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The effect of H₂S addition to methane on the ignition and oxidation at high pressures

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Experimental: Laminar Flow Reactor (FR)

- Temperature: 600–900 K
- Pressure: 50 bar
- Flow rate: 3.0 NL/min → Residence time: 6.6–10 s
- Downstream measurement via GC and Gas Analyzer
- H₂S/CH₄/O₂/N₂ mixtures ($\Phi = 22.8$, H₂S/CH₄ = 1.6% & $\Phi = 1.1$, H₂S/CH₄ = 13.5%)

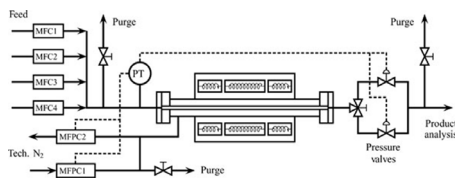


Fig 1. Schematic diagram of the high pressure laminar flow reactor

Experimental: Rapid Compression Machine (RCM)

- Temperature: 930–1050 K
- Pressure: 30–80 bar
- H₂S/CH₄/O₂/N₂/AR mixtures ($\Phi = 0.5$, H₂S/CH₄ = 0 & 1%)

Chemical Kinetics Model

- H₂/CO/HC's subsets from recent work by Glarborg et al. [1–3].
- H₂S subset is taken from a recent review by Glarborg et al. [4].
- Importance of SH+H₂O₂ = H₂S+HO₂ (R1):
→ calculated by Zhou et al. [5], adjusted by Mathieu et al. [6].

Results (RCM)

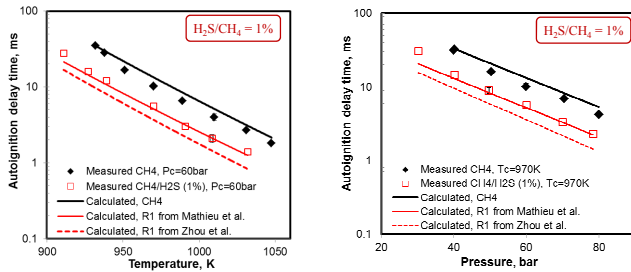


Fig 2. Measured (symbols) and calculated (lines) autoignition delay times (RCM). Left: ignition delay times at a fixed pressure of $P_c = 60$ bar. Right: Ignition delay times at a fixed temperature of $T_c = 970$ K.

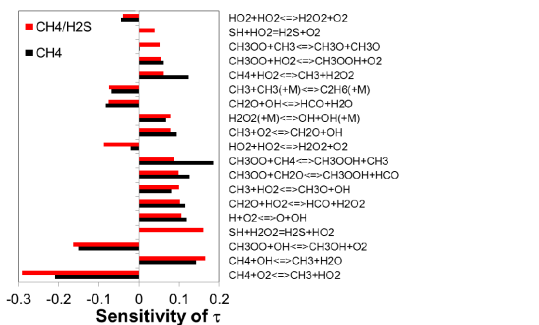


Fig 3. Sensitivity coefficients with respect to the autoignition delay time calculated at $T_c = 970$ K and $P_c = 80$ bar at fuel-lean conditions ($\Phi = 0.5$); for neat CH₄ (black bars) and for H₂S/CH₄ (red bars).

Results (FR)

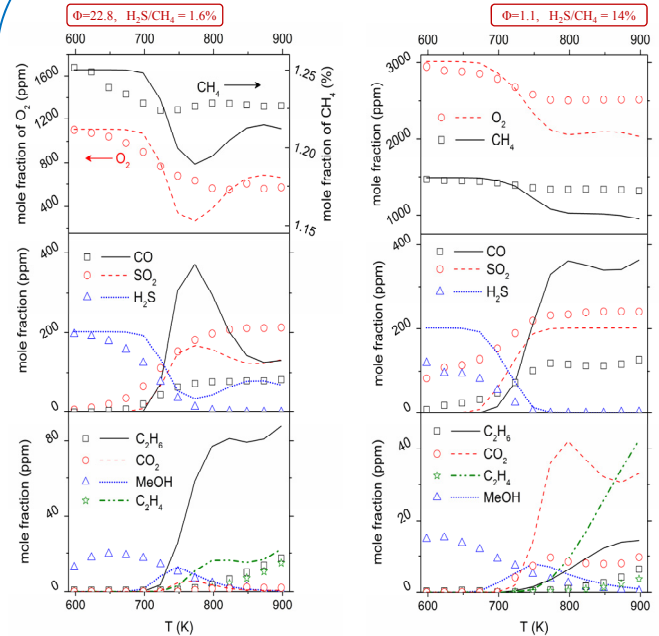


Fig 4. Results of experiments with CH₄/H₂S in the flow reactor at 50 bar. Left: 12516/1109/202 ppm of CH₄/O₂/H₂S in N₂ ($\Phi = 22.8$). Right: 1494/3012/202 ppm of CH₄/O₂/H₂S in N₂ ($\Phi = 1.1$). Gas residence time is given by $\tau[s] = 5990/T [K]$ and $\tau[s] = 5920/T [K]$, for fuel-rich and stoichiometric conditions, respectively.

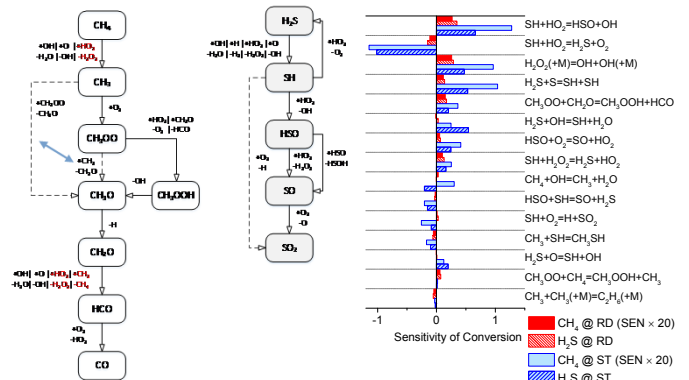


Fig 5. Left: Reaction pathways for CH₄ and H₂S oxidation under flow reactor conditions (750 K & 50 bar) and RCM conditions (970 K & 80 bar). The reactions coloured red are involved only under RCM conditions. Right: Sensitivity of reaction rate constants in predicting H₂S and CH₄ molar conversion at the end of the flow reactor at 725 K and 50 bar. RD: reducing, ST: stoichiometric conditions.

Summary & Future Work

- RCM:
 - Adding 1% H₂S to CH₄; reducing ignition delays by a factor of two.
 - Good prediction by the model
- FR:
 - Promoting effect of H₂S addition on CH₄ oxidation
 - Overestimation of the onset of CH₄ and H₂S oxidation by the model
- ROP & SEN: no change in reaction pathways of CH₄ by adding H₂S
→ H₂S interactions with H₂O₂ promote the ignition by producing radicals
- Further work is required for better understanding of intermediate-T/ high-P oxidation of H₂S and its interaction with CH₄.

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