An Iterative Real-time Optimization Scheme for the Optimal Operation of Chemical Processes under Uncertainty. *Proof of Concept in a Miniplant*

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Supporting Information

In this section the parameters of the different models are presented.

Table S1: Kinetic Model Parameters. Model I[1]

Parameters	**Unit**	**Value**
Catalyst Equilibrium		
$K_{cat,1}$	$m^3/kmol$	10
$K_{cat,2}$	$-$	1.01
Hydroformylation to linear and branched aldehyde		
Hydroformylation of 1-dodecene to linear aldehyde $\mathbf{r_1}$		
Frequency factor $k_{1,0}$	$m^9/(kg_{cat} \cdot min \cdot kmol^2)$	4.9×10^7
Activation Energy Ea_1	kJ/mol	113.08
$K_{1,1}$	m^3/mol	574.88
$K_{1,2}$	m^3/mol	3020.00
$K_{1,3}$	m^3/mol	1.17×10^4
Hydroformylation of iso-dodecene to branched aldehyde $\mathbf{r_5}$		
Frequency factor $k_{5,0}$	$m^9/(kg_{cat} \cdot min \cdot kmol^2)$	600.00
Activation Energy Ea_5	kJ/mol	120.844
Isomerization $\mathbf{r_2}$		
Frequency factor $k_{2,0}$	$m^3/(kg_{cat} \cdot min)$	696.23
Activation Energy Ea_2	kJ/mol	136.891
$K_{2,1}$	m^3/mol	38.63
$K_{2,2}$	m^3/mol	226.21
Hydrogenation of 1-dodecene and *iso*-dodecene		
Hydrogenation of 1-dodecene $\mathbf{r_3}$		
Frequency factor $k_{3,0}$	$m^6/(kg_{cat} \cdot min \cdot kmol)$	139.55
Activation Energy Ea_3	kj/mol	76.105
Equilibrium Constants		
$K_{3,1}$	m^3/mol	2.66
$K_{3,2}$	m^3/mol	7.10
$K_{3,3}$	m^3/mol	1.28
Hydrogenation of *iso*-dodecene $\mathbf{r_4}$		
Frequency factor $k_{4,0}$	$m^6/(kg_{cat} \cdot min \cdot kmol)$	0.70
Activation Energy Ea_4	kJ/mol	102.260

Table S2: Kinetic Model Parameters. Model II[2]

Parameters	**Unit**	**Value**
Catalyst Equilibrium		
$K_{cat,1}$	m^3/kmol	30.41
$K_{cat,2}$	–	0
$K_{cat,3}$	–	0.644
Hydroformylation to linear and branched aldehyde		
Hydroformylation of 1-dodecene to linear aldehyde $\mathbf{r_1}$		
Frequency factor $k_{1,0}$	$m^9/(kg_{cat} \cdot min \cdot kmol^2)$	4.9×10^7
Activation Energy Ea_1	kJ/mol	113.08
$K_{1,1}$	m^3/mol	574.88
$K_{1,2}$	m^3/mol	3020.00
$K_{1,3}$	m^3/mol	1.17×10^4
Hydroformylation of iso-dodecene to branched aldehyde $\mathbf{r_5}$		
Frequency factor $k_{5,0}$	$m^9/(kg_{cat} \cdot min \cdot kmol^2)$	37.02
Activation Energy Ea_5	kJ/mol	120.844
Hydroformylation of 1-dodecene to branched aldehyde $\mathbf{r_6}$		
Frequency factor $k_{6,0}$	$m^9/(kg_{cat} \cdot min \cdot kmol^2)$	395.1
Activation Energy Ea_6	kJ/mol	113.08
Isomerization $\mathbf{r_2}$		
Frequency factor $k_{2,0}$	$m^3/(kg_{cat} \cdot min)$	4.878×10^3
Activation Energy Ea_2	kJ/mol	136.891
$K_{2,1}$	m^3/mol	38.63
$K_{2,2}$	m^3/mol	226.21
Hydrogenation of 1-dodecene and *iso*-dodecene		
Hydrogenation of 1-dodecene $\mathbf{r_3}$		
Frequency factor $k_{3,0}$	$m^6/(kg_{cat} \cdot min \cdot kmol)$	272.4
Activation Energy Ea_3	kj/mol	76.105
Equilibrium Constants		
$K_{3,1}$	m^3/mol	2.66
$K_{3,2}$	m^3/mol	7.10
$K_{3,3}$	m^3/mol	1.28
Hydrogenation of *iso*-dodecene $\mathbf{r_4}$		
Frequency factor $k_{4,0}$	$m^6/(kg_{cat} \cdot min \cdot kmol)$	2.96×10^{-2}
Activation Energy Ea_4	kJ/mol	102.260

Table S3: Parameters for equilibrium constants estimation[3]

Variable	a_0 [kJ/mol]	a_1 [kJ/mol/K]	a_2 [kj/mol/K^2]
$\Delta G_{R,2}$	-11.00	0	0
$\Delta G_{R,3}$	-126.28	1.27×10^{-1}	6.80×10^{-6}

Table S4: Parameters for gas solubility[3]

Component	$H_0[(\mathrm{MPa}\cdot\mathrm{m}^3)/\mathrm{kmol}]$	$E[\mathrm{kJ/mol}]$
H_2	910	10.173
CO	35550	22.975

Table S5: Parameters for gas solubility[2]

Component	$H_0[(\mathrm{bar}\cdot\mathrm{m}^3)/\mathrm{kmol}]$	$E[\mathrm{J/mol}]$
H_2	66.4	-3.06
CO	73.9	-0.84

Table S6: Mass transfer coefficients for the G-L interface[1]

Component	$k_G[\mathrm{min}^{-1}]$
H_2	2.44
CO	2.31

Table S7: Parameters in the empirical decanter model. Note: Validity within temperature range 288-298 K with a fixed TMS composition of DMF/Decan 50:50.[4]

Parameter	(*l*-/*b*-)Aldehyde	(*n*-/*iso*-)Dodecene	*n*-Decane	DMF	Rhodium	Phosphous
A_1	-12.43	-7.040	-8.252	-7.928	-17.348	-20.843
A_2	2727.025	2579.235	3012.939	0.981	0.975	0.972
A_3	0.012	0	0	0.020	0.049	0.061

Table S8: Correlations used for density[3]

Component	a_0 [kg/m^3]	a_1 [kg/m^3/K]
n-Decane	981.60	-8.353×10^{-1}
DMF	1256.52	-1.0306
1-Dodecene	993.89	-7.8875×10^{-1}
Dodecane	977.04	-7.6743×10^{-1}
Tridecanal	1068.12	-8.0108×10^{-1}
iso-Dodecene	993.89	-7.8875×10^{-1}
Branced aldehydes	1068.12	-8.0180×10^{-1}

References

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(2) Hentschel, B.; Kiedorf, G.; Gerlach, M.; Hamel, C.; Seidel-Morgenstern, A.; Freund, H.; Sundmacher, K. Model-Based Identification and Experimental Validation of the Optimal Reaction Route for the Hydroformylation of 1-Dodecene. *Ind. Eng. Chem. Res.* **2015**, *54*, 1755–1765.

(3) Hentschel, B.; Peschel, A.; Freund, H.; Sundmacher, K. Simultaneous design of the optimal reaction and process concept for multiphase systems. *Chem. Eng. Sci.* **2014**, *115*, 69–87.

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