Supporting Information

Assessment of 1-dimensional catalytic reactors using constrained Gibbs free energy minimization method: water-gas-shift and carbon monoxide methanation case.

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The conservation matrix represented by its species and elements (components) is given here:

		CO(g)	CO2(g)	H2(g)	H2O(g)	CH4(g)	C(s)
A =	C	1	1	0	0	1	1
	H	0	0	2	2	4	0
	O	1	2	0	1	0	0

and the respective linear independent reactions considered are:

R1 $CO + H_2O \Leftrightarrow CO_2 + H_2$

R2 $CO + 3H_2 \Leftrightarrow CH_4 + H_2O$

R3 $2CO \Leftrightarrow C(s) + CO_2$

from which the reaction matrix ϑ is obtained:

	R1	R2	R3	
ϑ =	-1	-1	-2	CO(g)
	1	0	1	CO2(g)
	1	-3	0	H2(g)
	-1	1	0	H2O(g)
	0	1	0	CH4(g)
	0	0	1	C(s)

Hence, from these matrices, a new entity conservation matrix A' is formulated following the algorithm proposed by Blomberg and Koukkari[23]. Here, the *rx* extra columns are the respective rows used to facilitate the iterative steps taken, and Lx describes the species label changing based on the linear combinations of the rows. For the sake of visualization, zeros were omitted. The matrix A extending procedure starts adding the unitary matrix to the left side of the reaction matrix, as follows:

$$A' = [I \quad \vartheta] \therefore$$

		CO(g)	CO_2(g)	H_2(g)	H_2O(g)	CH_4(g)	C(s)	R1	R2	R3
r1	CO(g)	1						-1	-1	-2
r2	CO_2(g)		1					1		1
r3	H_2(g)			1				1	-3	
r4	H_2O(g)				1			-1	1	
r5	CH_4(g)					1			1	
r6	C(s)						1			1

The primary goal is the elimination of all negative values applying linear combinations on the rows only; a proper positive pivot (from the reactions columns) is then chosen. Briefly, strictly positive scaling factors must be employed and they can deviate from the unit in some cases. Sometimes it is necessary to choose negative pivots to proceed. A complete description of the steps can be found in the original article[23]. After eight iterations, the extended matrix becomes that presented in Eq. (9). One should notice that other combinations are possible, although this procedure is made in a stepwise fashion to ensure knowledge transfer. In our proposed example, in the first iteration, the pivot element was chosen from row 4 and column 8 in order to reduce the magnitude of the element (3, 8). The respective label now receives an opposite transformation undergone by the respective row receiving the "changing". The label update must be settled on the selected pivot row. Thus, in this first iteration, the label becomes: H_2(g) – H_2O(g) = O(g).

Iteration S1)

		CO(g)	CO_2(g)	H_2(g)	H_2O(g)	CH_4(g)	C(s)	R1	R2	R3	
r1	CO(g)	1						-1	-1	-2	
r2	CO_2(g)		1					1		1	
r3	H_2(g)			1	1				-2		r4+r3
r4	**O(g)**				1			-1	1		**L3-L4**
r5	CH_4(g)					1			1		
r6	C(s)						1			1	

Iteration S2)

		CO(g)	CO_2(g)	H_2(g)	H_2O(g)	CH_4(g)	C(s)	R1	R2	R3	
r1	CO(g)	1	1						-1	-1	r2+r1
r2	**O(g)**		1					1		1	**L1-L2**
r3	H_2(g)			1	1				-2		
r4	O(g)				1			-1	1		
r5	CH_4(g)					1			1		
r6	C(s)						1			1	

Iteration S3)

Here, when the label changing is applied to row 2, the first element "vanishing" turns out.

		CO(g)	CO_2(g)	H_2(g)	H_2O(g)	CH_4(g)	C(s)	R1	R2	R3	
r1	CO(g)	1	1						-1	-1	
r2	**v1**		1					1		1	**L4-L2**
r3	H_2(g)			1	1				-2		
r4	O(g)		1		1				1	1	r2+r4
r5	CH_4(g)					1			1		
r6	C(s)						1			1	

This means that an immaterial constraint, named here as v_1, is active on carbon dioxide and reaction R1.

Iteration S4)

		CO(g)	CO_2(g)	H_2(g)	H_2O(g)	CH_4(g)	C(s)	R1	R2	R3	
r1	**C(g)**	1	1						-1	-1	**L4-L1**
r2	v1		1					1		1	
r3	H_2(g)			1	1				-2		
r4	O(g)	1	2		1						r1+r4
r5	CH_4(g)					1			1		
r6	C(s)						1			1	

Iteration S5)

		CO(g)	CO_2(g)	H_2(g)	H_2O(g)	CH_4(g)	C(s)	R1	R2	R3	
r1	C(g)	1	1			1				-1	r5+r1
r2	v1		1					1		1	
r3	H_2(g)			1	1				-2		
r4	O(g)	1	2		1						
r5	**H_4(g)**					1			1		**L1-L5**
r6	C(s)						1			1	

Iteration S6)

		CO(g)	CO_2(g)	H_2(g)	H_2O(g)	CH_4(g)	C(s)	R1	R2	R3	
r1	C(g)	1	1			1				-1	
r2	v1		1					1		1	
r3	H_2(g)			1	1	2					2*r5+r3
r4	O(g)	1	2		1						
r5	**v2**					1			1		**2*L3-L5**
r6	C(s)						1			1	

Iteration S7)

		CO(g)	CO_2(g)	H_2(g)	H_2O(g)	CH_4(g)	C(s)	R1	R2	R3	
r1	**C(g)**	1	1			1				-1	**L2-L1**
r2	v1	1	2			1		1			r1+r2
r3	H_2(g)			1	1	2					
r4	O(g)	1	2		1						
r5	v2					1			1		
r6	C(s)						1			1	

Iteration S8)

		CO(g)	CO_2(g)	H_2(g)	H_2O(g)	CH_4(g)	C(s)	R1	R2	R3	
r1	C(g)	1	1			1	1				r6+r1
r2	v1	1	2			1		1			
r3	H_2(g)			1	1	2					
r4	O(g)	1	2		1						
r5	v2					1			1		
r6	**C(g)-C(s)**						1			1	**L1-L6**

Post-processing and transposition (tableaux matrix):

T	C	2H	O	v1	v2	v3
CO(g)	1		1	1		
CO_2(g)	1		2	2		
H_2(g)		1				
H_2O(g)		1	1			
CH_4(g)	1	2		1	1	
C(s)	1					1
WGS (R1)				1		
CO meth. (R2)					1	
Boudouard (R3)						1

Here, one can notice that the post-processed matrix contains the stoichiometric matrix A presented at the beginning, except for the scaling factor of the hydrogen element.