Performance of methanol kinetic mechanisms at oxy-fuel conditions

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ABSTRACT

Methanol premixed flames were studied under oxy-fuel conditions for the first time. Laminar burning velocities were measured with the heat flux method at atmospheric pressure for unburnt gas temperatures of 308–358 K within a stoichiometric range of ϕ = 0.8–1.5. A linear relationship between temperature and laminar burning velocity on a log–log scale was observed. The experimental results are discussed by comparison to modeling results from three kinetic mechanisms. All models gave an overprediction of the laminar burning velocity. It was demonstrated that implementation of recently advised rate constants for reactions of methanol with O_2, HO_2, H and OH, together with modification of the third-body efficiency for H_2O in the decomposition of the formyl radical, significantly improves model performance both for methanol combustion in air and at oxy-fuel conditions.

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1. Introduction

An approach to deal with emissions of the greenhouse gas carbon dioxide, CO_2, is carbon capture and sequestration (CCS). A novel and promising way to implement CCS is the oxy-fuel technology where air is replaced by molecular oxygen (O_2) and CO_2. The CO_2 is recycled from the flue gas and mixed with O_2. The high concentration of CO_2 in the gas downstream the burner facilitates separation of CO_2 for sequestration. As external gas recirculation creates CO_2-rich combustion conditions, combustion studies of fuel at these conditions is of high relevance. Also, many internal combustion engines employ External Gas Recirculation (EGR) regimes which creates CO_2-rich conditions. In special applications, like submarine engines, oxy-fuel combustion of liquid fuels is directly implemented.

Methanol's popularity as an alternative fuel for engines is increasing. In China, 6–8% of the transportation fuel pool is methanol (coal-based) in an effort to reduce dependency on imported oil. Methanol is used both as a blending component (with gasoline) and as a pure fuel in methanol cars. Methanol is also being considered as a viable alternative fuel for shipping (mainly in Europe). The Scandinavian EFFSHIP project [1], investigated a number of alternative fuels and advanced methanol as the most promising one. Within the SPIRETH project [2], a "spin-off" from EFFSHIP, a main engine was run on methanol in a laboratory setting, and an auxiliary diesel engine on a Swedish RoPax vessel was fueled with

a blend of primarily di-methyl ether (DME), with some residual methanol from the onboard fuel conversion process. Within a 2012 TEN-T Multi-Annual Programme funded project [3], an existing passenger vessel was retrofitted for operation on methanol.

In combustion research methanol is used as a model fuel for studying alcohol chemistry. A strength of methanol as a model fuel for kinetic studies is that the chemistry of the H-abstraction products CH_2OH and CH_3O is relatively isolated from methyl radical chemistry. This background gives value to methanol studies, not only for its own merits but as a representative for alcohol chemistry.

When changing the oxidizer from conventional air to CO_2 rich conditions the prerequisites for the combustion process are altered. CO_2 not only acts as a diluent for O_2, it changes combustion properties such as heat capacity and flame temperature and participates as a reactant in the combustion reactions [4–7].

Chemical kinetic models are commonly validated for combustion in normal air. To enable further understanding and development of oxy-fuel technology the performance of the models under CO_2-rich conditions need to be investigated and possibly improved. The present paper is part of a study of C1–C2 alcohols under oxy-fuel conditions; in a previous publication it was shown that models for ethanol + air overpredicted laminar burning velocities for ethanol under oxy-fuel conditions [8].

In the current work, the laminar burning velocity of methanol flames at atmospheric pressure and elevated temperatures under oxy-fuel conditions are presented for the first time. The temperature dependence of the laminar burning velocity (S_L) is interpreted using the relation $S_L = S_{L0} (T/T_0)^{\alpha}$, where S_{L0} is the laminar burning

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velocity at standard conditions, T is the temperature and T_0 is the reference temperature at standard conditions. The laminar burning velocities are modeled using kinetic mechanisms by Li et al. [9], Li et al. with changes according to Klippenstein et al. [10], and Aramco 1.3 [11]. Using sensitivity and rate of production analyses the mechanisms are evaluated for the CO_2-rich conditions of the study, aiming at the identification of possible improvements in reaction rate parameters.

2. Experimental

Premixed methanol + O_2 + CO_2 flames were stabilized using the heat flux method [12–14]. The principle of the method is based on a thermodynamic exchange between the flame, burner head and unburnt gas. The burner has a heated plenum chamber and a heated burner plate with 0.5 mm diameter holes. Heating jackets and thermostatically 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.

At the adiabatic laminar burning velocity, the net flux of the heat exchange is zero and the temperature profile of the burner plate is uniform. The temperature profile as a function of the radius of the burner plate is given by $T_p(r) = T_c + Cr^2$, where T_c is the temperature at the center of the burner plate; C is a coefficient in the fit and r the radius of the burner plate [14]. The adiabatic laminar burning velocity is found at $C = 0$. The temperature profile is measured by eight thermocouples (type T) inserted in holes at different radial positions of the burner plate and collected by a National Instrument 9213 thermocouple input module.

The flames were studied at atmospheric pressure, temperatures of 308, 318, 328, 338 and 358 K and equivalence ratios (ϕ) in the range 0.8–1.5. The laminar burning velocity at 298 K was not measured due to the limitations in the partial vapor pressure for methanol. The oxidizer mixture consisted of 35% O_2 and 65% CO_2, chosen to approximately match the flame temperature of equivalent methanol flames with air as an oxidizer [15,16].

The gases were taken from gas bottles, passing through a buffering vessel before a mass flow controller (MFC). To control the fuel flow, a liquid mass flow controller (Mini-Cori-Flow) was used. The fuel was mixed with the oxidizer gas and evaporated in a controlled evaporator mixer (CEM). All components of the experimental setup are schematically presented in Fig. 1. The MFC, CEM and Mini-Cori-Flow are all from Bronkhorst. The MFC used for the oxidizer mixture was originally calibrated for air, recalibration was performed with a piston meter Definer 220 from Bios, USA. From the calibration a third degree polynomial was obtained and used to recalculate the gas flow settings for the oxidizer mixture.

The methanol from Merck had a purity of 99.9 mol% with less than 0.1% water content. The oxidizer gas was premixed at AGA mixing plant, at 35.0 mol% O_2 in CO_2 within an accuracy of 0.7%.

One should note that variation of the oxygen content in the oxidizer of the order of 1% may significantly change the measured laminar burning velocity, as was experimentally demonstrated by, e.g., Dyakov et al. [17]. To eliminate this uncertainty, two series of measurements at 308 K and 328 K were performed with on-site mixing of O_2 and CO_2 using separate MFCs. As will be demonstrated in the following, both types of oxidizer preparation (from the plant or on-site) yield consistent results.

2.1. Experimental uncertainties

Experimental uncertainties are mainly due to uncertainties in gas mixture composition and scatter in temperature reading. These uncertainties need to be accurately quantified to evaluate the error in the results. Uncertainties in the equivalence ratio stem from the accuracy of the flows of oxidizer and fuel, and are quantified in the same manner as by Bosschaart and de Goey [14]. 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. The uncertainty from the temperature distribution is represented by the standard deviation from the thermocouples. This is calculated by a least square fit of the scatter in the temperature distribution. A mean value of the standard deviations of the C coefficient for each of the measured points is then calculated. This mean value is then divided by the slope from the fit of C vs. flow rate to produce the errors in C.

Due to tendencies of cell formation in flames burned with O_2 + CO_2 [18], all data were obtained at sub-adiabatic conditions and extrapolated to the laminar burning velocity. The experimental data points, C vs. laminar burning velocity, at a specific gas mixture composition show a linear relationship in the measured interval and based on the work of Bosschaart and de Goey [14] it is assumed that this linearity is valid to the adiabatic conditions ($C = 0$). At least four measurement points were taken to make sure the trend was indeed linear. A linear fit to the data was made, followed by an extrapolation to $C = 0$. The extent of the extrapolation range varies for different flame conditions with respect to equivalence ratio and unburnt gas temperature. At higher temperatures and richer conditions the flames had a tendency to form cellular structure around conditions that are expected to be adiabatic, and therefore the conditions at which the flame was uniformly flat and suitable for data collection are further below the adiabatic state compared to colder and leaner conditions. For the measurements at unburnt gas temperature of 308 K the extent of the extrapolation is 0.3–0.7 cm s^{-1} from the determined adiabatic laminar burning velocity, while at 358 K it is as far as 1.7–2 cm s^{-1}. This is clearly within the linear region as shown by Bosschaart and de Goey [14].

The highest initial temperature of the fresh gases, 358 K, was only 10 K lower than the temperature of the burner head, 368 K. Hermanns [19] noted that the measured laminar burning velocity does not depend on the temperature difference between the plenum chamber and the burner head, yet a difference smaller than about 30 K may lead to flame instabilities. This effect is manifested in the present work in the slightly increased uncertainty of the laminar burning velocity at 358 K due to the more extensive extrapolation, as explained in the previous paragraph. The procedure for evaluation of associated uncertainties is described in the Supplementary material.

In addition to the described major uncertainties in gas mixture composition and as a result of scatter in temperature readings, there are a number of other uncertainties. Examples are edge effects at limiting equivalence ratios, flow uniformity, radiative heat losses (discussed in the following), limited range of possible measurements defined by the perforation pattern of the burner plate, etc. The uncertainties are summarized and analyzed elsewhere [20,21] with advises of the methods to control them and the best laboratory practice to follow.

The uncertainties in the power exponent, α, are evaluated by considering the uncertainties from the laminar burning velocity for each experimental point. Each experimental S_L value is changed to its uncertainty limits, ΔS_L, and a new α_i is recalculated for each case. This is done for each experimental point individually in a sequence. Since:

$$\alpha = f(S_{L_i}, S_{L_{i+1}}, \ldots, S_{L_n}) \tag{1}$$

then the contribution of each measured flame speed to the total uncertainty in α equals $\Delta\alpha(S_{L_i}) = \alpha_i - \alpha_0$, where α_0 is the original power exponent α, calculated from the experimental data. The total