Simulation and optimization of the CWPO process by combination of Aspen Plus and 6-factor Doehlert Matrix: towards the autothermal operation

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SUPPLEMENTARY MATERIAL

Table S1**. Elementary reactions considered in the CWPO reactor according to the oxidation pathway and kinetic model reported in *Diaz de Tuesta et al. (2017)***

Compounds	Reactions		
PHENOL→HQ	C_6H_6O +	H_2O_2	→ $C_6H_6O_2 + H_2O$
PHENOL →RS	C_6H_6O +	H_2O_2	→ $C_6H_6O_2 + H_2O$
PHENOL → CTL	C_6H_6O +	H_2O_2	→ $C_6H_6O_2 + H_2O$
PHENOL → BQ	C_6H_6O +	$2{\cdot}H_2O_2$	→ $C_6H_4O_2 + 3{\cdot}H_2O$
PHENOL → MAL	C_6H_6O +	$8{\cdot}H_2O_2$	→ $C_4H_4O_4 + 9{\cdot}H_2O + 2{\cdot}CO_2$
PHENOL → FUM	C_6H_6O +	$8{\cdot}H_2O_2$	→ $C_4H_4O_4 + 9{\cdot}H_2O + 2{\cdot}CO_2$
PHENOL → MLO	C_6H_6O +	$10{\cdot}H_2O_2$	→ $C_3H_4O_4 + 11{\cdot}H_2O + 3{\cdot}CO_2$
PHENOL → OXA	C_6H_6O +	$13{\cdot}H_2O_2$	→ $C_2H_2O_4 + 15{\cdot}H_2O + 4{\cdot}CO_2$
PHENOL → ACE	C_6H_6O +	$10{\cdot}H_2O_2$	→ $C_2H_4O_2 + 11{\cdot}H_2O + 4{\cdot}CO_2$
PHENOL → FOR	C_6H_6O +	$8{\cdot}H_2O_2$	→ $CH_2O_2 + 10{\cdot}H_2O + 5{\cdot}CO_2$
PHENOL → CO_2	C_6H_6O +	$14{\cdot}H_2O_2$	→ $17{\cdot}H_2O + 6{\cdot}CO_2$
HQ → FUM	$C_6H_6O_2$ +	$7{\cdot}H_2O_2$	→ $C_4H_4O_4 + 8{\cdot}H_2O + 2{\cdot}CO_2$
HQ → ACE	$C_6H_6O_2$ +	$9{\cdot}H_2O_2$	→ $C_2H_4O_2 + 10{\cdot}H_2O + 4{\cdot}CO_2$
HQ → CO_2	$C_6H_6O_2$ +	$13{\cdot}H_2O_2$	→ $16{\cdot}H_2O + 6{\cdot}CO_2$
RS → FUM	$C_6H_6O_2$ +	$7{\cdot}H_2O_2$	→ $C_4H_4O_4 + 8{\cdot}H_2O + 2{\cdot}CO_2$
RS → MLO	$C_6H_6O_2$ +	$11{\cdot}H_2O_2$	→ $C_3H_4O_4 + 12{\cdot}H_2O + 3{\cdot}CO_2$
RS → OXA	$C_6H_6O_2$ +	$12{\cdot}H_2O_2$	→ $C_2H_2O_4 + 14{\cdot}H_2O + 4{\cdot}CO_2$
RS → FOR	$C_6H_6O_2$ +	$10{\cdot}H_2O_2$	→ $CH_2O_2 + 12{\cdot}H_2O + 5{\cdot}CO_2$
RS → CO_2	$C_6H_6O_2$ +	$13{\cdot}H_2O_2$	→ $16{\cdot}H_2O + 6{\cdot}CO_2$
CTL → MAL	$C_6H_6O_2$ +	$7{\cdot}H_2O_2$	→ $C_4H_4O_4 + 8{\cdot}H_2O + 2{\cdot}CO_2$
CTL → ACE	$C_6H_6O_2$ +	$9{\cdot}H_2O_2$	→ $C_2H_4O_2 + 10{\cdot}H_2O + 4{\cdot}CO_2$
CTL → CO_2	$C_6H_6O_2$ +	$13{\cdot}H_2O_2$	→ $16{\cdot}H_2O + 6{\cdot}CO_2$
BQ → FUM	$C_6H_4O_2$ +	$6{\cdot}H_2O_2$	→ $C_4H_4O_4 + 6{\cdot}H_2O + 2{\cdot}CO_2$
BQ → MLO	$C_6H_4O_2$ +	$8{\cdot}H_2O_2$	→ $C_3H_4O_4 + 8{\cdot}H_2O + 3{\cdot}CO_2$
BQ → CO_2	$C_6H_4O_2$ +	$12{\cdot}H_2O_2$	→ $14{\cdot}H_2O + 6{\cdot}CO_2$
MAL → ACE	$C_4H_4O_4$ +	$2{\cdot}H_2O_2$	→ $C_2H_4O_2 + 2{\cdot}H_2O + 2{\cdot}CO_2$
MAL → CO_2	$C_4H_4O_4$ +	$2{\cdot}H_2O_2$	→ $4{\cdot}H_2O + 4{\cdot}CO_2$
FUM → FOR	$C_4H_4O_4$ +	$5{\cdot}H_2O_2$	→ $CH_2O_2 + 6{\cdot}H_2O + 3{\cdot}CO_2$
MLO → FOR	$C_3H_4O_4$ +	$4{\cdot}H_2O_2$	→ $CH_2O_2 + 3{\cdot}H_2O + 2{\cdot}CO_2$
OXA → CO_2	$C_2H_2O_4$ +	H_2O_2	→ $2{\cdot}H_2O + 2{\cdot}CO_2$

Diaz de Tuesta, J. L.; Quintanilla, A.; Casas, J. A.; Rodriguez, J. J. Kinetic modeling of wet peroxide oxidation with a carbon black catalyst. Appl. Catal. B Env., 2017, 209, 701-710.

Table S2**. Binary coefficients (a_{ij}, a_{ji}, b_{ij}, b_{ji}) estimated for the implementation of the UNIQUAC thermodynamic model in the simulator software**

Compounds	a_{ij}	a_{ji}	b_{ij}	b_{ji}
$CO_2 - H_2O$	7.704327	1.592254	-6378.257600	-1816.906000
$O_2 - H_2O$	0.000000	0.000000	-376.687900	255.000318
PHENOL $- H_2O$	2.425187	-3.969134	-498.866040	696.592722
$H_2O_2 - H_2O$	0.513000	-0.340000	89.054500	147.824900
HQ or BQ $- H_2O$	-0.125420	1.050260	81.034700	-225.190000
CTL $- H_2O$	-1.220880	0.201203	348.271000	95.518500

RS – H_2O	-8.525242	2.302660	-10000.000000	-218.082000
MAL, MLO or FUM – H_2O	1.536310	-1.965010	-18.267400	-2822.150000
ACE or OXA – H_2O	1.306828	0.046200	-768.989980	219.875521
FOR – H_2O	0.465010	0.502277	-44.111860	71.727194
CO_2 – O_2	1.463940	-8.299810	0.000000	0.000000
O_2 – N_2	-0.511115	1.068730	54.998400	-147.231000

Table S3. **Theoretical oxygen demand (ThOD) and total organic carbon (TOC) of each compound (*i*).**

Compound	Oxidation reaction for ThOD calculation	TOC_i (g_{TOC}/g_i)	$ThOD_i$ (g_{ThOD}/g_i)
PHENOL (C_6H_6O)	$C_6H_6O + 7{\cdot}O_2 \rightarrow 6{\cdot}CO_2 + 3{\cdot}H_2O$	0.76	2.38
HQ ($C_6H_6O_2$)	$C_6H_6O_2 + 6{,}5{\cdot}O_2 \rightarrow 6{\cdot}CO_2 + 3{\cdot}H_2O$	0.65	1.89
CTL ($C_6H_6O_2$)	$C_6H_6O_2 + 6{,}5{\cdot}O_2 \rightarrow 6{\cdot}CO_2 + 3{\cdot}H_2O$	0.65	1.89
RS ($C_6H_6O_2$)	$C_6H_6O_2 + 6{,}5{\cdot}O_2 \rightarrow 6{\cdot}CO_2 + 3{\cdot}H_2O$	0.65	1.89
BQ ($C_6H_4O_2$)	$C_6H_4O_2 + 6{\cdot}O_2 \rightarrow 6{\cdot}CO_2 + 2{\cdot}H_2O$	0.67	1.78
MAL ($C_4H_4O_4$)	$C_4H_4O_4 + 3{\cdot}O_2 \rightarrow 4{\cdot}CO_2 + 2{\cdot}H_2O$	0.41	0.83
FUM ($C_4H_4O_4$)	$C_4H_4O_4 + 3{\cdot}O_2 \rightarrow 4{\cdot}CO_2 + 2{\cdot}H_2O$	0.41	0.83
MLO ($C_3H_3O_4$)	$C_3H_3O_4 + 0{,}75{\cdot}O_2 \rightarrow 3{\cdot}CO_2 + 3{\cdot}½{\cdot}H_2O$	0.35	0.62
OXA ($C_2H_2O_4$)	$C_2H_2O_4 + 0{,}5{\cdot}O_2 \rightarrow 2{\cdot}CO_2 + H_2O$	0.27	0.18
ACE ($C_2H_4O_2$)	$C_2H_4O_2 + O_2 \rightarrow 2{\cdot}CO_2 + 2{\cdot}H_2O$	0.40	1.07
FOR (CH_2O_2)	$CH_2O_2 + 0{,}5{\cdot}O_2 \rightarrow CO_2 + H_2O$	0.26	0.35

For the calculation of ThOD and TOC of a stream, all organic compounds in the stream are considered:

$$ThOD \ \ (g \cdot L^{-1}) = \sum_{i=1}^{n} C_i(g \cdot L^{-1}) \cdot ThOD_i$$

$$TOC \ \ (g \cdot L^{-1}) = \sum_{i=1}^{n} C_i(g \cdot L^{-1}) \cdot TOC_i$$

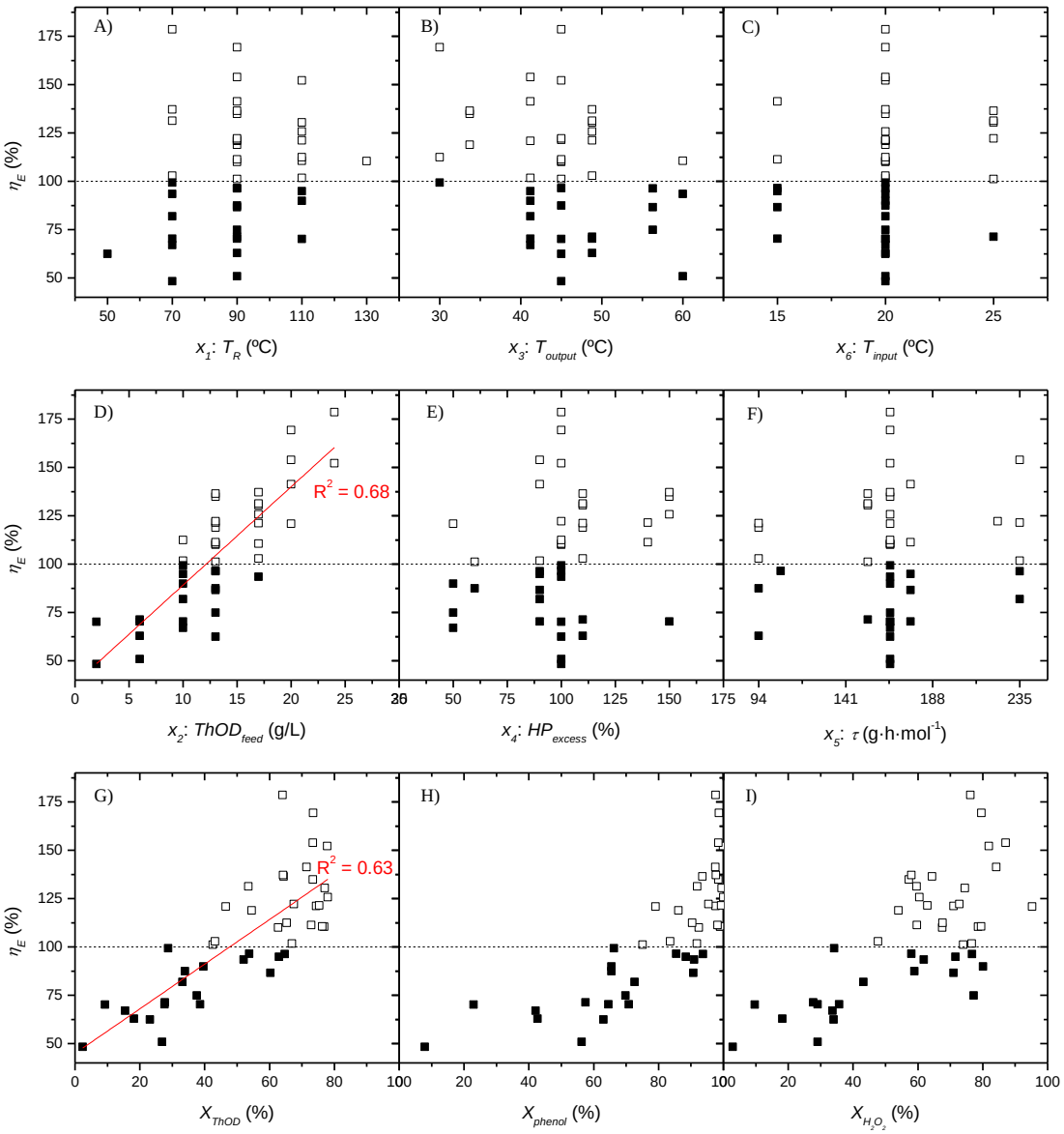

Figure S1. **Influence of the operating variables (A-F) and conversions (G-I) on the energetic efficiency of the CWPO process. Open symbols represent the cases under autothermal operation.**