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Fundamental limits of NO formation in fuel-rich premixed methane-air flames

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Document Version

Publisher's PDF, also known as Version of record

Publication date:

2007

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

van Essen, V. M. (2007). *Fundamental limits of NO formation in fuel-rich premixed methane-air flames*. [Thesis fully internal (DIV), University of Groningen]. University of Groningen.

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Designers of combustion equipment fired with natural gas have to meet increasingly stringent NO_x emission regulations. To satisfy these regulations, NO_x control strategies such as flue-gas recirculation and upstream heat loss are applied. In general, chemical mechanisms do a good job in predicting the effect of these control strategies on NO formation for fuel-lean and stoichiometric conditions, where the well-understood Zeldovich mechanism is the dominant route for NO formation. However, for fuel-rich conditions there are still significant uncertainties in the reaction kinetics describing NO formation, which hinder the ability to predict the effect of NO_x control strategies. The major route to NO formation under fuel-rich conditions occurs via the Fenimore mechanism, where the CH radical is the key intermediate (as discussed in Chapter 1). Since the CH radical is exceptionally difficult to measure at atmospheric pressure, the Fenimore mechanism is often studied at reduced pressures. This thesis provides insight into the effect of flue-gas recirculation and upstream heat loss on NO formation via the Fenimore mechanism by measuring temperature and key species such as CH, OH and NO in one-dimensional, low-pressure, fuel-rich methane flames. The measurements are compared with the computed results of flame structure, including NO formation, using the GRI-Mech 3.0 chemical mechanism. Thus, in addition to providing insight into the effects of two NO_x control strategies, to the benefit of the design of low-NO_x combustion systems, the experimental data presented in this thesis can also be used for improving chemical mechanisms to predict NO formation.

For performing experiments at reduced pressures, a low-pressure setup was constructed based on a design from University of Heidelberg (see Chapter 2). Determination of the working area for flat, premixed methane/air flames revealed that moderately fuel-rich ($\phi < 1.3$) flames could be stabilized at pressures as low as 22 Torr. When using O₂/N₂ mixtures with an oxygen concentration higher than that of air, the working area can be substantially increased towards richer equivalence ratios ($\phi \sim 2.4$ for 22 Torr methane/oxygen flames). For this reason, methane/oxygen/nitrogen mixtures are used in this work with O₂/N₂ ratios ranging from (0.30/0.70) to (0.40/0.60).

Chapter 3 of this thesis describes the procedure for determining the local temperature and concentrations of NO, OH and CH using laser-induced fluorescence (LIF). The LIF measurements are performed in the linear regime,

and corrected for quenching using directly measured fluorescence decay times. To test our calibration measurements, additional measurements of temperature, OH, CH and NO profiles were performed in a 'reference' flame used in the literature, for which these profiles have already been reported. Moreover, the reference flame is also used as benchmark for GRI-Mech 3.0, providing a link between experimental results and those computed using this mechanism. The local temperature is determined from a Boltzmann plot derived from the OH-LIF excitation spectrum, and for the reference flame agreed within 35 K of the literature values for the entire temperature profile. The overall estimated uncertainty of the temperature measurements is ± 50 -75 K. Both OH and CH mole fractions are determined through calibration of the LIF signal by Rayleigh scattering. The CH-LIF signals are corrected for chemiluminescence by subtracting the background signal from the temporal fluorescence signal. Experimental OH and CH mole fractions determined in the reference flame were in excellent agreement (within 10%) with measurements reported in the literature. The total uncertainty in CH and OH measurements is estimated to be 25 and 20%, respectively. NO mole fractions were determined by adding varying amounts of NO to the cold gas mixture of the reference flame and comparing seeded and non-seeded LIF signals. Here too, the measured NO mole fraction in the reference flame at 2 cm above the burner surface was in excellent agreement with the literature values. The estimated uncertainty of NO measurements is 15%. For measurements performed in other flames, the reference flame was used as a calibration for converting relative OH, CH and NO signals to absolute values.

In Chapter 4, the effects of burner stabilization on Fenimore NO formation in low-pressure, fuel-rich premixed methane/oxygen/nitrogen flames are discussed. Towards this end, axial profiles of temperature, OH, CH and NO are measured for equivalence ratios between 1.3 and 1.5. A decrease in flame temperature of 200-300 K and corresponding decrease in OH mole fraction are observed when lowering the total flow rate from 5 to 3 slpm, thus increasing the degree of burner stabilization. Also, a decrease in CH mole fraction (~50%) and NO mole fraction (~40%) in the flames studied is observed for this increase in burner stabilization. An estimation of the Fenimore contribution to NO formation, based on integrating the rate for the CH+N₂ reaction and using rate coefficient from GRI-Mech 3.0 (explained in Chapter 1), shows good agreement with experimental values for $\phi=1.3$ and 1.4 flames, which supports

the choice for the rate constant. An important factor when considering the effects of changes in CH mole fraction on NO formation at increased burner stabilization is the change in residence time. Discrepancies are observed between measured NO mole fractions and calculated Fenimore NO mole fractions at richer equivalence ratios, most likely due to slow oxidation of fixed nitrogen species (such as HCN) in burnt-gas zone. Detailed calculations using GRI-Mech 3.0 predict the experimental results for $\phi=1.3$ flames very well, but show increasing differences with measurements for higher equivalence ratios. Within the framework of the chemical mechanism used, these differences are attributed to uncertainties in CH formation and consumption, as well as to uncertainties in the routes to NO under very rich conditions.

The effects of ‘dry’ flue-gas recirculation (FGR) on Fenimore NO formation in 35 Torr, $\phi=1.3$ premixed methane/oxygen/nitrogen flames are discussed in Chapter 5. Detailed calculations using GRI-Mech 3.0 show a good quantitative agreement with measured profiles, but the predicted CH profiles are ~ 0.1 cm closer to the burner surface. However, the estimated Fenimore contribution to the NO mole fractions, using the experimental temperature and CH profiles, indicate that this shift in CH profiles has no effect on NO formation. The application of ‘dry’ FGR results in a ~ 200 K decrease in flame temperature, which is accompanied by a decrease in OH mole fraction by one-third. Another consequence of applying FGR is a $\sim 50\%$ lower maximum CH mole fraction and $\sim 20\%$ decrease in NO mole fraction. The effect of this decrease in CH mole fraction on NO formation is substantially compensated by the increase in molecular nitrogen in the cold gas mixture from the FGR, which accounts for the “only” 20% decrease observed in the NO mole fraction. According to calculations using GRI-Mech, additional recycling of water results in a substantial decrease in NO mole fraction. The Fenimore analysis indicates that this effect arises from the decrease in the N_2 mole fraction caused by water addition.

Finally, Chapter 6 presents a LIF study of the effect of pressure on NO formation in $\phi=1.3$ premixed methane flame with two different O_2/N_2 ratios (0.40/0.60 and that of air). During the experiments the flame temperature was kept constant, while changing the pressure between 35 and 760 Torr. For the flames studied, NO formation occurs primarily via the Fenimore mechanism regardless of the pressure and O_2/N_2 ratio. Moreover, the NO mole fractions

Summary

show only a very weak dependence on pressure. Detailed calculations using GRI-Mech 3.0 predict the experimentally observed trend for both O₂/N₂ ratios. The calculations predict the NO mole fractions for CH₄/O₂/N₂ flame well, but overpredict the results by ~30% for the methane/air flame flames. This difference may be addressed by improving the CH prediction.