Electronic Supplementary Information (ESI)

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

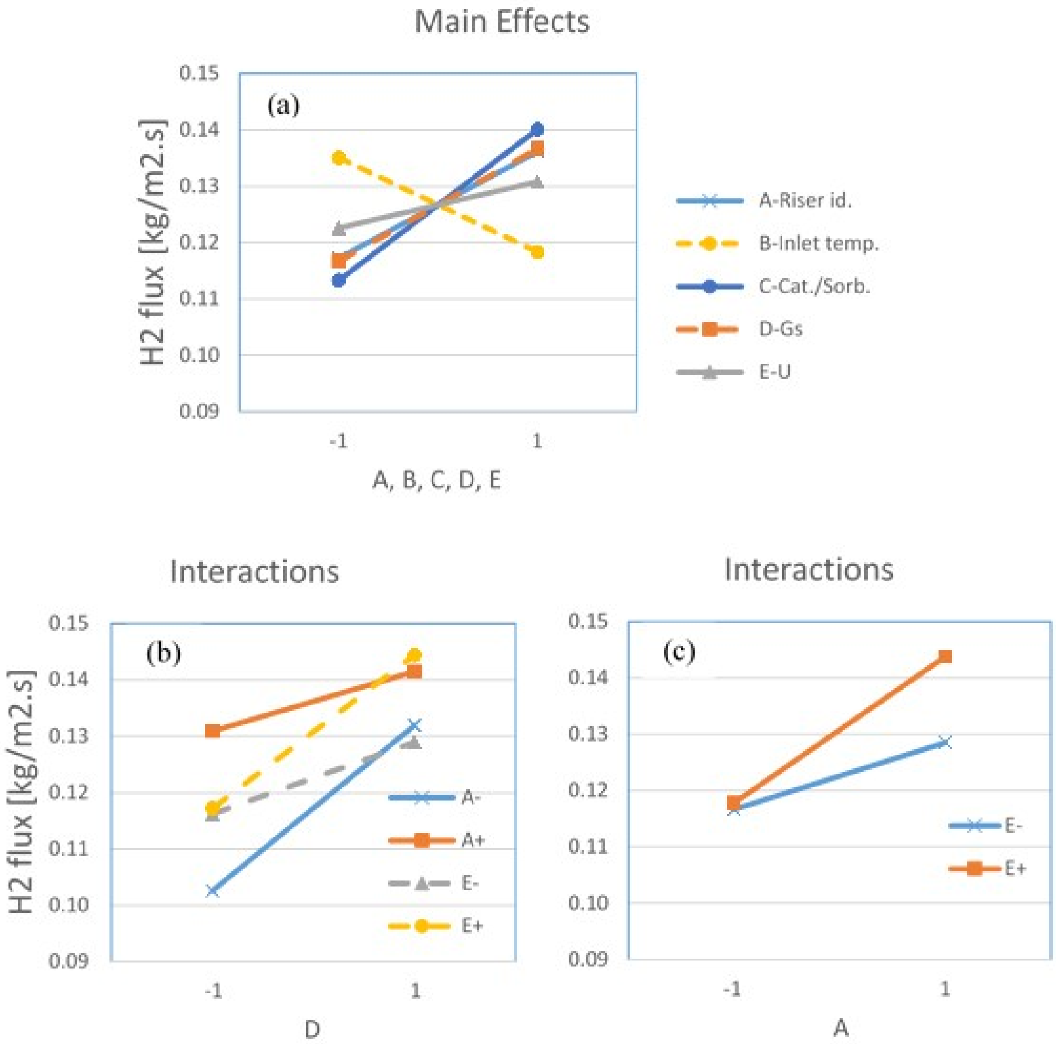

Fig. S1. The main effects (a) and the interactions (b and c) on the H_2 flux.

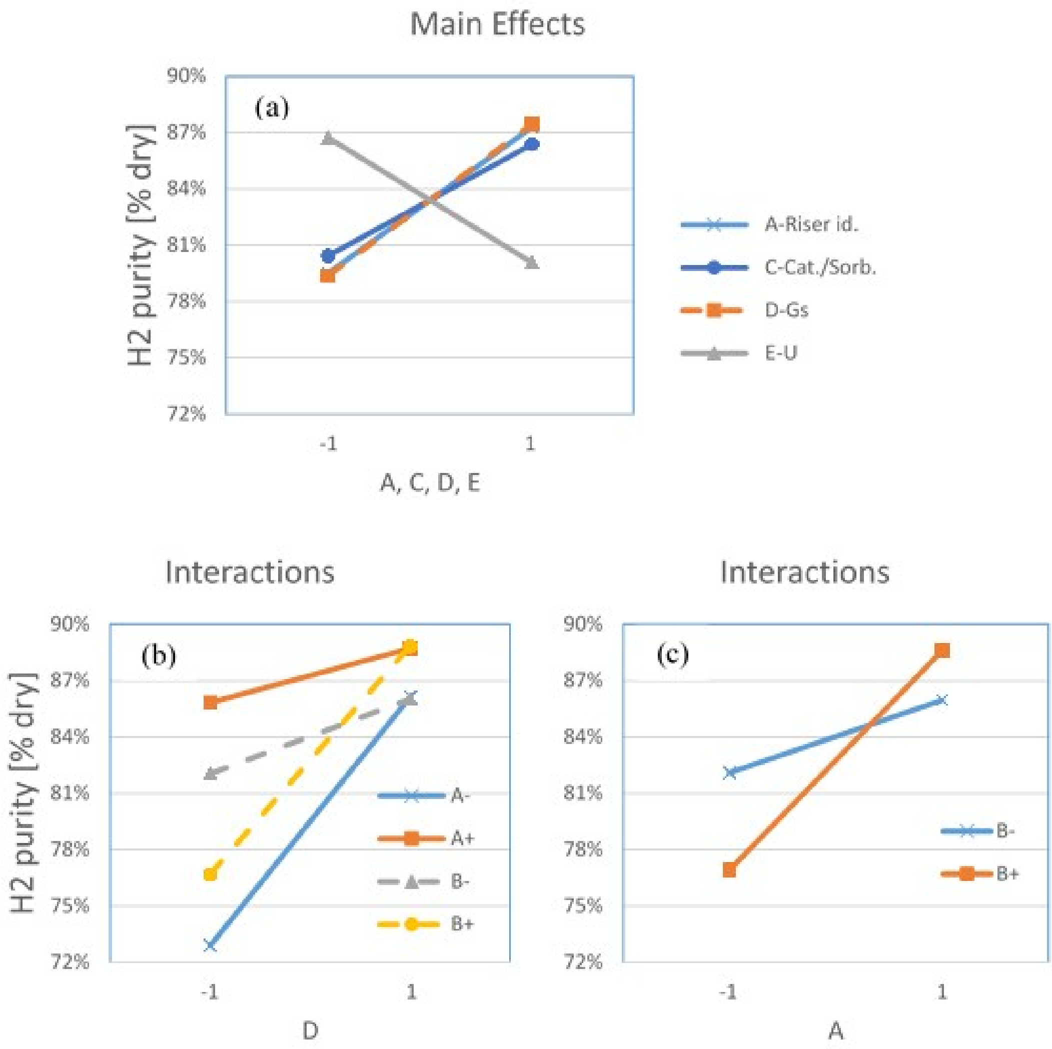

Fig. S2. The main effects (a) and the interactions (b and c) on the H_2 purity.

Table S1 Conservation equations used in the simulations.

a) Mass conservation for each phase q:

$$\frac{\partial}{\partial t}(\varepsilon_q\rho_q) + \nabla \cdot (\varepsilon_q\rho_q\vec{v}_q) = \sum_{p=1}^{n}(\dot{m}_{pq} - \dot{m}_{qp}) + S_{m,q} \tag{S1}$$

b) Momentum conservation

- for gas phase:

$$\frac{\partial}{\partial t}(\varepsilon_g\rho_g\vec{v}_g) + \nabla \cdot (\varepsilon_g\rho_g\vec{v}_g\vec{v}_g) = -\varepsilon_g\nabla p + \nabla \cdot \bar{\bar{\tau}}_g + \varepsilon_g\rho_g\vec{g} + \sum_{s=1}^{n}\left(K_{sg}(\vec{v}_s - \vec{v}_g) + \dot{m}_{sg}\vec{v}_{sg} - \dot{m}\right. \tag{S2}$$

- for solid phase:

$$\frac{\partial}{\partial t}(\varepsilon_s\rho_s\vec{v}_s) + \nabla \cdot (\varepsilon_s\rho_s\vec{v}_s\vec{v}_s) = -\varepsilon_s\nabla p - \nabla p_s + \nabla \cdot \bar{\bar{\tau}}_s + \varepsilon_s\rho_s\vec{g} + \sum_{l=1}^{n}\left(K_{ls}(\vec{v}_l - \vec{v}_s) + \dot{m}_{ls}\vec{v}_{ls} - \right. \tag{S3}$$

c) Energy conservation

- for gas phase:

$$\frac{\partial}{\partial t}(\varepsilon_g\rho_g H_g) + \nabla \cdot (\varepsilon_g\rho_g\vec{v}_g H_g) = \varepsilon_g\frac{\partial p_g}{\partial t} + \bar{\bar{\tau}}_g:\nabla\vec{v}_g - \nabla \cdot \vec{q}_g + S_{h,g} + \sum_{s=1}^{n}\left(Q_{sg} + \dot{m}_{sg}h_{sg} - \dot{m}_g\right. \tag{S4}$$

- kinetic fluctuation energy conservation for solid phase:

$$\frac{3}{2}\left[\frac{\partial}{\partial t}(\varepsilon_s\rho_s\Theta_s) + \nabla \cdot (\varepsilon_s\rho_s\vec{v}_s\Theta_s)\right] = (-p_s\bar{\bar{I}} + \bar{\bar{\tau}}_s):\nabla\vec{v}_s + \nabla \cdot (k_{\Theta_s}\nabla\Theta_s) - \gamma_{\Theta_s} + \phi_{ls} \tag{S5}$$

where γ_{Θ_s} is collisional dissipation of energy (Lun *et al*. [S1]):

$$\gamma_{\Theta_s} = \frac{12(1 - e_{ss}^2)g_{0,ss}}{d_s\sqrt{\pi}}\rho_s\varepsilon_s^2\Theta_s^{3/2} \tag{S6}$$

and ϕ_{ls} is kinetic energy exchange between phase l and solid phase:

$$\phi_{ls} = -3K_{ls}\Theta_s \tag{S7}$$

d) Chemical species conservation of the species k in phase q:

$$\frac{\partial}{\partial t}(\varepsilon^q\rho^q Y_k^q) + \nabla \cdot (\varepsilon^q\rho^q\vec{v}^q Y_k^q) = -\nabla \cdot (\varepsilon^q\vec{J}_k^q) + \varepsilon^q R_k^q + \varepsilon^q S_k^q + \sum_{p=1}^{n}(\dot{m}_{p^k q^k} - \dot{m}_{q^k p^k}) \tag{S8}$$

Table S2 Constitutive equations used in the simulations.

---

a) Stress tensor for each phase q:

$$\bar{\bar{\tau}}_q = \varepsilon_q \mu_q \left(\nabla \vec{v}_q + \nabla \vec{v}_q^T\right) + \varepsilon_q \left(\lambda_q - \frac{2}{3}\mu_q\right) \nabla \cdot \vec{v}_q \bar{\bar{I}} \tag{S9}$$

b) Solid shear viscosity:

$$\mu_s = \mu_{s,col} + \mu_{s.kin} + \mu_{s,fr} \tag{S10}$$

where $\mu_{s,col}$ is the collisional viscosity:

$$\mu_{s,col} = \frac{4}{5}\varepsilon_s \rho_s d_s g_{0,ss}\left(1 + e_{ss}\right)\left(\frac{\Theta_s}{\pi}\right)^{1/2} \varepsilon_s \tag{S11}$$

and $\mu_{s,kin}$ is the kinetic viscosity (Gidaspow *et al.* [S1]):

$$\mu_{s,kin} = \frac{10\rho_s d_s \sqrt{\Theta_s \pi}}{96\varepsilon_s\left(1 + e_{ss}\right)g_{0,ss}}\left[1 + \frac{4}{5}\varepsilon_s g_{0,ss}\left(1 + e_{ss}\right)\right]^2 \varepsilon_s \tag{S12}$$

c) Solid bulk viscosity (Lun *et al.* [S1]):

$$\lambda_s = \frac{4}{3}\varepsilon_s^2 \rho_s d_s g_{0,ss}\left(1 + e_{ss}\right)\left(\frac{\Theta_s}{\pi}\right)^{1/2} \tag{S13}$$

d) Solid Pressure (Lun *et al.* [S1]):

$$p_s = \varepsilon_s \rho_s \Theta_s + 2\varepsilon_s^2 \rho_s \Theta_s g_{0,ss}\left(1 + e_{ss}\right) \tag{S14}$$

e) Radial distribution coefficient

- for one solid phase (Lun *et al*. [S1]):

$$g_{0,ss} = \left[1 - \left(\frac{\varepsilon_s}{\varepsilon_{s,max}}\right)^{1/3}\right]^{-1} \tag{S15}$$

- the mutual radial distribution coefficient between two solid phases:

$$g_{0,ls} = \frac{d_s g_{0,ll} + d_l g_{0,ss}}{d_s + d_l} \tag{S16}$$

f) Granular temperature from KTGF:

$$\frac{3}{2}\frac{\partial}{\partial t}\left(\varepsilon_s\rho_s\Theta_s\right) = \left(-p_s\bar{I} + \bar{\tau}_s\right):\nabla\vec{v}_s - \gamma_{\Theta_s} + \phi_{ls} \tag{S17}$$

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

- for $\varepsilon_g > 0.8$:

$$K_{sg} = \frac{3}{4}C_D\frac{\varepsilon_s\varepsilon_g\rho_g\left|\vec{v}_s - \vec{v}_g\right|}{d_s}\varepsilon_g^{-2.65} \tag{S18}$$

where C_D is drag coefficient:

$$C_D = \frac{24}{\varepsilon_g Re_s}\left[1 + 0.15\left(\varepsilon_g Re_s\right)^{0.687}\right] \tag{S19}$$

- for $\varepsilon_g \leq 0.8$:

$$K_{sg} = 150\frac{\varepsilon_s\left(1 - \varepsilon_g\right)\mu_g}{\varepsilon_g d_s^2} + 1.75\frac{\rho_g\varepsilon_s\left|\vec{v}_s - \vec{v}_g\right|}{d_s} \tag{S20}$$

h) Solid-solid momentum exchange coefficient:

$$K_{ls} \equiv K_{sl} = \frac{3\left(1 + e_{ls}\right)\left(\frac{\pi}{2} + C_{fr,ls}\frac{\pi^2}{8}\right)\varepsilon_s\rho_s\varepsilon_l\rho_l\left(d_l + d_s\right)^2 g_{0,ls}}{2\pi\left(\rho_l d_l^3 + \rho_s d_s^3\right)}\left|\vec{v}_l - \vec{v}_s\right| \tag{S21}$$

i) Gas-solid heat exchange coefficient:

$$h_{sg} \equiv h_{gs} = \frac{k_g Nu_s}{d_s} \tag{S22}$$

where Nu_s is Nusselt number of solid phase (Gunn's model [S1]):

$$Nu_s = \left(7 - 10\varepsilon_g + 5\varepsilon_g^2\right)\left(1 + 0.7Re_s^{0.2}Pr^{1/3}\right) + \left(1.33 - 2.4\varepsilon_g + 1.2\varepsilon_g^2\right)Re_s^{0.7}Pr^{1/3} \tag{S23}$$

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

Phase properties	
Catalyst density [kg/m^3]	2,200
Calcined dolomite density [kg/m^3]	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 [m^2/s^2]	$1x10^5$
Packing limit of solid phases	0.60
Restitution coefficient of all phase interactions	0.90
<u>System properties</u>	
Outlet pressure [atm]	1
Wall type	Adiabatic
Shear condition	No slip

Table S4 The fixed parameters and the studied parameters of the 2^5 full factorial design.

Parameters	Low level	High level
<u>Design parameters</u>		
Gas inlet velocity: U [m/s]	3	4
Solid flux: G_s [kg/m^2s]	100	200
Diameter of the riser: id [m]	0.1	0.2
Height of the riser: H [m]	7 (fixed)	
<u>Reaction parameters</u>		
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: T_{in} [°C]	600	700
CaO conversion of inlet sorbent: $X_{CaO,in}$ [%]	0 (fixed)	

Table S5 The area-averaged H_2 flux, H_2 purity and CaO conversion (X_{CaO}) near the outlet of the riser from parametric study with the 2^5 factorial design.

Factor:	A	B	C	D	E	R1	R2	
Run	id [m]	T_{in} [°C]	Cat/Sb [kg/kg]	G_s [kg/m²s]	U [m/s]	H_2 flux [kg/m²s]	H_2 purity [% dry]	X_{CaO} [%]
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

27	0.2	700	2.54	200	3	0.133745	94.07	0.95
28	0.2	700	2.54	200	4	0.152288	89.07	1.07
29	0.2	700	0.58	100	3	0.112057	88.65	0.63
30	0.2	700	0.58	100	4	0.115007	81.31	0.60
31	0.2	700	0.58	200	3	0.121366	91.26	0.38
32	0.2	700	0.58	200	4	0.132704	86.25	0.41

Table S6 The results of the ANOVA of the H_2 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 (G_s)	0.003190	1	0.003190	44.4568	<0.0001
A (id)	0.002868	1	0.002868	39.96242	<0.0001
B (T_{in})	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 H_2 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	0.00092
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.