Kinetics of thermal dry reforming of methane for syngas production

and solid carbon capture

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1. Flowrate and residence times in the reactor

Table S1: Inlet volumetric flow rate corresponding to the residence time in the hot zone

Hot zone residence time (s)	Total inlet volume rate (ml/min) at 298 K	
1	1230.81	
3	410.28	
5	246.15	
7	175.82	

Table S2: Adjustment in flowrate to achieve a residence time of 5 s in the hot zone at different temperatures

Hot zone temperature (K)	Total inlet volume rate (ml/min) at 298 K
1273	323.49
1373	322.13
1473	300.23
1573	281.16
1673	246.15
1873	235.97

2. Kinetic mechanisms

The kinetic parameters of the deposition reactions along with hydrogen inhibition functions are given in Table below. The detailed gas-phase mechanisms are provided in a separate text files.

Deposition reaction kinetic data in Arrhenius format					
Species	A (m s ⁻¹)	$E_{\rm A}$ (kJ mol ⁻¹)	H ₂ inhibition function		
CH4	4.00E+12	446	$2.094/\left(2.094 + \frac{[H_2]}{[CH_4]}\right)$		
C ₂ H ₆	1.00E+13	268	$1.594 / \left(1.594 + \frac{[H_2]}{[C_2H_6]} \right)$		
C₂H₄	7.25E+03	155	$1.594 / \left(1.594 + \frac{[H_2]}{[C_2H_4]} \right)$		
C_2H_2	2.03E+02	126	$4.497 / \left(4.497 + \frac{[H_2]}{[C_2H_2]} \right)$		
C ₄ H ₆	7.25E+02	142	$6.042 / \left(6.042 + \frac{[H_2]}{[C_4H_6]} \right)$		
C_6H_6	2.35E+06	217	$0.519 / \left(0.519 + \frac{[H_2]}{[C_6 H_6]} \right)$		

Table S3: Kinetic parameters for deposition reactions.

The impact of temperature on the important species taking part in non-catalytic DRM is illustrated in Figure S1 for three different gas-phase mechanisms, namely Caltechmech (reference S1), ABF2000 (reference S2), and Polymech (reference S3).



Figure S1: Comparison of three different gas-phase mechanisms, namely Caltechmech, ABF2000, and Polymech for a temperature range (1073 K to 1873 K) at a CH_4 : CO_2 ratio of 2, a residence time of 5 s, and at a pressure of 1 bar.

3. Thermodynamic product distribution for hydrocarbon byproducts

Figure S2 depicts the hydrocarbon equilibrium by-product distribution for different $CH_4:CO_2$ ratios and pressure.



Figure S2: Effect of different $CH_4:CO_2$ ratios (1, 4) and pressure (1, 5 bar) on hydrocarbon byproduct equilibrium distribution

4. Impact of temperature on hydrocarbon by-products

Figure S3 illustrates the impact of temperature on the formatting of hydrocarbon byproducts.



Figure S3: End-of-pipe experiments vs. simulations for hydrocarbon by-products at different hot zone temperatures at constant CH₄:CO₂ ratio = 2, τ = 5 s, and p = 1 bar.

5. Impact of CH₄:CO₂ ratio on hydrocarbon by-products

Figure S4 illustrates the impact of the CH₄:CO₂ ratio on the formation of hydrocarbon by-products.



Figure S4: End-of-pipe experiments vs. simulations for hydrocarbon by-products at different CH₄:CO₂ ratios while keeping the other reaction conditions, namely T = 1673 K, τ = 5 s, and p = 1 bar, constant.

6. Impact of CH₄:CO₂ ratio on C₂H₂ production

Figure S5 depicts the impact of the CH_4 : CO_2 ratio on C_2H_2 formation along the reactor axis.



Figure S5: Axial profiles of C₂H₂ at CH4:CO2 ratios of 1 and 4; T = 1673 K, τ = 5 s, and p = 1 bar.

7. Impact of residence time on hydrocarbon by-products

Figure S6 illustrates the impact of the residence time on the formation of hydrocarbon by-products.



Figure S6: End-of-pipe experiments vs simulations for hydrocarbon by-products at different residence times, while keeping all other reaction conditions, namely T = 1673 K, CH₄:CO₂ ratio = 2, and p = 1 bar, constant.

References

[S1] G. Blanquart, P. Pepiot-Desjardins, H. Pitsch, Chemical mechanism for high temperature combustion of engine relevant fuels with emphasis on soot precursors, Combust. Flame. 156 (2009) 588–607. https://doi.org/10.1016/j.combustflame.2008.12.007.

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