Electrical Supplementary Information (ESI)

Factorial Design Analysis of Parameters for Sorption Enhanced Steam Reforming of Ethanol in a Circulating Fluidized Bed Riser using CFD

![Main Effects](Image)

- **Main Effects (a)**
  - $H_2$ flux [kg/m².s]
  - Variables: A-fiser id., B-Inlet temp., C-Cat./Sorb., D-Gs, E-U

![Interactions](Image)

- **Interactions (b)**
  - $H_2$ flux [kg/m².s]
  - Variables: D

- **Interactions (c)**
  - $H_2$ flux [kg/m².s]
  - Variables: A

**Fig. S1.** The main effects (a) and the interactions (b and c) on the $H_2$ flux.
Fig. S2. The main effects (a) and the interactions (b and c) on the H₂ purity.
Table S1  Conservation equations used in the simulations.

a) Mass conservation for each phase q:
\[
\frac{\partial}{\partial t} (\varepsilon_q \rho_q) + \nabla \cdot (\varepsilon_q \rho_q \mathbf{v}_q) = \sum_{p=1}^{n} (\dot{m}_{pq} - \dot{m}_{qp}) + S_{m,q} \tag{S1}
\]

b) Momentum conservation
- for gas phase:
\[
\frac{\partial}{\partial t} (\varepsilon_g \rho_g \mathbf{v}_g) + \nabla \cdot (\varepsilon_g \rho_g \mathbf{v}_g \mathbf{v}_g) = -\varepsilon_g \nabla \mathbf{p}_g + \varepsilon_g \mathbf{v}_g \cdot \mathbf{\tau}_g + \varepsilon_g \rho_g g + \sum_{s=1}^{n} (\mathbf{K}_{sg} (\mathbf{v}_s - \mathbf{v}_g) + \dot{m}_{sg} \mathbf{v}_sg - \mathbf{\hat{m}}_g) \tag{S2}
\]
- for solid phase:
\[
\frac{\partial}{\partial t} (\varepsilon_s \rho_s \mathbf{v}_s) + \nabla \cdot (\varepsilon_s \rho_s \mathbf{v}_s \mathbf{v}_s) = -\varepsilon_s \nabla \mathbf{p}_s + \varepsilon_s \mathbf{v}_s \cdot \mathbf{\tau}_s + \varepsilon_s \rho_s g + \sum_{l=1}^{n} (\mathbf{K}_{ls} (\mathbf{v}_l - \mathbf{v}_s) + \dot{m}_{ls} \mathbf{v}_ls - \mathbf{\hat{m}}_s) \tag{S3}
\]

c) Energy conservation
- for gas phase:
\[
\frac{\partial}{\partial t} (\varepsilon_g \rho_g H_g) + \nabla \cdot (\varepsilon_g \rho_g H_g \mathbf{v}_g) = \varepsilon_g \frac{\partial \mathbf{p}_g}{\partial t} + \mathbf{\tau}_g \cdot \mathbf{\hat{v}}_g + \nabla \cdot (\mathbf{\hat{q}}_g) + S_{h,g} + \sum_{s=1}^{n} (Q_{sg} + \dot{m}_{sg} h_{sg} - \dot{m}_g) \tag{S4}
\]
- kinetic fluctuation energy conservation for solid phase:
\[
\frac{3}{2} \frac{\partial}{\partial t} (\varepsilon_s \rho_s \mathbf{\Theta}_s) + \nabla \cdot (\varepsilon_s \rho_s \mathbf{\Theta}_s \mathbf{v}_s) = -\gamma_{\Theta_s} \mathbf{\Theta}_s + \phi_{ls} \tag{S5}
\]
where \(\gamma_{\Theta_s}\) is collisional dissipation of energy (Lun et al. [S1]):
\[
\gamma_{\Theta_s} = \frac{12(1 - e_{ss}^2) e_{0,ss} e_{s}^{2/3}}{d \sqrt{\pi} \rho_{s} e_{s}^{2/3}} \tag{S6}
\]
and \(\phi_{ls}\) is kinetic energy exchange between phase l and solid phase:
\[
\phi_{ls} = -3 K_{ls} \mathbf{\Theta}_s \tag{S7}
\]
d) Chemical species conservation of the species k in phase q:
\[
\frac{\partial}{\partial t} (\varepsilon_q \rho_q Y_q^k) + \nabla \cdot (\varepsilon_q \rho_q Y_q^k \mathbf{v}_q) = -\nabla \cdot (\varepsilon_q Y_q^k) + \varepsilon_q R_q^k + \varepsilon_q S_q^k + \sum_{p=1}^{n} (\dot{m}_{pq}^k - \dot{m}_{qp}^k) \tag{S8}
\]
Table S2  Constitutive equations used in the simulations.

a) Stress tensor for each phase $q$:
\[ \tau_q = \varepsilon_q \mu_q \left( \nabla \cdot \mathbf{v}_q + \nabla \mathbf{v}_q \right) + \varepsilon_q \left( \lambda_q - \frac{2}{3} \mu_q \right) \nabla \cdot \mathbf{v}_q \]  \hspace{1cm} (S9)

b) Solid shear viscosity:
\[ \mu_s = \mu_{s,\text{col}} + \mu_{s,\text{kin}} + \mu_{s,\text{fr}} \]  \hspace{1cm} (S10)

where $\mu_{s,\text{col}}$ is the collisional viscosity:
\[ \mu_{s,\text{col}} = \frac{4}{5} \varepsilon_s \rho_s d_s g_{0,ss} \left( 1 + e_{ss} \right) \frac{(\Theta_s)}{\pi}^{1/2} \varepsilon_s \]  \hspace{1cm} (S11)

and $\mu_{s,\text{kin}}$ is the kinetic viscosity (Gidaspow et al. [S1]):
\[ \mu_{s,\text{kin}} = \frac{10 \varepsilon_s \rho_s d_s \sqrt{\Theta_s \pi}}{96 \varepsilon_s \left( 1 + e_{ss} \right) g_{0,ss}} \left[ 1 + \frac{4}{5} \varepsilon_s g_{0,ss} \left( 1 + e_{ss} \right) \right]^{2/5} \varepsilon_s \]  \hspace{1cm} (S12)

c) Solid bulk viscosity (Lun et al. [S1]):
\[ \lambda_s = \frac{4}{3} \varepsilon_s^2 \rho_s d_s g_{0,ss} \left( 1 + e_{ss} \right) \left( \frac{\Theta_s}{\pi} \right)^{1/2} \varepsilon_s \]  \hspace{1cm} (S13)

d) Solid Pressure (Lun et al. [S1]):
\[ p_s = \varepsilon_s \rho_s \Theta_s + 2 \varepsilon_s^2 \rho_s \Theta_s g_{0,ss} \left( 1 + e_{ss} \right) \]  \hspace{1cm} (S14)

e) Radial distribution coefficient
- for one solid phase (Lun et al. [S1]):
\[ g_{0,ss} = \left[ 1 - \left( \frac{e_s}{e_{s,\text{max}}} \right)^{1/3} \right] \cdot 1 \]  \hspace{1cm} (S15)

- the mutual radial distribution coefficient between two solid phases:
\[ g_{0,ls} = \frac{d_s g_{0,li} + d_l g_{0,ss}}{d_s + d_l} \]  \hspace{1cm} (S16)
f) Granular temperature from KTGF:

\[
\frac{3 \partial}{\partial t} (\varepsilon_s \rho_s \Theta_s) = (-p_s I_s + \tau_s) \nabla v_s - \gamma \Theta_s + \phi_{ls}
\]  

(S17)

g) Gas-solid momentum exchange coefficient using Gidaspow's drag model [S1]

- for \( \varepsilon_g > 0.8 \):

\[
K_{sg} = \frac{3}{4} C_D \frac{\epsilon_g \rho_g |v_s - \nabla g|}{d_s} \varepsilon_g - 2.65
\]  

(S18)

where \( C_D \) is drag coefficient:

\[
C_D = \frac{24}{\epsilon_g \Re_s} \left[ 1 + 0.15(\epsilon_g \Re_s)^{0.687} \right]
\]  

(S19)

- for \( \varepsilon_g \leq 0.8 \):

\[
K_{sg} = 150 \frac{\epsilon_g (1 - \varepsilon_g) \mu_g}{\epsilon_g d_s^2} + 1.75 \frac{\rho_g \epsilon_g |v_s - \nabla g|}{d_s}
\]  

(S20)

h) Solid-solid momentum exchange coefficient:

\[
K_{ls} = K_{sl} = \frac{3(1 + \epsilon_l) \left( \frac{\pi}{2} + C_{fr,ls} \frac{\pi^2}{8} \right) \epsilon_l \rho_l \rho_l (d_l + d_s) \epsilon_l |v_l - \nabla l|}{2 \pi (\rho_l d_l^3 + \rho_s d_s^3)}
\]  

(S21)

i) Gas-solid heat exchange coefficient:

\[
h_{sg} = h_{gs} = \frac{k_A \text{Nu}_s}{d_s}
\]  

(S22)

where \( \text{Nu}_s \) is Nusselt number of solid phase (Gunn’s model [S1]):

\[
\text{Nu}_s = \left( 7 - 10 \epsilon_g + 5 \epsilon_g^2 \right) \left( 1 + 0.7 \Re_s^{0.2} \Pr^{1/3} \right) + \left( 1.33 - 2.4 \epsilon_g + 1.2 \epsilon_g^2 \right) \Re_s^{0.7} \Pr^{1/3}
\]  

(S23)

Table S3  The setting of phase and system properties in the simulations.

| Phase properties                     |           |
|--------------------------------------|-----------|
| Catalyst density [kg/m³]             | 2,200     |
| Calcined dolomite density [kg/m³]    | 1,540     |
Mean catalyst particle size [μm] 200
Mean dolomite particle size [μm] 250
MgO content in dolomite [wt %] 40
Inlet granular temperature of solid phases [m²/s²] 1x10⁵
Packing limit of solid phases 0.60
Restitution coefficient of all phase interactions 0.90

**System properties**
- Outlet pressure [atm] 1
- Wall type Adiabatic
- Shear condition No slip

**Table S4**  The fixed parameters and the studied parameters of the 2⁵ full factorial design.

| Parameters                                | Low level | High level |
|-------------------------------------------|-----------|------------|
| **Design parameters**                     |           |            |
| Gas inlet velocity: U [m/s]               | 3         | 4          |
| Solid flux: Gₛ [kg/m²s]                   | 100       | 200        |
| Diameter of the riser: id [m]             | 0.1       | 0.2        |
| Height of the riser: H [m]                | 7 (fixed) |            |
| **Reaction parameters**                   |           |            |
| Catalyst to sorbent ratio: Cat/Sb [kg/kg] | 0.58      | 2.54       |
| Steam/Ethanol molar ratio: S/E [mol/mol]  | 6 (fixed) |            |
| Temperature of inlets: Tᵢₙ [°C]           | 600       | 700        |
| CaO conversion of inlet sorbent: Xₑₜₙ [%] | 0 (fixed) |            |
Table S5  The area-averaged H<sub>2</sub> flux, H<sub>2</sub> purity and CaO conversion (X<sub>CaO</sub>) near the outlet of the riser from parametric study with the 2<sup>5</sup> factorial design.

| Run id | T<sub>in</sub> [°C] | Cat/Sb [kg/kg] | G<sub>s</sub> [kg/m<sup>2</sup>s] | U [m/s] | H<sub>2</sub> flux [kg/m<sup>2</sup>s] | H<sub>2</sub> purity [% dry] | X<sub>CaO</sub> [%] |
|--------|------------------|----------------|-----------------|------|-----------------|----------------|------|
| 1      | 0.1              | 600            | 2.54            | 100  | 3               | 0.132795       | 85.96 | 2.54 |
| 2      | 0.1              | 600            | 2.54            | 100  | 4               | 0.134116       | 78.85 | 2.36 |
| 3      | 0.1              | 600            | 2.54            | 200  | 3               | 0.142458       | 89.01 | 1.47 |
| 4      | 0.1              | 600            | 2.54            | 200  | 4               | 0.163118       | 85.17 | 1.53 |
| 5      | 0.1              | 600            | 0.58            | 100  | 3               | 0.107676       | 80.88 | 0.84 |
| 6      | 0.1              | 600            | 0.58            | 100  | 4               | 0.095864       | 72.13 | 0.71 |
| 7      | 0.1              | 600            | 0.58            | 200  | 3               | 0.118917       | 84.78 | 0.51 |
| 8      | 0.1              | 600            | 0.58            | 200  | 4               | 0.124579       | 80.10 | 0.50 |
| 9      | 0.1              | 700            | 2.54            | 100  | 3               | 0.122248       | 89.53 | 2.84 |
| 10     | 0.1              | 700            | 2.54            | 100  | 4               | 0.088973       | 59.58 | 0.08 |
| 11     | 0.1              | 700            | 2.54            | 200  | 3               | 0.129442       | 91.93 | 1.70 |
| 12     | 0.1              | 700            | 2.54            | 200  | 4               | 0.150081       | 87.67 | 1.88 |
| 13     | 0.1              | 700            | 0.58            | 100  | 3               | 0.069700       | 59.82 | 0.02 |
| 14     | 0.1              | 700            | 0.58            | 100  | 4               | 0.069147       | 56.47 | 0.02 |
| 15     | 0.1              | 700            | 0.58            | 200  | 3               | 0.110062       | 87.66 | 0.62 |
| 16     | 0.1              | 700            | 0.58            | 200  | 4               | 0.116549       | 82.74 | 0.55 |
| 17     | 0.2              | 600            | 2.54            | 100  | 3               | 0.138739       | 88.94 | 1.54 |
| 18     | 0.2              | 600            | 2.54            | 100  | 4               | 0.162809       | 85.04 | 1.64 |
| 19     | 0.2              | 600            | 2.54            | 200  | 3               | 0.146765       | 91.30 | 0.84 |
| 20     | 0.2              | 600            | 2.54            | 200  | 4               | 0.173570       | 87.57 | 0.96 |
| 21     | 0.2              | 600            | 0.58            | 100  | 3               | 0.119885       | 84.64 | 0.52 |
| 22     | 0.2              | 600            | 0.58            | 100  | 4               | 0.128142       | 79.93 | 0.53 |
| 23     | 0.2              | 600            | 0.58            | 200  | 3               | 0.128984       | 87.32 | 0.30 |
| 24     | 0.2              | 600            | 0.58            | 200  | 4               | 0.142326       | 82.94 | 0.32 |
| 25     | 0.2              | 700            | 2.54            | 100  | 3               | 0.126764       | 91.89 | 1.68 |
| 26     | 0.2              | 700            | 2.54            | 100  | 4               | 0.143514       | 86.29 | 1.82 |
Table S6  The results of the ANOVA of the H₂ flux.

| Source   | Sum of squares | Degree of freedom (DF) | Mean square | F-value   | P-value |
|----------|----------------|------------------------|-------------|-----------|---------|
| C (Cat/Sb) | 0.005737       | 1                      | 0.005737    | 79.93976  | <0.0001 |
| D (Gₐ)  | 0.003190       | 1                      | 0.003190    | 44.4568   | <0.0001 |
| A (id)  | 0.002868       | 1                      | 0.002868    | 39.96242  | <0.0001 |
| B (Tₐ)  | 0.002229       | 1                      | 0.002229    | 31.06468  | <0.0001 |
| AD      | 0.000702       | 1                      | 0.000702    | 9.77882   | 0.004733|
| E (U)   | 0.000538       | 1                      | 0.000538    | 7.493613  | 0.011736|
| DE      | 0.000419       | 1                      | 0.000419    | 5.836395  | 0.024042|
| AE      | 0.000399       | 1                      | 0.000399    | 5.552999  | 0.027341|
| Residual | 0.001651       | 23                     | 7.18E-05    |           |         |
| Cor Total | 0.017732      | 31                     |             |           |         |

Table S7  The results of the ANOVA of the H₂ purity.
| Source   | Sum of squares | Degree of freedom (DF) | Mean square | F-value | P-value |
|----------|----------------|------------------------|-------------|---------|---------|
| D (G_s)  | 519.2369       | 1                      | 519.2369    | 26.61521| <0.0001 |
| A (id)   | 481.9729       | 1                      | 481.9729    | 24.70513| <0.0001 |
| E (U)    | 354.6858       | 1                      | 354.6858    | 18.1806 | 0.000292|
| C (Cat/Sb) | 281.9324     | 1                      | 281.9324    | 14.45138| 0.000092|
| AD       | 213.7666       | 1                      | 213.7666    | 10.95732| 0.003054|
| BD       | 133.1668       | 1                      | 133.1668    | 6.825905| 0.015563|
| AB       | 122.3844       | 1                      | 122.3844    | 6.273218| 0.01979 |
| ABD      | 117.8375       | 1                      | 117.8375    | 6.040152| 0.021944|
| Residual | 448.7076       | 23                     | 19.50902    |         |         |
| Cor Total| 2673.691       | 31                     |             |         |         |

**References**

[S1] ANSYS Inc., ANSYS Fluent Theory Guide 15.0, SAS IP Inc., USA, 2013.