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Technical University of Denmark

Propane Oxidation at High Pressure and Intermediate Temperatures

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Motivations

- Propane: a major component in LPG
- Propane: a minor but sensitive component of natural gas
- Engines and gas turbines: need experimental data at high pressures and intermediate temperatures

Experimental: laminar flow reactor

- Quartz reactor to minimize surface reactions
- Steel pressure shell to achieve high pressures
- Temperature: 500—900 K
- Pressure: 100 bar
- Isothermal Zone Length: 42—44 cm
- Residence time: 8—11 s
- Measurement via GC

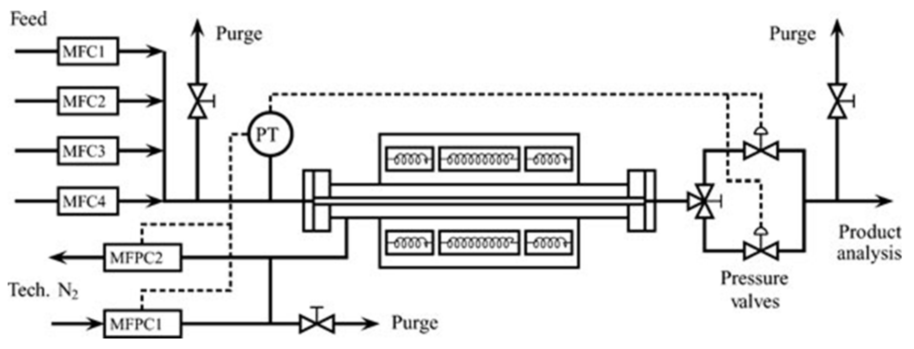

Fig 2. Schematic diagram of the high pressure laminar flow reactor

Chemical kinetics model

- H_2/CO/HC's subsets from recent work by Glarborg et al. [1—4].
- C_3 subset is reviewed and introduced in the present work.
- Low temperature sequences for propane oxidation is adopted from Goldsmith et al. [5].

Results: fuel-rich mixture

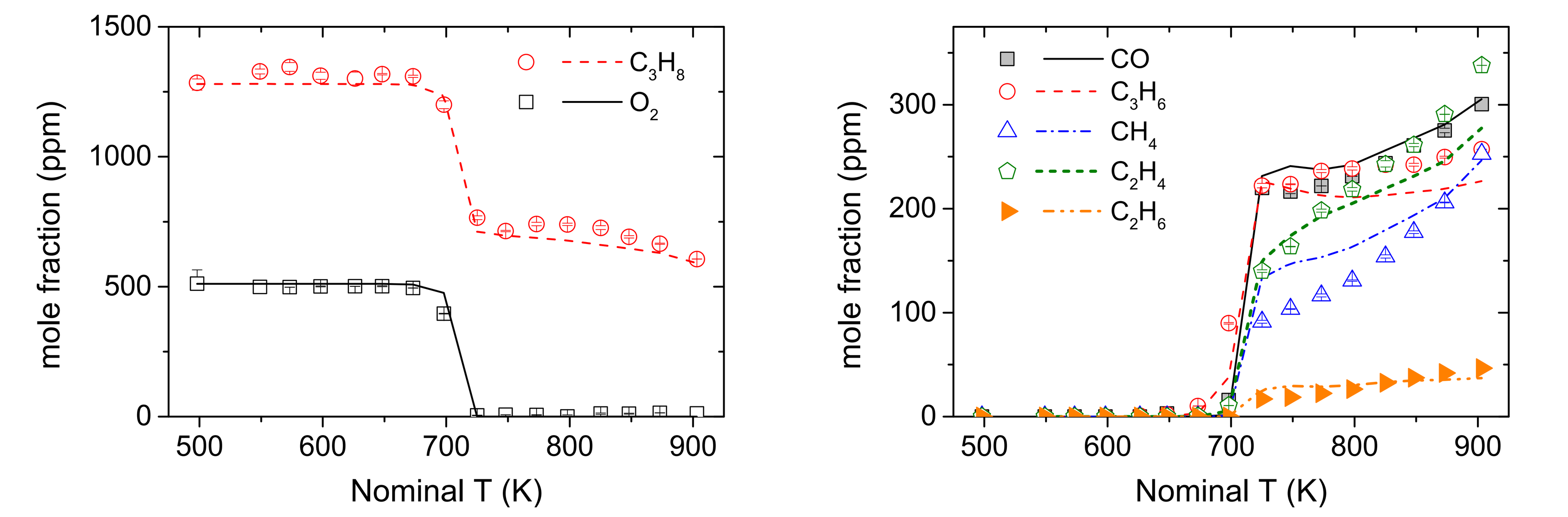

Fig 3. Results of experiments under reducing conditions (1285 ppm C_3H_8 and 511 ppm O_2 in N_2, Φ=12.5) at 100 bar pressure.

The fuel oxidation started at 700–725 K for a fuel-rich mixture (reducing conditions), and the major detected products have been CO, C_3H_6, CH_4, and C_2H_4. The model was able to reproduce the onset of oxidation as well as the concentrations of intermediate components precisely.

Results: stoichiometric mixture

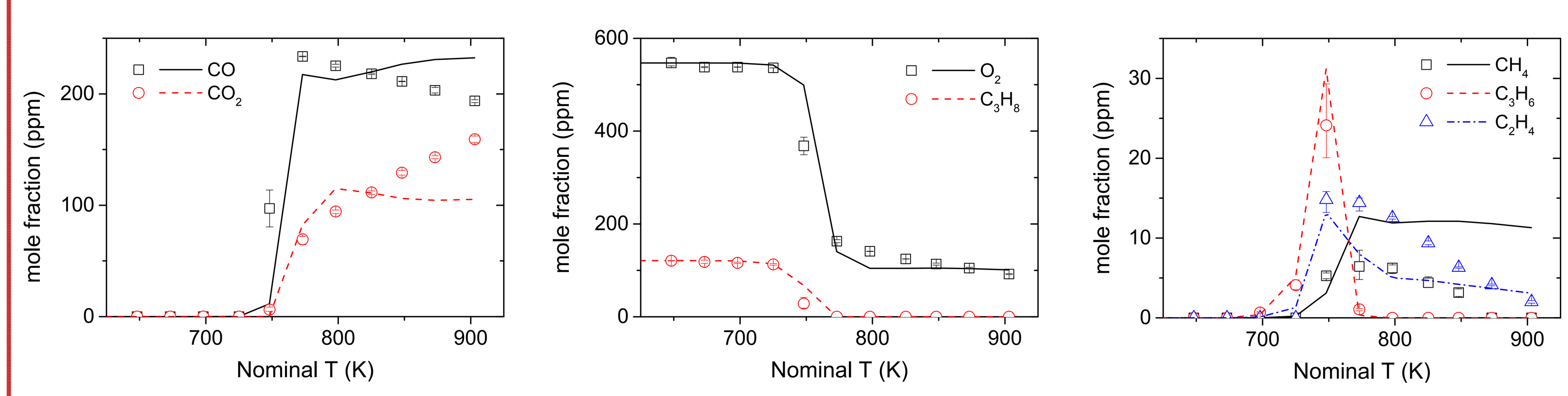

Fig 4. Results of experiments under stoichiometric conditions (121 ppm C_3H_8 and 547 ppm O_2 in N_2, Φ=1.1) at 100 bar pressure.

For a stoichiometric mixture, the fuel conversion started around 725 K. At T>750 K, propane was oxidized almost completely. The major products of the oxidation were CO and CO_2 and the concentration of propene and ethene decreased sharply at T>775 K. The model captured the onset temperature of ignition accurately but it seems that CO oxidation to CO_2 at high temperatures was not precisely captured by the model.

Results: fuel-lean mixture

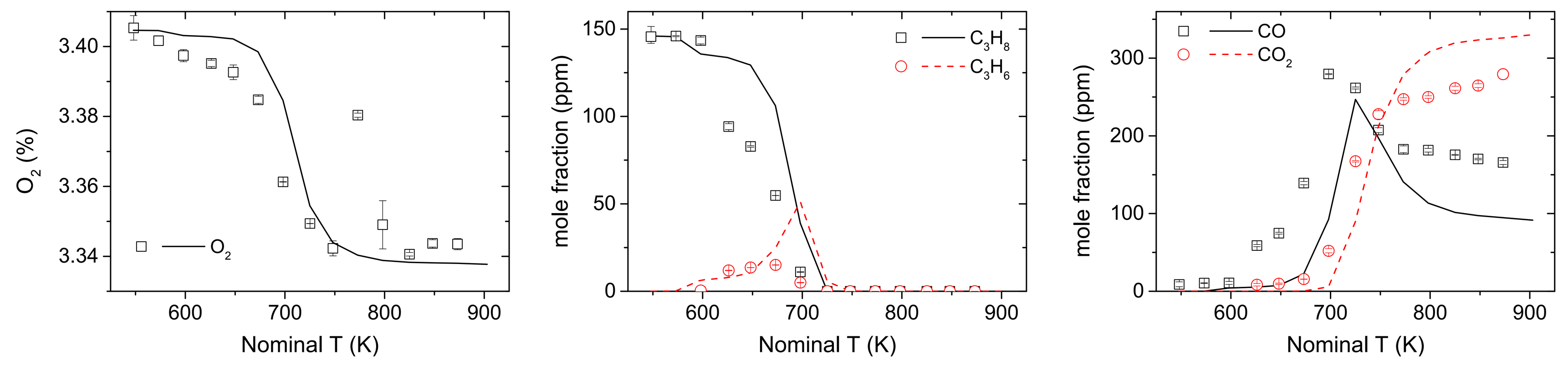

Fig 5. Results of experiments under oxidizing conditions (146 ppm C_3H_8 and 3.405% O_2 in N_2, Φ=0.02) at 100 bar pressure.

Propane concentration dropped sharply at T>600 K for a fuel-lean mixture (oxidizing conditions), and propane vanished from the exhaust at T>725 K. The model predicted slower reactivity compared to the experiments, so the fuel conversion was slightly underpredicted by the model.

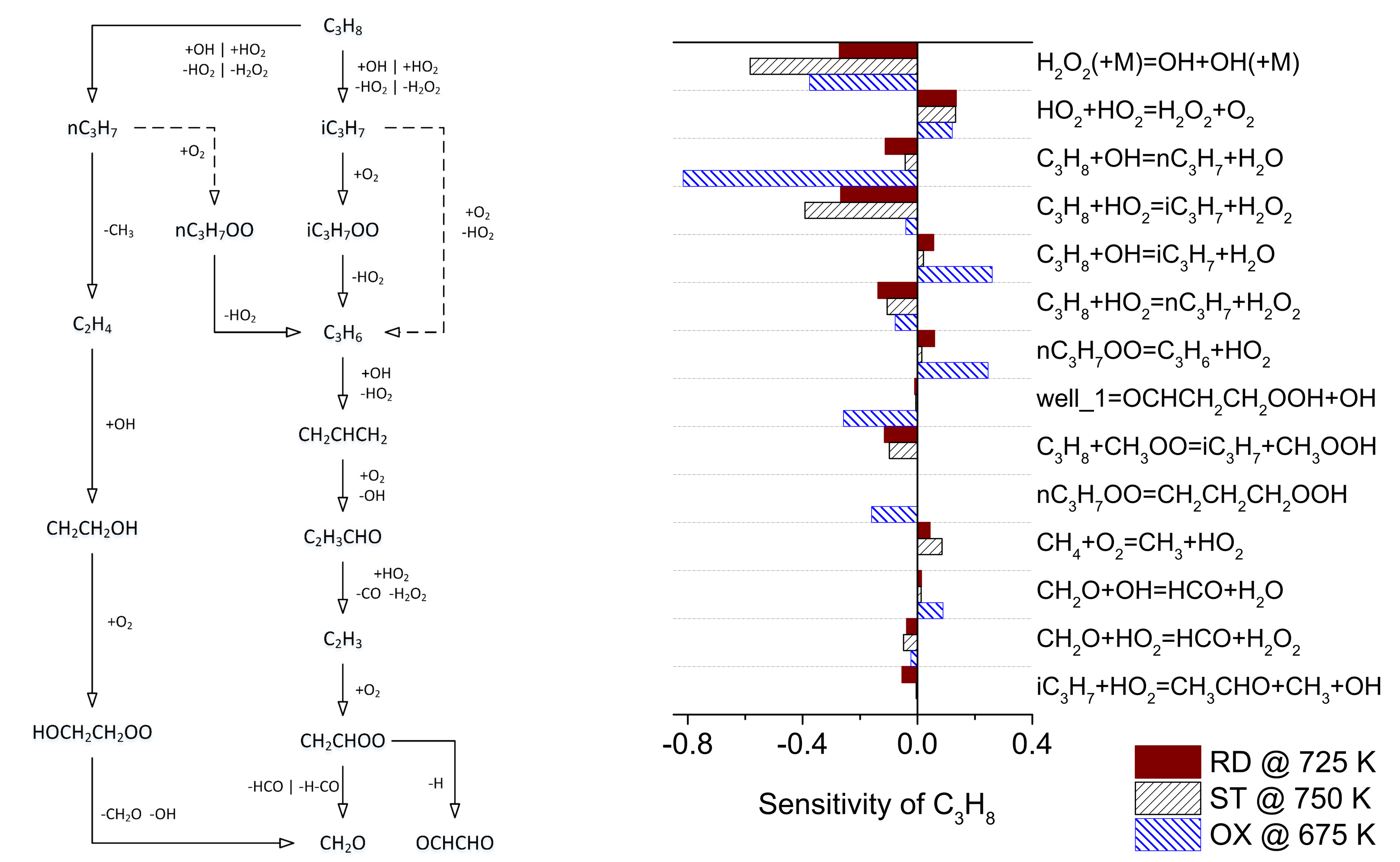

Fig 6. ***Left:*** Reaction pathways for propane oxidation under stoichiometric conditions (750 K, 100 bar). ***Right:*** Sensitivity of C_3H_8 prediction under flow-reactor conditions (RD: reducing, ST: stoichiometric, OX: oxidizing conditions) at 100 bar. The component $HOOCH_2CH_2CH_2OO$ is named "well_1" in above.

According to the results of sensitivity analyses, propane oxidation is largely controlled by H-abstraction by HO_2 from propane (R1). The branch leading to iC_3H_7 shows a larger sensitivity compared to the other one (except for oxidizing conditions). The reaction between C_3H_8 and OH (R2) is also sensitive. While the branch to nC_3H_7 promotes the oxidation, the other branch to iC_3H_7 inhibits the fuel conversion. The H-abstraction by CH_3OO from propane (R3) is also sensitive for reducing and stoichiometric conditions.

$C_3H_8 + HO_2 = nC_3H_7 + H_2O_2$	(R1a)
$C_3H_8 + HO_2 = iC_3H_7 + H_2O_2$	(R1b)
$C_3H_8 + OH = nC_3H_7 + H_2O$	(R2a)
$C_3H_8 + OH = iC_3H_7 + H_2O$	(R2b)
$C_3H_8 + CH_3OO = iC_3H_7 + CH_3OOH$	(R3)

Analysing the reaction pathway of propane oxidation revealed that for stoichiometric conditions and at 750 K, the major path for propane oxidation begins with H-abstraction by OH and HO_2 (R1 & R2). If the H-abstraction results in an iC_3H_7 radical, it will add to molecular oxygen to give iC_3H_7OO, which later decomposes to propene. If R1 and R2 yield nC_3H_7, then decomposition to ethene is favoured compared to addition of nC_3H_7 to molecular oxygen.

Summary

Propane oxidation at intermediate temperatures (500—900 K) and high pressure (100 bar) has been characterized by conducting experiments in a laminar flow reactor over a wide range of stoichiometries. The onset of fuel oxidation was found to be 600—725 K, depending on mixture stoichiometry. The model agreed well with the measurements of fuel-rich and stoichiometric mixtures while the model underpredicted the fuel conversion for fuel-lean conditions. Sensitivity analyses revealed the importance of H-abstraction reactions by HO_2, OH, and CH_3OO in controlling propane oxidation at 750 K.

References

[1] H. Hashemi, J. M. Christensen, S. Gersen, P. Glarborg, *"Hydrogen oxidation at high pressure and intermediate temperatures: Experiments and kinetic modeling"*, Proc. Combust. Inst. 35 (2015) 553—560.

[2] H. Hashemi, J. M. Christensen, S. Gersen, H.B. Levinsky, S.J. Klippenstein, P. Glarborg, *"High-pressure oxidation of methane"*, Combust. Flame 172 (2016) 349—364.

[3] J. Lopez, C. Rasmussen, H. Hashemi, M. Alzueta, Y. Gao, P. Marshall, C. Goldsmith, P. Glarborg, *"Experimental and kinetic modeling study of C_2H_2 oxidation at high pressure"*, Int. J. Chem. Kinet. 48 (2016) 724—738.

[4] H. Hashemi, J.G. Jacobsen, C.T. Rasmussen, J.M. Christensen, P. Glarborg, S. Gersen, M. Essen, H.B. Levinsky, S.J. Klippenstein, *"High-pressure oxidation of ethane"*, Combust. Flame (2017), accepted.

[5] C. F. Goldsmith, W. H. Green, S. J. Klippenstein, *"Role of O_2 + QOOH in low-temperature ignition of propane. 1. Temperature and pressure dependent rate coefficients"*, J. Phys. Chem. A 116 (2012) 3325—3346.