September, 21st - 24th 2014
FLAME STRUCTURE 2014
8th International Seminar on Flame Structure

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LAMINAR BURNING VELOCITY FOR NITROMETHANE + AIR

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Introduction

Nitromethane, CH_3NO_2, is used as a fuel in motor racing and as an additive to other fuels to increase the power output of the engine. It is also useful in scientific research concerning combustion of fuel nitrogen since it is simple specie with a C-N bond. As a part of this the fundamental burning properties of pure nitromethane in air are of interest.

A major part of the research on nitromethane focuses on its properties as a monopropellant and its properties related to explosions, such as detonation and shock waves. Experimental flame studies of nitromethane+air have not been published.

Two studies concerning flame propagation of nitromethane flames have been performed [1, 2]. De Jaeger and van Tiggelen measured flame propagation velocities for nitromethane flames with molecular oxygen (O_2) and varied concentrations of molecular nitrogen (N_2) [1]. They correlated these measurements with the flame temperatures and concluded that nitromethane has a low flame propagation velocity considering its low global activation energy. Fells and Rutherford studied the effect of addition of nitromethane on the burning rate of methane flames [2]. An increase in burning velocity for methane flames with < 3 % nitromethane was seen for both lean and rich flames. Based on this observation it was suggested that nitromethane has the possibility of participating as both a fuel and an oxidant simultaneously.

A few mechanisms for nitromethane combustion have been developed in recent years [3-5]; none of them has been validated for the conditions of the present study. The burning rates were modeled by Boyer and Kuo, for pressures above 3 MPa and compared to experimental results with good agreement up to 15 MPa [3]. Tian et al. studied a rich nitromethane+O_2+Ar flame at low pressure [4], several new species were experimentally observed in the study and a kinetic model was presented. Zhang et al. studied rich and stoichiometric premixed nitromethane+O_2+Ar flames at low pressures and presented experimental temperature and species profiles [5, 6]. The authors also constructed a kinetic model that satisfactory reproduced their experimental results.

The aim of the present study is to present new fundamental experimental data on nitromethane flames burning with air and

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evaluate the ability of a recent model to predict the laminar burning velocity at atmospheric pressure.

Experimental section

Premixed nitromethane+air flames were stabilized using the Heat Flux method. The principle of the method is based on a thermodynamic exchange between the flame, burner head and unburnt gas. At the adiabatic conditions the heat exchange is zero and the temperature distribution on the burner plate is uniform.

The burner has a heated plenum chamber and a heated perforated burner plate of brass with 0.5 mm diameter holes. Heating jackets and thermostatic controlled water is used to keep the burner head at a constant temperature of 368 K and the plenum chamber at the desired unburnt gas temperature.

To regulate the gas flow mass flow controllers (MFC) were used. The liquid fuel was controlled and evaporated by a mini-Cori-flow MFC and a controlled evaporator mixer, all from Bronkhorst. A schematic overview of the experimental setup is shown in fig. 1.

The flames were studied at atmospheric pressure, initial temperatures of 338, 348 and 358 K and equivalence ratios (ϕ) in the range 0.8 to 1.5. The partial vapour pressure of nitromethane limits the lower experimental unburnt gas temperature of 338 K and above and the accessible ϕ at 338 K to 1.2.

The uncertainty in the laminar burning velocities is dependent on the accuracy of the flows of oxidizer and fuel, and the scatter in the temperature distribution of the thermocouples.

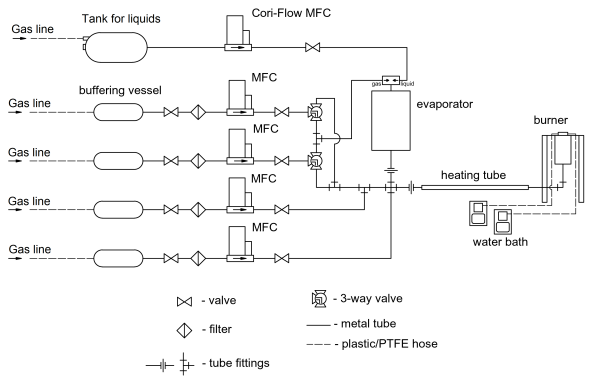

Figure 1: A schematic overview of the experimental setup.

Kinetic modeling

The nitromethane+air flames were modelled using CHEMKIN IV [7]. The parameters GRAD=0.05 and CURV=0.05 were used, which yield

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> 300 grid points. Trace species approximation, multicomponent transport and thermal diffusion were taken into ac account. The absolute tolerance was set to 10^{-9}. To facilitate conversion 0.09 ppm Ar was added to the fuel in the calculations.

Sensitivity analysis with respect to flow rate is performed for a stoichiometric flame at atmospheric pressure and unburnt gas temperature of 358 K.

Upon the recommendation of the authors of the most recent nitromethane model [8] a mechanism recently expanded to include nitroethane+O_2+Ar flames was used. This model contains 115 species and 729 reactions, of which 13 nitromethane reaction. The mechanism was validated against low pressure flames.

Results and Discussion

Laminar burning velocities for nitromethane+air have been measured using the Heat Flux method. When calculating ϕ, NO was taken into account as a final product in the stoichiometric balance.

$$2\ CH_3NO_2 + 2.5\ O_2 \rightarrow 2\ CO_2 + 3\ H_2O + 2\ NO$$

Figure 2 shows the experimental laminar burning velocity with associated uncertainties for the nitromethane+air flames presented together with modeled flames for the three temperatures 338, 348 and 358 K. Experimentally the flames were reexamined at 338 K for ϕ=0.8-1.2 and the results were reproducible within the experimental uncertainty. The laminar burning velocity is increasing with increasing unburnt gas temperature. The maxima were found at ϕ=1.2 for all three investigated temperatures: 33.0 cm s^{-1} at 338 K, 34.3 cm s^{-1} at 348 K and 36.1 cm s^{-1} at 358 K.

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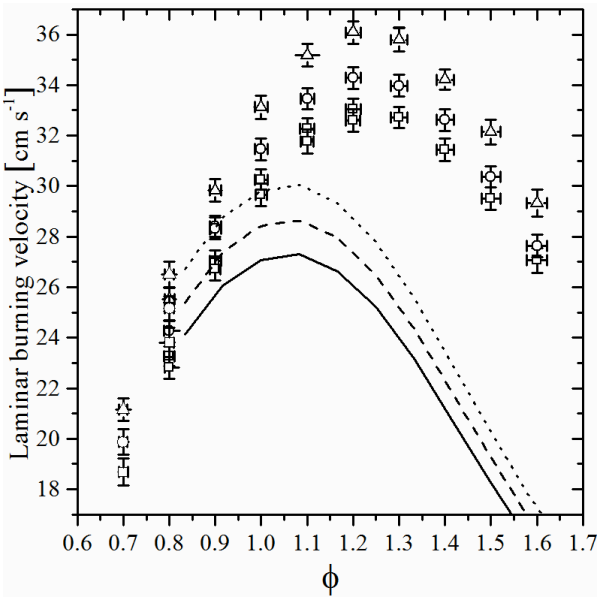

Figure 2: Laminar burning velocities vs. equivalence ratio for nitromethane. Both experimental (symbols) and calculated (lines) results using the model of [8] are displayed for at 338 K (square) (solid), 348 K (circle) (dash) and 358 K (triangle) (dot).

The measured laminar burning velocity showed a linear relationship to unburnt gas temperature on a log-log-scale as seen in fig. 3. The temperature dependence of the laminar burning velocity (SL) was interpreted using relation $SL = SL_0(T/T_0)^{\alpha}$. In fig. 4 the power exponent α is presented with corresponding uncertainties. The uncertainties in α were evaluated by considering the uncertainties from the laminar burning velocity for each experimental point and changing each experimental point to the extreme values in a sequence and all possible α are calculated. From these α, the uncertainty for each ϕ is calculated through standard deviation.
The experimental results were compared with the latest published model suitable for nitromethane flames [8]. As seen in fig. 2 the agreement is satisfactory at the lean side. At stoichiometric and rich conditions the modeling significantly underpredict the experimental results and also place the maximum laminar burning velocity lower (ϕ=1.05) compared to the experimental maximum at ϕ=1.2.

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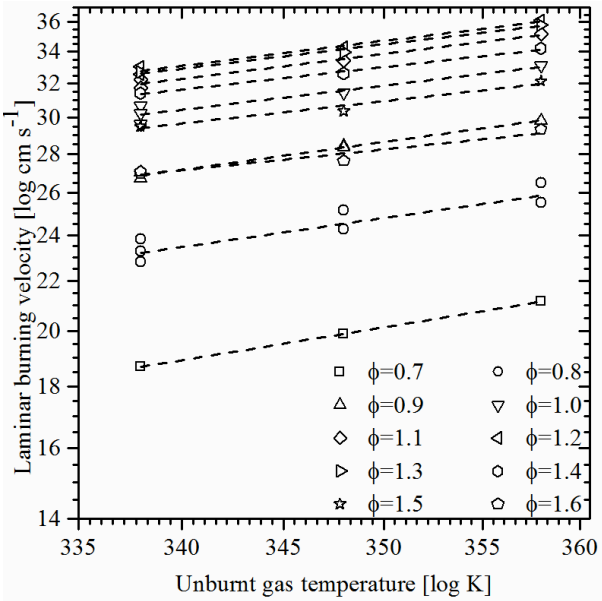

Figure 3: The logarithms of laminar burning velocity as a function of temperature for nitromethane+air flames.

The experimental power exponents α are compared with power exponents α derived from modeling results. The experimental power exponent α is decreasing towards richer conditions. As seen in fig. 4, the model displays a different temperature dependence as compared to the experimental results with a local minimum and increasing power α after ϕ=1.1. Between ϕ=0.9-1.2 the model predicts the temperature dependence within the experimental uncertainties. For rich flames the model predicts a slight increase of power α, whereas the experimental results display a decrease.

The discrepancy between the model and experiments call for improvement of the understanding of C-N flame chemistry. The model performance was investigated through sensitivity analysis. The sensitivity analysis is presented for the twenty most sensitive reactions at ϕ=1.0 in fig. 5. The radical NO is participating in nine of the twenty sensitive reactions. Many of these reactions have a strong temperature dependence, which may imply a corresponding strong temperature dependence of the overall flame chemistry.

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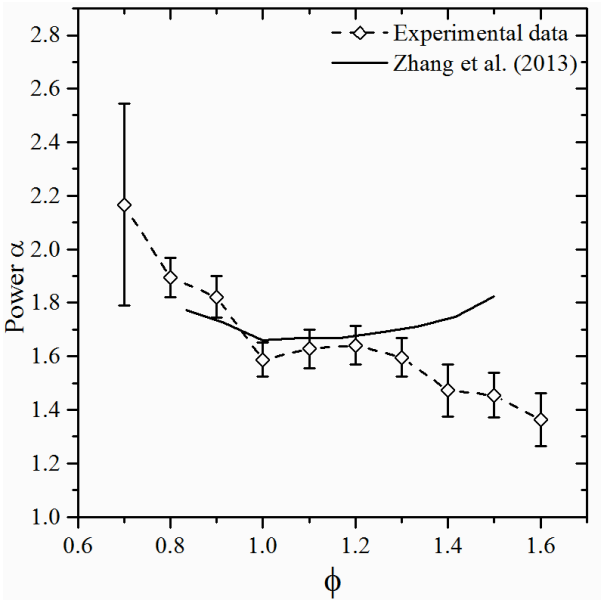

Figure 4: Power exponents α vs. equivalence ration for nitromethane+air. Symbols with errorbars represent experimental results and solid line - calculated results using the model of [8].

As seven of the sensitive reactions have negative sensitivity they would have a dampening effect on the burning velocity. The radical HNO has seven reactions among the twenty most sensitive, which is an indication of its importance for the nitromethane flames. In four H-abstraction reactions HCO is participating, with CO as a product. The CH_3O radical involved in three sensitive reactions, uni-molecular decomposition and recombination with NO to form CH_2O radical, and reaction with HNO to form NO and methanol.

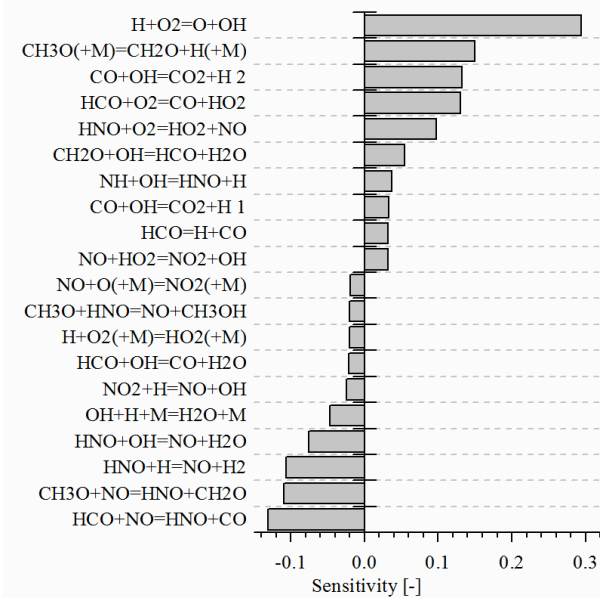

Figure 5: The twenty most sensitive reactions for nitromethane+air at ϕ=1.0 and 358 K.

Conclusions

Laminar burning velocities for nitromethane+air flames are presented for a range of initial gas mixture temperatures and equivalence ratios, at atmospheric pressure. The maximum in laminar burning velocity is found at ϕ=1.2 at all temperatures.

A recently developed chemical kinetics mechanism by Zhang et al. [8] was used to model the flames. It was concluded that this model, validated for low pressure flames, was not able to satisfactory model the flames of the present study.

The power exponent α describing the temperature dependence was derived from both experimental and modeling results. In the range of ϕ from 0.8 to 1.2 the modeling results are within the errorbars of the experimental data, while at richer flames the deviation is significant.

From the sensitivity analysis it can be concluded that CH_3O-chemistry as well as NO-chemistry likely is of importance for these nitromethane+air flames. Further work is required to understand the chemistry of radicals involved in nitromethane flames and model development is necessary to be able to predict laminar burning velocities

Acknowledgements

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