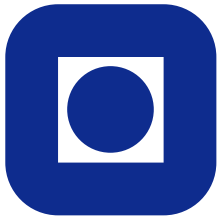


NTNU
Norwegian University of
Science and Technology

Comparison of reduced mechanisms for gasifying applications

J. Krüger[1], T. Løvås[1], N. Haugen[2], F. Mauss[3], C. Perlman[4] and L. Seidel[3]

[1] *NTNU EPT, Trondheim, Norway*
[2] *SINTEF Energy Research, Trondheim, Norway*
[3] *Brandenburg University of Technology, Cottbus,Germany*
[4] *LOGE AB, Lund, Sweden*

Motivation

- IGCC plants with CCS can be part of the transition to renewable energy production
- coal gasification is a vital part of this process
- enhancing the predictive capabilities of models helps developing and operating gasifiers

NTNU
Norwegian University of
Science and Technology

Objective: Reduction of a detailed heterogeneous char gasification mechanism for use in CFD

- investigation of the dependence of heterogeneous reactions on flow turbulence
- 26-step mechanism for gasification of coal in H_2O, CO_2 and O_2 atmosphere[1]
- high computational cost for high number of particles (>200k)
- $\Rightarrow$ reduction via sensitivity analysis in LOGEsoft PaSR (partially stirred reactor) module

[1] Coal and Biomass Char Reactivities in Gasification and Combustion Environments

NTNU
Norwegian University of
Science and Technology

Why reduction in LOGE?

- high influence of stochastics in CFD
- effect of reaction rate vs. effect of flow field
- SRM (stochastic reactor model) approach models the effects of turbulent mixing without actually modeling turbulence
- $\Rightarrow$ similar, but better defined

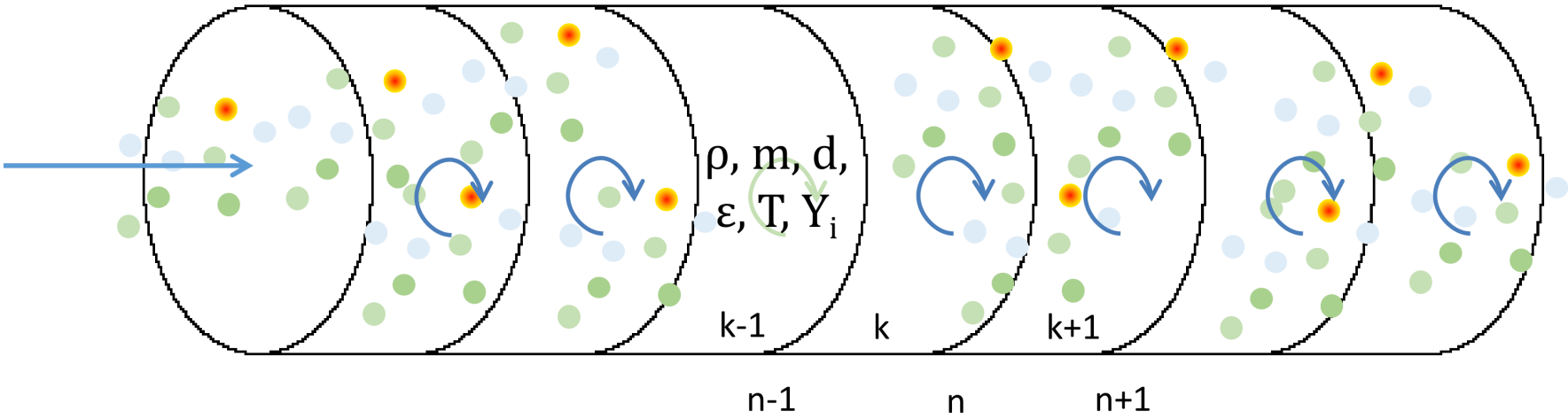
Method

- implementation of the mechanism into the PaSR gasifier model in LOGEsoft
- Reduction of the mechanism using sensitivity analysis for target species (H2O,CO,CO2,O2,H2)
- implementation of the reduced mechanism into the char gasification code Stanford code
- comparison of target species concentrations for mechanisms of increasing reduction

PaSR gasifier in LOGEsoft

- modeled as a series of coupled PaSR cells
- gas in each cell is divided into several gas particles
- each gas particle contains an amount of solid particles with one representative diameter
- gas particles exchange mass, species and enthalpy with other gas particles
- gas particles exchange heat with the reactor walls dictated by an exponential waiting time

PaSR, continued



Gasifier model in LOGEsoft from [2]

[2] CPU Efficient Modelling of Biomass Gasification Using a Stochastic Reactor Approach and Chemistry Guided Reduction

NTNU
Norwegian University of
Science and Technology

Stanford code reactive particle model

- used to predict mass loss rates of TGA (thermogravimetric analysis) experiments of the Stanford group[3]
- accounts for particle mass loss by shrinking and decreasing density
- can account for particle-particle and particle-wall radiation
- assumes a cloud of gas with uniformly behaving particles
- uses a Thiele modulus to model influence of diffusion on internal reactions
- can be used standalone and as a CFD sub-model (Pencil code)

[4] Coal and Biomass Char Reactivities in Gasification and Combustion Environments

NTNU
Norwegian University of
Science and Technology

Sensitivity/Necessity analysis with LOGEsoft

- good results for gas phase mechanism reduction[4]
- chemical perturbations for sensitivity analysis
- sensitivity of flow species or attributes on reactions/species
- can be automatized for large mechanisms
- full necessity analysis not straightforward for heterogeneous mechanisms with stochastics

[3] CPU Efficient Modelling of Biomass Gasification Using a Stochastic Reactor Approach and Chemistry Guided Reduction

NTNU
Norwegian University of Science and Technology

Sensitivity analysis, theory

Evolution of species during combustion:

$$\frac{\partial Y}{\partial t} = P(Y, u, T) + \omega(Y, T) \tag{1}$$

(P=species transport term, ω = species source term) Sensitivity of species concentration Y on rate coefficient k_j:

$$\frac{d}{dt}\frac{\partial Y}{\partial k_j} = \frac{\partial P}{\partial Y}\frac{\partial Y}{\partial k_j} + \frac{\partial P}{\partial k_j} + \frac{\partial \omega(t)}{\partial Y}\frac{\partial Y}{\partial k_j} + \frac{\partial \omega(t)}{\partial k_j} \tag{2}$$

NTNU
Norwegian University of
Science and Technology

Sensitivity analysis, theory

For a homogeneous reactor $P = 0$ and equation 2 simplifies to:

$$\frac{d}{dt}\frac{\partial Y}{\partial k_j} = \frac{\partial \omega(t)}{\partial Y}\frac{\partial Y}{\partial k_j} + \frac{\partial \omega(t)}{\partial k_j} \tag{3}$$

Sensitivity S of a parameter A in the vector of unknowns ψ in respect to species i, with r_k being the reaction rate of reaction k and c_i the concentration of species i.

$$S^S_{A,i} = \frac{\partial \psi_A}{\partial c_i} \approx \sum_{k=1}^{N_r} \frac{\partial \psi_A}{\partial r_k}\frac{\partial r_k}{\partial c_i} \tag{4}$$

NTNU
Norwegian University of
Science and Technology

Sensitivity analysis, theory

Expressing $\frac{\partial r_k}{\partial c_i}$ as:

$$\frac{\partial r_k}{\partial c_i} = \nu'_{i,k} c_i^{|\nu'_{i,k}-1|} \prod_{j \neq i}^{N_s} c_j^{\nu'_{j,k}} k_k = \frac{\nu'_{i,k}}{c_i} r_k \tag{5}$$

yields the sensitivity S of an arbitrary parameter A to species i:

$$S^S_{A,i} = |\sum_{k=1}^{N_r} \frac{\partial \psi_A}{\partial r_k} \frac{\nu'_{i,k}}{c_i} r_k| \tag{6}$$

NTNU
Norwegian University of
Science and Technology

Reaction mechanism

Coal gasification mechanism parameters: Preexponential factor A_k, activation energy $E_k[\mathrm{kJ}/\mathrm{mol}]$ and variance of activation energy $\sigma_k[\mathrm{kJ}/\mathrm{mol}]$

Nr	Reaction			A_k	E_k	σ_k
1	2Cf + H2O	$\leftrightarrow$	C(OH)+C(H)	2.1e06	105.	
2	C(OH) + Cf	$\leftrightarrow$	C(O) + C(H)	4.1e11	80.	
3	2C(H)	$\leftrightarrow$	2Cf + H2	1.4e11	67.	
4	C(O) + Cb	$\rightarrow$	CO+Cf	1.0e13	353.	28
5	C(OH) + Cb	$\leftrightarrow$	HCO+Cf	1.0e13	393.	28
6	Cb+Cf+C(H)+H2O	$\leftrightarrow$	CH3+C(O)+Cf	1.0e13	300.	
7	Cb+Cf+C(H)+H2	$\leftrightarrow$	CH3+2Cf	1.0e13	300.	
8	Cf+C(H)+CO	$\rightarrow$	HCO+2Cf	1.0e13	300.	
9	2C(H)	$\rightarrow$	CH2+Cf	3.0e11	426.	
10	Cf+CO2	$\leftrightarrow$	C(O)+CO	3.7e03	161.	
11	Cb+CO2+C(O)	$\rightarrow$	2CO+Cf	1.26e08	276.	
12	Cf+CO	$\leftrightarrow$	C(CO)	1.0e13	455.	33
13	CO+C(CO)	$\rightarrow$	CO2+2Cf	9.8e06	270.	
14	2Cf+O2	$\rightarrow$	C(O)+CO	5.0e10	150.	
15	2Cf + O2	$\rightarrow$	C2(O2)	4.0e07	93.	
16	2Cf+Cb+C(O)+O2	$\rightarrow$	CO2+C(O)+Cf	1.5e07	78.	
17	Cf+Cb+C(O)+O2	$\rightarrow$	CO+2C(O)	2.1e07	103.	
18	Cb+C2(O2)	$\rightarrow$	CO2+2Cf	1.0e13	304.	33

NTNU
Norwegian University of
Science and Technology

Reaction mechanism for sensitivity analysis

21-step coal gasification mechanism parameters: Preexponential factor A_k, activation energy $E_k[\mathrm{kJ/mol}]$ and variance of activation energy $\sigma_k[\mathrm{kJ/mol}]$

Nr	Reaction			A_k	E_k	σ_k
1	2Cf + H2O	$\rightarrow$	C(OH)+C(H)	2.1e06	105.	
2	C(OH) + Cf	$\rightarrow$	C(O) + C(H)	4.1e11	80.	
3	2C(H)	$\rightarrow$	2Cf + H2	1.4e11	67.	
4	C(O) + Cb	$\rightarrow$	CO+Cf	1.0e13	353.	28
5	C(OH) + Cb	$\leftrightarrow$	HCO+Cf	1.0e13	393.	28
6	Cb+Cf+C(H)+H2O	$\rightarrow$	CH3+C(O)+Cf	1.0e13	300.	
7	Cb+Cf+C(H)+H2	$\rightarrow$	CH3+2Cf	1.0e13	300.	
8	Cf+C(H)+CO	$\rightarrow$	HCO+2Cf	1.0e13	300.	
⋮	⋮	⋮	⋮	⋮	⋮	

NTNU
Norwegian University of Science and Technology

Boundary conditions

General boundary conditions: Reactor, fuel and oxidizer data for LOGEsoft and Stanford code runs [5]

Attribute	Value
$T_{gas,in}$	1640K
T_{wall}	1500K
Gas mechanism	GRI 3.0
$Y_{O2,in}$	0.79
$Y_{H2O,in}$	0.08
$Y_{N2,in}$	0.13
$\mathrm{m_{carbon}}/\mathrm{m_{gas}}$	0.65
porosity	0.9
$d_{particle}$	$50\mu m$

[5] Transient simulations of char gasification, 8^{th} US National Combustion Meeting

NTNU
Norwegian University of Science and Technology

Reduction

- target species for sensitivity: O_2, CO_2, H_2O, CO, H_2 of the pore gas ($Y_{gas} \approx Y_{gas,pore}$)
- reactions are ranked by how sensitive all target species are to them
- low ranked reactions are candidates for reduction
- mechanisms are run in Stanford code until conversion 99%

NTNU
Norwegian University of
Science and Technology

18-step mechanism

18-step coal gasification mechanism parameters: Preexponential factor A_k, activation energy $E_k[\mathrm{kJ/mol}]$ and variance of activation energy $\sigma_k[\mathrm{kJ/mol}]$. Removed: CH2

Nr	Reaction			A_k	E_k	σ_k
1	2Cf + H2O	$\rightarrow$	C(OH)+C(H)	2.1e06	105.	
2	C(OH) + Cf	$\rightarrow$	C(O) + C(H)	4.1e11	80.	
3	2C(H)	$\rightarrow$	2Cf + H2	1.4e11	67.	
4	C(O) + Cb	$\rightarrow$	CO+Cf	1.0e13	353.	28
5	C(OH) + Cb	$\leftrightarrow$	HCO+Cf	1.0e13	393.	28
6	Cb+Cf+C(H)+H2O	$\rightarrow$	CH3+C(O)+Cf	1.0e13	300.	
~~7~~	~~Cb+Cf+C(H)+H2~~	$\rightarrow$	~~CH3+2Cf~~	~~1.0e13~~	~~300.~~	
~~8~~	~~Cf+C(H)+CO~~	$\rightarrow$	~~HCO+2Cf~~	~~1.0e13~~	~~300.~~	
~~9~~	~~2C(H)~~	$\rightarrow$	~~CH2+Cf~~	~~3.0e11~~	~~426.~~	
10	Cf+CO2	$\leftrightarrow$	C(O)+CO	3.7e03	161.	
11	Cb+CO2+C(O)	$\rightarrow$	2CO+Cf	1.26e08	276.	
⋮	⋮	⋮	⋮	⋮	⋮	

NTNU
Norwegian University of
Science and Technology

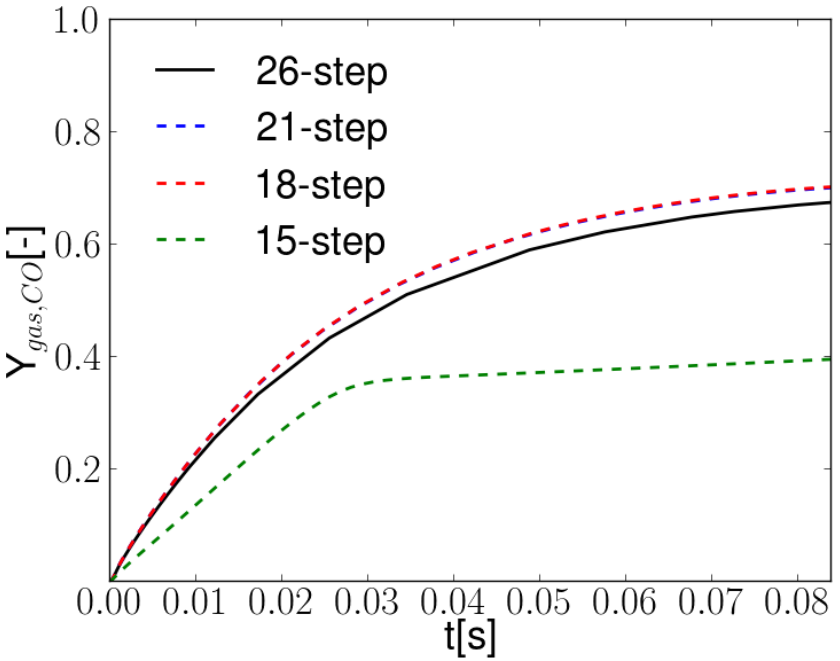
15-step mechanism

15-step coal gasification mechanism parameters: Preexponential factor A_k, activation energy $E_k[\mathrm{kJ/mol}]$ and variance of activation energy $\sigma_k[\mathrm{kJ/mol}]$. Removed: CH2, HCO, H2O

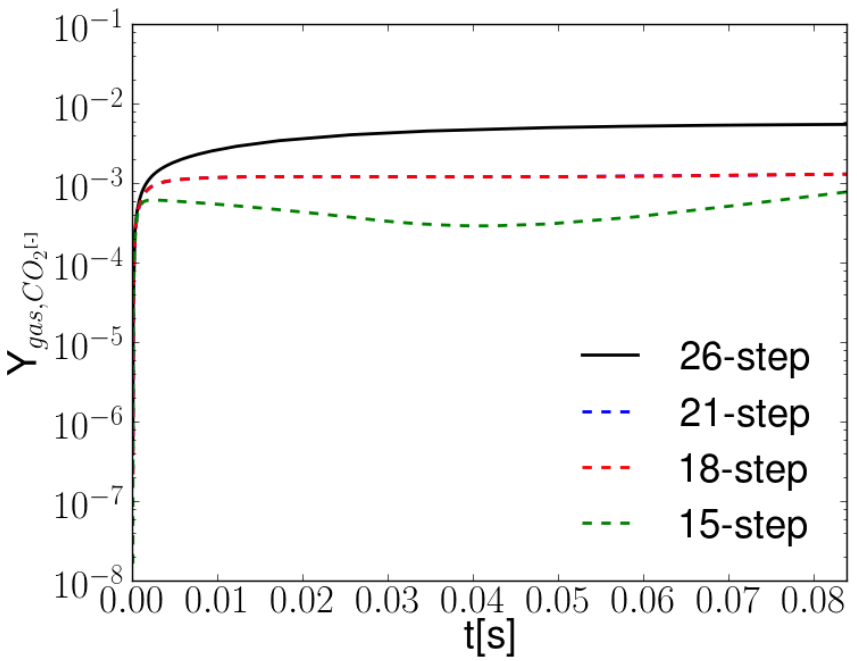
Nr	Reaction			A_k	E_k	σ_k
~~1~~	~~2Cf + H2O~~	$\rightarrow$	~~C(OH)+C(H)~~	~~2.1e06~~	~~105.~~	
2	C(OH) + Cf	$\rightarrow$	C(O) + C(H)	4.1e11	80.	
3	2C(H)	$\rightarrow$	2Cf + H2	1.4e11	67.	
4	C(O) + Cb	$\rightarrow$	CO+Cf	1.0e13	353.	28
~~5~~	~~C(OH) + Cb~~	$\leftrightarrow$	~~HCO+Cf~~	~~1.0e13~~	~~393.~~	~~28~~
6	Cb+Cf+C(H)+H2O	$\rightarrow$	CH3+C(O)+Cf	1.0e13	300.	
~~7~~	~~Cb+Cf+C(H)+H2~~	$\rightarrow$	~~CH3+2Cf~~	~~1.0e13~~	~~300.~~	
~~8~~	~~Cf+C(H)+CO~~	$\rightarrow$	~~HCO+2Cf~~	~~1.0e13~~	~~300.~~	
~~9~~	~~2C(H)~~	$\rightarrow$	~~CH2+Cf~~	~~3.0e11~~	~~426.~~	
10	Cf+CO2	$\leftrightarrow$	C(O)+CO	3.7e03	161.	
11	Cb+CO2+C(O)	$\rightarrow$	2CO+Cf	1.26e08	276.	
⋮	⋮	⋮	⋮	⋮	⋮	

NTNU
Norwegian University of Science and Technology

Simulations with the Stanford code



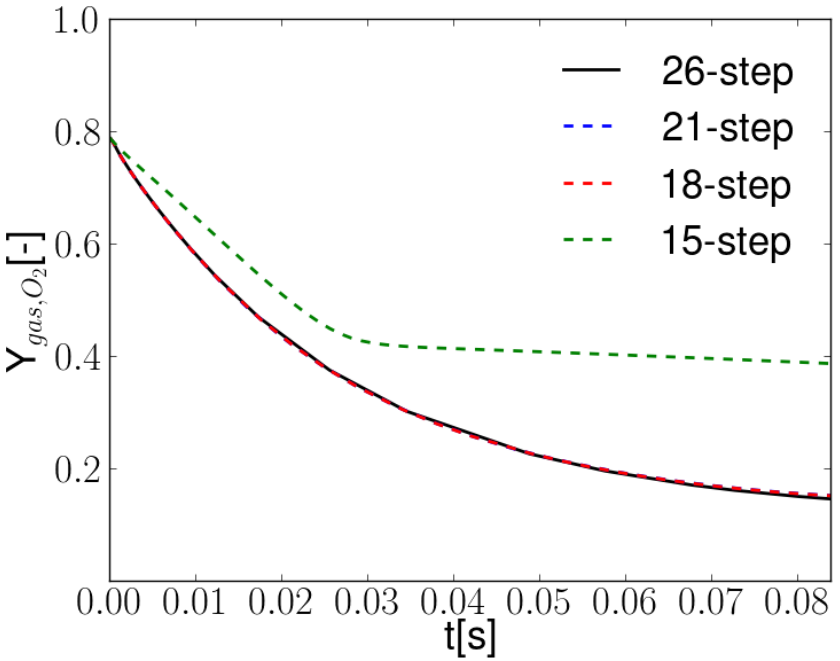
Influence of reduction on gas phase species: CO over time for different reductions



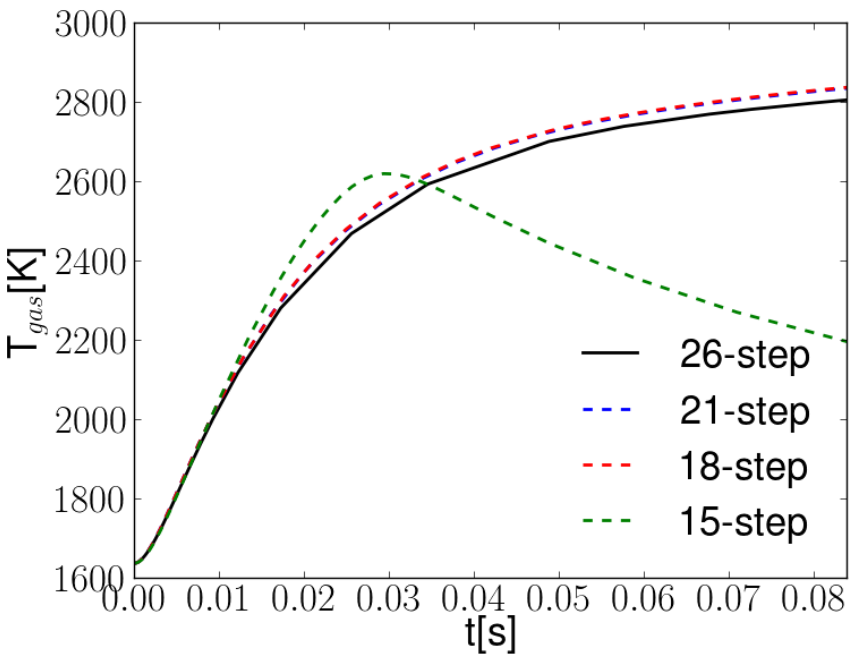
Influence of reduction on gas phase species: CO2 over time for different reductions

NTNU
Norwegian University of Science and Technology

Simulations with the Stanford code



Influence of reduction on gas phase species: O2 over time for different reductions



Influence of reduction on gas phase: temperature over time for different reductions

NTNU
Norwegian University of Science and Technology

Conclusions

- a simple sensitivity analysis was performed on a heterogeneous mechanism
- under the given conditions, reduction from 26 to 18 steps is possible
- gas phase compositions from LOGEsoft and the Stanford code are not comparable
- calculations in LOGEsoft are unstable for higher temperatures
- $\Rightarrow H_2O$ based reactions are understated

NTNU
Norwegian University of
Science and Technology

Future work

- increase the numerical stability of the mechanism at higher temperatures
- implement quasi state species for solid phase in LOGEsoft
- implementation of quasi-steady state species in Stanford code

Thank you for your attention! Questions?

NTNU
Norwegian University of
Science and Technology

Runtime

Comparison of speed-up

Nr of Steps	Time until 99% conversion	Runtime[s]	Comments
26	8.862E-02	53	
21	8.390E-02	197	lower tol.
18	8.404E-02	71	lower tol.
15	1.700E+00	190	lower tol.

NTNU
Norwegian University of
Science and Technology