Detailed Reaction Mechanism for the Combustion of Hydrogen and Syngas

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**Auto ignition (Ignition delay)**

<table>
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<th>Fuel</th>
<th>$\phi$</th>
<th>$P$ (atm)</th>
<th>$T$ (K)</th>
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<tbody>
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<td>Hydrogen</td>
<td>0.1 – 4.0</td>
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<td>925 – 2000</td>
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<tr>
<td>Syngas</td>
<td>0.5 – 1.0</td>
<td>1 – 32</td>
<td>870 – 2200</td>
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**Laminar flame speed**

<table>
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<th>$\phi$</th>
<th>$P$ (atm)</th>
<th>$T$ (K)</th>
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<tbody>
<tr>
<td>Hydrogen</td>
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<td>1 - 10 atm</td>
<td>298-443</td>
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<tr>
<td>Syngas</td>
<td>0.2 – 5.5</td>
<td>1 - 40 atm</td>
<td>298-460</td>
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1. **Hydrogen - Syngas Mechanism Validation**

This section deals with the kinetic model validation. The mechanism is validated against laminar flame speed, ignition delay time, species prediction in burner stabilized flame, JST stirred reactor and flow reactor.

For the laminar flame speed and burner stabilized flame solid line represents prediction implying the mixture average transport model and dash line represents the prediction implying the multi component transport model with current kinetic scheme unless stated. The solid or dash in the ignition delay, JSR and flow reactor plots represents prediction from the current kinetic model. All Symbols in the plots represents the experimental data from the published literature. Colors of lines and symbols are assigned to match each other for particular experimental condition or specific species.
1.1 Laminar Flame Speed

**Figure S1.1:** Comparison of Laminar flame speed of H$_2$–air mixture at 1 atm and 303, 373 and 443 K. Filled square [21], open triangle [22] and crosses [23].

**Figure S1.2:** Comparison of laminar flame speed of H$_2$–O$_2$–He [O$_2$/He: 1/7] at 298 K and 5, 10 atm. Open triangle [23], half-filled circle [24].
Figure S1.3: Laminar flame speed comparison of CO/H$_2$-air at 298 K and 2 atm. Half-filled square [17], open star [25].

Figure S1.4: Laminar flame speed comparison of CO/H$_2$ (50/50) –O$_2$/He (1/7) at 298 K and 5, 10 atm. Half-filled square [17], half-filled circle [26], open triangle [23] with uncertainty bars.
**Fig S1.5**: Laminar flame speed comparison of H\textsubscript{2}/CO (25/75) – O\textsubscript{2}/He (1/7) at 298 K and 5, 10, 20 atm. Filled square [17] and filled circle [27].

**Fig S1.6**: Laminar flame speed comparison of H\textsubscript{2}/CO (5/95) – O\textsubscript{2}/He (1/7) at 298 K and 5, 10, 20, 40atm. Filled squares [17], filled triangles [3].
Equivalence ratio, $\phi$

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Syngas composition: $H_2/CO/N_2/CO_2(33.55/40.26/13.20/12.99)$ %, $O_2/Ar$ ratio: 1/3.76, $O_2/He$ ratio: 1/6. Symbols measurements from [28].

**Figure S1.7:** Laminar flame speed comparison of syngas / air, syngas /$O_2$/Ar and syngas /$O_2$/He at 1 bar and 298 K. Syngas composition: $H_2/CO/N_2/CO_2(33.55/40.26/13.20/12.99)$ %. $O_2$/ Ar ratio: 1/3.76, $O_2$/He ratio: 1/6. Symbols measurements from [28].

Equivalence ratio, $\phi$

<table>
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<th>LFS [cm/s]</th>
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<td>250</td>
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**Figure S1.8:** Laminar flame speed comparison of syngas / air at 1 bar and 298, 380, 460 K. Syngas composition: $H_2/CO/N_2/CO_2 (33.55/40.26/13.20/12.99)$ %. Symbols measurements from [28].
**Figure S1.9:** Laminar flame speed comparison of syngas/O$_2$/He at 298 K and 1, 5, 10 bar. Syngas composition: H$_2$/CO/N$_2$/CO$_2$ (33.55/40.26/13.20/12.99) %. O$_2$/He ratio: 1/6. Symbols measurements from [28].

**Figure S1.10:** Laminar flame speed comparison of equimolar H$_2$/CO at different N$_2$ dilution at 1 bar and 302 K with air. Symbols measurements: filled squares [29] and filled triangles [30].
Figure S1.11: Laminar flame speed comparison of equimolar H₂/CO at different CO₂ dilution at 1 bar and 302 K with air. Symbols measurements: filled circles [31], filled triangles [30] and filled squares [32].

Figure S1.12: Laminar flame speed comparison of H₂/H₂O–air mixture with 15 % H₂O dilution at 1 atm and 323 K. Symbols measurements from [23].
Figure S1.13: Laminar flame speed comparison of H$_2$ / CO(50/50) / H$_2$O – air mixture with 15 % H$_2$O dilution at 1 atm and 423 K. Symbols measurements from [23].

Figure S1.14: Laminar flame speed comparison of H$_2$ / CO(5/95) / H$_2$O – air mixture with 7.5 % H$_2$O dilution at 1 atm and 323 K. Symbols measurements from [23].
Figure S1.15: Laminar flame speed comparison of H\textsubscript{2}/CO-air mixture at 1 atm and 298 K for H\textsubscript{2} composition 1, 3, 5 and 10 % in fuel mixture. Symbols measurements: open circle [17], open triangle [33], open square [25], open diamond [34], open star [26], crossed circle [35] and half-filled square [36].

Figure S1.16: Laminar flame speed comparison of H\textsubscript{2}/CO-air mixture at 1 atm and 298 K for H\textsubscript{2} composition 20, 30, 40 and 50 % in fuel mixture. Symbols measurements: open triangle [33] and half-filled square [36].
Figure S1.17: Laminar flame speed comparison of H₂/CO-air mixture at 1 atm and 298 K for H₂ composition 60, 70, 80 and 90 % in fuel mixture. Symbols measurements: open triangle [33] and half-filled circle [36].

1.2 Burner Stabilized Flame

Figure S1.18: Comparison between model prediction and measurements for H₂/O₂/Ar flame at 4.75kpa and 298 K. Symbols :measurements from [37] see Table III mixture 1 for initial condition and mixture
composition. Lines: prediction without using the experimental temperature profile. Same condition and legend information applies to figure S1.19 to S1.21.

**Figure S1.19:** Comparison between model prediction and measurements for H radical. Symbols measurements from [37]. See Figure S1.18 for initial condition.

**Figure S1.20:** Comparison between model prediction and measurements for O radical. Symbols measurements from [37]. See Figure S1.18 for initial condition.
**Figure S1.21:** Comparison between model prediction and measurements for OH radical. Symbols: measurements from [37]. See Figure S1.18 for initial condition.

**Figure S1.22:** Comparison between model prediction and measurements for H₂/O₂/Ar flame at 3 atm and 333 K. Symbols: measurements from [38] see Table III mixture 5 for initial condition and mixture composition. Lines: prediction without using the experimental temperature profile. Same condition and legend information applies to figure S1.23 to S1.26.
Figure S1.23: Comparison between model prediction and measurements for HO$_2$ and H$_2$O$_2$. Symbols measurements from [38]. See Figure S1.22 for initial condition.

Figure S1.24: Comparison between model prediction and measurements for H radical. Symbols measurements from [38]. See Figure S1.22 for initial condition.
**Figure S1.25**: Comparison between model prediction and measurements for O radical. Symbols measurements from [38]. See Figure S1.22 for initial condition.

**Figure S1.26**: Comparison between model prediction and measurements for OH radical. Symbols measurements from [38]. See Figure S1.22 for initial condition.
**Figure S1.27:** Comparison between model prediction and measurements for H₂/O₂/Ar flame at 1 atm and 333 K. Symbols: measurements from [38] see Table III, mixture 5 for initial condition and mixture composition. Lines: prediction using the experimental temperature profile. Same initial condition and legend information applies to figure S1.28 to S1.31.

**Figure S1.28:** Comparison between model prediction and measurements for HO₂ and H₂O₂. Symbols: measurements from [38]. See Figure S1.27 for initial condition.
Figure S1.29: Comparison between model prediction and measurements for H radical. Symbols measurements from [38]. See Figure S1.27 for initial condition.

Figure S1.30: Comparison between model prediction and measurements for O radical. Symbols measurements from [38]. See Figure S1.27 for initial condition.
Figure S1.31: Comparison between model prediction and measurements for OH radical. Symbols measurements from [38]. See Figure S1.27 for initial condition.

Figure 2.32: Comparison between model prediction and measurements for H₂/O₂/Ar flame at 10 atm and 363 K. Symbols: measurements from [39] see Table III, mixture 4 for initial condition and mixture composition. Lines: prediction using the experimental temperature profile.
Ignition Delay (Shock Tube)

Figure S1.33: Comparison between model prediction and measurements for H\textsubscript{2}/O\textsubscript{2}/Ar ignition delay time. Lines: model prediction; Symbols measurements from [3], see Table IV, mixture 1 for experimental condition.

Figure S1.34: Comparison between model prediction and measurements for H\textsubscript{2}/O\textsubscript{2}/N\textsubscript{2} ignition delay time. Lines: model prediction; Symbols measurements from [3], see Table IV, mixture 2 for experimental condition.
Figure S1.35: Comparison between model prediction and measurements for H$_2$/O$_2$/Ar ignition delay time. Lines: model prediction; Symbols measurements from [3], see Table IV, mixture 3 for experimental condition.

Figure S1.36: Comparison between model prediction and measurements for H$_2$/CO (5/95)-O$_2$/Ar ignition delay time. Lines: model prediction; Symbols measurements from [3], see Table IV, mixture 12 for experimental condition.
Figure S1.37: Comparison between model prediction and measurements for H₂/CO - O₂/Ar ignition delay time at 4 bar. Lines: model prediction; Symbols measurements from [3], see Table IV, mixture 13(H₂/CO:50/50), mixture 14 (H₂/CO:5/95) and mixture 1(H₂) for experimental condition.

Figure S1.38: Comparison between model prediction and measurements for H₂/O₂/Ar ignition delay time. Lines: model prediction; Symbols measurements from [3], see Table IV, mixture 15 for experimental condition.
Figure S1.39: Comparison between model prediction and measurements for H₂/O₂/Ar ignition delay time. Lines: model prediction; Symbols measurements from [3], see Table IV, mixture 16 for experimental condition.

Figure S1.40: Comparison between model prediction and measurements for H₂/O₂/Ar ignition delay time. Lines: model prediction; Symbols measurements from [3], see Table IV, mixture 17 for experimental condition.
**Figure S1.41:** Comparison between model prediction and measurements of H₂/O₂/Ar ignition delay at 33 atm. Lines: model prediction; Symbols: measurements from [40]. See Table IV, mixture 4 and 5 for initial condition.

**Figure S1.42:** Comparison between model prediction and measurements of H₂/O₂/Ar ignition delay at 57 and 64 atm. Lines: model prediction; Symbols: measurements from [40]. See Table IV, mixture 6, 7 and 8 for initial condition.
Figure S1.43: Comparison between model prediction and measurements of H$_2$/O$_2$/Ar ignition delay at 101 kPa and 6485 kPa. Lines: model prediction; Symbols: measurements from [41]. See Table IV, Mixture 9 for initial condition.

Figure S1.44: Comparison between model prediction and measurements for H$_2$/CO-O$_2$/Ar ignition delay time at different H$_2$/CO ratio, in 1 % O$_2$ and 98 % Ar at 12 atm. Lines: model prediction; Symbols measurements from [21].
Figure S1.45: Comparison between model prediction and measurements for H₂/CO-O₂/Ar ignition delay time at different H₂/CO ratio, in 1 % O₂ and 98 % Ar at 32 atm. Lines : model prediction; Symbols: measurements from [21].

1.3 Jet Stirred Reactor

Lines represents the model prediction from this work. Symbols represents the published experimental measurements. All the experimental data for JSR are extracted from the plots from the original paper. The initial mole fraction of the mixture are also taken from the graph to match the experimental work of respective group.
Figure S1.46: Comparison between model prediction and measurements for H₂/O₂/N₂ oxidation at 1atm, τ= 0.24 s and Ø=0.2. Symbols: measurements from [42]. See table V, Mixture 2 for initial condition and mixture composition.

Figure S1.47: Comparison between model prediction and measurements for H₂/O₂/N₂ oxidation at 1atm, τ= 0.24 s and φ =0.5. Symbols: measurements from [42]. See table V, Mixture 2 for initial condition and mixture composition.
Figure S1.48: Comparison between model prediction and measurements for H$_2$/O$_2$/N$_2$ oxidation at 10atm, $\tau=1.0$ s and $\phi=0.1$. Symbols: measurements from [42]. See table V, Mixture 1 for initial condition and mixture composition.

Figure S1.49: Comparison between model prediction and measurements for H$_2$/O$_2$/N$_2$ oxidation at 10atm, $\tau=1.0$ s and $\phi=1.5$. Symbols: measurements from [42]. See table V, Mixture 1 for initial condition and mixture composition.
Figure S1.50: Comparison between model prediction and measurements for H$_2$/O$_2$/N$_2$ oxidation at 1atm, $\tau = 0.12$ s and $\phi = 0.2$. Symbols: measurements from [43]. See table V, Mixture 3 for initial condition and mixture composition.

Figure S1.51: Comparison between model prediction and measurements for H$_2$/O$_2$/N$_2$ oxidation at 1atm, $\tau = 0.12$ s and $\phi = 0.5$. Symbols: measurements from [43]. See table V, Mixture 3 for initial condition and mixture composition.
Figure S1.52: Comparison between model prediction and measurements for H₂/O₂/N₂ oxidation at 1atm, \( \tau = 0.12 \) s and \( \phi = 2.0 \). Symbols: measurements from [43]. See table V, Mixture 3 for initial condition and mixture composition.

Figure S1.53: Comparison between model prediction and measurements for H₂/H₂O/O₂/N₂ oxidation at 1atm, \( \tau = 0.12 \) s and \( \phi = 0.24 \), with 10 % H₂O dilution. Symbols: measurements from [43]. See table V, Mixture 4 for initial condition and mixture composition.
Figure S1.54: Comparison between model prediction and measurements for H$_2$/H$_2$O/O$_2$/N$_2$ oxidation at 1atm, $\tau$= 0.12 s and $\phi$=0.5, with 10 % H$_2$O dilution. Symbols: measurements from [43]. See table V, Mixture 4 for initial condition and mixture composition.

Figure S1.55: Comparison between model prediction and measurements for H$_2$/H$_2$O/O$_2$/N$_2$ oxidation at 1atm, $\tau$= 0.12 s and $\phi$=1.05, with 10 % H$_2$O dilution. Symbols: measurements from [43]. See table V, Mixture 4 for initial condition and mixture composition.
Figure S1.56: Comparison between model prediction and measurements for H₂/H₂O/O₂/N₂ oxidation at 1atm, τ= 0.12 s and φ ≈2.38, with 10 % H₂O dilution. Symbols: measurements from [43]. See table V, Mixture 4 for initial condition and mixture composition.

Figure S1.57: Comparison between model prediction and measurements for CO/H₂/O₂/N₂ oxidation at 1atm, τ= 0.12 s and φ =0.1. Symbols: measurements from [44]. See table V, Mixture 5 for initial condition and mixture composition.
Figure S1.58: Comparison between model prediction and measurements for CO/H₂/O₂/N₂ oxidation at 1atm, τ= 0.12 s and ϕ =2.0. Symbols: measurements from [44]. See table V, Mixture 5 for initial condition and mixture composition.

1.4 Flow Reactor

Lines represents the model prediction from this work. Symbols represents the published experimental measurements. All the experimental data for flow reactor are extracted from the plots from the original paper. The closed homogenous reactor model is used for simulation assuming the constant pressure and enthalpy except for the plots in Figure S1.68 and S1.69 where plug flow reactor model is assumed. The simulation which are performed assuming constant P-H are time shifted to match the 50 % of the initial fuel consumption to account for the mixing non idealities.
Figure S1.59: Comparison between model prediction and measurements for H<sub>2</sub>/O<sub>2</sub>/N<sub>2</sub> oxidation at T: 880 K, P: 0.3 atm and Ø=1.0. Symbols: measurements from [45]. See table VI, Mixture 9 for initial condition and mixture composition.

Figure S1.60: Comparison between model prediction and measurements for H<sub>2</sub>/O<sub>2</sub>/N<sub>2</sub> oxidation at T: 934 K, P: 6 atm. Symbols: measurements from [45]. See table VI, Mixture 8 for initial condition and mixture composition.
Figure S1.61: Comparison between model prediction and measurements for H_2/O_2/N_2 oxidation at T: 935 K, P: 2.55 atm. Symbols: measurements from [45]. See table VI, Mixture 12 for initial condition and mixture composition.

Figure S1.62: Comparison between model prediction and measurements for H_2/O_2/N_2 oxidation at 0.6 atm; T: 897 K, φ=0.75 and T: 896 K, φ=0.33. Symbols: measurements from [45]. Circle (φ=0.75), triangle (φ =0.33). See table VI, Mixture 10 and 11 for initial condition and mixture composition.
Figure S1.63: Comparison between model prediction and measurements for H₂/O₂/N₂ oxidation at P: 15.7 atm; T: 914 K, ϕ=1.0 and 0.27. Symbols: measurements from [45]. Circle (Ø=1.0), star (Ø=0.27). See table VI, Mixture 14 and 15 for initial condition and mixture composition.

Figure S1.64: Comparison between model prediction and measurements for H₂/O₂/N₂ oxidation at P: 2.55 atm, T: 935 K, φ=1.0 and P: 2.5 atm, T: 943, Ø=0.33. Symbols: measurements from [45]. Circle (Ø=1.0), square (φ=0.33). See table VI, Mixture 12 and 13 for initial condition and mixture composition.
**Figure S1.65:** Comparison between model prediction and measurements for $\text{H}_2/\text{O}_2/\text{N}_2$ oxidation at $P$: 1 atm, $T$: 910 K, $\Theta$=0.28. Symbols: measurements from Yetter et.al. [46]. See table VI, Mixture 1 for initial condition and mixture composition.

**Figure S1.66:** Comparison between model prediction and measurements for $\text{CO}/\text{H}_2\text{O}/\text{O}_2/\text{N}_2$ oxidation at $T$: 1040 K and different initial pressure. Symbols: CO concentration profile, measurements from Kim et.al. [47]. See table VI, Mixture 3 for initial condition and mixture composition.
Figure S1.67: Comparison between model prediction and measurements for CO/H₂O/O₂/N₂ oxidation at P: 6.5 atm and different initial temperature. Symbols: CO concentration profile, measurements from Kim et.al. [47]. See table VI, Mixture 4 for initial condition and mixture composition.

Figure S1.68: Comparison between model prediction and measurements for H₂/O₂/N₂ oxidation at P: 6.5 atm and different initial temperature. Symbols: H₂ concentration profile, measurements from Mueller et.al. [45]. See table VI, Mixture 16 -20 for initial condition and mixture composition.
Figure S1.69: Species profile comparison between model prediction and measurements for H$_2$ (0.161%)/O$_2$ (1.6039%) / N$_2$; $\phi=0.05$ oxidation at 50 bar. Symbols: measurements from Hashemi et.al. [48]; lines: model prediction. The simulation lines are shifted by $+5$ K within the experimental uncertainty of $\pm5$ K.
1.5 Oxidation in Shock Wave Condition

![Figure S1.70](image1.png)

**Figure S1.70**: H₂O profile comparison between model prediction and measurements for H₂O₂ (2540 ppm)/ H₂O (1234 ppm)/ O₂ (617 ppm)/ Ar oxidation in shock tube at initial condition of 1.91 atm and 1398 K. Symbols measurements from Hong et.al. [49]. Lines are model prediction; solid line: prediction with this work adopting the rate constant for reaction R19 (H₂O₂+OH=HO₂+H₂O) from Hong et.al. [49], dash line: prediction when using the rate constant for R19 from Baulch et.al. [1] in this work.

![Figure S1.71](image2.png)

**Figure S1.71**: OH profile comparison between model prediction and measurements for H₂O₂ /H₂O / O₂ / Ar oxidation in shock tube. The mixture composition, initial condition and legend information are same as in Figure S1.71.
Figure S1.72: H$_2$O profile comparison between model prediction and measurements for H$_2$O$_2$ (860 ppm) / H$_2$O (663 ppm) / O$_2$ (332 ppm) / Ar oxidation in shock tube at initial condition of 1.83 atm and 1057 K. Symbols measurements from Hong et.al [50]; Line model prediction from this work.

Figure S1.73: H$_2$O profile comparison between model prediction and measurements for H$_2$ (2.9 %) / O$_2$ (0.1%) / Ar oxidation in shock tube at initial condition of 1.95 atm and 1100 K. Symbols measurements from Hong et.al. [51]. Line model prediction from this work.
References


