

Experimental Studies and Kinetic Modeling of Ethyl Valerate: Flat Flame Structures and Laminar Burning Velocities

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Abstract

The aim of this study is the characterization of ethyl valerate combustion by analysing a rich flat flame structure at low pressure and by determining the laminar burning velocities. A rich flame was stabilized on a burner at 55 mbar and analysed by gas chromatography. Oxygenated species are the first intermediates and the main pathway of the ethyl valerate decomposition is through the formation of valeric acid and ethylene. Laminar burning velocities measured at 1 atm and 318, 328 and 338 K are presented and discussed in relation to the only available dataset from the literature. A kinetic model has been elaborated and tested against the low pressure flame to check its validity. It contains 1733 elementary reactions and 274 chemical species.

Introduction

Next generation biofuels will have to rely on more abundant and sustainable supply chains. Progresses in biomass processing have made lignocellulose more attractive for the production of liquid biofuel, such as ethyl valerate. Indeed, levulinic acid obtained from lignocellulose can be converted into esters by hydrogenation and esterification.

Nowadays, biofuels are used as fuels in engines (spark and diesel engines) in replacement or mixed with traditional fuels as gasoline and diesel [1-4]. Pentanoate esters, methyl and ethyl valerate ($C_6H_{12}O_2$ and $C_7H_{14}O_2$) can be used, as fuels, in a spark engine. The heaviest ones, propyl and butyl valerate ($C_8H_{16}O_2$ and $C_9H_{18}O_2$) are used in a diesel engine [3-5]. Results on the characterization of ethyl valerate (EPE) combustion are very scarce [4-5]: very few data are available at high pressure and there are no results at low or atmospheric pressure.

To develop a detailed kinetic model of methyl octanoate, Dayma et al. [5] studied, experimentally at 1 atm, its oxidation both in an opposed-flow diffusion flame and in a jet-stirred reactor. They elaborated a kinetic model containing 383 species and 2781 reversible reactions.

Recently, Dayma et al. [6] studied experimentally the ethyl valerate combustion at high pressure (10 atm) in a jet stirred reactor, and the laminar burning velocities in a spherical combustion chamber. Laminar burning velocities were determined at initial gas mixture temperature of 423 K and pressures of 1, 3, 5 and 10 atm. According to the experimental results, they elaborated a mechanism containing 522 species and 2719 reactions.

The present work reports two experimental studies that are used to further characterize ethyl valerate combustion and for validation of a new chemical kinetics mechanism for ethyl valerate combustion. First, the experimental structure of rich ethyl valerate flat flame ($\Phi=1.35$: 3.9%EPE, 28.2% O_2 and 67.9%Ar) at low pressure (55 mbar) is investigated. The premixed flame has been stabilized on a Spalding-Botha burner

and investigated by means of gas chromatography. Second, laminar burning velocities of ethyl valerate+air flames are determined using the heat flux method at atmospheric pressure.

The UCL kinetic model [7] has been extended to ethyl valerate kinetics using Dayma's mechanism [6], and tested at low pressure, to assess its validity.

Experimental setups

Flat flame study at UCL

One of the challenges is the adaptation of the setup to work with these esters because they have a high boiling point at atmospheric pressure (145°C for EPE). The fuel must be evaporated and blended to the oxidizer and the diluent before the combustion chamber to obtain perfectly premixed conditions.

The present experimental set up is thus composed by the evaporation system (EV), the combustion chamber (CC), the compression system (CS) and the gas chromatography (GC) (Fig. 1). The EV and CC are kept at low pressure with a maximum pressure of 60 mbar during the test.

In the evaporation system the liquid and the gas are mixed and evaporate in the evaporator controller at around 180°C. To keep the evaporated fuel in gaseous phase, a heated conduit at 250°C connects the EV and the CC.

The rich ethyl valerate flame is stabilized at low pressure of 55 mbar (3.9%EPE, 28.2% O_2 and 67.9%Ar). The total flow rate of the gases is 7.37 l/min and the total mass flux is 0.045 $kg s^{-1} m^{-2}$.

The combustion chamber incorporates a movable Spalding-Botha type circular burner with a diameter of 8 cm. A conical quartz nozzle with an angle of 45° is facing the burner surface. A small hole with a diameter of 0.2 mm allows sampling to be performed through the flame.

As the experiment is performed at low pressure (55 mbar in the CC and 18 mbar after the nozzle) while the GC is working at atmospheric pressure, a piston compression system is used to increase the pressure of

the collected gases before its injection in the gas chromatography.

The gases are admitted in the heated cylinder at around 18 mbar and compressed to 2431 mbar. Due to the limited amount of gas in the cylinder, the process is nearly isothermal with a temperature of 72°C. To avoid condensation from the nozzle to the GC, the piping line is heated at 130°C.

To analyse different stable chemical compounds formed during the EPE combustion, a gas chromatography is used. The sample collected through the flame and compressed in the CS is separated in two columns (CPSIL5CB for hydrocarbons and oxygenated species and Molsieve for permanent gases). The separated species are analysed by two detectors (TCD: thermal conductivity detector and FID: flame ionisation detector). The analysed chemical compounds are: $C_7H_{14}O_2$ (ethyl valerate), O_2 , CO , CO_2 , H_2 , H_2O , CH_2O (formaldehyde), CH_3CHO (acetaldehyde), C_2H_5OH (ethanol), CH_3COCH_3 (acetone), CH_3COOH (acetic acid), $C_5H_{10}O_2$ (valeric acid), CH_4 , and C_2H_4 (ethylene).

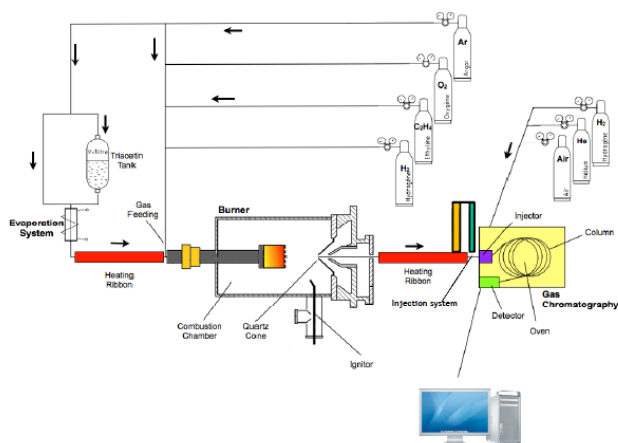


Fig. 1. Schematic setup of the burner connected with the EV, CS and GC for flat flame analysis.

The final flame temperature, corrected to compensate radiation losses, measured using a PtRh6%-PtRh30% coated thermocouple 0.1 mm in diameter, is 2243 K in the EPE flame.

Heat flux setup in Lund

Laminar burning velocities of ethyl valerate and air were determined using a heat flux setup at Lund University. A schematic of the setup is shown in Fig. 2. The setup has been described elsewhere [9], and the principle of the method and the components of the setup are only briefly outlined in the following.

Measurements were performed at atmospheric pressure, initial gas mixture temperatures of 318, 328 and 338 K, and equivalence ratios in the range 0.7-1.2. The gas mixture temperature was limited to a lower value of 318 K since below this there was condensation of the fuel. The upper limit for the temperature was 338

K since at higher temperatures the flames showed a cellular structure.

The heat flux method for determination of laminar burning velocities was developed by de Goey and co-workers [10]. First the method was applied to fuel mixtures of gaseous fuels, but eventually it was further developed for investigations of liquid fuels [11]. The strength of the method is that the laminar burning velocity is determined directly in a stretch free flame under adiabatic conditions, no corrections for flame stretch are required. The one dimensional flame is stabilized on a perforated plate burner heated to a temperature at least 20 K above the temperature of the combustible gas mixture, in the present study the plate was kept at 368 K. Burner plate temperature and the temperature of the plenum chamber of the burner, setting the temperature of the gas mixture, were regulated using separate water-baths circulating thermostated water.

The heat flux method build on that at adiabatic conditions there is no net heat transfer between the flame and the burner head. At adiabatic conditions the temperature of the burner plate is therefore uniform. The temperature profile is measured using eight thermocouples positioned in holes of the burner plate.

The composition of the combustible mixture of fuel and oxidizer is controlled using a mixing panel consisting of Mass Flow Controllers (MFCs) for metering the air, a Cori-Flow liquid mass flow controller for the liquid fuel and a Controlled Evaporator Mixer (CEM) for evaporation of the fuel. The gas MFC is calibrated for the air used as oxidizer, using a piston meter, Definer from Bios. Uncertainties in gas mixture composition as well as in the laminar burning velocity were assessed as described in [12].

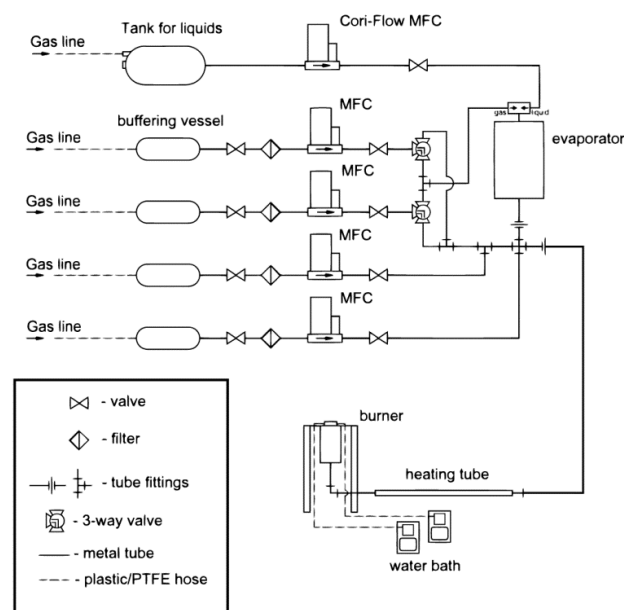


Fig. 2. Schematic of the heat flux setup used for determination of the laminar burning velocities.

Numerical simulation

Previously, a complete kinetic model named UCL was elaborated and validated against several compounds as hydrocarbons and oxygenated species [7, 8].

In this work, we combine the Dayma's and the UCL mechanisms to build an improved detailed kinetic model suitable to model the low pressure EPE flame. It contains 1733 elementary reactions and 274 species. The numerical simulation of the investigated one-dimensional flame has been performed using the COSILAB© software from SoftPredict [13].

Results and discussion

Low pressure flame structure

The comparison between experimental mole fraction profiles and the computed ones are presented in Figs. 3-5.

The mechanism is able to simulate with good agreement the experimental mole fraction profiles of the main species, as shown in Fig. 3.

The experimental mole fraction profile of ethyl valerate is below the simulated profile. This observation is justified by the condensation of this compound before its injection in the gas chromatography. We notice that after compression, the temperature in the GC is only 110°C at atmospheric pressure, this explains the condensation.

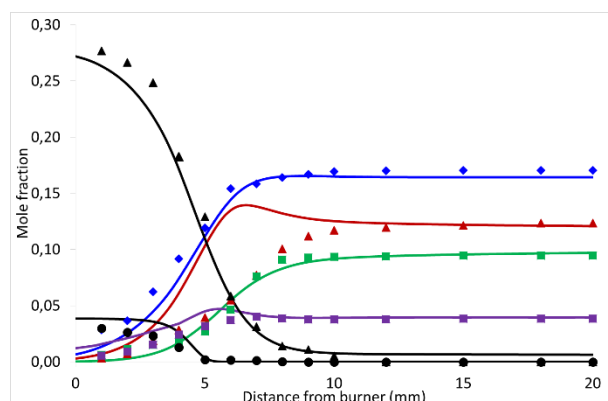


Fig. 3. Experimental (symbols) and simulated (lines) mole fraction profiles of O₂ (black triangles), EPE (black circles), H₂O (blue diamonds), CO (red triangles), CO₂ (green squares) and H₂ (purple crosses).

The combustion of ethyl valerate produces, as first intermediate species, the oxygenated compounds (valeric acid: C₄H₉COOH and acetaldehyde: CH₃CHO). As shown in Fig. 4, the valeric acid and the acetaldehyde are the first intermediates and their simulated maxima concentrations are at the same position as the experimental ones. However, the simulated mole fraction profiles of both compounds are well above the measured ones.

The valeric acid is produced by the decomposition of ethyl valerate in the following reaction $\text{EPE} = \text{C}_4\text{H}_9\text{COOH} + \text{C}_2\text{H}_4$.

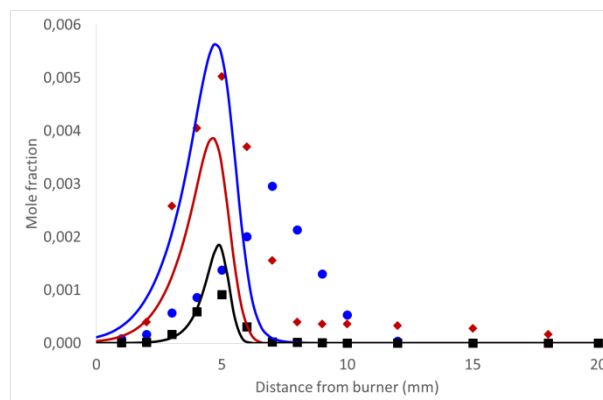


Fig. 4. Experimental (symbols) and simulated (lines) of CH₂O (circles), CH₃CHO (diamonds) and C₄H₉COOH (squares).

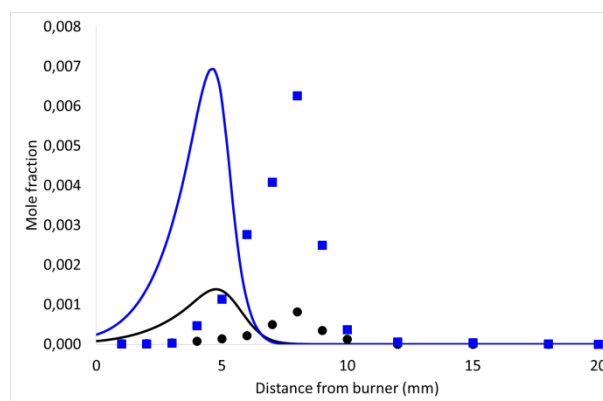


Fig. 5. Experimental (symbols) and simulated (lines) mole fraction profiles of CH₄ (circles) and C₂H₄ (squares).

The valeric acid concentration is overpredicted in the current simulation. As other ways of the valeric acid production are not present in this mechanism, we have to find out a good prediction of the production and the consumption of this molecule to reduce its concentration as related to the experiment. This species is important because propene (C₃H₆) is produced from it after the formation of the radical BuCOOH-4 (CH₃CHCH₂CH₂COOH): $\text{C}_4\text{H}_9\text{COOH} + \text{H} = \text{BuCOOH-4}$. Propene is produced from the reaction $\text{BuCOOH-4} = \text{C}_3\text{H}_6 + \text{CH}_2\text{COOH}$ (12%).

Acetaldehyde is produced by the reaction, $\text{EPE} + \text{H} = \text{CH}_3\text{CHO} + \text{NC}_4\text{H}_9\text{CO}$, with a contribution of 48%. The good prediction of acetaldehyde will influence the profile of C₃H₆ formation and then as a consequence those of the smaller molecules.

The simulated mole fraction profile of ethylene is in a good agreement with the experimental one as shown in Fig. 5. However, the simulated profile is shifted by 2 mm compared to the experimental ones.

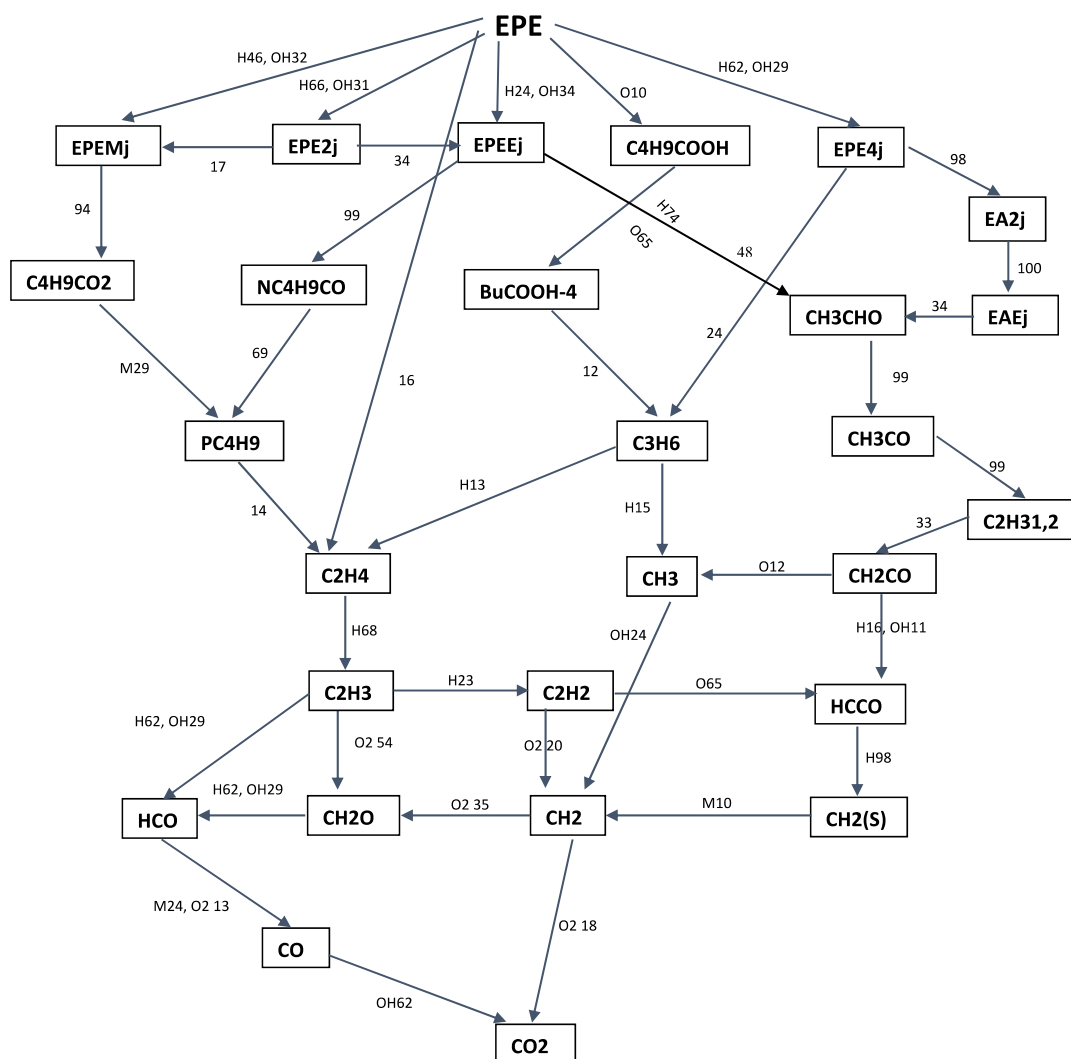


Fig. 6. Reaction pathways of ethyl valerate combustion.

Reaction pathways of ethyl valerate combustion in the low-pressure flame discussed above are shown in Fig. 6. From the reaction: $\text{EPE} = \text{C}_4\text{H}_9\text{COOH} + \text{C}_2\text{H}_4$, 16% of ethylene comes from ethyl valerate, 14% from the butyl radical PC_4H_9 ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2$) and finally 13% from C_3H_6 .

In the case of valeric acid and ethylene, the decomposition of ethyl valerate, seems to be the important challenge that must be taken into account in the improvement of the present kinetic model.

Methane (CH_4) is produced, in this model, by the radical CH_3 for 47% with the radical CH_3CO in the reaction: $\text{CH}_3 + \text{CH}_3\text{CO} = \text{CH}_4 + \text{CH}_2\text{CO}$.

The CH_3 radical is produced for 15% from the reaction $\text{C}_3\text{H}_6 + \text{H} = \text{CH}_3 + \text{C}_2\text{H}_4$ and for 24% from $\text{CH}_2\text{CO} + \text{H} = \text{CH}_3 + \text{CO}$.

Formaldehyde is produced from C_2H_3 following the step $\text{C}_2\text{H}_4 + \text{H} = \text{C}_2\text{H}_3 + \text{H}_2$ and then $\text{C}_2\text{H}_3 + \text{O}_2 = \text{CH}_2\text{O} + \text{OH}$ with a contribution of 54%.

The formation of the HCO radical comes from the reaction of CH_2O , with O (30%), H (14%) and OH (11%). Finally, the radical HCO produces CO that leads to the production of CO_2 .

The simulated profile of CH_2O is shifted by 2 mm in comparison with the experimental profile. The consequence of this shift is that the CO profile is also shifted at the same position as shown in Fig. 3. Indeed, the formaldehyde is responsible for the production of the radical HCO that produces CO .

We can conclude that the main stable compounds that must be taken in account to further improve the recently extended UCL kinetic model are $\text{C}_4\text{H}_9\text{COOH}$, CH_3CHO and CH_2O . The first and the second are underestimated compared to the experiments. However, the third one is overestimated.

The C_2H_4 profile is well simulated but a shift of 2mm must be done to agree with the experimental profile.

Laminar burning velocities

Laminar burning velocities at three temperatures are presented in Fig. 7. Maximum in laminar burning velocity is at $\phi=1.1$ for the dataset at 328 K that extends further than this, peak value is 41.3 cm s^{-1} . Errorbars in Fig. 7 mainly originate from uncertainties in flows of fuel and oxidizer and from temperature scatter in the burner plate, evaluated as outlined in [12]. Typical uncertainties in the present study are ± 0.01 for equivalence ratios and in a range from 0.6 cm s^{-1} to 0.9 cm s^{-1} for the laminar burning velocities.

The only earlier determination of the laminar burning velocities of ethyl valerate was performed at a significantly higher temperature, 423 K [6]. Temperature correlation of laminar burning velocity is commonly made using the expression $S_L = S_{L0}(T/T_0)^\alpha$, here it is used to enable comparison of the dataset of Dayma et al. to the results of the present study. Plotting laminar burning velocity vs temperature on a loglog scale will according to this correlation give a straight line. Fig. 8 shows filled symbols representing the experimental data of the present study and lines that are linear fits to these data. The lines are extended to 423 K, where the dataset of Dayma et al. [6] is represented by open symbols. The data at 423 K fall below the line around peak velocities and above the line at lean conditions.

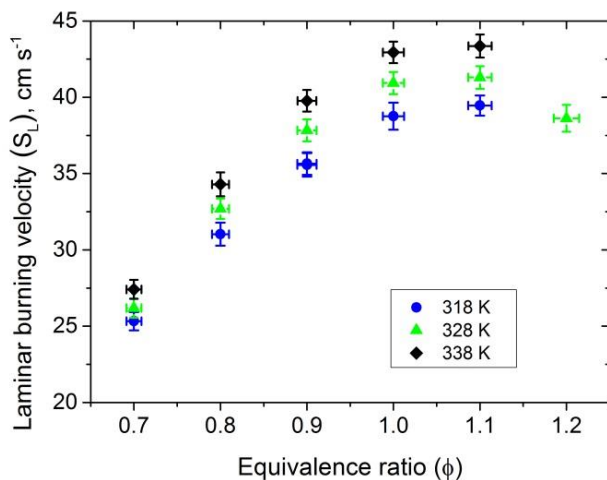


Fig. 7: Laminar burning velocities of ethyl valerate + air flames at 1 atm, determined using the heat flux method.

The trends in Fig. 8 indicate discrepancies between the present dataset, obtained at lower temperatures using the heat flux method, and the dataset of Dayma et al. [6] produced using a spherical combustion chamber at a significantly higher temperature. It is important to note that the two studies are at significantly different temperatures and the present study cover a very narrow temperature range. Also, from an experimental point of view the handling of the fuel is challenging since it has a low vapor pressure and easily condenses. Further

determinations of the laminar burning velocities at intermediate temperatures are needed.

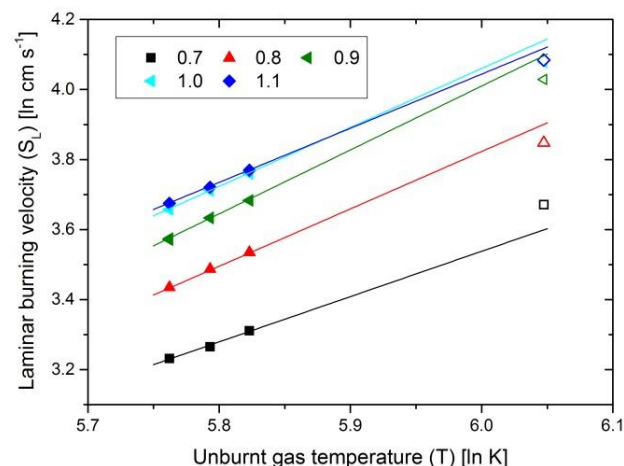


Fig. 8: Laminar burning velocities vs unburnt gas temperature. Closed symbols: present study; open symbols: Dayma et al. [6]. Lines are fits to the data of the present study.

Conclusion

A rich flame of ethyl valerate ($\Phi=1.35$) has been stabilized and studied at 55 mbar on a flat burner. The test bench has been adapted to the high boiling point of this ester by adding evaporation system. The experimental mole fraction profiles of stable species have been used to validate a kinetic model.

Laminar burning velocities were determined, at 1 atm and 318, 328, and 338 K, using the heat flux method. Maximum in laminar burning velocity was found at $\Phi=1.1$. Comparison with data of Dayma et al. [6] at 423 K, are not in agreement with the present dataset. The discrepancies call for further investigations of the laminar burning velocity at intermediate temperatures.

The UCL model improved using part of Dayma's mechanism has been used to model the ethyl valerate combustion at low pressure. The improved kinetic model predicts well the profiles of oxygen and the main products (CO , CO_2 , H_2 and H_2O). The measured fuel (EPE) mole fraction is underestimated due to some condensation in the sampling line.

The simulation of intermediate profiles need to be improved. The numerical simulation is in progress towards a good agreement between the experiment and the modelled mole fraction profiles by adjusting the first and important intermediate species that are the valeric acid and the acetaldehyde.

Further work will include validation of the model by simulation of the atmospheric pressure flames to determine laminar burning velocities.

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