Electronic Supplementary Information

A Mathematical Model of a Slurry Reactor for the Direct Synthesis of Hydrogen Peroxide

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INTERPHASE MASS EXCHANGE

Estimation of bubble diameter

In order to evaluate bubble dimensions, it is useful, to a first approximation, the Sauter's diameter estimation.

When *Re > 50000* (high turbulence), bubble dimension d_b is determined by the energy intensity turbulent dissipation e_D, which limits the maximum stable bubble dimension.

$$d_b = \frac{2}{e_D^{0.4}} \left(\frac{\sigma}{\hat{\rho}_L} \right)^{0.6} \varepsilon^{0.5} \left(\frac{\mu_G}{\mu_L} \right) \tag{1s}$$

Where e_D, σ, μ_G and μ_L are the turbulent dissipation of energy per unit mass, the interface tension and the viscosity of the two phases. Eq. (1s) gives immediately the Sauter's diameter. The intensity of the turbulent dissipation can be estimated through Kolmogorov's equation or through specific correlations. For example, let us consider the situation of smooth pipes, because it is being evaluate the energy dissipation in the middle of the fluid and not in correspondence of the walls. In this case:

$$e_D = 2 C_D u_L^3 / d_R \tag{2s}$$

$$\frac{1}{\sqrt{C_D}} =- 4\log_{10} \left[\left(\frac{7}{Re} \right)^{0.9} \right] \tag{3s}$$

Eqs. (1s), (2s) and (3s) are independent to the type of the fluid considered.

An alternative way to determine the diameter is the one that gives directly the maximum stable bubble diameter, strictly valid for ascent bubbles in liquid at rest and determined for liquid systems with low viscosity.

In this case, the Sauter's diameter is about 40-50% of the maximum diameter:

$$d_b = (0.4 \div 0.5)\sqrt{\frac{\sigma}{g\hat{\rho}_L}} \tag{4s}$$

Another correlation usually used to estimate bubble diameter in gas/liquid systems is the one of Akita and Yoshida:

$$\frac{d_b}{d_R} = 26\left(\frac{g\hat{\rho}_L d_R^2}{\sigma}\right)^{-0.5}\left(\frac{g\hat{\rho}_L^2 d_R^3}{\mu_L^2}\right)^{-0.12}\left(\frac{u_G}{\sqrt{gd_R}}\right)^{-0.12} \tag{5s}$$

MODEL EQUATIONS

Energy balance

Energy balance equation ($cal/\ cm_t^3/\ s$) can be written as:

$$\begin{aligned} & u_{sl}\left[\left((1-\alpha)+\alpha\varepsilon_p\right)C_{PL}\hat{\rho}_L + \alpha C_{PS}\hat{\rho}_S\right]\frac{\partial T}{\partial z} = \\ & = -\frac{4U}{d_R}\left(T - T_{ext}\right) + \varepsilon\sum_k \tilde{r}_k^G\left(-\Delta\tilde{H}_{k,G}\right) + \\ & +\ \alpha(1-\varepsilon)\hat{\rho}_S\left(1-\varepsilon_p\right)\sum_k \tilde{r}_k^S\left(-\Delta\tilde{H}_{k,S}\right) + \\ & +\ \alpha(1-\varepsilon)a_p N_i\left(-\Delta\tilde{H}_{ads,j}\right) \end{aligned} \tag{6s}$$

Where C_p, U and $\Delta\tilde{H}$ indicate specific heats, global exchange coefficient and enthalpic variations associated to chemical reactions and adsorption processes. In Eq. (6s) we have neglected the heat storage in the gaseous phase because irrelevant compared to the one in the slurry phase.

It is possible to express the global exchange coefficient as function of the liminal coefficients of external thermal exchange h_e and the internal one h_i, and of the tubes thermal conductivity k_T:

$$\frac{1}{U}=\frac{1}{h_i}+\frac{s_{m\,ln}}{k_T}+\frac{d_R}{d_e h_e} \tag{7s}$$

Where $s_{m\,ln}=d_R/\ 2ln(d_e\ /d_R)$ is the logarithmic mean thickness. To evaluate the internal liminal coefficient it is possible to use Dittus-Boelter correlation, valid for intubated motion:

$$Nu=\frac{h_i d_R}{k_{sl}}=0.023\ Re^{0.8}Pr^{0.333} \tag{8s}$$

For the external one, given that is unknown the fluid dynamic configuration that will be adopted, in the code is proposed the inclusion of a coefficient externally evaluated.

PHYSICO-CHEMICAL PROPERTIES AND MODEL PARAMETERS

Here we propose the estimation of the physico-chemical properties and parameters that were implemented in the simulations.

Henry's constants and vapor pressures

We found in literature Henry's constants values for H_2/H_2O, O_2/H_2O and N_2/H_2O systems, as well as vapor pressures of H_2O_2 and H_2O. These values (in atmospheres) were interpolated through the following expressions:

$$lnP^{\circ}=A+\frac{B}{T+C}+\frac{D}{T^2}+\frac{E}{T^3} \tag{9s}$$

$$lnH = A + \frac{B}{T + C} + \frac{D}{T^2} + \frac{E}{T^3} \tag{10s}$$

Coefficients are summarized in Table 1s. Actually, in the implemented expressions, coefficient C is zero, but is was left to insert eventual Antoine's expressions. We need to make clear that the amount of gas dissolved in the liquid phase is almost negligible compared to the one adsorbed on the catalyst. The liquid phase behaves like a buffer with limited capacity for the material exchange between gas and solid. The reason for that is the high value of the Henry's constant for the two principal reactants (in the order of 10^4 *atm*).

Density, viscosity and interfacial tension

To estimate the density of the liquid phase we refer only to water and hydrogen peroxide, even if the contribution of the last one is important only when we analyze process where high concentrations are reached.

$$\hat{\rho}_{H_2O} = 1.000\ g/cm^3 \tag{11s}$$

$$\hat{\rho}_{H_2O_2} = 1.450\ g/cm^3 \tag{12s}$$

$$\hat{\rho}_L = \left[\sum_i \frac{x_i M_i}{M_T \hat{\rho}_i}\right]^{-1} g/cm^3 \tag{13s}$$

For the system viscosity it was adopted the correspondent value of only water because of high dilution of the system:

$$ln\mu_L = -29.31 + \frac{4209}{T} + 0.04527T - 3.376 * 10^{-5}T^2 \qquad \left[\frac{g}{cm\ s}\right] \tag{14s}$$

In order to obtain values related to the slurry we referred to the following correlations:

$$\hat{\rho}_{sl} = \left[\frac{W}{\hat{\rho}_S} + \frac{1 - W}{\hat{\rho}_L}\right]^{-1} \tag{15s}$$

$$\mu_{sl} = \frac{\mu_L}{\left(1 + \frac{\alpha}{0.71}\right)^2} \tag{16s}$$

The interfacial tension was estimated with the value relative to the air/water system:

$$\sigma = 71.40 + 0.000 * T \quad dyn/cm \tag{17s}$$

For first attempt calculations, it was not considered the dependence on temperature, because it significantly depends on the system composition and, therefore, it is necessary to proceed with experimental measurements.

The estimation of some transport parameters requires the knowledge of gaseous phase viscosity. In this case, due to the marginal importance of this property in the system, we just considered the value relative to air:

$$\mu_G = 1812 * 10^{-7} g/cm/s \tag{18s}$$

Finally, for the catalyst density it was taken into account an alumina particle with 20% of porosity and the mean diameter of 50 μm:

$$\varepsilon_p = 0.2 \tag{19s}$$

$$\hat{\rho}_S = 3.97 \quad g/cm^3 \tag{20s}$$

$$\hat{\rho}_C = (1 - \varepsilon_p)\hat{\rho}_S = 3.18 \quad g/cm^3 \tag{21s}$$

Specific heats, latent heats of vaporization, formation enthalpies, thermal conductivities, adsorption heats and adsorption equilibrium constants

Relevant specific heats in the system are those of the solid and of the liquid phases. We implemented in the code some linear dependences on the temperature:

$$C_{P,L} = 1.000 + 0.00 * 10^{-3}T \quad \frac{cal}{g\,K} \tag{22s}$$

$$C_{P,S} = 0.185 + 0.00 * 10^{-3}T \quad \frac{cal}{g\,K} \tag{23s}$$

For the catalytic phase we made reference to alumina. Due to the preliminary nature of this work, it was not considered the dependence on temperature. In any case, it is possible to include this dependence in the software data file. Values of latent heats of vaporization for water and hydrogen peroxide and formation enthalpies for all the species of the system were found from literature and are summarized in Table1s.

The two important values of thermal conductivities are those related to the liquid phase and to the tubes metal:

$$k_{T,L} = 1.36 * 10^{-3} \frac{cal}{cm\,s\,K} \tag{24s}$$

$$k_{T,tubes} = 0.107 \quad \frac{cal}{cm\,s\,K} \tag{25s}$$

It is more complex the question of the adsorption parameters because usually the reference is made to experimental measurements. Therefore, we approximatively considered typical values of latent heats of adsorption in the order of 5000 *cal/mol* (exothermic process).

For the adsorption constants, we supposed high values in order to make the form of the adsorption isotherm as much "rectangular" as possible. Anyway, adsorption constants can be expressed with the following relation:

$$b_i = b_i^\circ e^{\Delta H_{ads}/RT} \tag{26s}$$

In these conditions, the most significant parameter becomes the loading capacity of the catalyst. From literature, it is known that adsorption capacity of hydrogen on Pd is in the order of one-two atoms of H for one Pd atom. Therefore, adopting a conservative approach, we can assume a 1:1 ratio between the two atomic species. This means that we can estimate an adsorption of ½ mole of H_2 for 1 mole of Pd present in the catalyst. For a catalyst containing the 5% of Pd, we have:

$$\Gamma_{H_2}^{\infty} = (0.5 \div 1.0)\frac{w_{Pd}}{106.5} \approx 0.25 \div 0.50 * 10^{-3} \ \frac{mol}{g} \tag{27s}$$

In absence of more information, this data was assumed also for the other species taking part to the reaction. In any case, it is essential that this data is determined through a number of experimental proofs on the catalyst. Obviously, the amount adsorbed on the catalyst is strongly dependent on the value of the adsorption thermodynamic constant b.

Considerations on the adsorption are important also to define the order in which the gaseous reactants are fed in the reactor. In fact, hydrogen is fed before oxygen because the amount of hydrogen that can adsorb on the catalyst is higher than the one of oxygen. This is usually true for catalysts made of supported metals, but it has to be experimentally verified anyway.

Diffusivities, molecular weights

Diffusivities in the liquid phase and molecular weights of the species involved in the process can be found in literature. Values here used are summarized in Table 1s. The dependence on temperature of the diffusivities is evaluable from the following equation:

$$\frac{D_i \mu_L}{T} = cost \tag{28s}$$

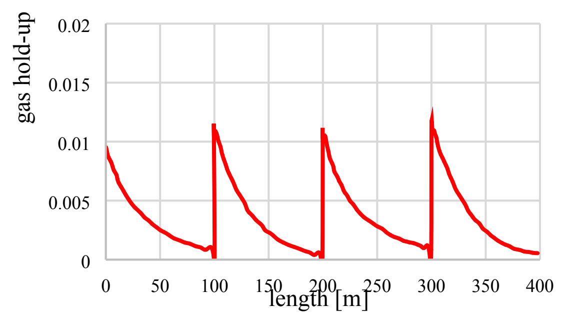
Table 1s. Summary of physical properties values used in simulations. Please note: values reported in the italic font are characterized by a great uncertainty.

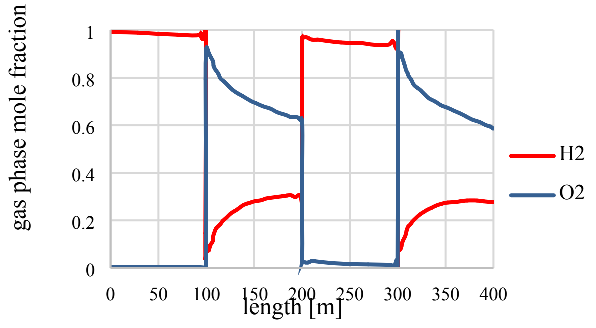
	ρ_L	T_b	ΔH_{ev}	Henry and vapor pressure parameters $[atm]$				
	$[g/cm^3]$	$[°C]$	$[cal/mol]$	A	B	C	D	E
N_2	-	-	-	3.9477	5709.60	0.0	$-1.00 * 10^{6}$	0.0
H_2	-	-	-	7.1150	2903.50	0.0	$-5.06 * 10^{5}$	0.0
O_2	-	-	-	3.7766	5560.30	0.0	$-1.00 * 10^{6}$	0.0
H_2O_2	1.450	100.0	11265	10.3050	-3493.30	0.0	$-4.01 * 10^{5}$	0.0

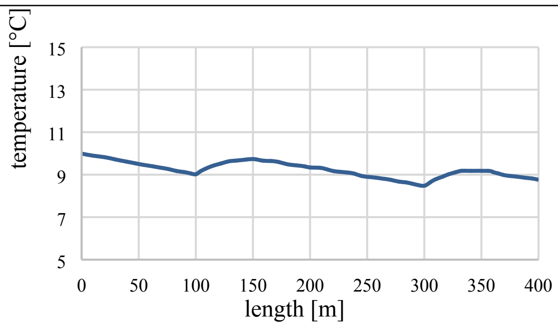
H_2O	1.000	150.2	9680.	11.0820	-3150.90	0.0	-4.21 $* 10^{5}$	2.00 $* 10^{7}$

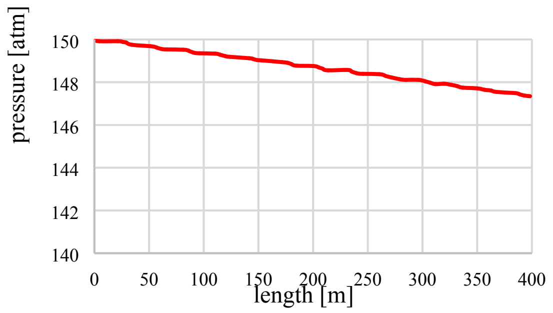
	M_i	D_i (25°C)	$\Delta H°_i$ (25°C)	$\Delta H°_{ads,i}$ (25°C)	Γ_i^{∞}	$b_i°$
	$[g/mol]$	$[cm^2/s]$	$[cal/mol]$	$[cal/mol]$	$[mol/g]$	-
N_2	28	1.90 $* 10^{-5}$	0.0	*0.0*	*0.50* $* 10^{-3}$	*0.00* $* 10^{7}$
H_2	2	5.85 $* 10^{-5}$	0.0	*-5000.*	*0.50* $* 10^{-3}$	*1.00* $* 10^{7}$
O_2	32	2.50 $* 10^{-5}$	0.0	*-5000.*	*0.50* $* 10^{-3}$	*1.00* $* 10^{7}$
H_2O_2	*34*	*1.00* $* 10^{-5}$	-44900.	*-5000.*	*0.50* $* 10^{-3}$	*1.00* $* 10^{7}$
H_2O	*18*	*1.00* $* 10^{-5}$	-68320	*0.0*	*0.50* $* 10^{-3}$	*0.00* $* 10^{7}$

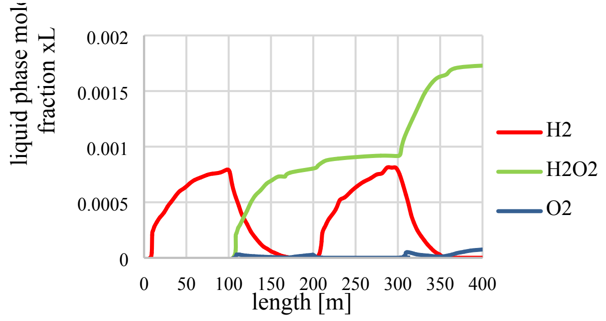
Additional plots

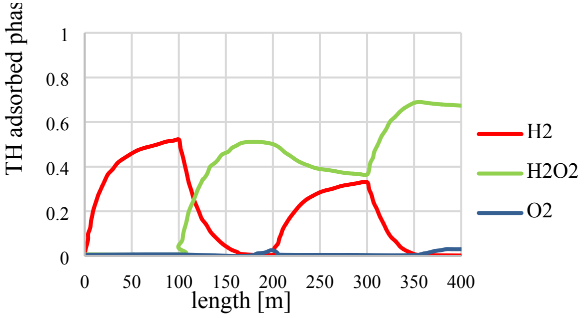


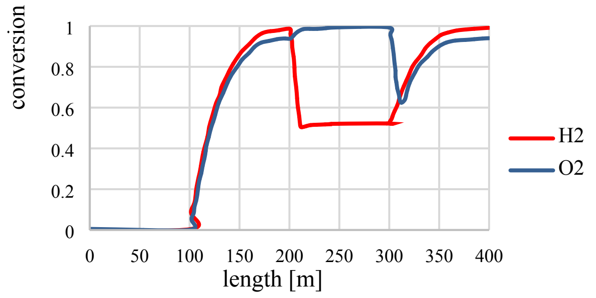


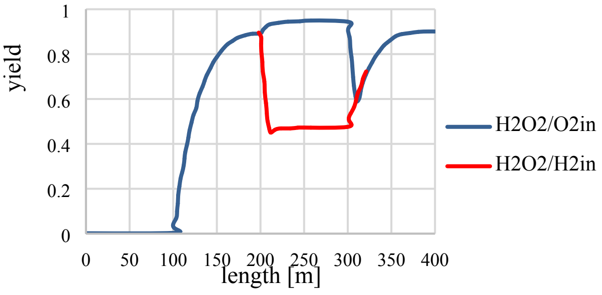












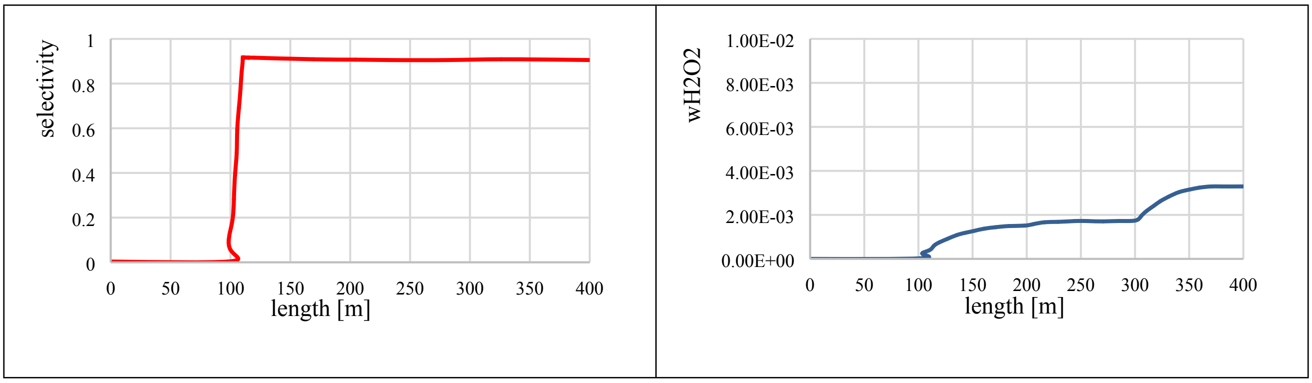


Figure. **S1.** 400 m of reactor divided into 4 sections each 100 m long.

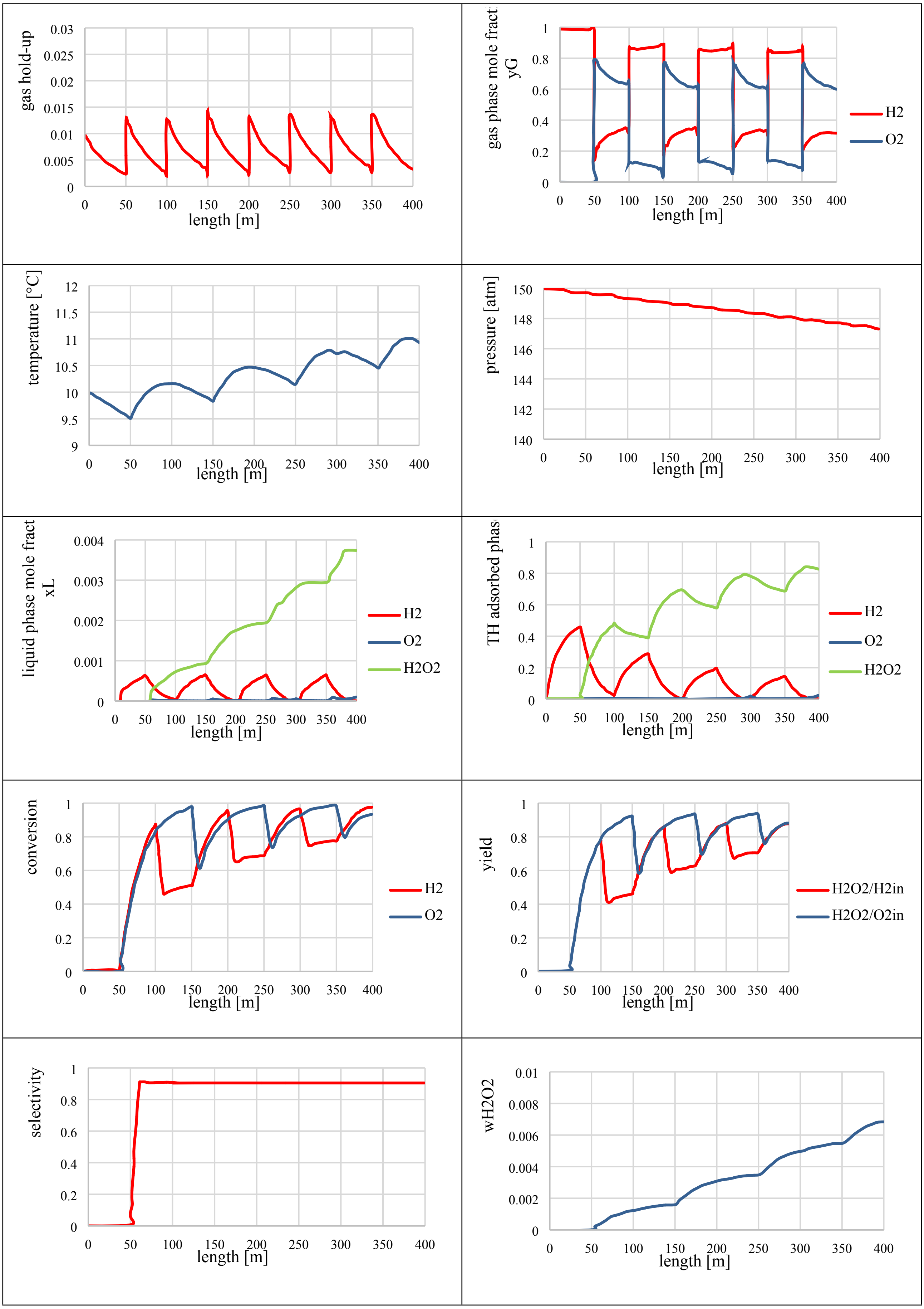
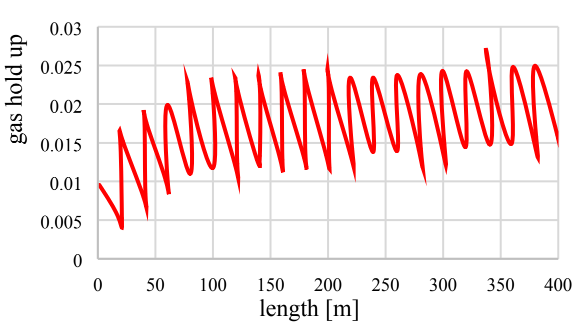


Figure S2. 400 m of reactor divided into 8 sections each 50 m long.


gas hold up
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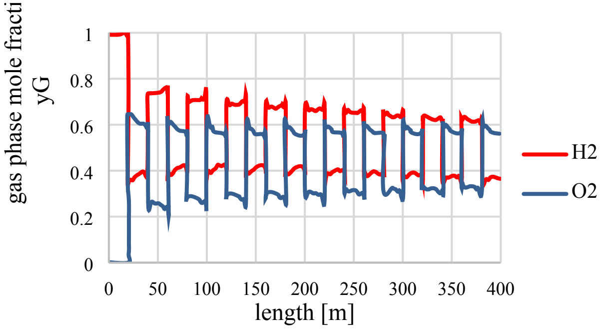
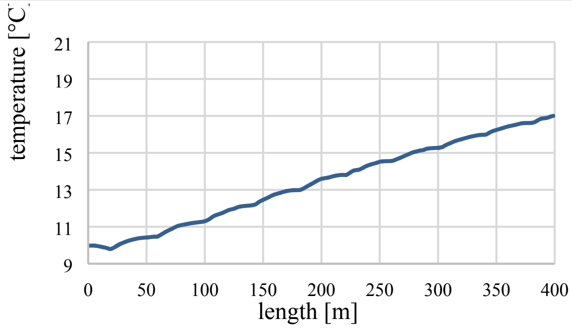
0.025
0.02
0.015
0.01
0.005
0
0
50
100
150
200
250
300
350
400
length [m]


gas phase mole fracti
yG
1
0.8
0.6
0.4
0.2
0
0
50
100
150
200
250
300
350
400
length [m]
H2
O2


temperature [°C
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17
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11
9
0
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100
150
200
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300
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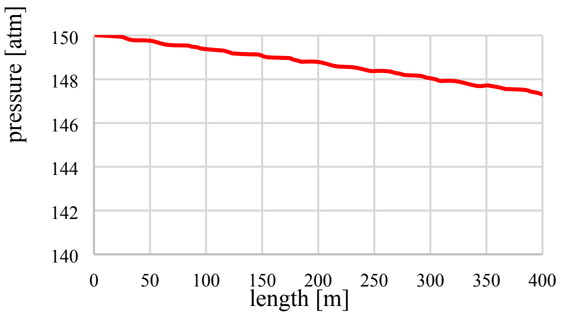
400
length [m]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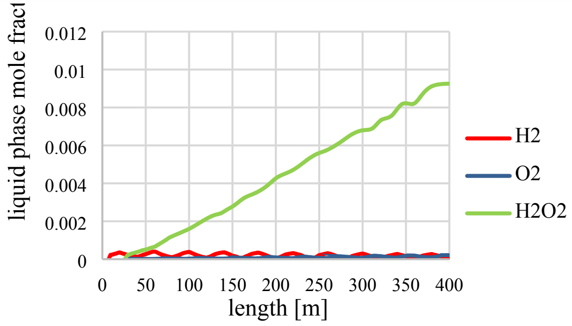
146
144
142
140
0
50
100
150
200
250
300
350
400
length [m]


liquid phase mole fract
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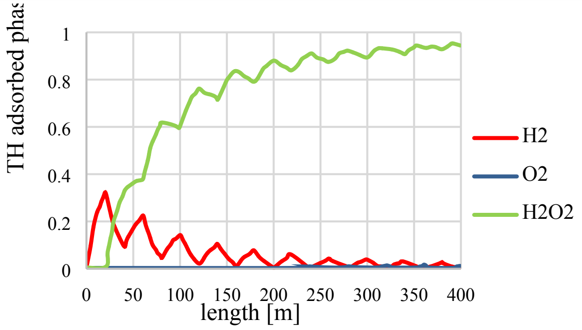
0.01
0.008
0.006
0.004
0.002
0
0
50
100
150
200
250
300
350
400
length [m]
H2
O2
H2O2


TH adsorbed phas
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0.6
0.4
0.2
0
0
50
100
150
200
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300
350
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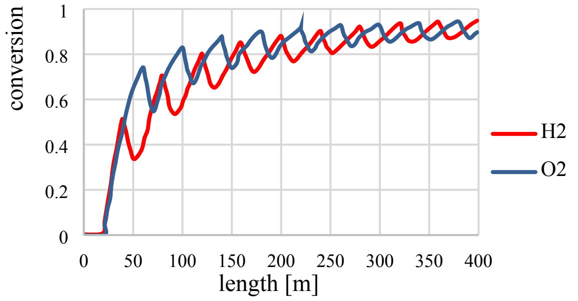
length [m]
H2
O2
H2O2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0
50
100
150
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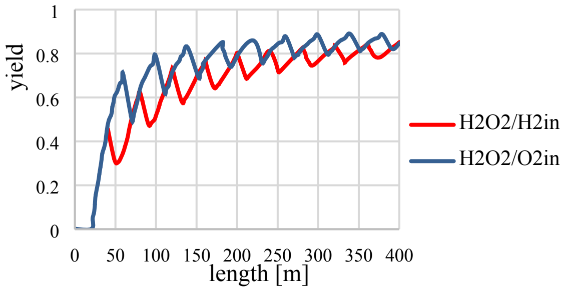
250
300
350
400
length [m]
H2
O2


yield
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0.8
0.6
0.4
0.2
0
0
50
100
150
200
250
300
350
400
length [m]
H2O2/H2in
H2O2/O2in

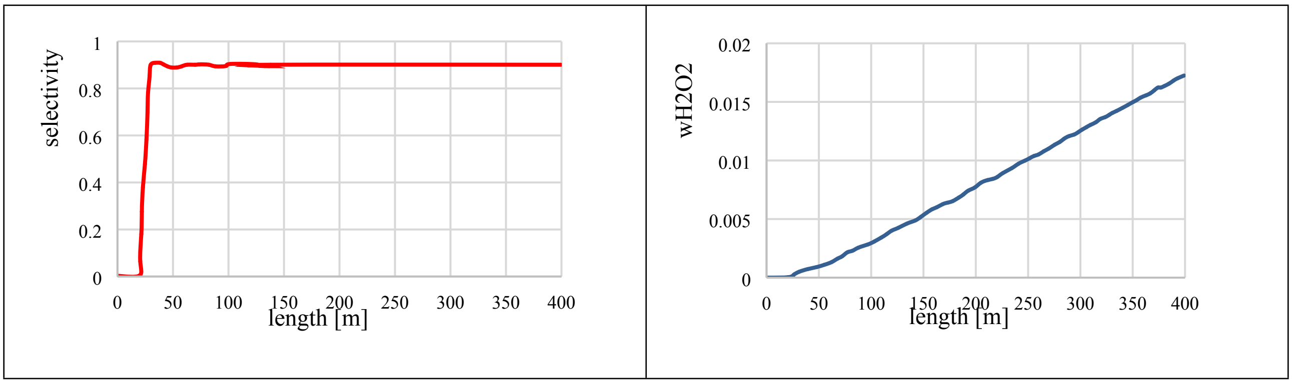

Figure S3. 400 m of reactor simulation.