1st International Conference on Chemical Looping
An Alternative Concept for Efficient and Clean Use of Fossil Resources

CLC Modelling: the fuel-reactor at fast fluidization Conversion of CH_4 using a NiO-based oxygen-carrier in a 140 kW_{th} unit

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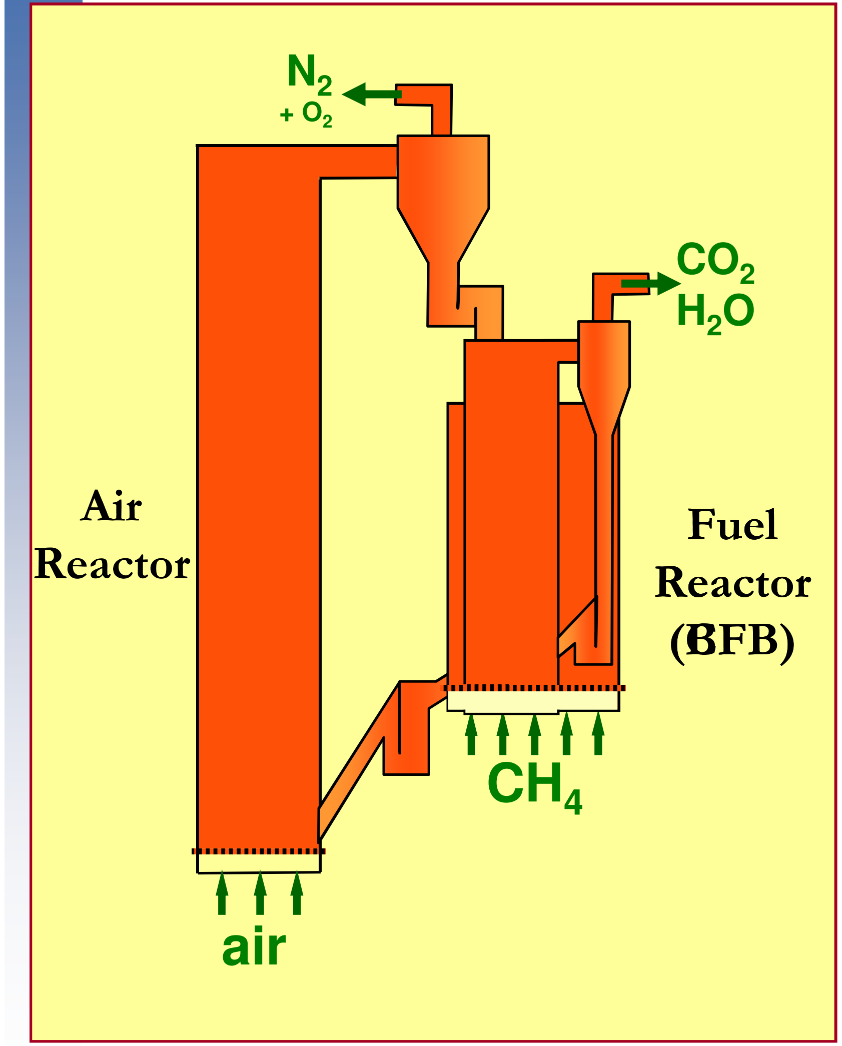
Presentation overview

Fuel Reactor Modelling

- Description of the mathematical model
- Outputs from the model
- Validation of the model against experimental results in a 140 kW CLC unit
  (Vienna University of Technology)

The Fuel Reactor

CLC system



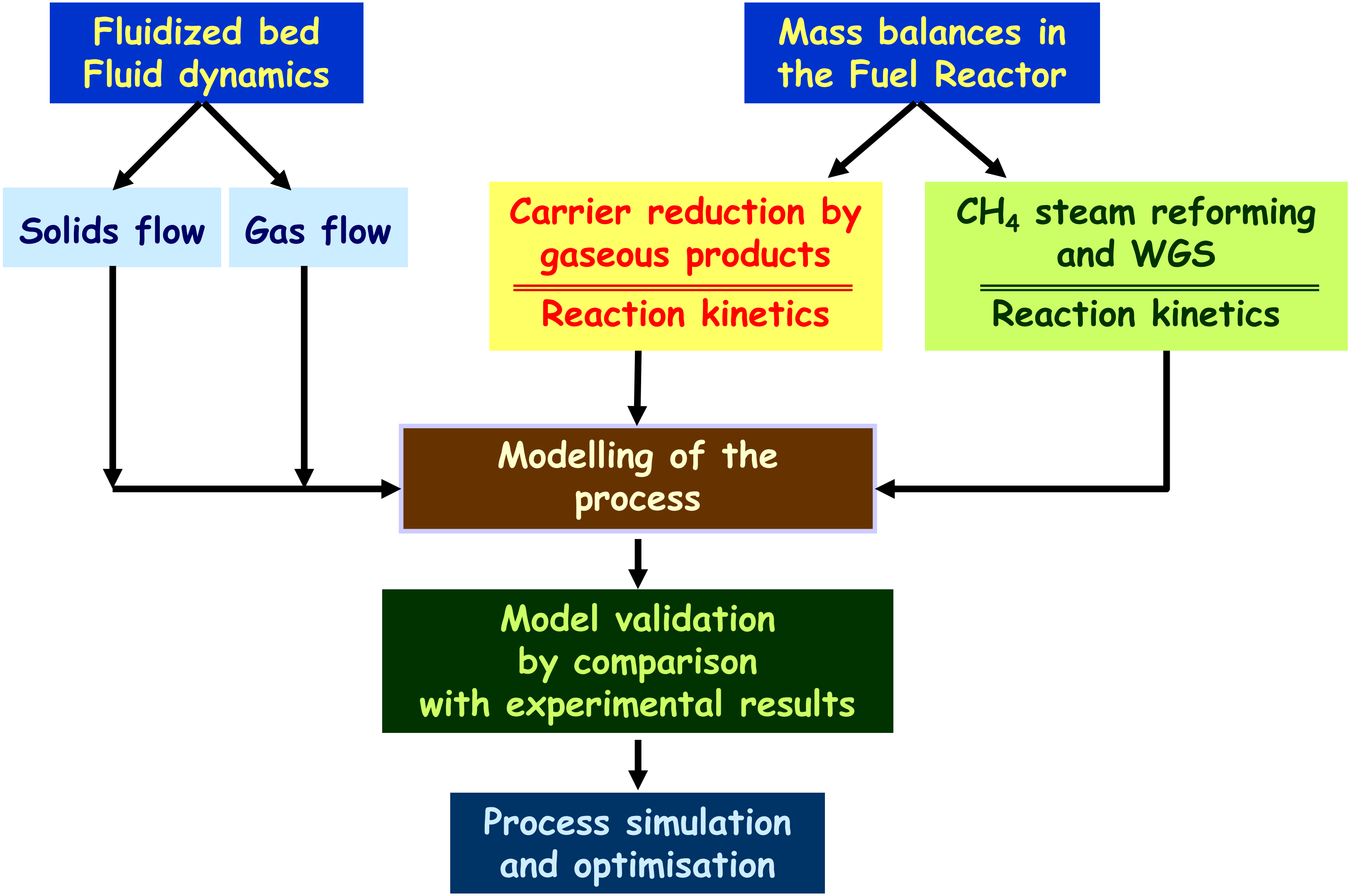
➢Bubbling Fluidized Bed

- Gas bypass through the bubble phase
- Low gas velocity: relatively large cross-sectional areas

➢ Circulating Fluidized Bed:

- Potential to convert the gas in the freeboard
- High gas velocity: smaller size of the reactor

Modelling the Fuel Reactor



Fluidized bed Fluid dynamics

Solids flow

Gas flow

Mass balances in the Fuel Reactor

Carrier reduction by gaseous products

Reaction kinetics

CH_4 steam reforming and WGS

Reaction kinetics

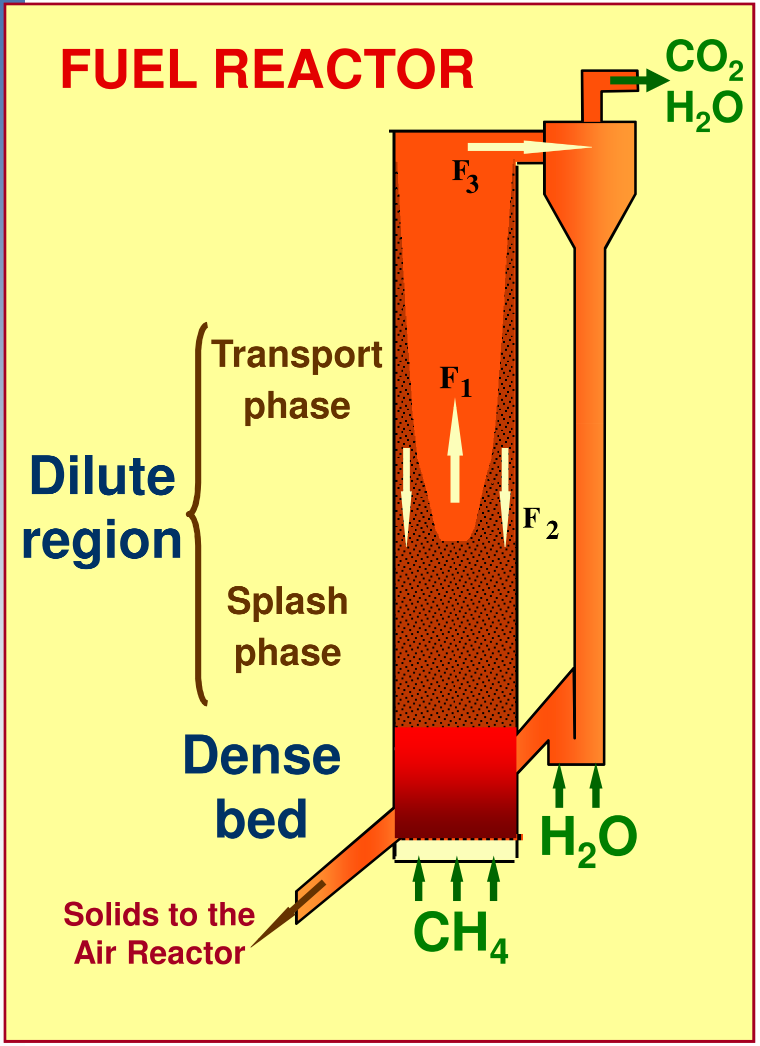
Modelling of the process

Model validation by comparison with experimental results

Process simulation and optimisation

Fluid dynamics

High-velocity Fluidized Bed



Pallarès & Johnsson model*

➢ DENSE BED:

- Two phases: bubble/emulsion
- Plug flow gas in each region
- Gas exchange between phases
- Perfect mixing of solids

➢ SPLASH PHASE:

- Plug flow gas
- Perfect mixing of solids
- Decay in solids concentration

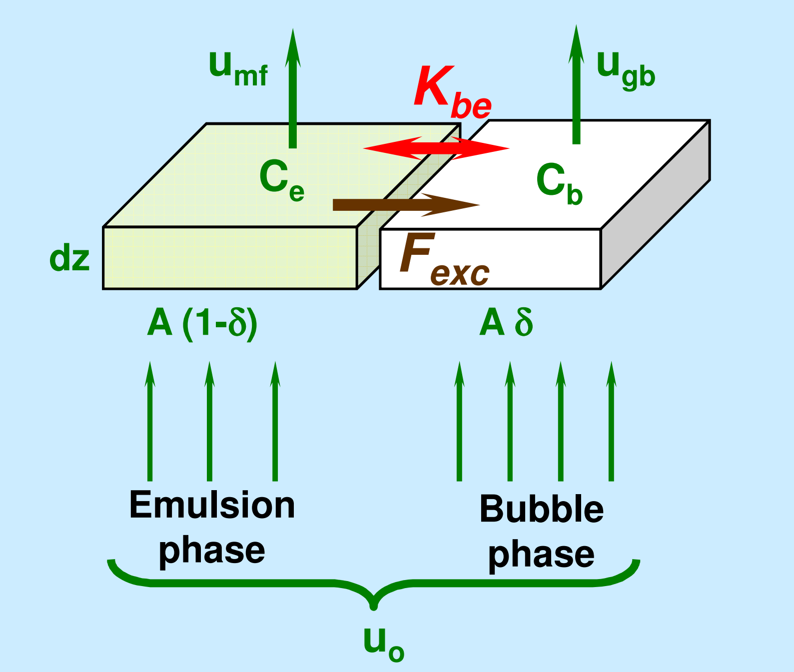
➢ TRANSPORT PHASE:

- Core-annulus structure

* Progress in Energy and Combustion Science 32 (2006) 539–569

Fluid dynamics in the dense bed

The emulsion phase and the bubbles phase are considered



- **Gas sharing between emulsion and bubbles**

$$u_g = (1-\delta_b)u_{mf} + u_{vis} + u_{tf}$$

- **Gas exchange between phases**
  - **Diffusive flow**

$$k_{be} = 1.631\, u_g \mathrm{Sc}^{0.37}$$

  - **Bulk flow**

F_{exc} to maintain u_{mf} in emulsion because of the gas expansion during CH_4 conversion

$$CH_4\,(g) + NiO\,(s) \longrightarrow CO_2\,(g) + 2\,H_2O\,(g) + Ni\,(s)$$

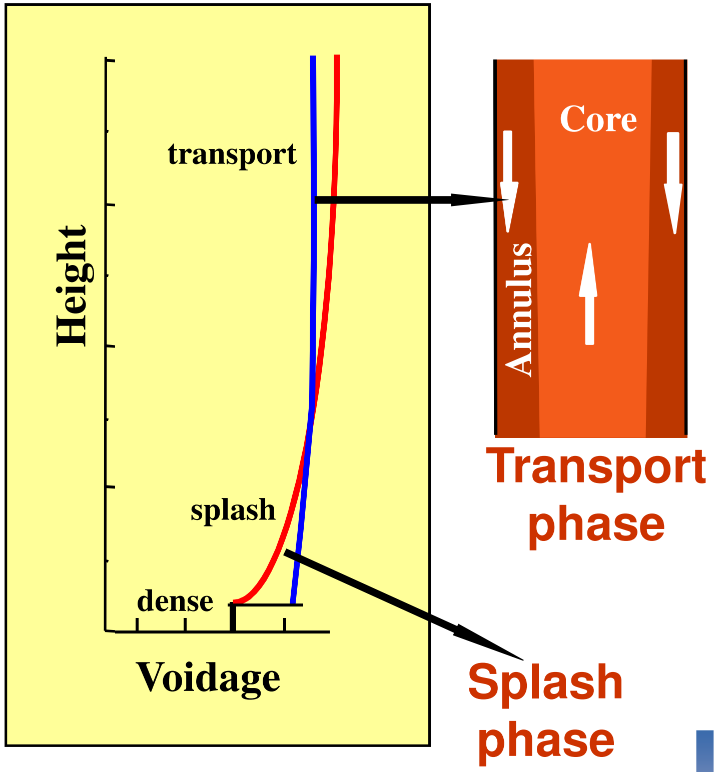
Fluid dynamics in the dilute region

The splash phase and the transport phase are considered

- **Solid concentration in the dilute region**

Exponential decay in each phase

Splash phase	**Transport phase**
$\frac{\mathrm{d}C_{spl}}{\mathrm{d}z} = -aC_{spl}$	$\frac{\mathrm{d}C_{tr}}{\mathrm{d}z} = -KC_{tr}$
Perfect mixing of solids with dense bed	**Core – Annulus structure**



- **Gas flow**
  - **Plug flow of gas through the core**
  - **Contact efficiency with solids**

$$\xi_{g-s} = 1 - 0.75\left(\frac{C_{dil}}{C_{b,H_b}}\right)^{0.4}$$

Mass balances

❖ Reactions with the oxygen carrier (NiO-based)

$$CH_4 + 4\ NiO \longrightarrow CO_2 + 2\ H_2O + 4\ Ni$$

$$CO + NiO \longrightarrow CO_2 + Ni$$

$$H_2 + NiO \longrightarrow H_2O + Ni$$

❖ Gas-phase reactions

- **CH_4 steam reforming: catalyzed by Ni**

$$CH_4 + H_2O \xrightarrow{Ni} CO + 3\ H_2$$

$$CH_4 + 2\ H_2O \xrightarrow{Ni} CO_2 + 4\ H_2$$

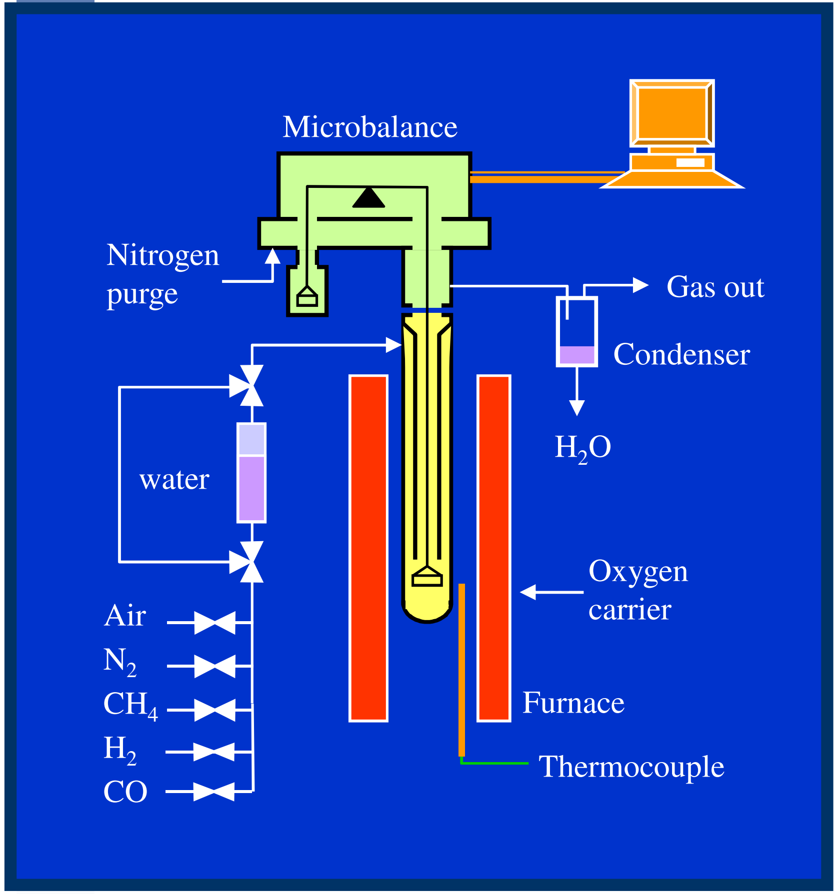
- **Water-Gas Shift equilibrium (WGS)**

$$CO + H_2O \longrightarrow CO_2 + H_2$$

Reaction kinetics

❖ Reactions with the oxygen carrier (NiO-based)

CI Electronics TGA



- **Oxygen carrier: $NiO/NiAl_2O_4$**
  - Prepared by the spray-drying method
  - Main properties of the particles

Particle size: +90-212 µm

NiO content ≈ 40 wt%

Aparent density = 3870 kg/m^3

  - Reactions

$$CH_4 + 4\,NiO \longrightarrow CO_2 + 2\,H_2O + 4\,Ni$$
$$CO + NiO \longrightarrow CO_2 + Ni$$
$$H_2 + NiO \longrightarrow H_2O + Ni$$

Sample weight: 20 - 60 mg
Temperature: 1050-1250 K
Gas concentration: 5-50%

Reaction kinetics

❖ Reactions with the oxygen carrier (NiO-based)

- **Oxygen carrier: $NiO/NiAl_2O_4$**
  - **Shrinking Core Model (SCM) in the grain**

Kinetic control

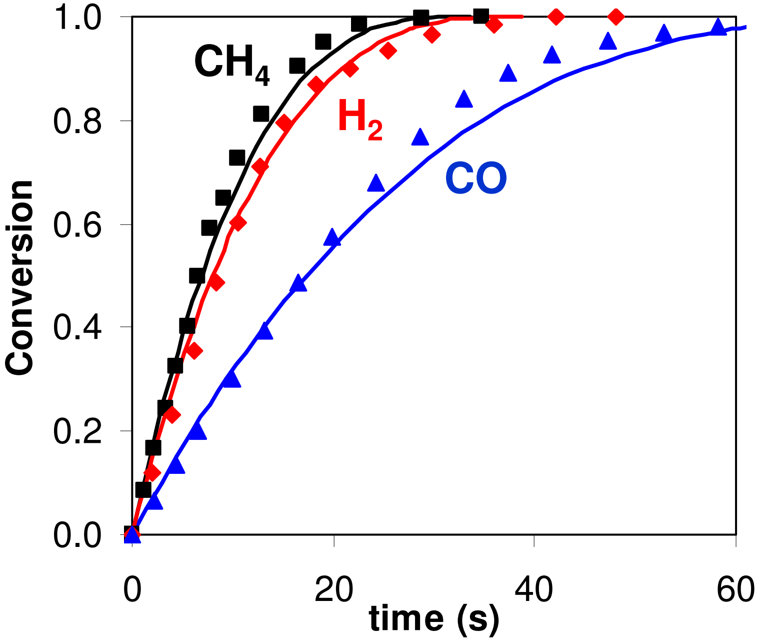
$$\frac{t}{\tau_{chr}} = 1-(1-X)^{1/3}$$

$$\tau_{chr} = \frac{\rho_m \, r_g}{b\, k_s \, \left(C_g^n - C_{eq}^n\right)}$$

$$k_s = k_{s,0} \; e^{(-E_k/RT)}$$

- - **Kinetics parameters**

	CH_4	CO	H_2
Reaction order (n)	0.6	0.8	0.8
$k_{S,0}$ (m s^{-1}(mol/m^3)$^{1-n}$)	2.5	0.11	0.25
E_S (kJ mol^{-1})	70	34	35



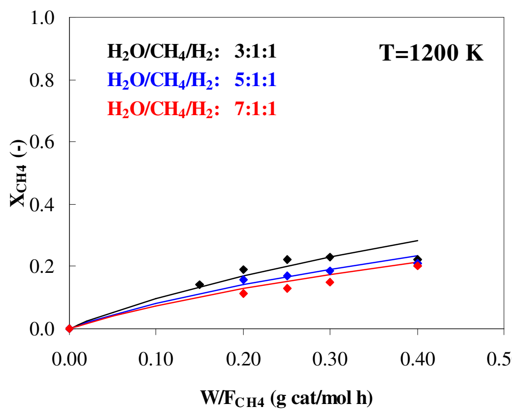
Reaction kinetics

❖ Gas-phase reactions

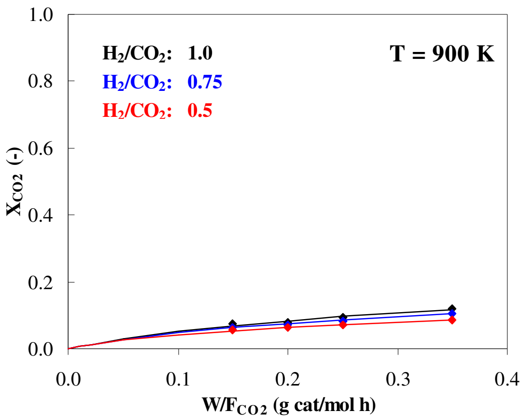
➢ **Combined method*:**

(1) $CH_4 + H_2O \longrightarrow CO + 3\,H_2$
(2) $CO + H_2O \longrightarrow CO_2 + H_2$
(3) $CH_4 + 2\,H_2O \longrightarrow CO_2 + 4\,H_2$

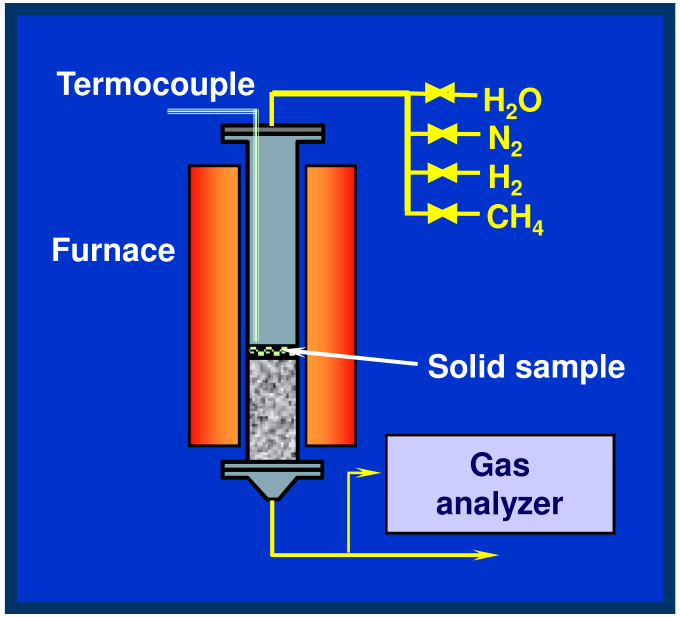
CH_4 SR (1 & 3): high T (1000-1200 K)



R-WGS (2): low T (800-1000 K)



Fixed Bed Reactor



* Xu & Froment. AIChE J. 35 (1989), 88-96

Reaction kinetics

❖ Gas-phase reactions

➢ **Combined method*:**

(1) $CH_4 + H_2O \longrightarrow CO + 3\,H_2$

(2) $CO + H_2O \longrightarrow CO_2 + H_2$

(3) $CH_4 + 2\,H_2O \longrightarrow CO_2 + 4\,H_2$

Reaction rates mol/(g cat s)

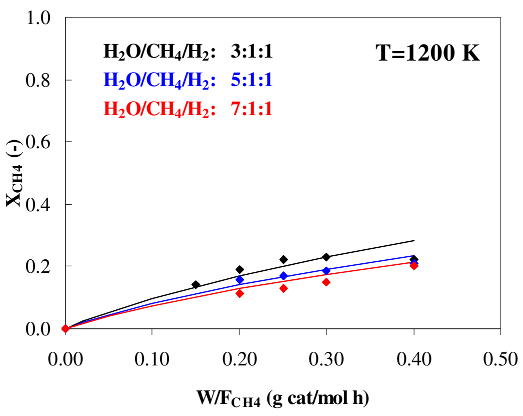
$$(-r_1) = \frac{k_1\left(y_{CH_4}\,y_{H_2O} - y_{H_2}^3\,y_{CO}\big/K_{eq,1}\right)}{y_{H_2}^{2.5}\left(1+K_{H_2O}\,y_{H_2O}\big/y_{H_2}\right)^2}$$

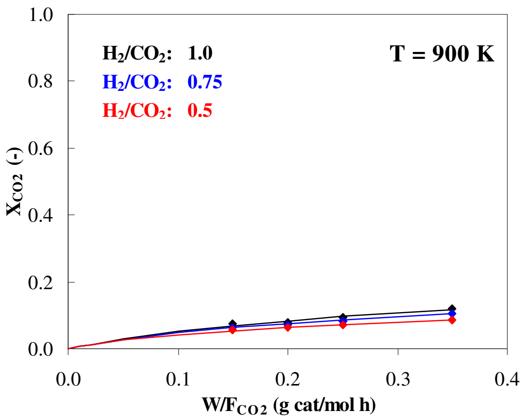
$$(-r_2) = \frac{k_2\left(y_{CO}\,y_{H_2O} - y_{H_2}\,y_{CO_2}\big/K_{eq,2}\right)}{y_{H_2}\left(1+K_{H_2O}\,y_{H_2O}\big/y_{H_2}\right)^2}$$

$$(-r_3) = \frac{k_3\left(y_{CH_4}\,y_{H_2O}^2 - y_{H_2}^4\,y_{CO}\big/K_{eq,3}\right)}{y_{H_2}^{3.5}\left(1+K_{H_2O}\,y_{H_2O}\big/y_{H_2}\right)^2}$$

CH_4 SR (1 & 3):
high T (1000-1200 K)

R-WGS (2):
low T (800-1000 K)





Kinetic parameters

	k_i	E_a
k_1	$1.01\cdot10^{11}$	236.5
k_2	$1.76\cdot10^{-3}$	18.4
k_3	$1.02\cdot10^{9}$	200.2
K_{H2O}	$3.18\cdot10^{6}$	96.9

* Xu & Froment. AIChE J. 35 (1989), 88-96

Fuel Reactor Modelling: Mass Balances

Mass balances for CH_4, H_2, CO, H_2O and CO_2

Dense bed:

$$\frac{\mathrm{d}F_{\mathrm{e,i}}}{\mathrm{d}V} = -\delta_{\mathrm{b}} k_{\mathrm{be}} \left(C_{\mathrm{e,i}} - C_{\mathrm{b,i}}\right) - y_{\mathrm{e,i}} \frac{\mathrm{d}F_{\mathrm{exc}}}{\mathrm{d}V} - \frac{\mathrm{d}F_{\mathrm{WGS,i}}}{\mathrm{d}V} - \left(1-\delta_{\mathrm{b}}\right) \sum \left(-\bar{r}_{\mathrm{g,i}}\right)_{\mathrm{e}} - \frac{\mathrm{d}F_{\mathrm{ref,i}}}{\mathrm{d}V}$$

$$\frac{\mathrm{d}F_{\mathrm{b,i}}}{\mathrm{d}V} = +\delta_{\mathrm{b}} k_{\mathrm{be}} \left(C_{\mathrm{e,i}} - C_{\mathrm{b,i}}\right) + y_{\mathrm{e,i}} \frac{\mathrm{d}F_{\mathrm{exc}}}{\mathrm{d}V} - \frac{\mathrm{d}F_{\mathrm{WGS,i}}}{\mathrm{d}V}$$

Gas exchange

- **Diffusive flow**
- **Bulk flow**

Fuel Reactor Modelling: Mass Balances

Mass balances for CH_4, H_2, CO, H_2O and CO_2

Dense bed:

$$\frac{\mathrm{d}F_{\mathrm{e,i}}}{\mathrm{d}V} = -\delta_{\mathrm{b}} k_{\mathrm{be}} \left(C_{\mathrm{e,i}} - C_{\mathrm{b,i}} \right) - y_{\mathrm{e,i}} \frac{\mathrm{d}F_{\mathrm{exc}}}{\mathrm{d}V} - \frac{\mathrm{d}F_{\mathrm{WGS,i}}}{\mathrm{d}V} - \left(1 - \delta_{\mathrm{b}} \right) \sum \left(-\overline{r}_{\mathrm{g,i}} \right)_{\mathrm{e}} - \frac{\mathrm{d}F_{\mathrm{ref,i}}}{\mathrm{d}V}$$

$$\frac{\mathrm{d}F_{\mathrm{b,i}}}{\mathrm{d}V} = +\delta_{\mathrm{b}} k_{\mathrm{be}} \left(C_{\mathrm{e,i}} - C_{\mathrm{b,i}} \right) + y_{\mathrm{e,i}} \frac{\mathrm{d}F_{\mathrm{exc}}}{\mathrm{d}V} - \frac{\mathrm{d}F_{\mathrm{WGS,i}}}{\mathrm{d}V}$$

Gas exchange

- **Diffusive flow**
- **Bulk flow**

WGS reaction

- **Fast reaction**
- **Considered at equilibrium conditions**

Fuel Reactor Modelling: Mass Balances

Mass balances for CH_4, H_2, CO, H_2O and CO_2

Dense bed:

$$\frac{\mathrm{d}F_{e,i}}{\mathrm{d}V} = -\delta_b k_{be}\left(C_{e,i} - C_{b,i}\right) - y_{e,i}\frac{\mathrm{d}F_{exc}}{\mathrm{d}V} - \frac{\mathrm{d}F_{WGS,i}}{\mathrm{d}V} - \left(1-\delta_b\right)\sum\left(-\bar{r}_{g,i}\right)_e - \frac{\mathrm{d}F_{ref,i}}{\mathrm{d}V}$$

$$\frac{\mathrm{d}F_{b,i}}{\mathrm{d}V} = +\delta_b k_{be}\left(C_{e,i} - C_{b,i}\right) + y_{e,i}\frac{\mathrm{d}F_{exc}}{\mathrm{d}V} - \frac{\mathrm{d}F_{WGS,i}}{\mathrm{d}V}$$

Gas exchange

- **Diffusive flow**
- **Bulk flow**

WGS reaction

- **Fast reaction**
- **Considered at equilibrium conditions**

Reaction in the emulsion

- **OC: perfect mixing**

Conversion of particles depends on the residence time distribution

$$\bar{X}_s = \int_0^{\tau} X_s(t)\cdot\frac{e^{-t/t_{mr}}}{t_{mr}}\cdot dt$$

- **CH_4 Steam Reforming**

Fuel Reactor Modelling: Mass Balances

Mass balances for CH_4, H_2, CO, H_2O and CO_2

Dilute region:

$$\frac{\mathrm{d}F_{\mathrm{dil,i}}}{\mathrm{d}V} = -\xi_{g-s}\left[\sum\left(-\bar{r}_{\mathrm{g,i}}\right)_{\mathrm{sp}} + \sum\left(-\bar{r}_{\mathrm{g,i}}\right)_{\mathrm{tr}}\right] - \sum\frac{\mathrm{d}F_{\mathrm{ref,i}}}{\mathrm{d}V} - \frac{\mathrm{d}F_{\mathrm{WGS,i}}}{\mathrm{d}V}$$

- **Reaction in the splash phase**

  Solids in perfect mixing with the dense bed

- **Reaction in the transport phase**

  Variation of OC conversion with the reactor heigth

$$\frac{\mathrm{d}X_s}{\mathrm{d}z} = \frac{\mathrm{d}X_s}{\mathrm{d}t}\frac{\mathrm{d}t}{\mathrm{d}z} = \frac{\mathrm{d}X_s}{\mathrm{d}t}\frac{1}{u_{s,c}}$$

- **Reactions in the gas phase**

  WGS reaction: at equilibrium

  (2) $CO + H_2O \longleftrightarrow CO_2 + H_2$

  CH_4 Steam Reforming

  (1) $CH_4 + H_2O \longrightarrow CO + 3\,H_2$

  (3) $CH_4 + 2\,H_2O \longrightarrow CO_2 + 4\,H_2$

Fuel Reactor Modelling

Visual Fortran ® Code

Initial conditions

- The amount of solids in the fuel–reactor should be that required to give the pressure drop initially assumed:

$$\Delta P = \int_0^{H_b} C_b \rho_s g dz + \int_{H_b}^{H_r} C_{dil} \rho_s g dz$$

- The oxygen supplied by the oxygen–carrier must be equal to the oxygen reacted with the fuel gas:

$$F_{OC} \frac{R_{OC}}{M_O} \Delta X_{OC} = 4\eta_c F_{CH_4}$$

Input data:

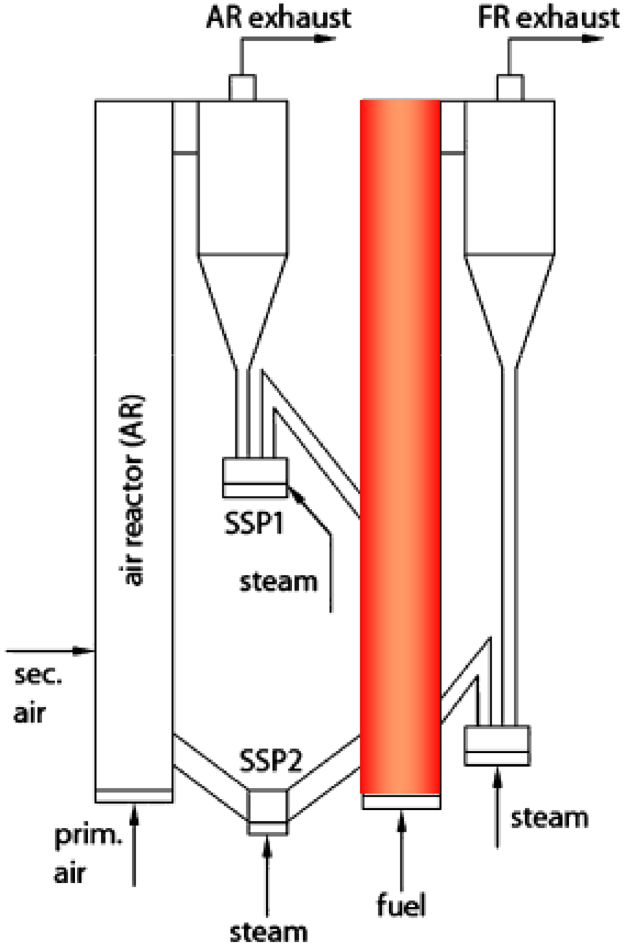
- Reactor geometry (H_r, D_r, H_{LS})
- Operating conditions (T, ΔP, F_g, F_s)
- Properties of OC (phys. & chem.)

Output results

- Axial profiles of gas and solids
- Conversion of the OC
- Combustion efficiency

Fuel Reactor Modelling

Dual Circulating Fluidized Bed
Vienna University of Technology



Fuel Reactor
Fast fluidization regime

Reactor geometry

Heigth:	3 m
Diameter:	0.16 m

Oxygen carrier $NiO/NiAl_2O_4$

Particle size: +90-212 µm

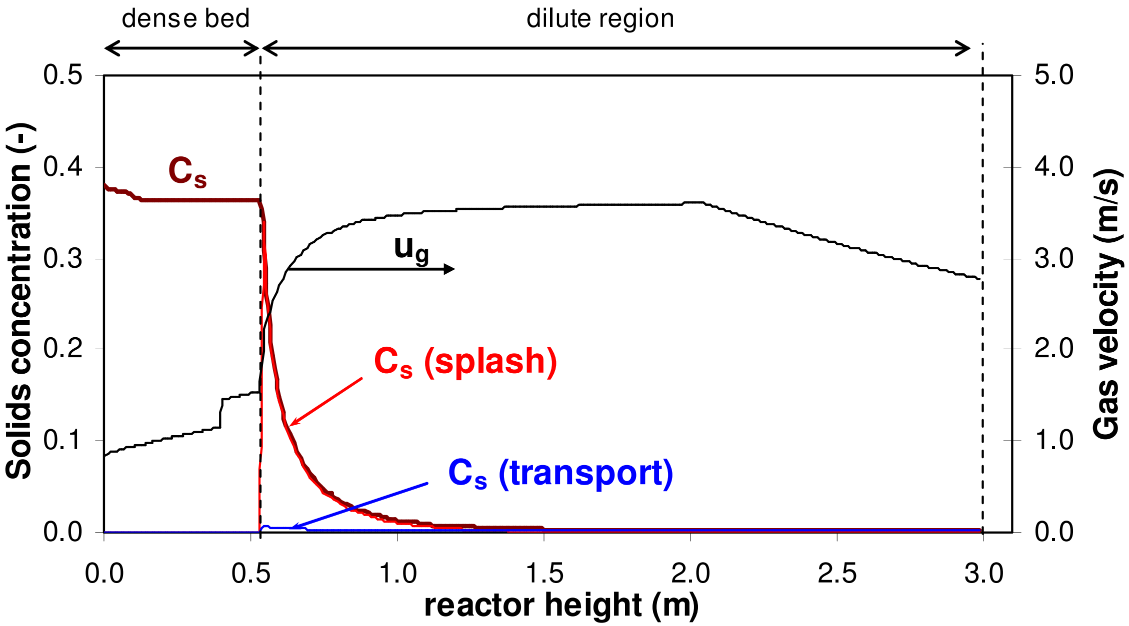
NiO content ≈ 40 wt%

Aparent density = 3870 kg/m^3

Kolbitsch et al. Ind. Eng. Chem. Res. 48 (2009) 5542-5547

Fuel Reactor Modelling: Results

Axial profiles in the dilute region: **Solids concentration**

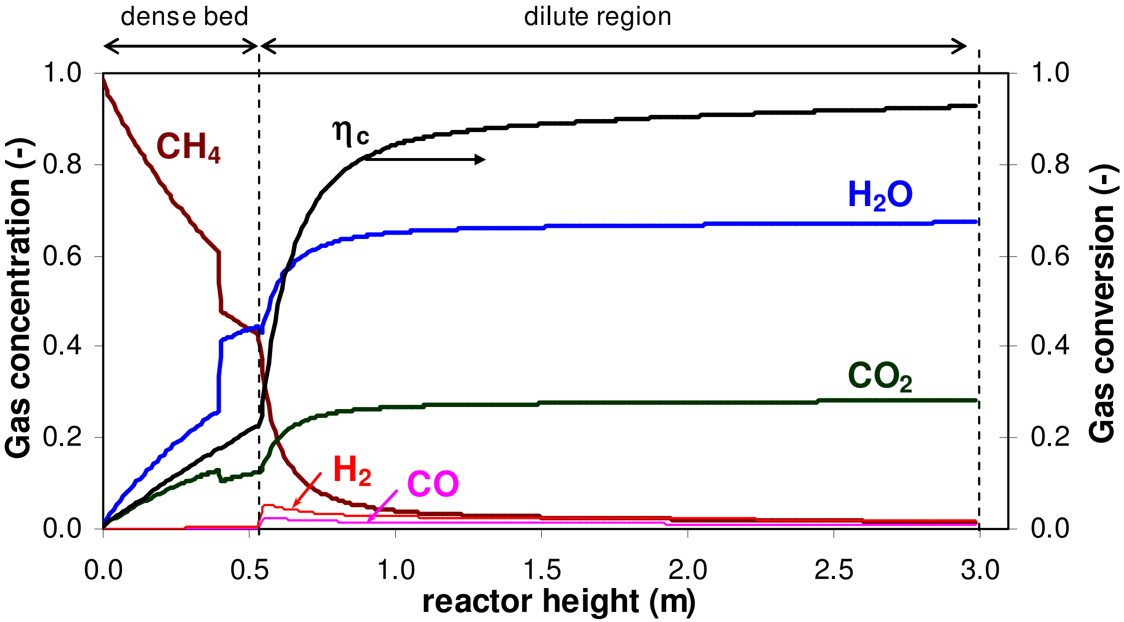


Teperature:	1170 K
Flow of CH_4:	14.2 Nm^3/h
Solids inventory:	20 kg
Solids conversion:	0.20
OC/fuel:	10

- **The dense bed is characterized by a roughly constant concentration of solids**
- **The splash phase dominates the solids concentration in the first 1 m of the dilute region. After that, the transport phase is dominating**
- **The gas velocity increases with the reactor height because the gas expansion as CH_4 is converted to CO_2 and H_2O**

Fuel Reactor Modelling: Results

Axial profiles in the dilute region: **Gas concentration**

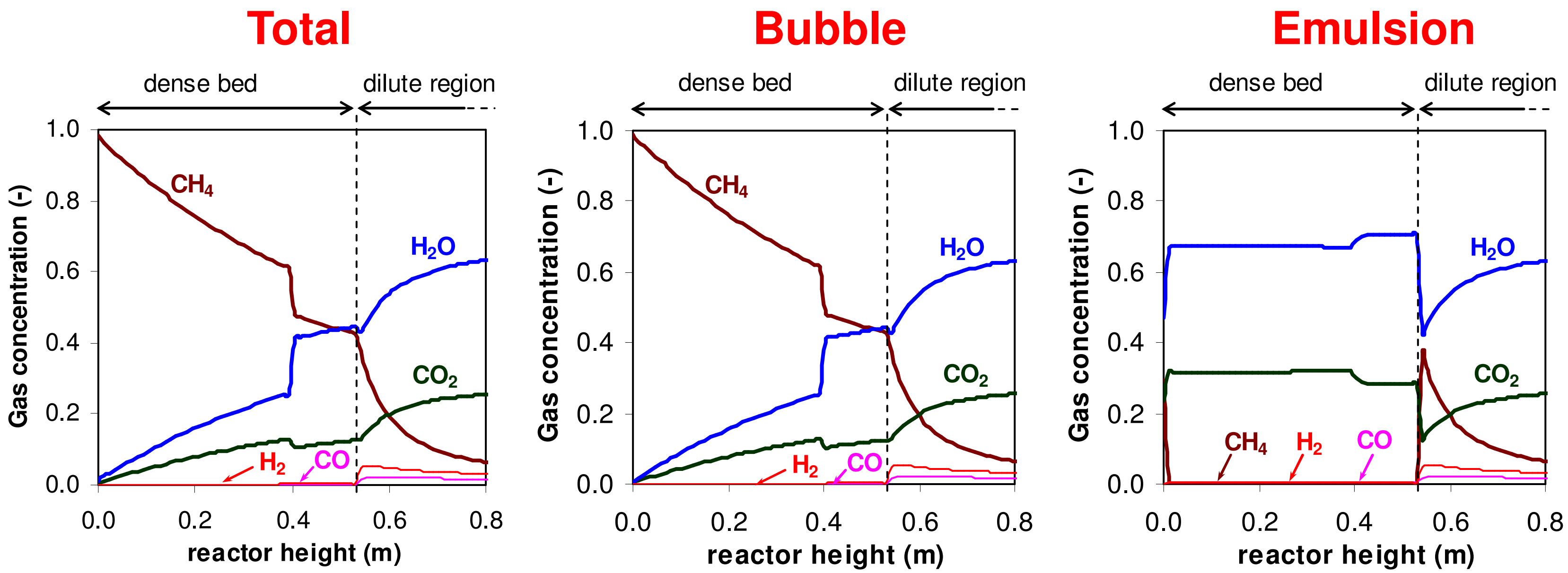


Temperature:	1170 K
Flow of CH_4:	14.2 Nm^3/h
Solids inventory:	20 kg
Solids conversion:	0.20
OC/fuel:	10

- **Most of methane is converted in the dilute region**
  - **Limited by gas exchange between emusulsion and bubbles**
  - **Better gas-solid contact in the dilute region**
- **H_2 and CO concentrations are low because:**
  - **High reactivity with H_2**
  - **Reaction rate for SMR is low**

Fuel Reactor Modelling: Results

Gas flow in the dense bed

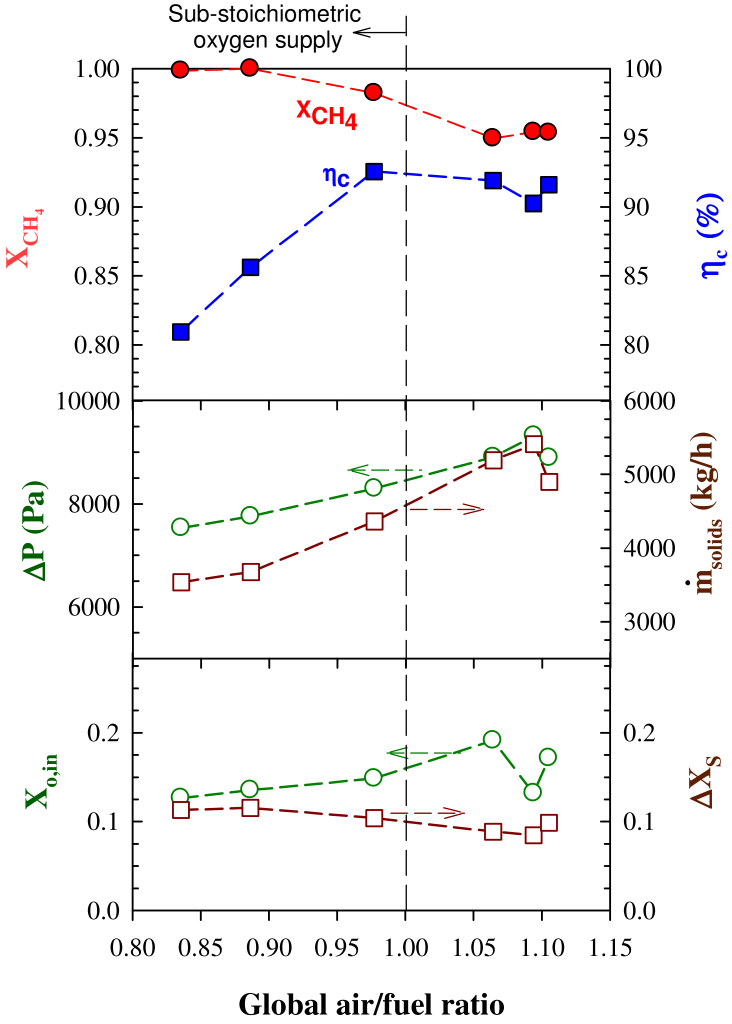


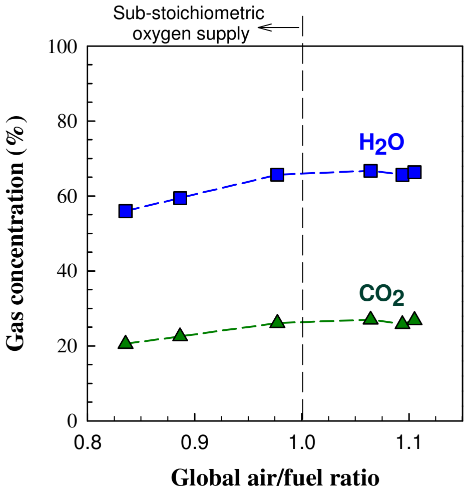
- Most of gas flows through the bubbles
  - Unconverted methane must to diffuse to the emulsion phase to react
- The gaseous products (H_2O, CO_2 , H_2 and CO) are generated in the emulsion
  - H_2O and CO_2 are the main compounds in the emulsion phase

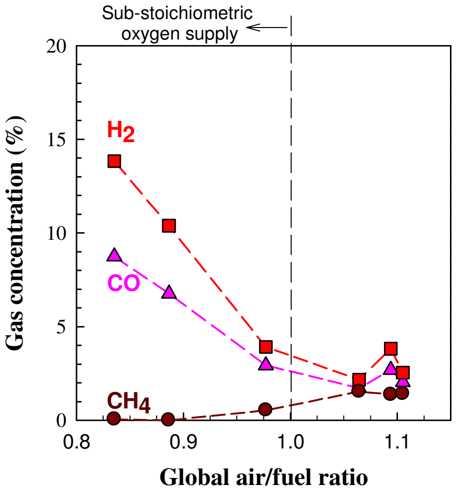
Validation of the Model

Experimental results from 140 kW unit

- The combustion efficiency was maintained roughly constant at Global air/fuel ratio above the stoichiometric conditions, but methane was not fully converted
- CH_4 was fully converted at sub-stoichiometric conditions, but low efficiencies were obtained due to high H_2 and CO concentrations at the exit



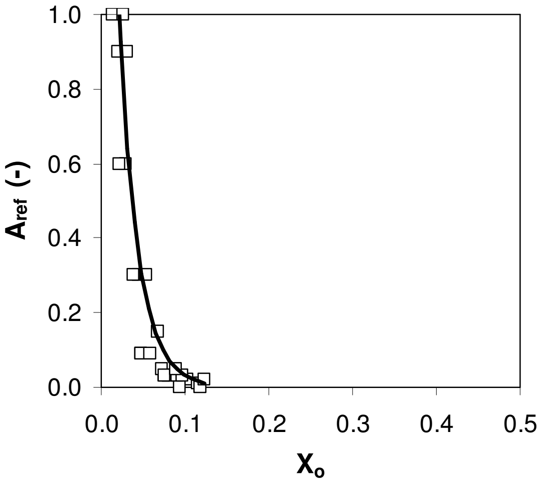


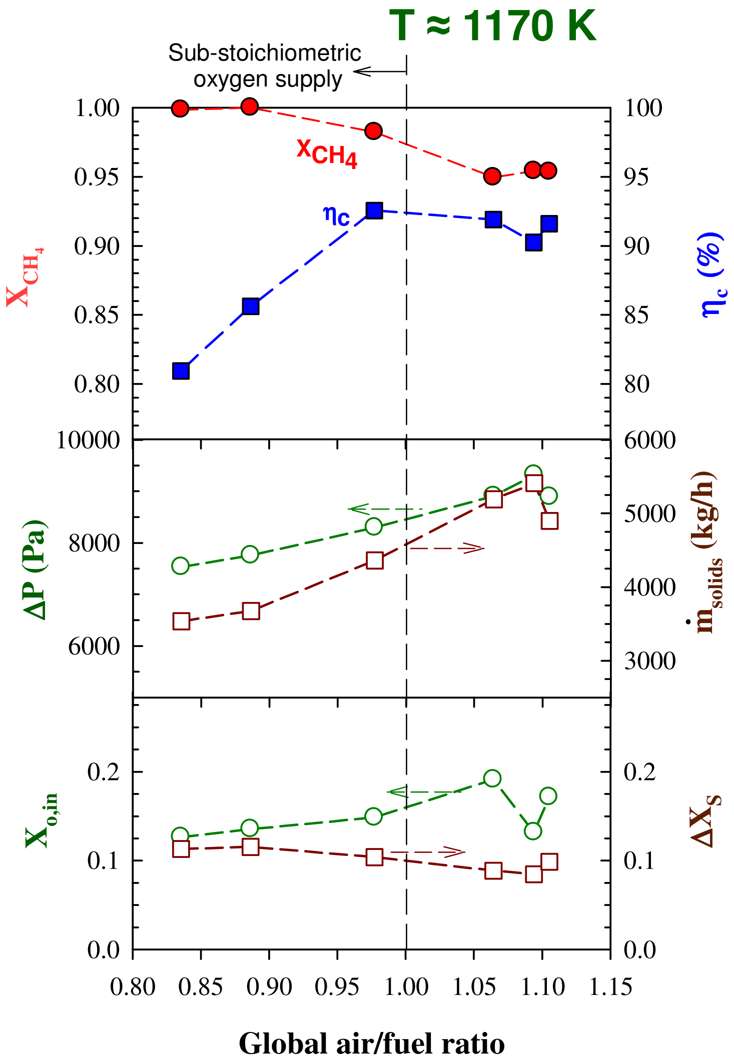


SMR: catalytic activity of the OC

- **The catalytic activity of the OC towards the SMR reaction depends on the oxidation degree, X_O**

$$A_{ref} = \frac{actual\ reforming\ reactivity}{reforming\ activity\ of\ fully\ reduced\ OC}$$



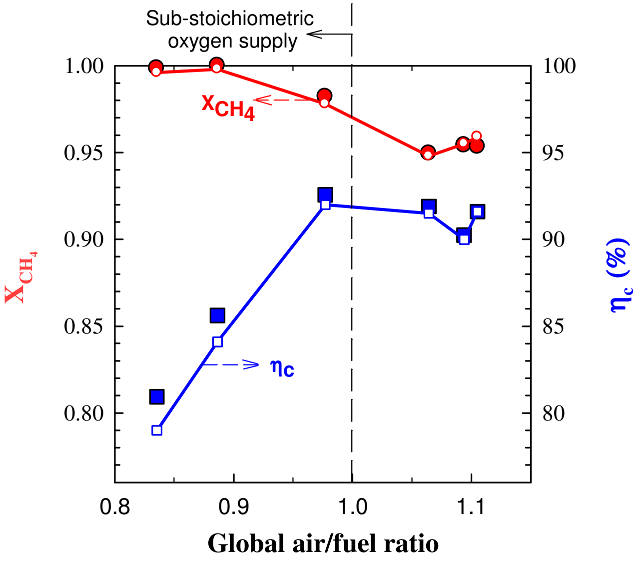


Fuel Reactor Modelling: Results

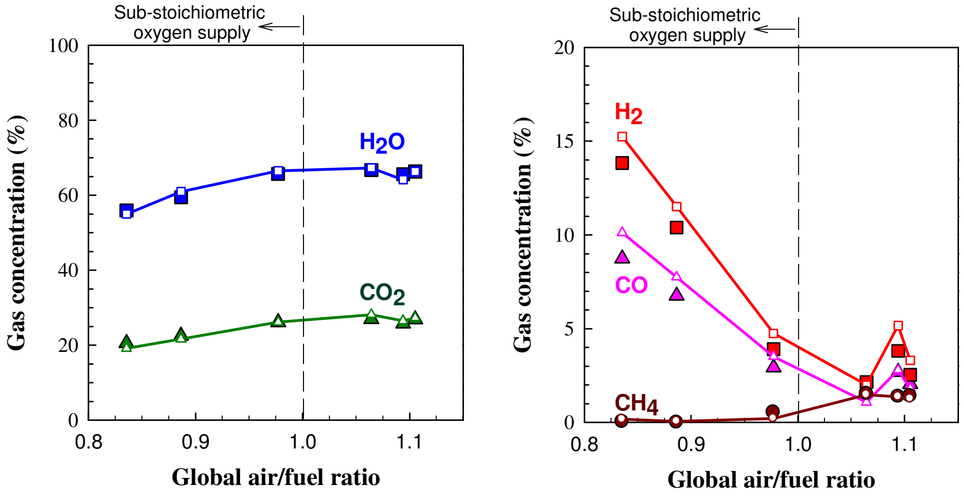
Experimental vs predictions of the model

Effect of the air/fuel ratio

Gas conversion



Gas concentration



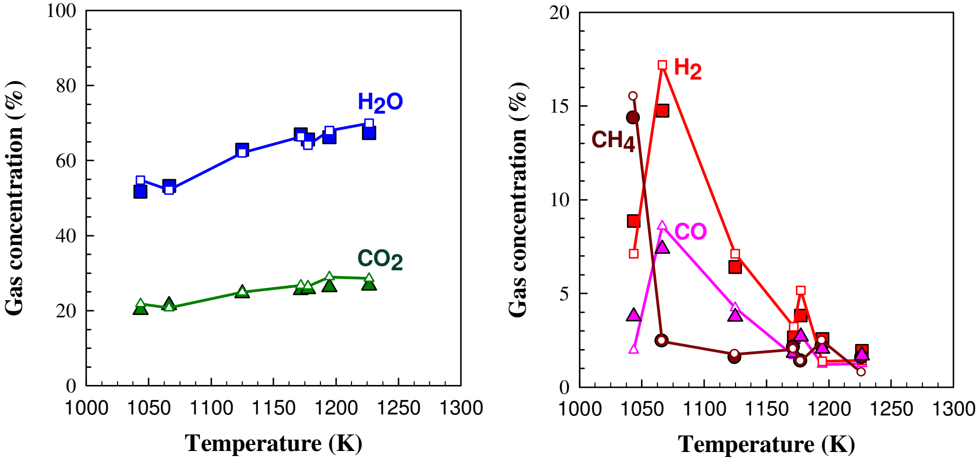
- **Good agreement was found between predicted and experimental data**

Validation of the Model

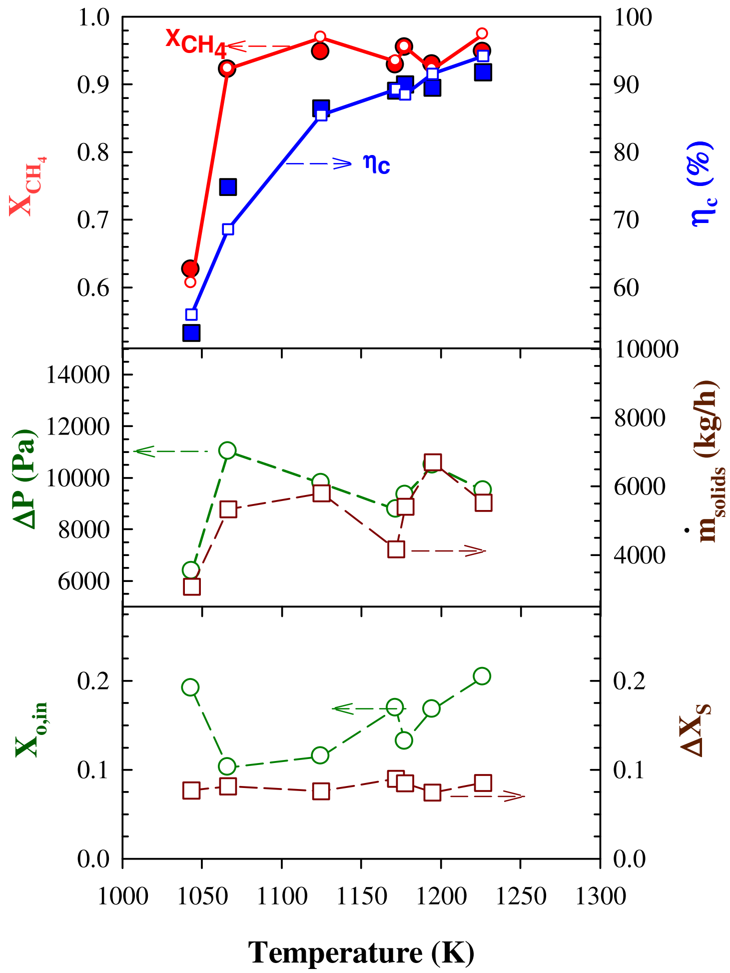
Experimental vs predictions of the model

Effect of the temperature

- Good agreement was found between predicted and experimental data
- The temperature has a strong influence on the combustion efficiency in the range 1000-1150 K
- Lower effect was obtained at higher temperatures



Air/fuel ratio ≈ 1.1



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Conclusions

- A mathematical model describing the fuel-reactor has been developed, being the reactor a fast fluidized bed
- The model includes the fluid dynamics of the system and the chemical reactions involved during the conversion of methane using a Ni-based oxygen carrier
- The model was validated against experimental results obtained in a 140 kW_{th} CLC prototype. Good agreement was found between predicted and experimental data
- The fuel conversion in the dilute region and the steam reforming reaction had decisive importance to obtain high combustion efficiency
- The model will can be used to optimize and design a CLC system when it was joined to a mathematical model for the Air Reactor

Thank you for your attention

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