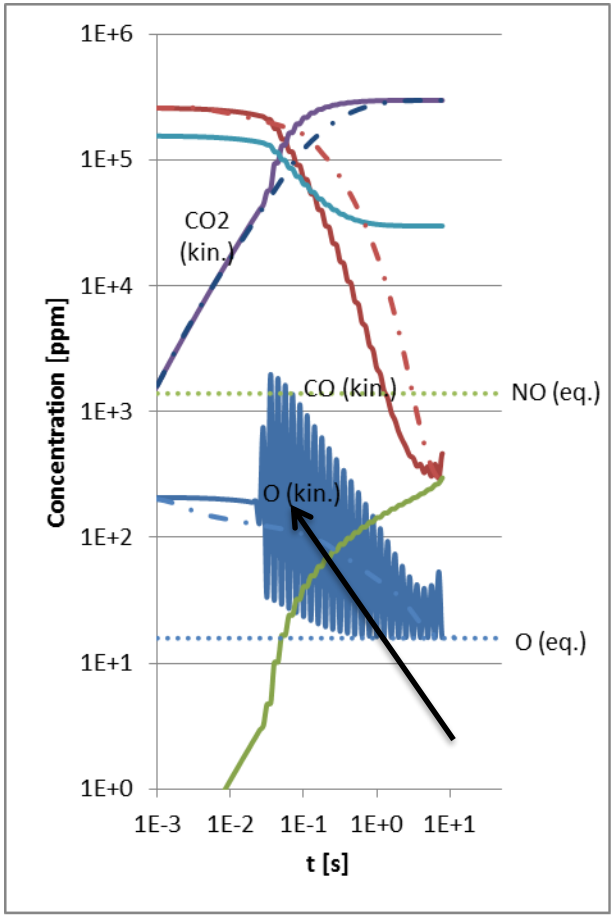


Figure 16. NO formation; Euler-method

- Two competing reactions (O-radical)
  - r_2: $CO+O_2 \leftrightarrow CO_2+O$
  - r_3: $CO+O+M \leftrightarrow CO_2+M$
- Oscillation, when $\Delta r_2 \approx \Delta r_3 \approx n_O$
- One possible solution is quasi steady-state assumption
  - d[O]/dt=0=>
  - $k_3[CO][O][M]=k_2[CO][O_2]$
  - $[O]=k_2/k_3*[O_2]/[M]$

⇒Improves stability

⇒Fails close to O(eq.)

Quasi steady-state

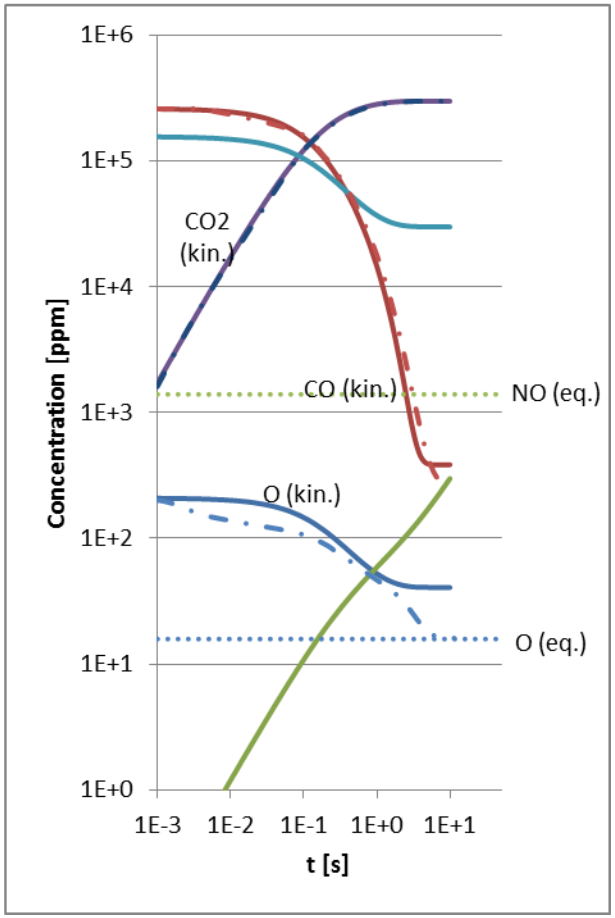


Figure 18. NO formation; Steady-state assumption.

(iv) NO emissions - Combustion of CH_4

- Larger amount of reactions are involved for CH_4 combustion and related
- Several hydrocarbons involved for NO_X formation

⇒Need for extending stoichiometric matric further

⇒Several competing reactions could cause numerical problems during simulation; stiff chemical system

⇒**Global kinetic model applied** instead of models based on the elementary kinetic reactions

Table 6. Applied global kinetic model

Reaction	
R1	$N+NO \leftrightarrow N_2+O$
R2	$CH_4+1½O_2 \rightarrow CO+2H_2$
R3	$CH_4+H_2O \rightarrow CO+3H_2$
R4	$H_2+1½O_2 \rightarrow H_2O$
R5	$H_2O \rightarrow H_2+1½O_2$
R6	$CO+H_2O \leftrightarrow CO_2+H_2$
R7	$NH_3+O_2 \rightarrow NO+H_2O+1½H_2$
R8	$NH_3+NO \rightarrow N_2+H_2O+1½H_2$

(iv) NO emissions - Combustion of CH_4

Table 6. Extended stoichiometric matrix; Total 60 gaseous species and 5 immaterial constraints;

Phase	Constituent	O	H	C	N	Ar	CH_4*	CO*	NH_3*	NO*	H_2*
Gas	CO	1		1				1			
	CO_2	2		1							
	H_2		2								1
	H_2O	1	2								
	O	1									
	CH_4		4	1			1				
	NH_3		3		1				1		
	NO	1			1					1	
	Ar					1					
	…										
Constraints	r_1: $\Sigma\Delta r_{CH4}$						1				
	r_2: $\Sigma\Delta r_{CO}$							1			
	r_3: $\Sigma\Delta r_{NH3}$								1		
	r_4: $\Sigma\Delta r_{NO}$									1	
	r_5: $\Sigma\Delta r_{H2}$										1

(iv) NO emissions - Combustion of CH_4

- Separate models for:
  - oxidation of methane
  - oxidation of carbon monoxide
  - oxidation of ammonia
- CFE method is applicable for modelling fuel NO emissions if global kinetic models are used

=> However timing is slightly off as model does not consider radical build-up

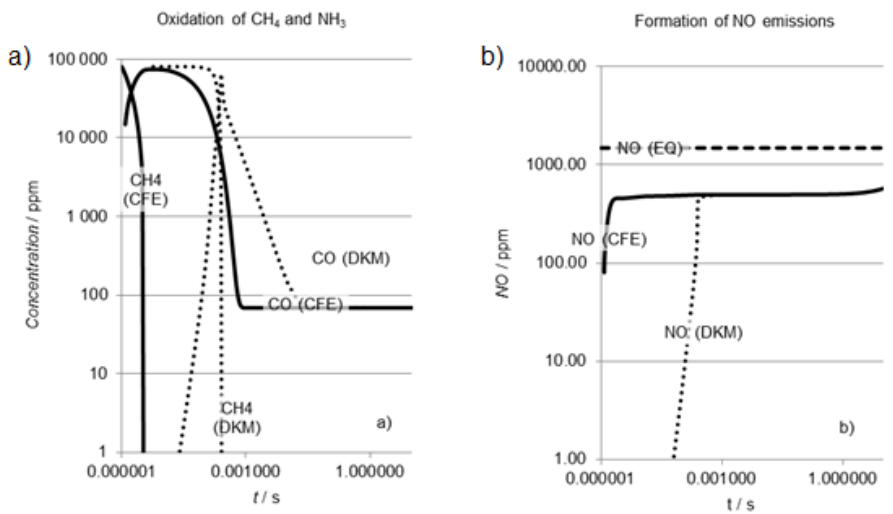


Figure 12. Fuel NO emissions [IV]. Biomass is modelled as methane, and nitrogen in biomass as ammonia. a) Combustion of hydrocarbons. b) NO emissions. The temperature is 1,500°C and λ=1.2. Here EQ refers to the equilibrium concentrations, CFE to the super-equilibrium concentrations and DKM to the validation data obtained from the detailed kinetic model.

Gasification

Gasification - Background

- During biomass gasification light hydrocarbons (e.g. : CH_4, C_2H_2, C_2H_4, C_2H_6, C_3H_8, C_6H_6), ammonia, tars and char are formed among syngas.
- This affects on the composition of major species in syngas (CO, CO_2, H_2, H_2O)

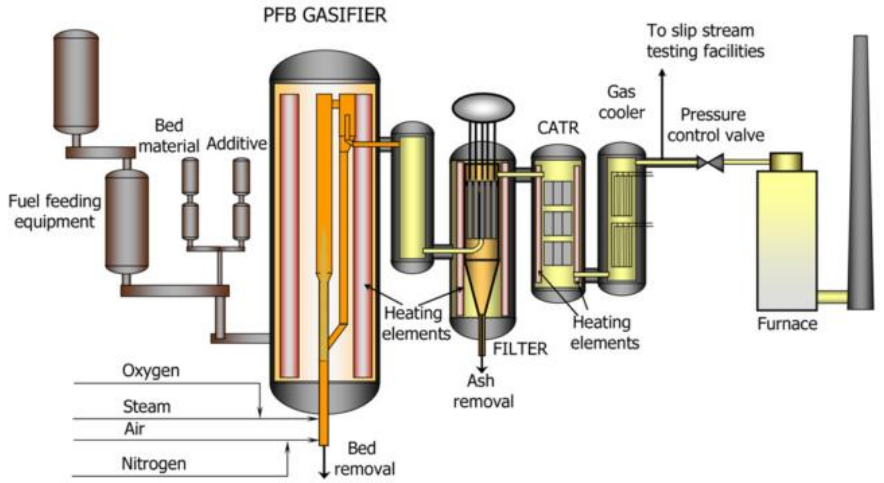


Figure 1. E

- Assuming thermodynamic equilibrium the 'super-equilibrium' of hydrocarbons, ammonia, tar and char is not taken into account
- Phenomena based and semi-empirical models have been developed for describing the super-equilibrium
- Phenomena based models become tedious with several parameters. Current semi-empirical models provide only ad-hoc solution.
- **Aim: evaluate the use of experimental models with CFE and to study different model structures**

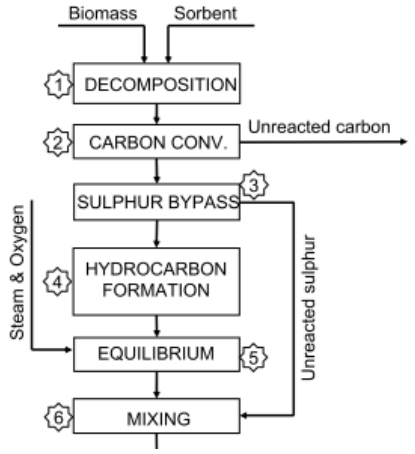


Figure 2. Example of multi-step semi-empirical model.

Gasification - Cases with different sets of constraints

- **EQ**: Thermodynamic equilibrium is used as base case**.** No additional constraints are defined.
- **Super-EQ1:** super-equilibrium where carbon conversion, tar and ammonia formation are defined is studied. In addition the amount of carbon in volatile hydrocarbons (CH_4, C_2H_2, C_2H_4, C_2H_6, C_3H_8 and C_6H_6) is fixed.
- **Super-EQ2** where previous case is extended by introducing additional constraint for the amount of hydrogen in volatile hydrocarbons.
- **Super-EQ3** replaces the hydrogen constraint by introducing a constraint for CH_4
- **Super-EQ4** defines the amount of carbon bound to unsaturated hydrocarbons hydrocarbons (C_2H_2 and C_2H_4) and benzene (C_6H_6)
- **Super-EQ5** introduces a fully constrained system where the amount of every hydrocarbon constituent is defined by empirical models. However the water-gas shift reaction is not constrained, but local equilibrium is assumed.

Gasification – Extended stoichiometric matrix

- Components: C-O-H-N-S
- Phases: gas (14 constituents), biomass (4), water, char and ash.
- Extending matrix with CFE method:
  - 12 virtual components
  - 12 virtual constituents
- Extended model is used to predict the super-equilibrium of char, tar, ammonia, and light hydrocarbons in syngas.
- **Different combinations of immaterial constraints are evaluated from thermodynamic equilibrium to fully constrained system**

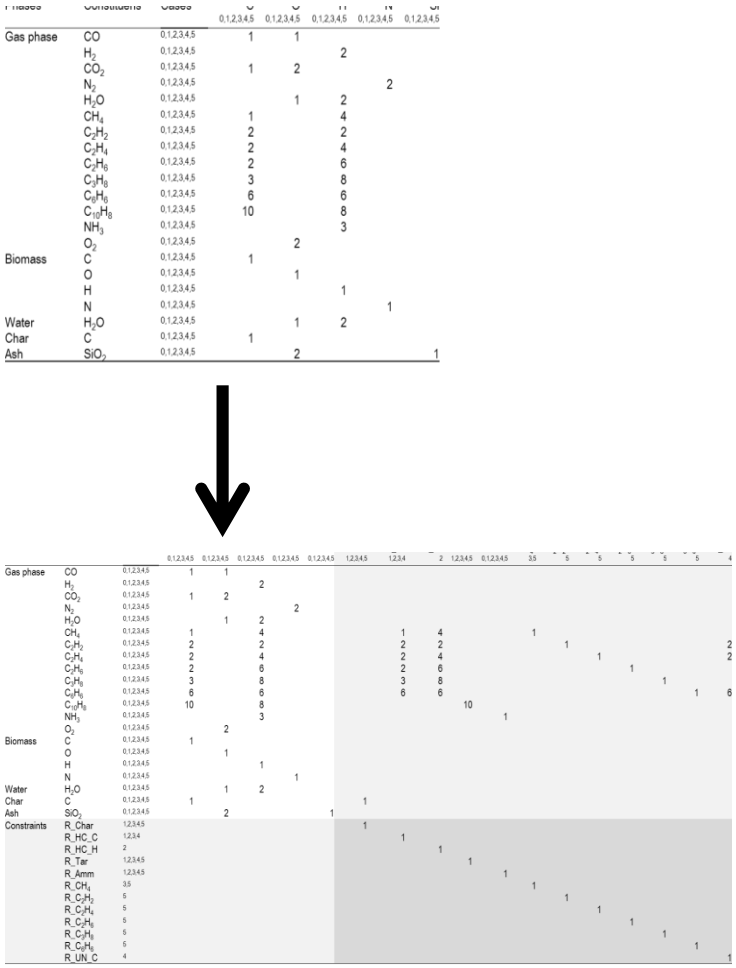


Figure 6. Extending chemical system with additional immaterial constraints.

Gasification - EQ - stoichiometric matrix

Table 1. Extended stoichiometric matrix C-O-H-N-Si system.

Phases	Constituents	Cases	C	O	H	N	Si
			0,1,2,3,4,5	0,1,2,3,4,5	0,1,2,3,4,5	0,1,2,3,4,5	0,1,2,3,4,5
Gas phase	CO	0,1,2,3,4,5	1	1			
	H_2	0,1,2,3,4,5			2		
	CO_2	0,1,2,3,4,5	1	2			
	N_2	0,1,2,3,4,5				2	
	H_2O	0,1,2,3,4,5		1	2		
	CH_4	0,1,2,3,4,5	1		4		
	C_2H_2	0,1,2,3,4,5	2		2		
	C_2H_4	0,1,2,3,4,5	2		4		
	C_2H_6	0,1,2,3,4,5	2		6		
	C_3H_8	0,1,2,3,4,5	3		8		
	C_6H_6	0,1,2,3,4,5	6		6		
	$C_{10}H_8$	0,1,2,3,4,5	10		8		
	NH_3	0,1,2,3,4,5			3		
	O_2	0,1,2,3,4,5		2			
Biomass	C	0,1,2,3,4,5	1				
	O	0,1,2,3,4,5		1			
	H	0,1,2,3,4,5			1		
	N	0,1,2,3,4,5				1	
Water	H_2O	0,1,2,3,4,5		1	2		
Char	C	0,1,2,3,4,5	1				
Ash	SiO_2	0,1,2,3,4,5		2			1

No additional virtual constraints

Gasification – Super-EQ1 - Extended stoichiometric matrix

Table 2. Extended stoichiometric matrix. C-O-H-N-Si system.

Phases	Constituents	Cases	C	O	H	N	Si	Char*	HC_C*	Tar*	Amm*
			0,1,2,3,4,5	0,1,2,3,4,5	0,1,2,3,4,5	0,1,2,3,4,5	0,1,2,3,4,5	1,2,3,4,5	1,2,3,4	1,2,3,4,5	0,1,2,3,4,5
Gas phase	CO	0,1,2,3,4,5	1	1							
	H_2	0,1,2,3,4,5			2						
	CO_2	0,1,2,3,4,5	1	2							
	N_2	0,1,2,3,4,5				2					
	H_2O	0,1,2,3,4,5		1	2						
	CH_4	0,1,2,3,4,5	1		4				1		
	C_2H_2	0,1,2,3,4,5	2		2				2		
	C_2H_4	0,1,2,3,4,5	2		4				2		
	C_2H_6	0,1,2,3,4,5	2		6				2		
	C_3H_8	0,1,2,3,4,5	3		8				3		
	C_6H_6	0,1,2,3,4,5	6		6				6		
	$C_{10}H_8$	0,1,2,3,4,5	10		8					10	
	NH_3	0,1,2,3,4,5			3						1
	O_2	0,1,2,3,4,5		2							
Biomass	C	0,1,2,3,4,5	1								
	O	0,1,2,3,4,5		1							
	H	0,1,2,3,4,5			1						
	N	0,1,2,3,4,5				1					
Water	H_2O	0,1,2,3,4,5		1	2						
Char	C	0,1,2,3,4,5	1					1			
Ash	SiO_2	0,1,2,3,4,5		2			1				
Constraints	R_Char	1,2,3,4,5						1			
	R_HC_C	1,2,3,4							1		
	R_Tar	1,2,3,4,5								1	
	R_Amm	1,2,3,4,5									1

Constraints for char, tar, ammonia, and carbon in hydrocarbons

Gasification – Super-EQ2 - Extended stoichiometric matrix

Table 3. Extended stoichiometric matrix. C-O-H-N-Si system.

Phases	Constituents	Cases	C	O	H	N	Si	Char*	HC_C*	HC_H*	Tar*	Amm*
			0,1,2,3,4,5	0,1,2,3,4,5	0,1,2,3,4,5	0,1,2,3,4,5	0,1,2,3,4,5	1,2,3,4,5	1,2,3,4	2	1,2,3,4,5	0,1,2,3,4,5
Gas phase	CO	0,1,2,3,4,5	1	1								
	H_2	0,1,2,3,4,5			2							
	CO_2	0,1,2,3,4,5	1	2								
	N_2	0,1,2,3,4,5				2						
	H_2O	0,1,2,3,4,5		1	2							
	CH_4	0,1,2,3,4,5	1		4				1	4		
	C_2H_2	0,1,2,3,4,5	2		2				2	2		
	C_2H_4	0,1,2,3,4,5	2		4				2	4		
	C_2H_6	0,1,2,3,4,5	2		6				2	6		
	C_3H_8	0,1,2,3,4,5	3		8				3	8		
	C_6H_6	0,1,2,3,4,5	6		6				6	6		
	$C_{10}H_8$	0,1,2,3,4,5	10		8						10	
	NH_3	0,1,2,3,4,5			3							1
	O_2	0,1,2,3,4,5		2								
Biomass	C	0,1,2,3,4,5	1									
	O	0,1,2,3,4,5		1								
	H	0,1,2,3,4,5			1							
	N	0,1,2,3,4,5				1						
Water	H_2O	0,1,2,3,4,5		1	2							
Char	C	0,1,2,3,4,5	1					1				
Ash	SiO_2	0,1,2,3,4,5		2			1					
Constraints	R_Char	1,2,3,4,5						1				
	R_HC_C	1,2,3,4							1			
	R_HC_H	2								1		
	R_Tar	1,2,3,4,5									1	
	R_Amm	1,2,3,4,5										1

Constraints for char, tar, ammonia, carbon in hydrocarbons and hydrogen in hydrocarbons

Gasification – Super-EQ3 - Extended stoichiometric matrix

Table 4. Extended stoichiometric matrix. C-O-H-N-Si system.

Phases	Constituents	Cases	C	O	H	N	Si	Char*	HC_C*	Tar*	Amm*	CH_4*
			0,1,2,3,4,5	0,1,2,3,4,5	0,1,2,3,4,5	0,1,2,3,4,5	0,1,2,3,4,5	1,2,3,4,5	1,2,3,4	1,2,3,4,5	0,1,2,3,4,5	3,5
Gas phase	CO	0,1,2,3,4,5	1	1								
	H_2	0,1,2,3,4,5			2							
	CO_2	0,1,2,3,4,5	1	2								
	N_2	0,1,2,3,4,5				2						
	H_2O	0,1,2,3,4,5		1	2							
	CH_4	0,1,2,3,4,5	1		4				1			1
	C_2H_2	0,1,2,3,4,5	2		2				2			
	C_2H_4	0,1,2,3,4,5	2		4				2			
	C_2H_6	0,1,2,3,4,5	2		6				2			
	C_3H_8	0,1,2,3,4,5	3		8				3			
	C_6H_6	0,1,2,3,4,5	6		6				6			
	$C_{10}H_8$	0,1,2,3,4,5	10		8					10		
	NH_3	0,1,2,3,4,5			3						1	
	O_2	0,1,2,3,4,5		2								
Biomass	C	0,1,2,3,4,5	1									
	O	0,1,2,3,4,5		1								
	H	0,1,2,3,4,5			1							
	N	0,1,2,3,4,5				1						
Water	H_2O	0,1,2,3,4,5		1	2							
Char	C	0,1,2,3,4,5	1					1				
Ash	SiO_2	0,1,2,3,4,5		2			1					
Constraints	R_Char	1,2,3,4,5						1				
	R_HC_C	1,2,3,4							1			
	R_Tar	1,2,3,4,5								1		
	R_Amm	1,2,3,4,5									1	
	R_CH_4	3,5										1

Constraints for char, tar, ammonia, carbon in hydrocarbons and CH_4

Gasification – Super-EQ4 - Extended stoichiometric matrix

Table 5. Extended stoichiometric matrix. C-O-H-N-Si system.

Phases	Constituents	Cases	C	O	H	N	Si	Char*	HC_C*	Tar*	Amm*	UN_C*
			0,1,2,3,4,5	0,1,2,3,4,5	0,1,2,3,4,5	0,1,2,3,4,5	0,1,2,3,4,5	1,2,3,4,5	1,2,3,4	1,2,3,4,5	0,1,2,3,4,5	4
Gas phase	CO	0,1,2,3,4,5	1	1								
	H_2	0,1,2,3,4,5			2							
	CO_2	0,1,2,3,4,5	1	2								
	N_2	0,1,2,3,4,5				2						
	H_2O	0,1,2,3,4,5		1	2							
	CH_4	0,1,2,3,4,5	1		4				1			
	C_2H_2	0,1,2,3,4,5	2		2				2			2
	C_2H_4	0,1,2,3,4,5	2		4				2			2
	C_2H_6	0,1,2,3,4,5	2		6				2			
	C_3H_8	0,1,2,3,4,5	3		8				3			
	C_6H_6	0,1,2,3,4,5	6		6				6			6
	$C_{10}H_8$	0,1,2,3,4,5	10		8					10		
	NH_3	0,1,2,3,4,5			3						1	
	O_2	0,1,2,3,4,5		2								
Biomass	C	0,1,2,3,4,5	1									
	O	0,1,2,3,4,5		1								
	H	0,1,2,3,4,5			1							
	N	0,1,2,3,4,5				1						
Water	H_2O	0,1,2,3,4,5		1	2							
Char	C	0,1,2,3,4,5	1					1				
Ash	SiO_2	0,1,2,3,4,5		2			1					
Constraints	R_Char	1,2,3,4,5						1				
	R_HC_C	1,2,3,4							1			
	R_Tar	1,2,3,4,5								1		
	R_Amm	1,2,3,4,5									1	
	R_UN_C	4										1

Constraints for char, tar, ammonia, carbon in hydrocarbons and carbon in unsaturated hydrocarbons + aromatics

Gasification – Super-EQ5 - Extended stoichiometric matrix

Table 6. Extended stoichiometric matrix. C-O-H-N-Si system.

Phases	Constituents	Cases	C	O	H	N	Si	Char*	Tar*	Amm*	CH_4*	C_2H_2*	C_2H_4*	C_2H_6*	C_3H_8*	C_6H_6*
			0,1,2,3,4,5	0,1,2,3,4,5	0,1,2,3,4,5	0,1,2,3,4,5	0,1,2,3,4,5	1,2,3,4,5	1,2,3,4,5	0,1,2,3,4,5	3,5	5	5	5	5	5
Gas phase	CO	0,1,2,3,4,5	1	1												
	H_2	0,1,2,3,4,5			2											
	CO_2	0,1,2,3,4,5	1	2												
	N_2	0,1,2,3,4,5				2										
	H_2O	0,1,2,3,4,5		1	2											
	CH_4	0,1,2,3,4,5	1		4						1					
	C_2H_2	0,1,2,3,4,5	2		2							1				
	C_2H_4	0,1,2,3,4,5	2		4								1			
	C_2H_6	0,1,2,3,4,5	2		6									1		
	C_3H_8	0,1,2,3,4,5	3		8										1	
	C_6H_6	0,1,2,3,4,5	6		6											1
	$C_{10}H_8$	0,1,2,3,4,5	10		8				10							
	NH_3	0,1,2,3,4,5			3					1						
	O_2	0,1,2,3,4,5		2												
Biomass	C	0,1,2,3,4,5	1													
	O	0,1,2,3,4,5		1												
	H	0,1,2,3,4,5			1											
	N	0,1,2,3,4,5				1										
Water	H_2O	0,1,2,3,4,5		1	2											
Char	C	0,1,2,3,4,5	1					1								
Ash	SiO_2	0,1,2,3,4,5		2			1									
Constraints	R_Char	1,2,3,4,5						1								
	R_Tar	1,2,3,4,5							1							
	R_Amm	1,2,3,4,5								1						
	R_CH_4	3,5									1					
	$R\_C_2H_2$	5										1				
	$R\_C_2H_4$	5											1			
	$R\_C_2H_6$	5												1		
	$R\_C_3H_8$	5													1	
	$R\_C_6H_6$	5														1

Constraints for char, tar, ammonia, CH_4, C_2H_2, C_2H_4, C_2H_6, C_3H_8 and C_6H_6

Gasification – Full extended stoichiometric matrix

Table 7. Extended stoichiometric matrix. C-O-H-N-Si system.

Phases	Constituents	Cases	C	O	H	N	Si	Char*	HC_C*	HC_H*	Tar*	Amm*	CH_4*	C_2H_2*	C_2H_4*	C_2H_6*	C_3H_8*	C_6H_6*	UN_C*
			0,1,2,3,4,5	0,1,2,3,4,5	0,1,2,3,4,5	0,1,2,3,4,5	0,1,2,3,4,5	1,2,3,4,5	1,2,3,4	2	1,2,3,4,5	0,1,2,3,4,5	3,5	5	5	5	5	5	4
Gas phase	CO	0,1,2,3,4,5	1	1															
	H_2	0,1,2,3,4,5			2														
	CO_2	0,1,2,3,4,5	1	2															
	N_2	0,1,2,3,4,5				2													
	H_2O	0,1,2,3,4,5		1	2														
	CH_4	0,1,2,3,4,5	1		4				1	4			1						
	C_2H_2	0,1,2,3,4,5	2		2				2	2				1					2
	C_2H_4	0,1,2,3,4,5	2		4				2	4					1				2
	C_2H_6	0,1,2,3,4,5	2		6				2	6						1			
	C_3H_8	0,1,2,3,4,5	3		8				3	8							1		
	C_6H_6	0,1,2,3,4,5	6		6				6	6								1	6
	$C_{10}H_8$	0,1,2,3,4,5	10		8						10								
	NH_3	0,1,2,3,4,5			3							1							
	O_2	0,1,2,3,4,5		2															
Biomass	C	0,1,2,3,4,5	1																
	O	0,1,2,3,4,5		1															
	H	0,1,2,3,4,5			1														
	N	0,1,2,3,4,5				1													
Water	H_2O	0,1,2,3,4,5		1	2														
Char	C	0,1,2,3,4,5	1					1											
Ash	SiO_2	0,1,2,3,4,5		2			1												
Constraints	R_Char	1,2,3,4,5						1											
	R_HC_C	1,2,3,4							1										
	R_HC_H	2								1									
	R_Tar	1,2,3,4,5									1								
	R_Amm	1,2,3,4,5										1							
	R_CH_4	3,5											1						
	$R\_C_2H_2$	5												1					
	$R\_C_2H_4$	5													1				
	$R\_C_2H_6$	5														1			
	$R\_C_3H_8$	5															1		
	$R\_C_6H_6$	5																1	
	R_UN_C	4																	1

Gasification – Applied constraints

- Temperature dependent constraints:
  - carbon in char
  - carbon in hydrocarbons
  - hydrogen in hydrocarbons
  - carbon in unsaturated and aromatics
  - carbon in CH_4,C_2H_2,C_2H_4,C_2H_6, C_3H_8
- Constant values:
  - carbon in tar
  - nitrogen in ammonia
  - carbon in C_6H_6
- Models based on empirical data.

Table 8. Applied constraints for SuperEQ1 – SuperEQ5 cases. Experimental model is taken from literature.

Constraint	Unit	Expression	Case
C in char	[mol/kg $_{\text{carbon in dry biomass}}$]	71.664+0.012906*T	1,2,3,4,5
C in tar	[mol/kg $_{\text{dry biomass}}$]	3.0	1,2,3,4,5
N in ammonia	[mol/kg $_{\text{dry biomass}}$]	0.042	1,2,3,4,5
C in hydrocarbons	[mol/kg $_{\text{dry biomass}}$]	17.642 - 0.009545*T	1,2,3
H in hydrocarbons	[mol/kg $_{\text{dry biomass}}$]	50.376 - 0.02732*T	2
C in unsaturated and aromatic	[mol/kg $_{\text{dry biomass}}$]	7.7231 - 0.00408*T	4
CH_4	[mol/kg $_{\text{dry biomass}}$]	7.074-0.003*T	3,5
C_2H_2	[mol/kg $_{\text{dry biomass}}$]	0.06454-0.00004*T	5
C_2H_4	[mol/kg $_{\text{dry biomass}}$]	2.987-0.002*T	5
C_2H_6	[mol/kg $_{\text{dry biomass}}$]	1.196-0.001*T	5
C_3H_8	[mol/kg $_{\text{dry biomass}}$]	0.150921-0.000155*T	5
C_6H_6	[mol/kg $_{\text{dry biomass}}$]	0.27	5

Gasification – Validation

- Five different gasification setups modelled (A-E)
- Six different model construction evaluated (Cases EQ, Super-EQ1-Super-EQ5)

Table 9. Validation data. Nitrogen removed. Data from [1].

		A	B	C	D	E
C in dry biomass	[w-%]	50.7	50.7	50.7	51.3	51.1
H in dry biomass	[w-%]	6.2	6.2	6.2	6.1	6.1
N in dry biomass	[w-%]	0.1	0.1	0.1	0.5	0.1
O in dry biomass	[w-%]	42.8	42.8	42.8	39.5	42.3
Ash in dry biomass	[w-%]	0.2	0.2	0.2	2.6	0.4
Fuel moisture	[%]	6.9	6.9	6.9	10.4	7.4
Gasifier temp	[C]	823	838	886	830	868
Pressure	[MPa]	0.250	0.250	0.250	0.250	0.250
Oxygen-to-fuel ratio	[kg/kg dry fuel]	0.31	0.37	0.42	0.37	0.46
Steam-to-fuel ratio	[kg/kg dry fuel]	0.5	0.54	0.54	0.54	0.75
CO	[v-%]	0.144	0.132	0.133	0.122	0.103
CO_2	[v-%]	0.211	0.220	0.222	0.222	0.207
H_2	[v-%]	0.167	0.154	0.156	0.167	0.149
CH_4	[v-%]	0.056	0.055	0.056	0.056	0.046
H_2O	[v-%]	0.400	0.418	0.411	0.411	0.483

Gasification – Validation: Measured vs. modelled syngas components (CO, H_2O, CO_2, H_2 and CH_4)

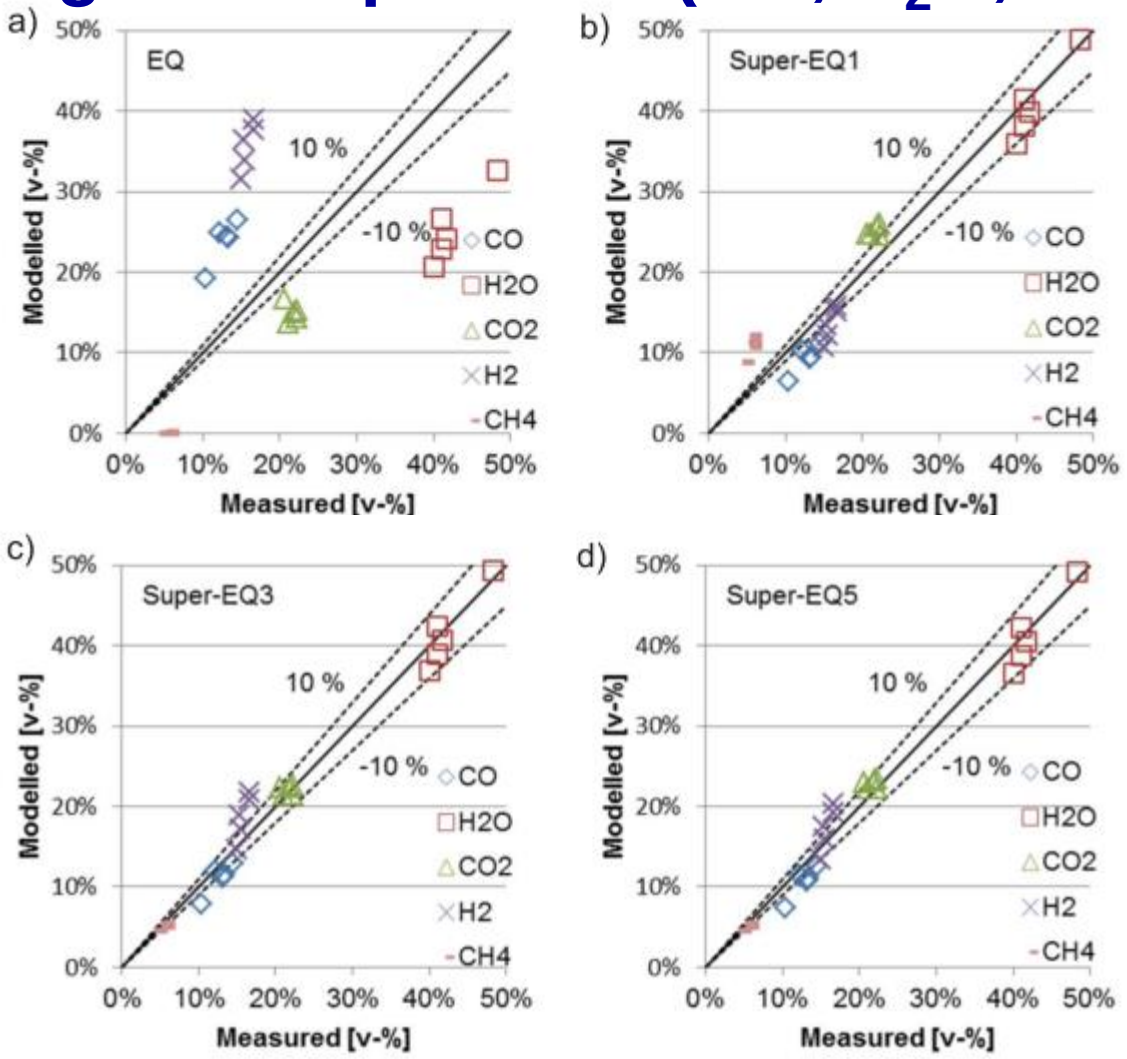


Figure 7. Biomass gasification and major synthesis gas species (CO, H_2O, CO_2, H_2 and CH_4) [II]. Four different models structures presented: a) Thermodynamic equilibrium without constraints. b) Carbon conversion, tar and ammonia formation and the total amount of light hydrocarbons are constrained. c) An additional constraint for methane is defined. d) The amount of every hydrocarbon is constrained and only water-gas is considered as local equilibrium. Validation data is obtained from [41].

Ref: Kangas, P., et al, 2014.. Fuel 129, 86–94. doi:10.1016/j.fuel.2014.03.034

Gasification - Validation of CFE model with other gasifiers

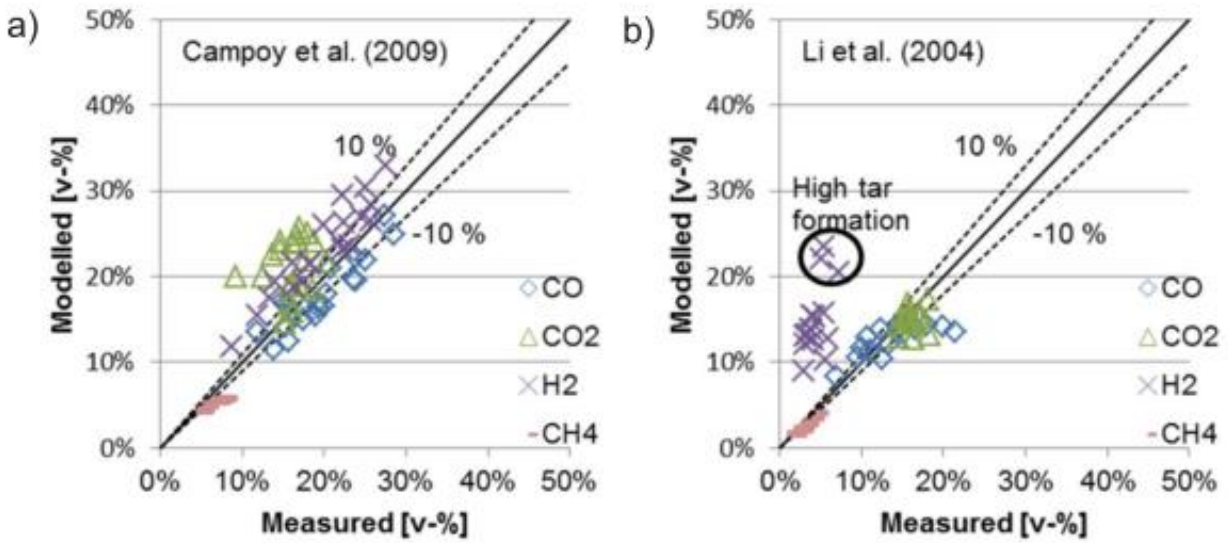


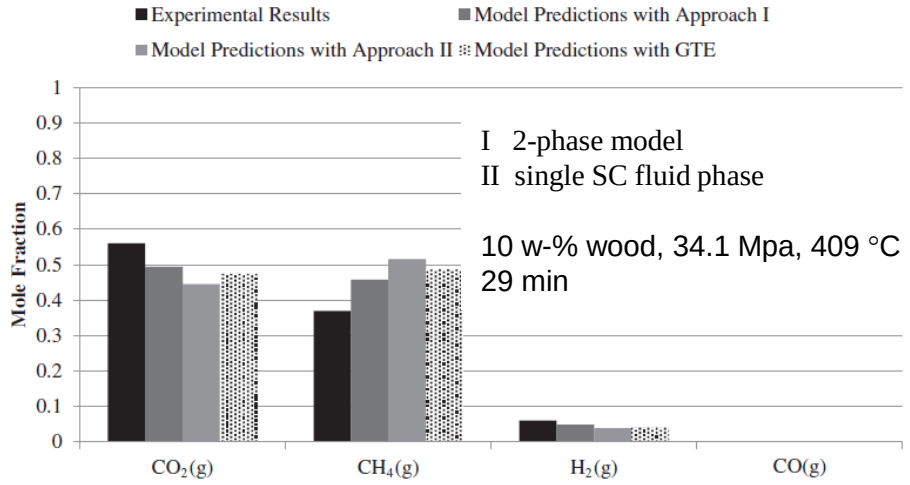
Figure 8. Validation of the biomass gasification model [II] in a) an air/steam-blown fluidised bed gasifier and in b) an air-blown circulating bed gasifier. Major syngas components (CO, CO_2, H_2 and CH_4) in dry gas are presented. Validation data of is obtained from [104,105].

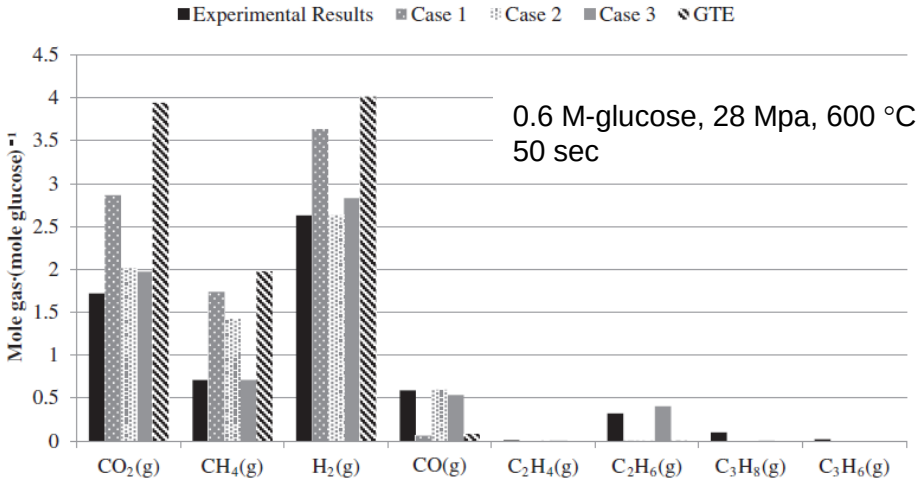
Ref: Kangas, P., et al, 2014.. Fuel 129, 86–94. doi:10.1016/j.fuel.2014.03.034

In Delft: Biomass gasification in supercritical water

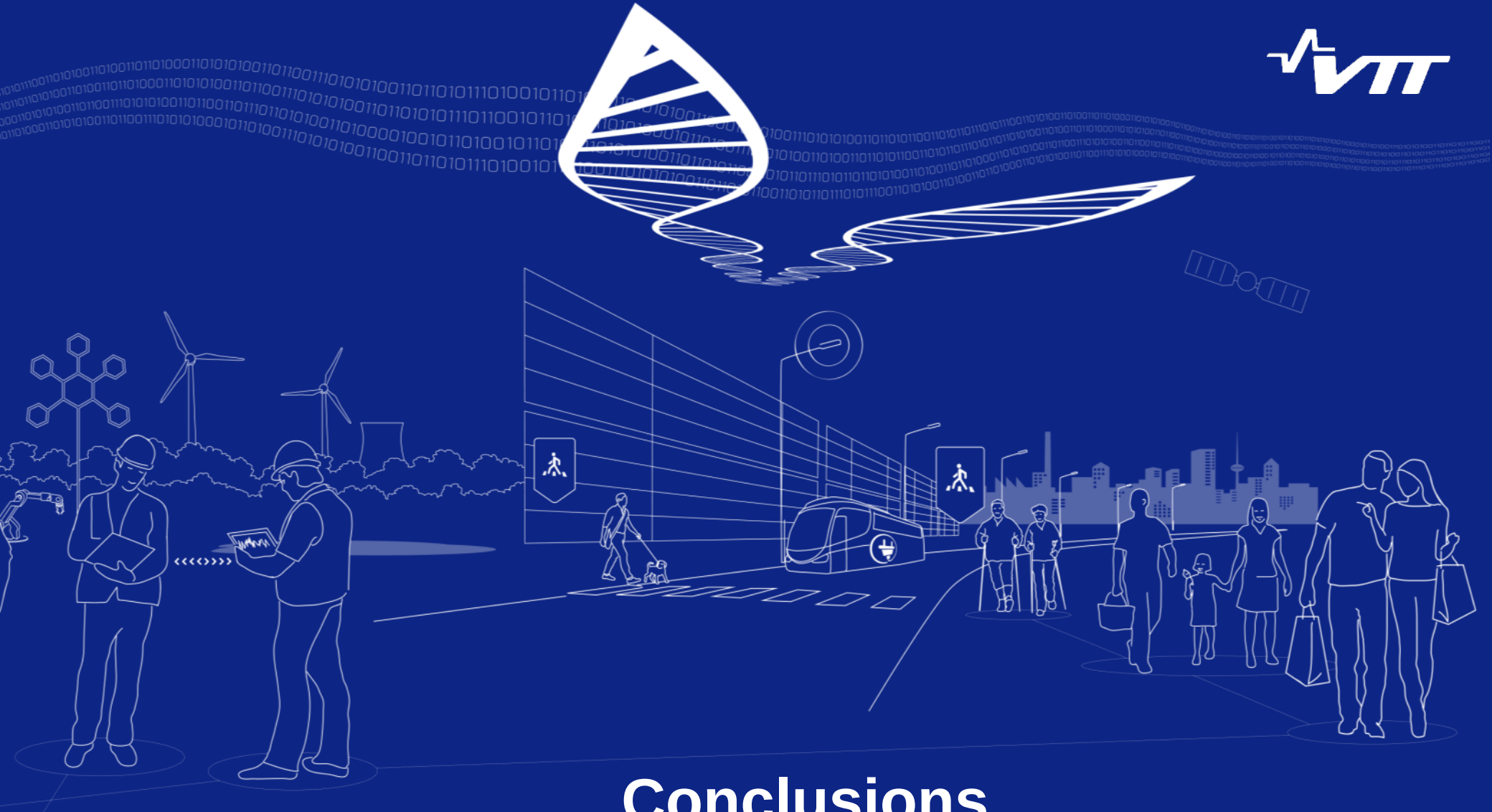
Table B.1
The constraints that have been used for the different cases shown in Figs. 1–9.

Figures	Constraints							
		CGE	DCC	HGE	H_2 amount	CH_4 amount	CO_2 amount	C_2H_6 amount
Fig. 1	Approach I	×	×					
	Approach II	×	×					
	GTE							
Fig. 2	Approach I	×	×					
	Approach II	×	×					
	GTE							
Fig. 3	Approach I	×	×					
	Approach II	×	×					
	GTE							
Fig. 4	Approach I	×	×					
	Approach II	×	×					
	GTE							
Fig. 5		×	×					
Fig. 6	Case 1	×						
	Case 2	×		×	×			
	Case 3	×		×		×		
	GTE							
Fig. 7	Case 1	×						
	Case 2	×			×			
	Case 3	×				×		
Fig. 8	Case 1	×						
	Case 2	×			×			
	Case 3	×				×		
Fig. 9	Case 1	×			×	×		
	Case 2	×			×	×	×	
	Case 3	×			×	×		×





Yakaboylu,O. et al., Fuel Processing Technology, 138, (2015), 74-85



Conclusions

Conclusions – this study

- CFE is successfully applied for modelling biomass gasification and NO emissions
- Experimental model, global kinetic models and reactions based elementary kinetic reactions can be implemented as constraints in CFE calculation
- Requires less parameters than a mechanistic kinetic approach.
- Best result are achieved when moderate amount of reactions are limiting the system.

Table 2. Applications and type of applied constraints.

Applications	**Types of constraints**			
	Constant values	Experimental Models	Global kinetic models	Models based on elementary kinetic reactions
Torrefaction			+ Applicable for char conversion [I] - Not feasible for predicting gaseous phase [I]	
Pyrolysis			+ Applicable for char conversion [I] - Not feasible for predicting gaseous phase [I]	
Gasification	+ Applicable to predicting, tar, and ammonia [II]	+ Applicable to predicting methane and char [II]	+ Applicable for char gasification [I]	
Recovery boiler	+ Applicable to the enrichment of alkali metals, sulfur and chlorine [III]			
NO emissions			+ Applicable for Fuel NO emissions [IV]	± Plausible for Thermal NO emissions [IV] - Not feasible for Fuel NO emissions [IV]

+ implies advantages in applying CFE method; - implies drawbacks in applying CFE method; ± indicates possibilities of using CFE method

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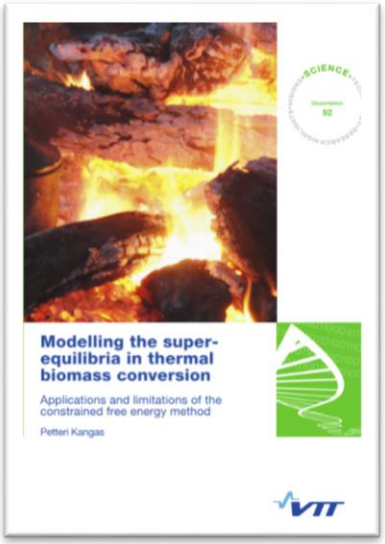
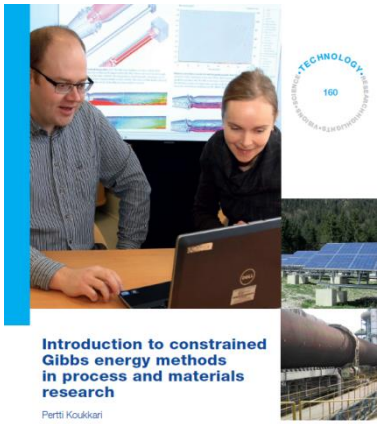
Conclusions - Other uses of kinetic constraints

- In chemical and metallurgical reactors for improved control of autogenic energy efficiency (up to 40 % savings in energy and/or CO_2 release)
- In rotary drums and other furnaces for replacement of fossil fuels with biofuel
- In pulp and papermaking processes for control of chemical dosage and process pH
- In developing new chemistry concepts for in-situ reactions

Conclusions

- CFE provides a rigorous method to include work-related and dynamic factors to min(G)
- Serves for quantitative calculation of both partial equilibria and para-equilibrium systems in chemistry and materials science
- Can be used for approximate local equilibria in complex reaction systems
- With accurate reaction kinetics, will provide data of reaction rate controlled local chemical equilibrium systems
- Has gained increasing interest with its wide applicability in both materials and process research*
- Overviews published in: www.vtt.fi/inf/pdf/technology/2014/T160.pdf
  www.vtt.fi/inf/pdf/science/2015/S92.pdf





*https://www.mendeley.com/groups/2493581/constrained-free-energy-cfe-method/