TECHNISCHE
UNIVERSITÄT
WIEN
Vienna University of Technology

Institute of Chemical Engineering
Research Platform Future Energy Technology
Prof. Hermann Hofbauer

Getreidemarkt 9/166
1060 Wien
www.vt.tuwien.ac.at

Sulfur Deactivation Effects on Hydrogen Production by Catalytic Steam Reforming of Methane Produced by Biomass Gasification

Parham Sadooghi & Reinhard Rauch

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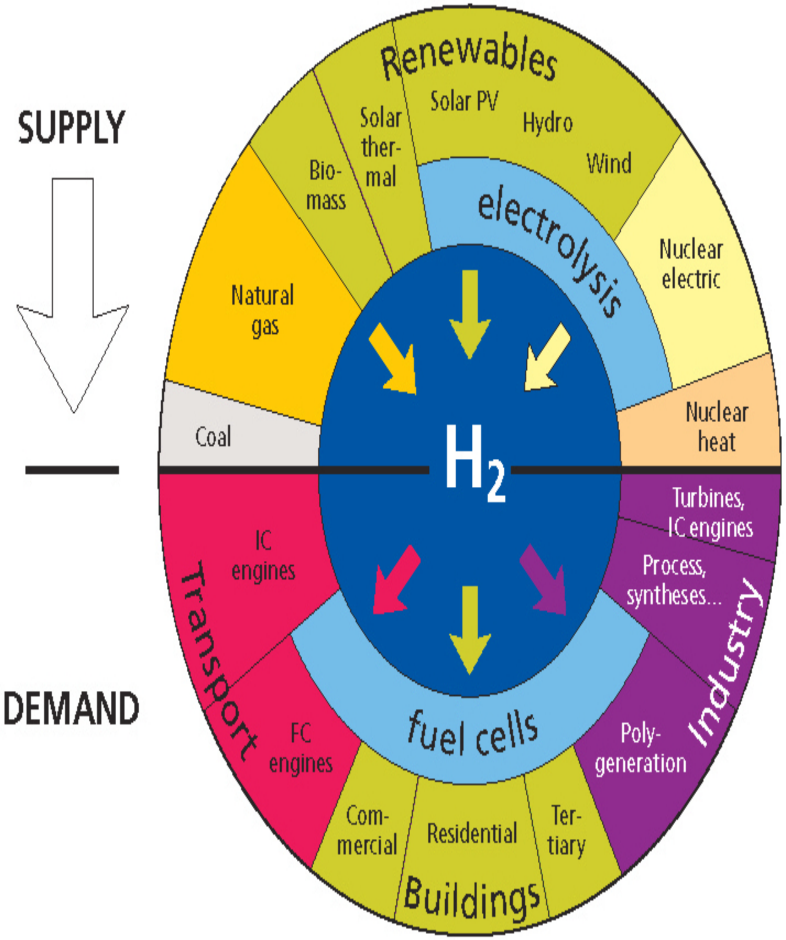
Why Hydrogen?

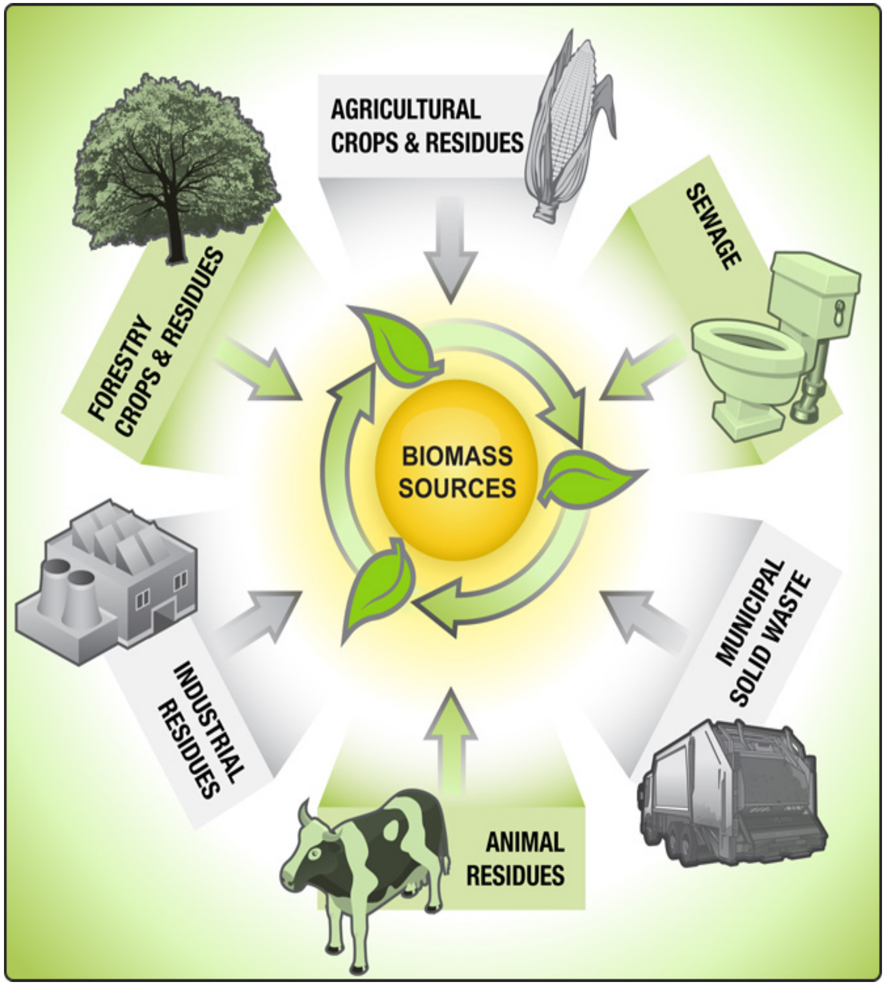
- **Limit of coal, petroleum and fossil fuels resources**
- **Increasing demand for clean transportation fuel**
- **Greenhouse gases and environmental problems**
- **Hydrogen play key role in chemical and refinery industries**



Hydrogen Production

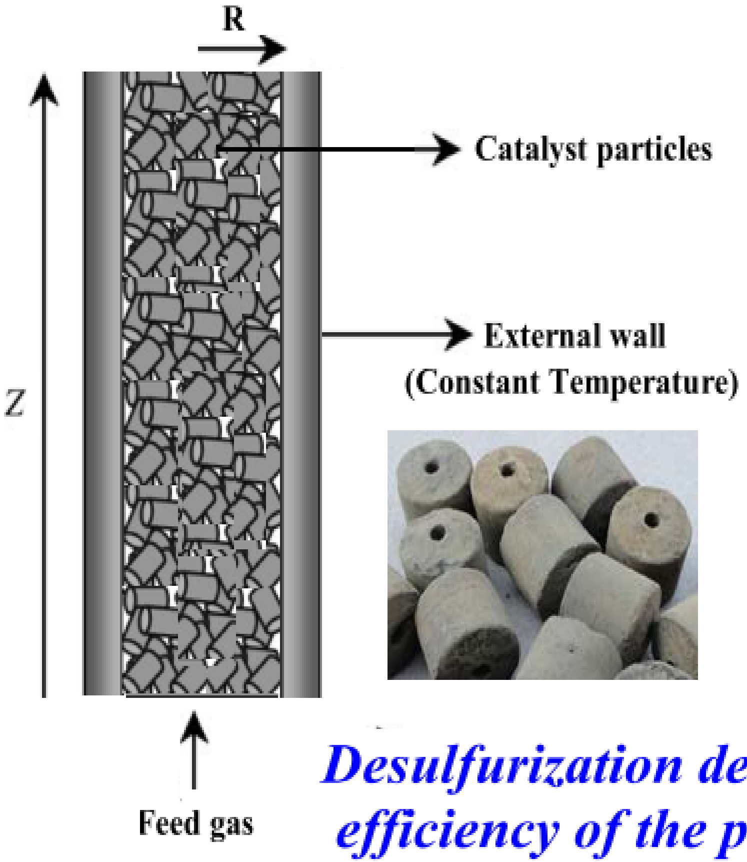
Why Biomass?

- Availability of biomass
- Decreasing the use of fossil fuels
- Decreasing dependence on nuclear power
- Decreasing environmental problems



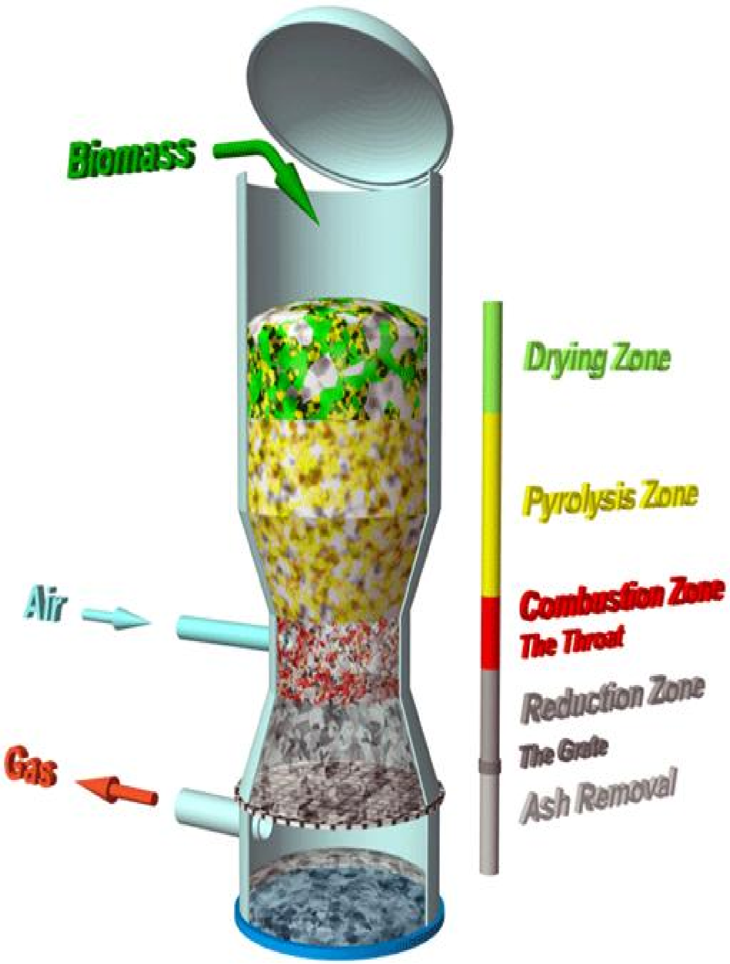
Produced Gas:

CH_4, CO_2, CO, H_2S, H_2,N_2, Hydrocarbons, Impurities



Desulfurization decreases efficiency of the process

Biomass Gasification:



Steam Reforming of Methane

Methane steam reforming reaction

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \qquad \Delta H_1 = 206\ kJ/mol$$

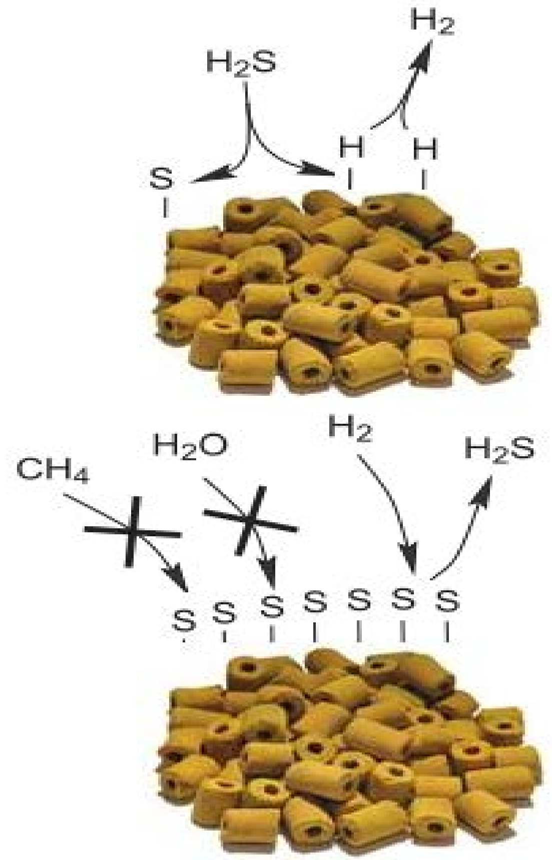
Water gas-shift reaction:

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad \Delta H_2 = -41\ kJ/mol$$

Reverse Methanation Reaction

$$CH_4 + 2H_2O \leftrightarrow CO_2 + 4H_2 \qquad \Delta H_3 = 165\ kJ/mol$$

Sulfur effects: 100 ppm (Typical)



$$H_2S + Ni \leftrightarrow Ni - S + H_2$$

Highlights of Steam Reforming Reactions:

- **Water gas shift reaction highly exothermic**
- **Methane Steam reforming reactions highly endothermic**
- **High temperature low pressure in favor of synthesis**
- **Heat transfer into the reactor is important**

Governing Equations, Boundary Conditions

- ***Mass Balance***

$$\frac{\partial xCH_4}{\partial z} = \frac{D_{er}\rho_g}{G}\left[\frac{1}{r}\frac{\partial CH_4}{\partial r} + \frac{\partial^2 xCH_4}{\partial r^2}\right] + \frac{\rho_b M}{Gy^0 CH_4}(R_1\eta_1 + R_3\eta_3)$$

$$\frac{\partial xCO_2}{\partial z} = \frac{D_{er}\rho_g}{G}\left[\frac{1}{r}\frac{\partial CO_2}{\partial r} + \frac{\partial^2 xCO_2}{\partial r^2}\right] + \frac{\rho_b M}{Gy^0 CH_4}(R_2\eta_2 + R_3\eta_3)$$

- ***Energy Balance:***

$$GC_p\frac{\partial T}{\partial z} = \lambda_{er}\left[\frac{1}{r}\frac{\partial T}{\partial r} + \frac{\partial^2 T}{\partial r^2}\right] + \rho_b\left(\sum_{i=1}^{3}(-\Delta H_i)r_i\eta_i\right)$$

- ***Initial Conditions:***

$C_i = C_0$ at all r and z

$T = T_0$

- ***Boundary Conditions***

$\frac{\partial C}{\partial r} = 0$ at $r = 0$ and r=R all z

$\frac{\partial T}{\partial z} = -\frac{U}{\lambda_{er}}(T - T_a)$ at r=R all z

$C_i = C_0$ at $z = 0$ $0 \le r \le R$

$T = T_0$

$\frac{\partial C}{\partial z} = \frac{\partial T}{\partial z} = 0$ at $z = L$ $0 \le r \le R$

Reactor & Catalyst Data:

Inner tube diameter	**0.02155 (m)**
Tube thickness	**0.0026 (m)**
Tube length	**0.7 (m)**
Outside wall temperature	**1173(K)**
Pellet size	**0.005*0.005(m**
Catalyst bulk density	**0.76(kg/m3)**
Inlet temperature	**1173(K)**
Inlet Pressure	**117300(Pa)**

Maxed model for Sulfur Poisoning:

$$R_{sp} = K_s e^{\frac{-32100}{T}} P_{CH4^{0.8}} * P_{H2^{0.3}} * P_{H2S^{-0.9}}$$

Temkin Isotherm:

$$R_{sp} = R^0{}_{sp} (1-\theta_s)^3$$

$$\theta_s = 1.45 - 9.53.10^{-5}.T + 4.17.10^{-5}.T \ln\left(\frac{p_{H2S}}{p_{H2}}\right)$$

Xu & Froment Kinetics

$$R_1 = \frac{k_1}{p_{H_2}^{2.5}}\left(p_{CH_4}p_{H_2O} - \frac{p_{H_2}^{2.5}p_{CO}}{K_{e1}}\right) \times \frac{1}{DEN^2}$$

$$R_2 = \frac{k_2}{p_{H_2}}\left(p_{CO}p_{H_2O} - \frac{p_{H_2}p_{CO_2}}{K_{e2}}\right) \times \frac{1}{DEN^2}$$

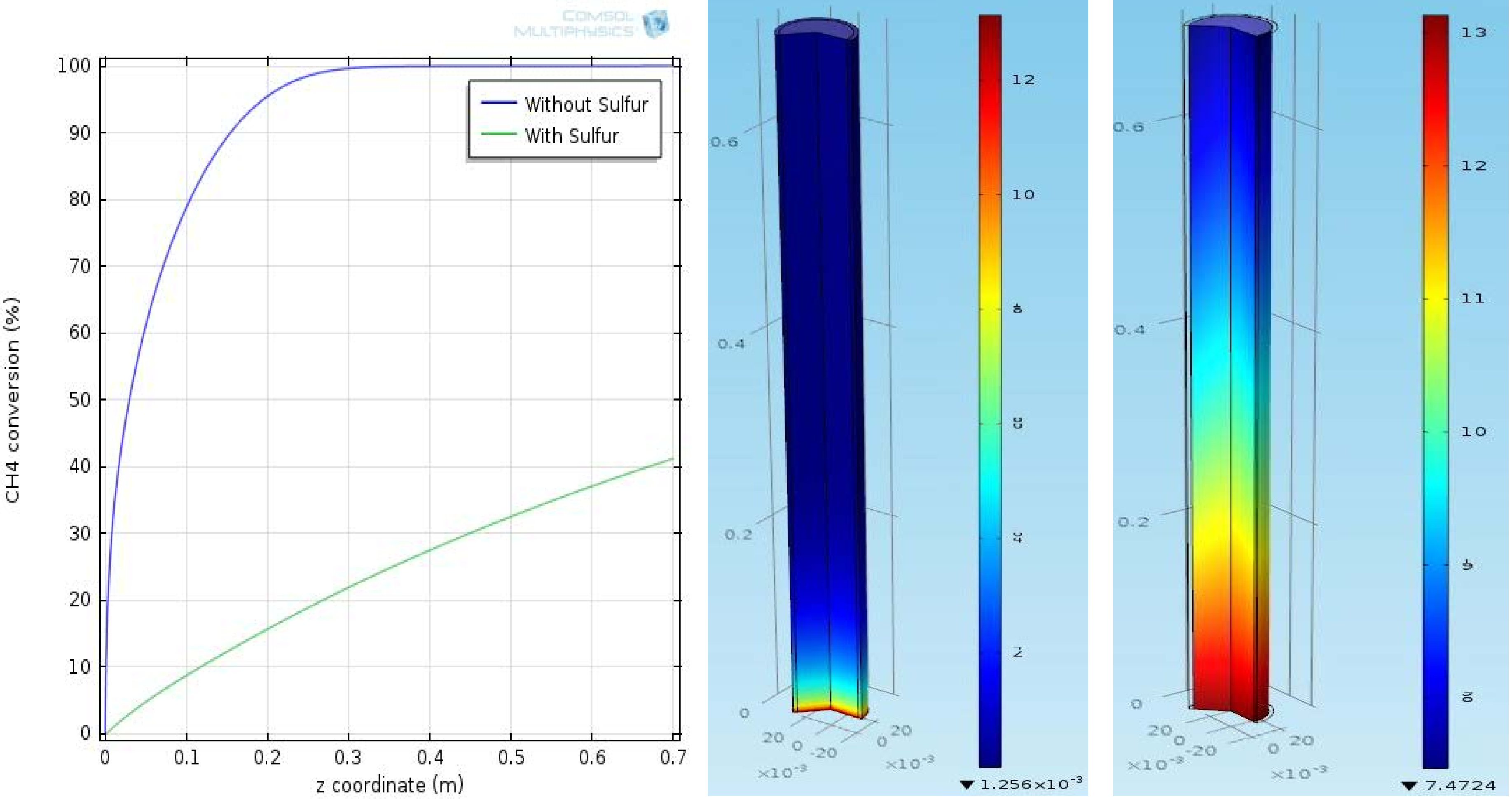
$$R_3 = \frac{k_3}{p_{H_2}^{3.5}}\left(p_{CH_4}p_{H_2O}^2 - \frac{p_{H_2}^4 p_{CO_2}}{K_{e3}}\right) \times \frac{1}{DEN^2}$$

$$DEN = 1 + K_{CO}p_{CO} + K_{H_2}p_{H_2} + K_{CH_4}p_{CH_4} + \frac{K_{H_2O}p_{H_2O}}{p_{H_2}}$$

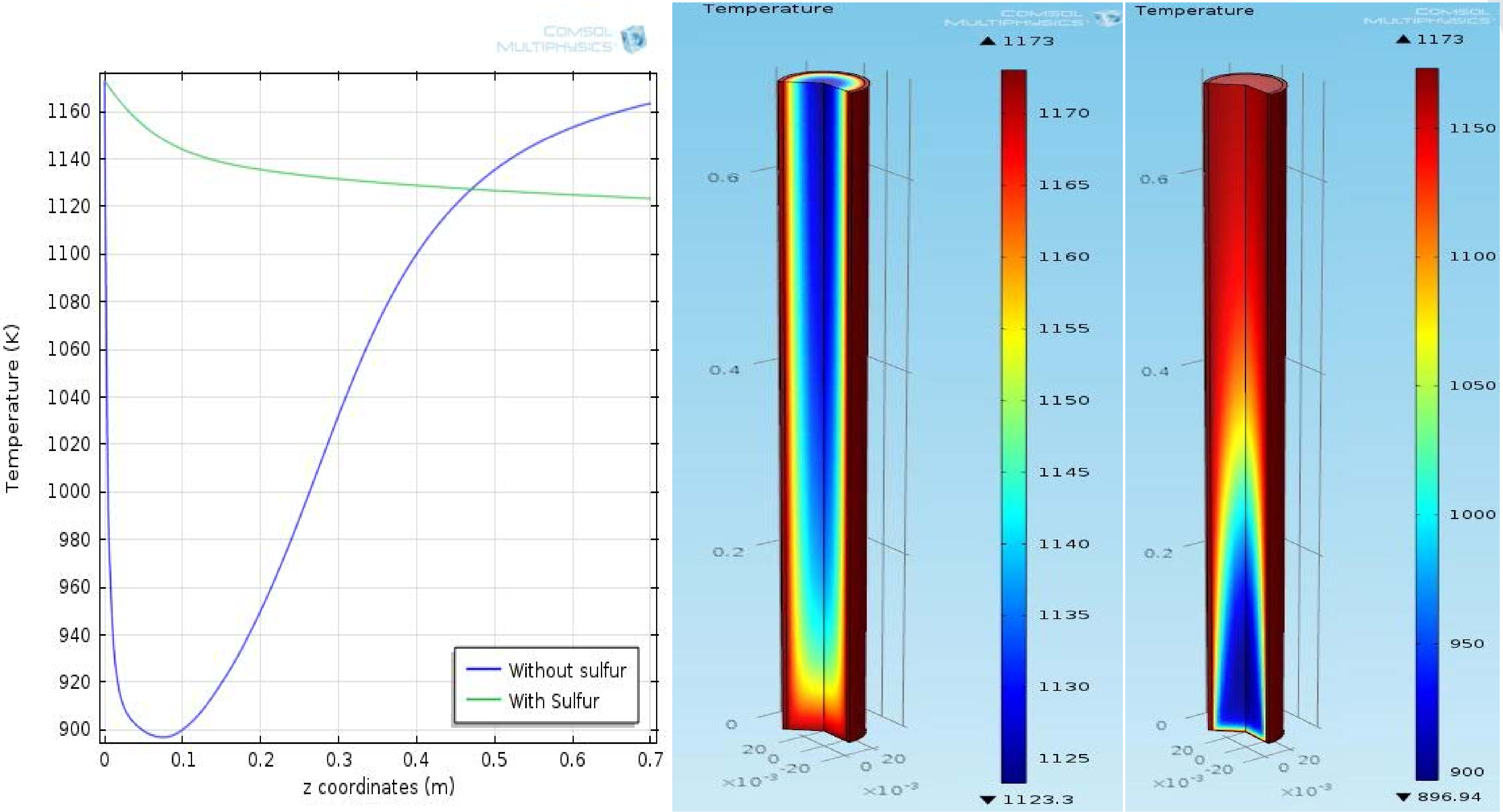
Gas Composition: Güssing Plant, Austria

Gas Species	Gas_dry [Vol%]	Gas_wet [Vol%]
H2O		40
H2	40.0	24.0
CO	22.0	13.2
CO2	23.0	13.8
CH4	10.0	6.0
N2	1.5	0.9
C2H4	3.5	2.1
H2S	0.001	0.001
Rest to 100%	0.0	0.0

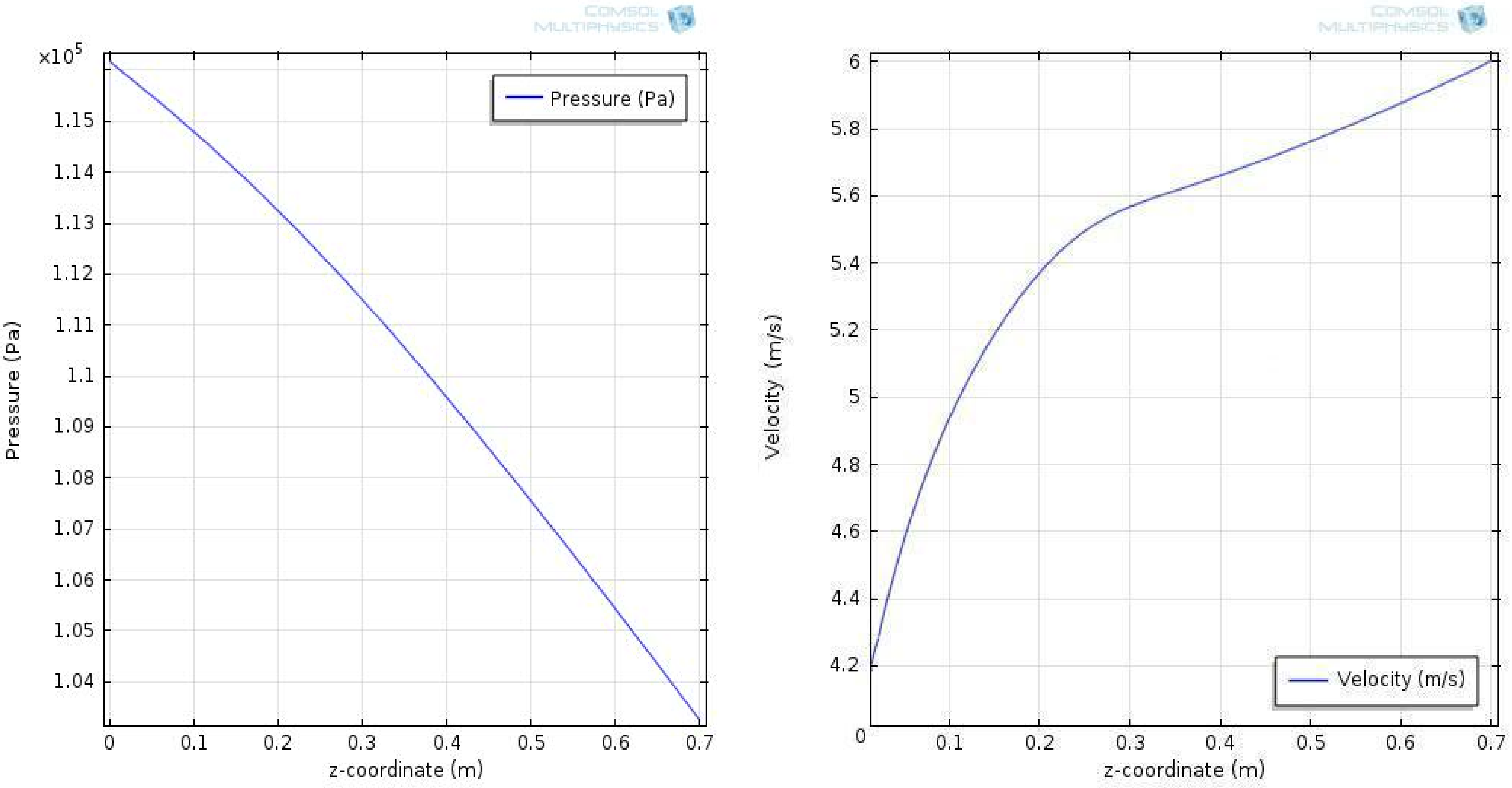
Result & Discussion:



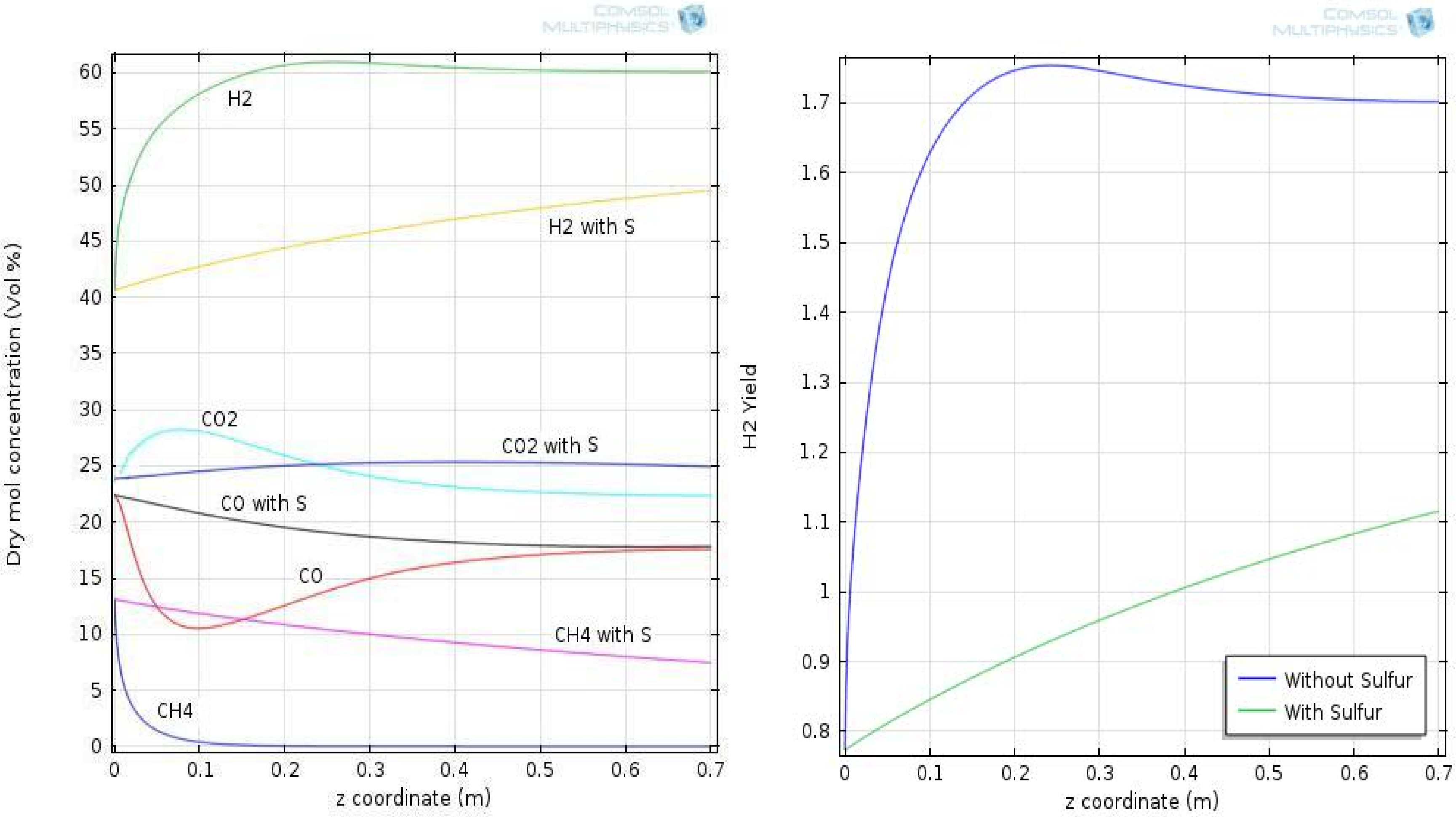
Methane conversion in the reactor with and without sulfur included in the gas. T=1173 (K)



Temperature distribution along the centerline of the reactor with and without sulfur in the gas, T=1173 (K)



Pressure drop and velocity change in the reactor with and without sulfur included in the gas. T=1173 (K)



Molar concentration and hydrogen yield in the reactor with and without sulfur included in the gas. T=1173 (K)

Conclusion:

- The result of the modeling is in good agreement with experimental results.
- Heat transfer in axial and radial direction is exactly simulated by two dimensional model.
- Even at very small amount (100 ppm) hydrogen sulfide has significant effect on the efficiency
- The predicting results are going to be used for optimization and design of an actual reactor.

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Thank You For Your Kind Attention!

Contact: Parham Sadooghi
Parham.sadooghi@tuwien.ac.at

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