NTNU

Innovation and Creativity

SINTEF

Numerical Investigation of the Sorption Enhanced Steam Methane Reforming in a Fluidized Bed Reactor

Financed through GASSMAKS program and PAFFrx project of the Norwegian Research Council

Z. Chao, Y. Wang, J.P. Jakobsen, M. Fernandino, H.A. Jakobsen

Outline

1 Background and Objectives

Background:

SMR (Steam Methane Reforming)

$$CH_4(g) + H_2O(g) = CO(g) + 3H_2(g) \qquad \Delta H_{298} = 206.2\,\mathrm{kJ/mol}$$

$$CO(g) + H_2O(g) = CO_2(g) + H_2(g) \qquad \Delta H_{298} = -41.5\,\mathrm{kJ/mol}$$

$$CH_4(g) + 2H_2O(g) = CO_2(g) + 4H_2(g) \qquad \Delta H_{298} = 164.7\,\mathrm{kJ/mol}$$

SE-SMR (Sorption Enhanced SMR)

$$\mathrm{CaO} + \mathrm{CO_2} \Leftrightarrow \mathrm{CaCO_3} \qquad \Delta H_{298} = -178\,\mathrm{kJ/mol}$$

Advantages:

1. Separation of the green house gas CO_2
2. Higher purity of Hydrogen

NTNU
Innovation and Creativity

1 Background and Objectives

Syetem: Catalyst – Sorbent – Gas mixture

combined

2-phase

3-phase

Reactor: Fixed Bed

Fluidized Beds: Bubble bed, riser

Lindborg et al.(2008), Wang et al.(2010,2011) From Reactor Technology Group, NTNU Have conducted 2D,3D 2-phase modeling.

Objective: 3-phase Bubble bed modeling.

NTNU

Innovation and Creativity

1 Background and Objectives

- Applying Gas-Catalyst-Sorbent 3- phase reactive flow model for SE-SMR fluidized bed reactor

- Check Catalyst-Sorbent segregation-mixing behavior

Johnsen et at.(2006):

Dolomite: 125-300um, 1560kg/m3

Catalyst: 150-250um, 2200kg/m3

- Check other Flow and Reaction performance

NTNU

Innovation and Creativity

2 Model Equations and Modeling

Three-fluid model is used.

Gas Phase : K- Epsilon turbulent model

Particle Phase: KTGF

particle billiard ball collision theory + some statistical methods

N-S like momentum Eqns

Continuity Eqns

Other transport Eqns

Chao et al.,2011, Derivation and Validation of a Binary Multi-fluid Eulerian Model for Fluidized Beds, Chemical Engineering Science, Vol.66,3605-3616.

2 Model Equations and Modeling

Subscript: 0 Gas, i = 1 (catalyst), 2 (sorbent)

Continuity Equations

$$\frac{\partial}{dt}(\alpha_i\rho_i) + \nabla\cdot(\alpha_i\rho_i\mathbf{v}_i) = \Gamma_i$$

i = 0,1,2

Gas particle coupling

Gas momentum Equation

$$\frac{\partial}{dt}(\alpha_0\rho_0\mathbf{v}_0) + \nabla\cdot(\alpha_0\rho_0\mathbf{v}_0\mathbf{v}_0) = -\alpha_0\nabla p_0 - \nabla\cdot\alpha_0(\boldsymbol{\tau}_0 + \boldsymbol{\tau}_t) + \sum_{k=1}^{2}\beta_{0k}(\mathbf{v}_k - \mathbf{v}_0) + \alpha_0\rho_0\mathbf{g}$$

Particle momentum Equations

i = 1,2

$$\frac{\partial}{dt}(\alpha_i\rho_i\mathbf{v}_i) + \nabla\cdot(\alpha_i\rho_i\mathbf{v}_i\mathbf{v}_i) = -\alpha_i\nabla p_0 - \nabla\cdot\mathbf{p}_i + \beta_{0i}(\mathbf{v}_0 - \mathbf{v}_i) + \sum_{k=1}^{2}\beta_{ik}(\mathbf{v}_k - \mathbf{v}_i) + \alpha_i\rho_i\mathbf{g}$$

Granular temperature Equations

i = 1,2

P-P coupling

$$\frac{3}{2}\frac{\partial}{dt}(\alpha_i\rho_i\Theta_i) + \frac{3}{2}\nabla\cdot(\alpha_i\rho_i\Theta_i\mathbf{v}_i) = -\mathbf{p}_i : \nabla\mathbf{v}_i - \nabla\cdot\mathbf{q}_i + 3\beta_{0i}\Theta_i + \gamma_i$$

2 Model Equations and Modeling

Gas turbulent kinetic engergy Equation

$$\frac{\partial}{dt}(\alpha_0\rho_0 k_0)+\nabla\cdot(\alpha_0\rho_0 k_0\mathbf{v}_0)=\alpha_0(-\boldsymbol{\tau}_t:\nabla\mathbf{v}_0+S_t)+\nabla\cdot(\alpha_0\frac{\mu_0^t}{\sigma_0}\nabla k_0)-\alpha_0\rho_0\varepsilon_0$$

Gas turbulent kinetic engergy dissipation rate Equation

$$\frac{\partial}{dt}(\alpha_0\rho_0\varepsilon_0)+\nabla\cdot(\alpha_0\rho_0\varepsilon_0\mathbf{v}_0)=\alpha_0 C_1\frac{\varepsilon_0}{k_0}(-\boldsymbol{\tau}_t:\nabla\mathbf{v}_0+S_t)+\nabla\cdot(\alpha_0\frac{\mu_0^t}{\sigma_\varepsilon}\nabla\varepsilon_0)-\alpha_0\rho_0 C_2\frac{\varepsilon_0^2}{k_0}$$

Gas molecular temperature Equation

$$\alpha_0\rho_0 C_{p,0}\frac{DT_0}{Dt}=\nabla\cdot\alpha_0\lambda_0^{\text{eff}}\nabla T_0+\boxed{Q_{01}+Q_{02}}+\boxed{\sum_{j=1}^{3}R_j^{SMR}\Delta H_j^{SMR}}$$

Catalyst molecular temperature Equation

$$\alpha_1\rho_1 C_{p,1}\frac{DT_1}{Dt}=\nabla\cdot\alpha_1\lambda_1^{\text{eff}}\nabla T_1-\boxed{Q_{01}}$$

Sorbent molecular temperature Equation

$$\alpha_2\rho_2 C_{p,2}\frac{DT_2}{Dt}=\nabla\cdot\alpha_2\lambda_2^{\text{eff}}\nabla T_2+\boxed{R^{Sorb}\Delta H^{Sorb}}-\boxed{Q_{02}}$$

Gas species transport Equation

$$\frac{\partial}{\partial t}(\rho_0\omega_j)+\nabla\cdot(\rho_0\mathbf{v}_0\omega_j)=\nabla\cdot\left(\rho_0 D_0^{\text{eff}}\nabla\omega_j\right)+\boxed{R_j+\frac{\Gamma_0}{\alpha_0}\omega_j^i}$$

NTNU

Innovation and Creativity

2 Model Equations and Modeling

Xu and Froment (1989)

$$R_1^{SMR} = \frac{k_1}{p_{H_2}^{2.5}} \left[\frac{p_{CH_4} p_{H_2O} - p_{H_2}^3 p_{CO}/K_1}{DEN^2} \right]$$

$$R_2^{SMR} = \frac{k_2}{p_{H_2}} \left[\frac{p_{CO} p_{H_2O} - p_{H_2} p_{CO_2}/K_2}{DEN^2} \right]$$

$$R_3^{SMR} = \frac{k_3}{p_{H_2}^{3.5}} \left[\frac{p_{CH_4} p_{H_2O}^2 - p_{H_2}^4 p_{CO_2}/K_3}{DEN^2} \right]$$

Sun et al. (2008)

$$R^{Sorb} = 56 k_s (1 - X)(p_{CO_2} - p_{CO_{2,eq}})^n S$$

NTNU
Innovation and Creativity

2 Model Equations and Modeling

Phase coupling:

(1) Gas—catalysts—sorbents momentum

$$\beta_{0k} = \begin{cases} \frac{150\mu_0(1-\alpha_0)\alpha_k}{\alpha_0 d_k^2} + \frac{1.75\alpha_k\rho_0|\mathbf{v}_0-\mathbf{v}_k|}{d_k} & \text{if } \alpha_0 \le 0.8 \\ \frac{3C_D\rho_0\alpha_k|\mathbf{v}_0-\mathbf{v}_k|}{4d_k}\alpha_0^{-1.65} & \text{if } \alpha_0 > 0.8 \end{cases}$$

$$\beta_{12} = \frac{m_1 m_2 n_1 n_2}{m_1+m_2} d_{12}^2 (1+e_{12}) g_{12} \{ (\sqrt{2\pi}\Theta_1^{0.5} + \sqrt{2\pi}\Theta_2^{0.5} - \sqrt{2}\Theta_{12}^{0.25}\Theta_2^{0.25}) + [\frac{\pi}{2} v_{12} - 1.135 v_{12}^{0.5} (\Theta_1^{0.25} + \Theta_1^{0.25} + 0.8\Theta_1^{0.125}\Theta_1^{0.125})] \} + \beta_{12}^{fri}$$

(2) Gas—catalysts (sorbents) heat transfer

$$Q_{0k} = \frac{6\alpha_k}{d_k} h_{0k} (T_k - T_0)$$

NTNU
Innovation and Creativity

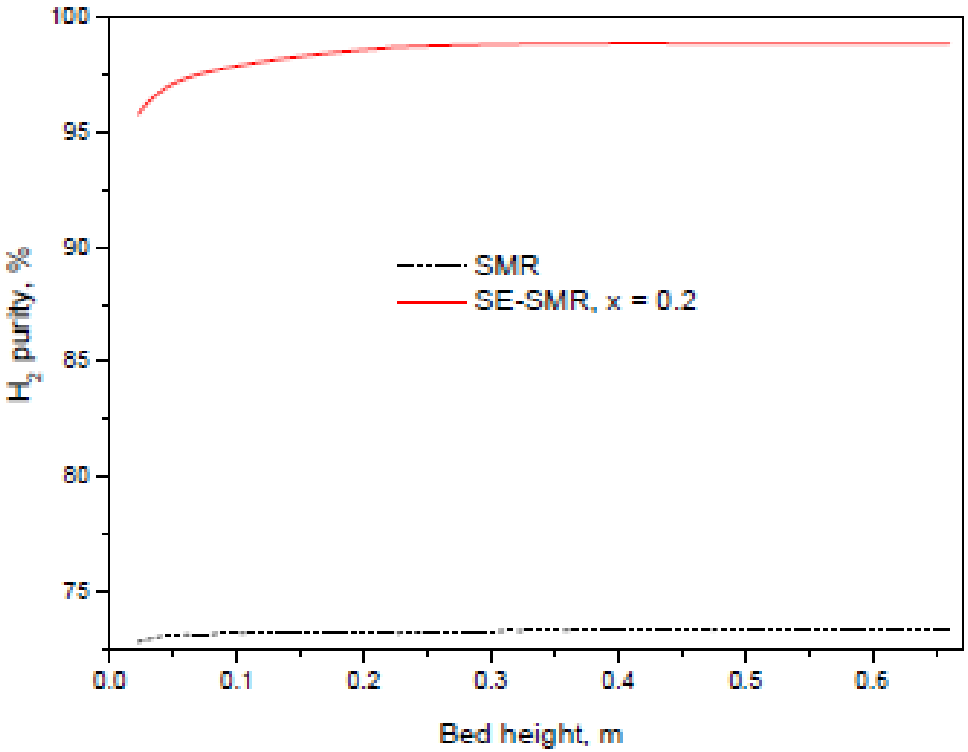
2 Model Equations and Modeling

Parameters	Values
Bed height (m)	0.66
Bed diameter (m)	0.1
Total mass of the particles(kg)	3.1
Catalyst to calcined dolomite mass ratio	2.5
Static bed height (m)	0.3
Catalyst particle size (μm)	150-250
Dolomite particle size (μm)	125-300
Reforming Temperature (^oC)	600
Superficial gas velocity(m/s)	0.096
Steam to Carbon molar feed ratio	3
Catalyst density (kg/m^3)	2200
Dolomite particle density (kg/m^3)	1560

Laboratory Scale bubble bed reactor from Johnson et al. (2006) is investigated.

3 Results

3.1 Hydrogen purity for SMR, SE-SMR



Axial hydrogen purity distribution for SMR and SE-SMR.

$x = q/q_{max}$

SE-SMR process can improve H_2 purity apparently than SMR

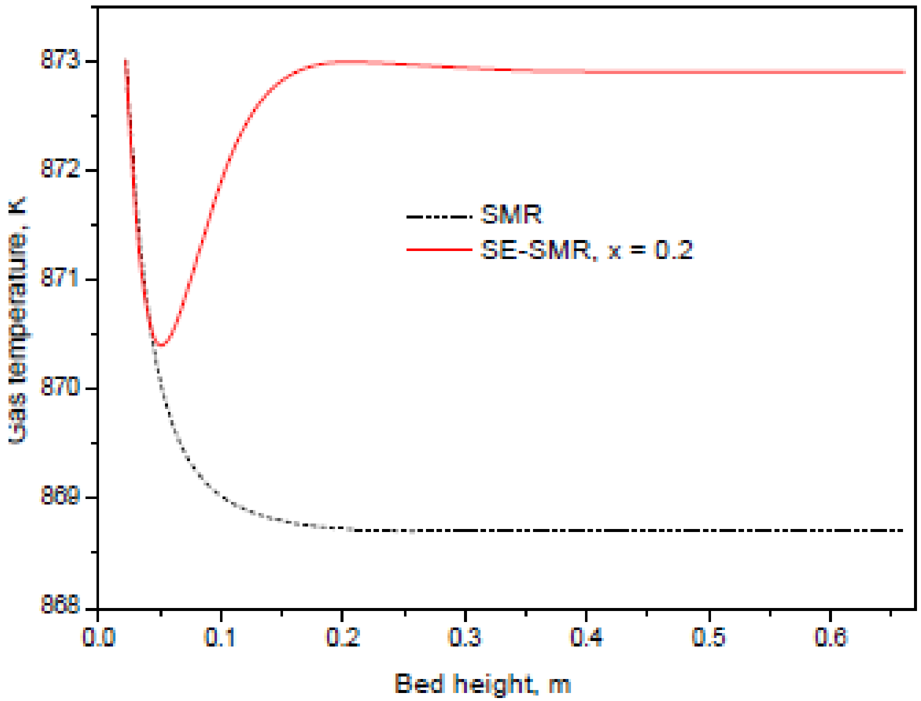
EXP. From Johnsen et at.(2006):

H_2 purity: 98-99% around

NTNU
Innovation and Creativity

3 Results

3.2 Gas temperatures for SMR, SE-SMR



Gas temperature distribution for SMR and SE-SMR.

SMR reaction:

Endothermic

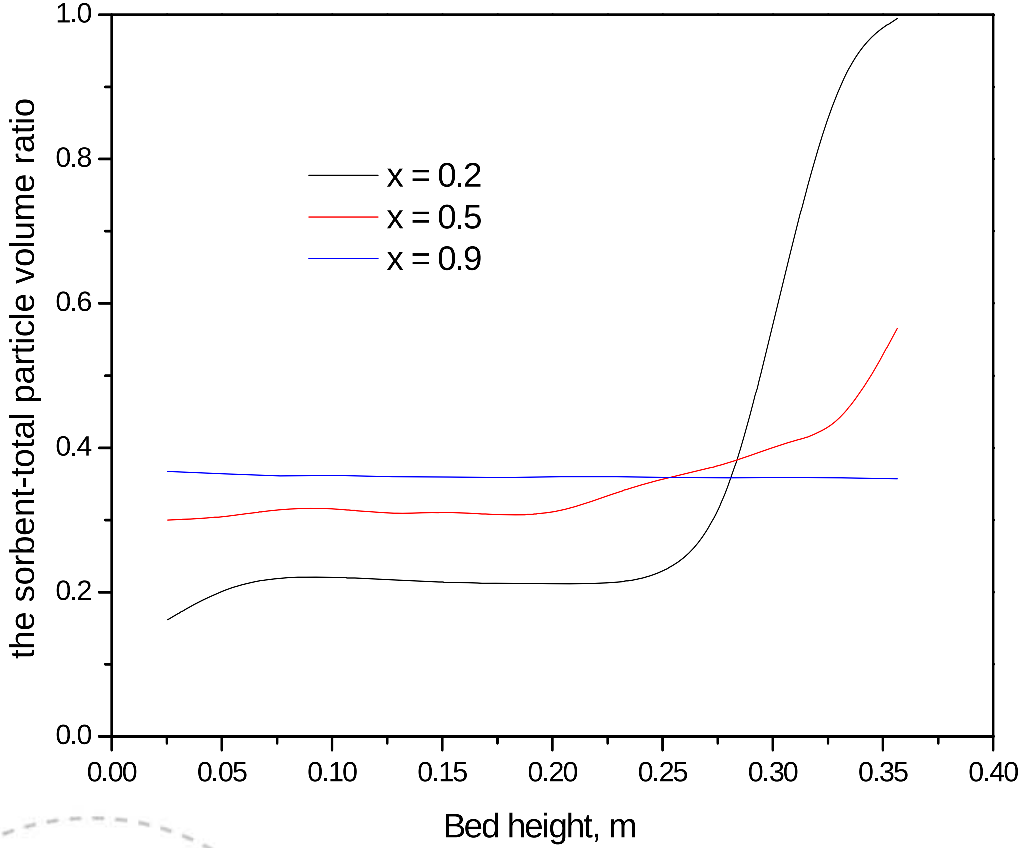
SE-(CO_2 sorption) reaction:

exothermic

NTNU
Innovation and Creativity

3 Results

3.3 Catalyst-Sorbent Segregation



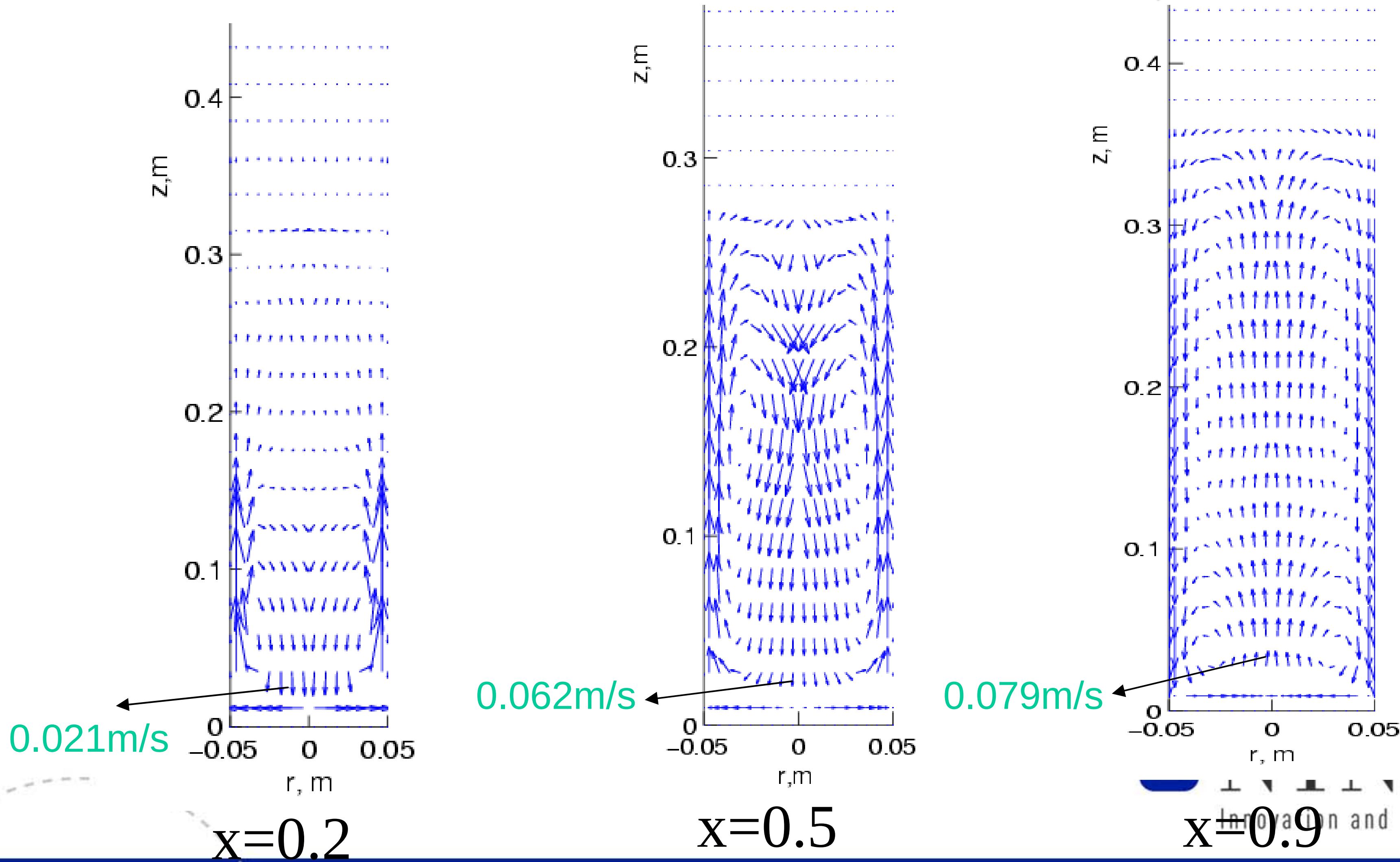
x= q/q_{max}	$\rho_s (kg/m^3)$
0.2	1694
0.5	1895
0.9	2163

$$\rho_c = 2200 kg/m^3$$

NTNU
Innovation and Creativity

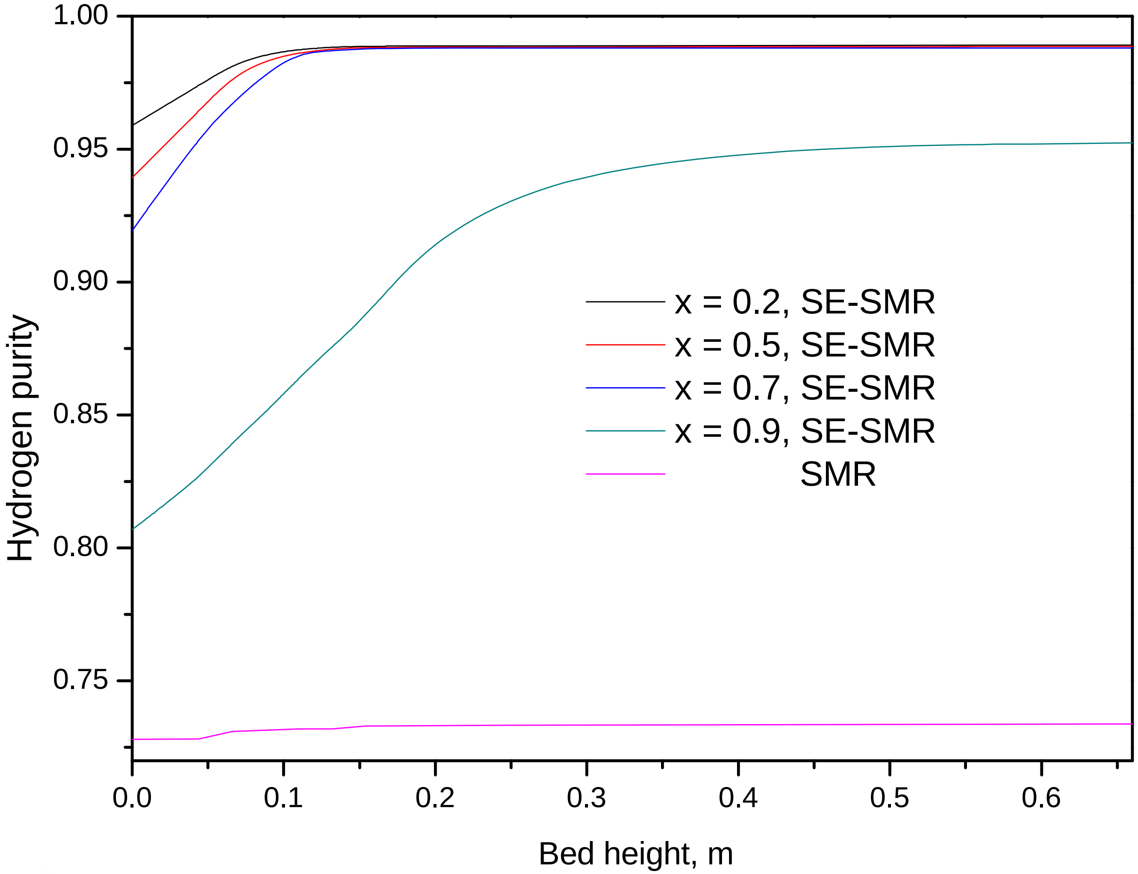
3 Results

3.4 Particle flow profiles, sorbent



3 Results

3.5 Sorption-enhanced performance in the adsorption process



x= q/q_{max}	$\rho_s (kg/m^3)$
0.2	1694
0.5	1895
0.7	2029
0.9	2163

$$\rho_c = 2200 kg/m^3$$

NTNU
Innovation and Creativity

4 Conclusions and Further Work

4.1 Conclusions

- A three-fluid reactive flow model was applied to SE-SMR reactor, reasonable results are obtained:

  --SE objective could be realized.

  --The hydrogen purity agrees well with the experiment.

- SE-SMR Process are characterized by:

  -- Sorbent weight increases

  -- changed particle flow profiles.

  -- binary particles: segregated to mixed.

  -- Even when x =0.7, the outlet H_2 purity can get 98%.

NTNU
Innovation and Creativity

4.2 Further work

Natural sorbents used in the present investigation

Dolomite: 1560kg/m3

Catalyst: 2200kg/m3

If synthetic sorbents are to be used

Synthetic CaO: 2500kg/m3 (Rout et al.2011)

Catalyst: 2200kg/m3

NTNU
Innovation and Creativity

Thank you for your attention!

SINTEF

NTNU
Innovation and Creativity