Trends in Laminar Burning Velocities of C2-C7 Esters

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Abstract
Laminar burning velocities, S_L, for straight chain saturated esters with total numbers of carbons from 2 to 7 are presented. The results are discussed with respect to trends in S_L as a result of chain length in the acid and alkyl chains. Ten esters were studied, for five of these this is the first ever determination of S_L. This extended comparative study brought the following major conclusions: 1) formates have generally higher S_L than acetates, 2) the C3 esters, ethyl formate and methyl acetate, stand out by having highest and lowest S_L, respectively, 3) in general S_L are similar for different esters at lean conditions, while at rich conditions the divergence can be significant.

Introduction

Biodiesel is a fuel already in production and use as replacement for conventional diesel. The main constituents of biodiesel are fatty acid methyl and ethyl esters with carbon chains in the range C12-C18. A strategic advantage is that biodiesel can be produced from a wide range of plant and animal fats, but this is also a drawback since it gives variation in composition of the resulting fuels. Research efforts in understanding the combustion characteristics of biodiesel components are limited by the low vapour pressure of the long chain species, resulting in experimental challenges. As a result smaller ester compounds are investigated to understand the combustion and reactivity of esters [1].

Experimental flame studies in combination with chemical kinetics models are essential in improvement of the understanding of biodiesel combustion. Flame propagation as well as flame structure of well defined laboratory flames are useful. A complete review of experimental data concerning oxygenated fuels and stable intermediate oxygenates, including both laminar burning velocities and flame structures, was recently published [2].

To build experimental data sets for a wide range of esters is valuable to increase the general understanding of ester reactivity. Comparative studies of species profiles in low pressure flames of esters has revealed that the abundance of different combustion intermediates are highly dependent on the length of the hydrocarbon chains, the degree of saturation and branching. This lead to differences in reactivity that will inevitably affect combustion properties like laminar burning velocity and ignition delays.

The most studied small esters, for which several kinetic mechanisms also have been developed, are methyl formate ($C_2H_4O_2$) and methyl butanoate ($C_5H_{10}O_2$). An unsaturated ester that has gotten some attention is methyl crotonate ($C_5H_8O_2$). A few studies were designed to investigate the effects of the lengths of the hydrocarbon chains [3, 4] and degree of unsaturation [5, 6] on the laminar burning velocity .

Figure 1 show a general ester structure and two examples of C5 ester isomers with different number of carbons in the hydrocarbon chains, methyl butanoate and propyl acetate. Most of the esters studied this far has a methyl or ethyl group as the alkyl chain, R_1 in Fig.

1, since these compounds are most relevant as biodiesel components. Some esters, mainly small species with only one carbon in one or both of the carbon chains, have high laminar burning velocities as a result of that they produce an abundance of small reactive intermediates [7].
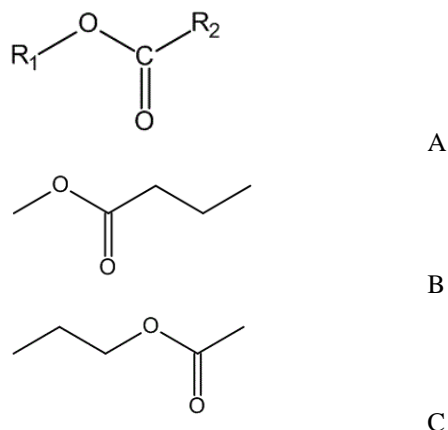

Fig. 1. A: the general ester structure with the hydrocarbon chains denoted R_1 for the alkyl chain and R_2 for the acid chain. B and C: esters with the formula $C_5H_{10}O_2$, methyl butanoate and propyl acetate, respectively.

For ethyl esters it was shown in two comparative studies that ethyl acetate is the slowest burning ethyl ester when compared to the smaller ethyl formate [3], and the larger ethyl propionate [3, 4] and ethyl butanoate [4]. When similar trends were investigated for saturated methyl esters [3] it was seen that the methyl acetate and methyl butanoate, with even numbers of carbons in the alkyl chains, burn slower than methyl formate and methyl propanoate. The trend is attributed to chemical effects since adiabatic flame temperatures are close to identical [3]. To investigate the effect of unsaturation, the C5 esters methyl butanoate and methyl crotonate were compared in an experimental study by Wang et al. [5] and the results were further investigated and compared to methyl acrylate and methyl formate by Grana et al. [6]. It was concluded that unsaturation increase the laminar burning velocity.

The above mentioned studies were performed at elevated temperatures of 333 K [3], 403 K [5], 323-473

K [4], with none of these studies presenting data at the same temperature.

The work presented here is part of an extensive experimental study of ester laminar burning velocities, including esters with 2-7 carbon atoms. Here we demonstrate how different length of the alkyl chain and the acidic chain in straight chain saturated esters affects the laminar burning velocity. Series of esters with increasing number of carbons in either alkyl- or acidic chain are compared, as well as isomers of $C_3H_6O_2$ and $C_5H_{10}O_2$. The experimental study was performed using the heat flux method at atmospheric pressure and at initial gas mixture temperatures of 298 K and 338 K.

The esters presented in this work are (where the number of carbons is for the whole fuel molecule) for C2: methyl formate (MF); C3: ethyl formate (EF), methyl acetate (MA); C4: propyl formate (PF), ethyl acetate (EA); C5: propyl acetate (PA), methyl butanoate (MB); C6: butyl acetate (BA), methyl valerate (MV); C7: n-amyl acetate (AA).

Experimental

The heat flux method for determination of laminar burning velocities is a method where the property is determined directly in a stretch free flame under adiabatic conditions [8]. 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. Heat transfer between the flame and the burner head is at adiabatic conditions equal in both directions, which mean there is no net heat transfer. At these conditions the temperature of the burner plate is uniform. By varying the flow of gas while monitoring the temperature profile, measured by eight thermocouples in the burner plate, the adiabatic laminar burning velocity is found.

The combustible mixture of fuel and oxidizer is created using a mixing panel with gas Mass Flow Controllers (MFCs), a Cori-Flow liquid mass flow controller and a Controlled Evaporator Mixer (CEM) for evaporation of the fuel. All these components are from Bronkhorst. The gas MFCs are regularly calibrated for air, using a piston meter, Definer from Bios. The use of the heat flux method for liquid fuels has been described earlier [9] as well as the setup used for the present experiments [10]. Uncertainties in gas mixture composition and laminar burning velocity were assessed, as previously described [11]. Typical uncertainties are ± 1 cm s^{-1} for laminar burning velocity and ± 0.01 in equivalence ratio.

Experiments were performed at 1 atm pressure, initial gas mixture temperatures of 298 and 338 K and ϕ in the range 0.6-1.6. The temperature of the burner head was kept constant at 368 K. The mixture of fuel and oxidizer was transported through a heated tube from the evaporator to the plenum chamber of the burner, to avoid condensation of the fuel in the gas line.

The gas mixture temperature of 298 K was visited for those esters where it was practically possible. For some of the longer chained esters this was, however, not possible because of condensation at high fuel content in the gas mixtures. Due to this all esters were also investigated at 338 K, since this is a temperature where all the studied compounds are stable in the gas phase at the investigated equivalence ratios. Due to formation of cellular structures in the rich flames at higher equivalence ratios for the temperature of 338 K, the measurements at this temperature was in most cases limited to equivalence ratios up to 1.1.

Results and Discussion

The formates are esters with hydrogen at position R_2 as defined in panel A of Fig. 1. These esters commonly show a high reactivity since the formate moiety contains no C-C bond and produce an abundance of small reactive species. Figure 2 presents laminar burning velocities of formates with 2-4 carbons in the alkyl chain (R_1). While MF and PF have close to identical laminar burning velocities, the middle sized one, EF, burns faster by several cm s^{-1} at the lean side and around stoichiometry. At the rich side the relation between EF and PF remains the same, but here MF shows comparably higher laminar burning velocities, reaching the same values as EF.
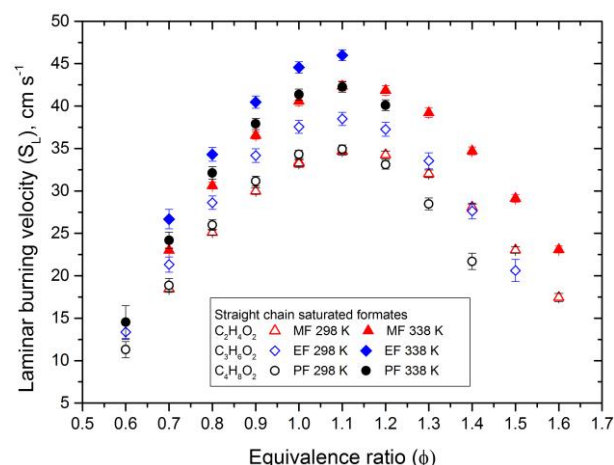

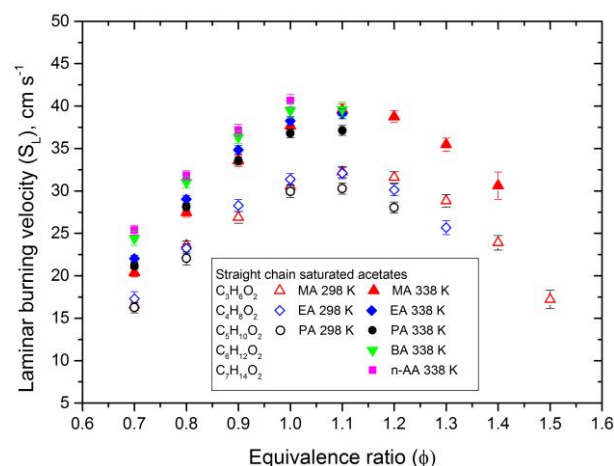**Fig. 2.** Laminar burning velocities of formates (H at R_2) at 1 atm, 298 and 338 K.

Fig. 3. Laminar burning velocities of acetates (C1 at R_2) at 1 atm, 298 and 338 K.
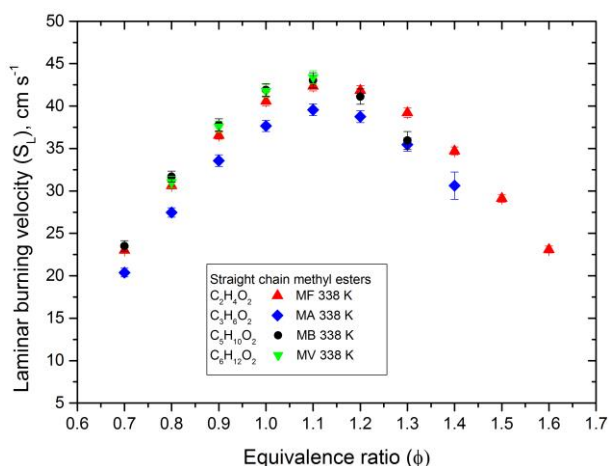
Fig. 4. Laminar burning velocities of methyl esters (C1 at R_1) at 1 atm, 338 K.
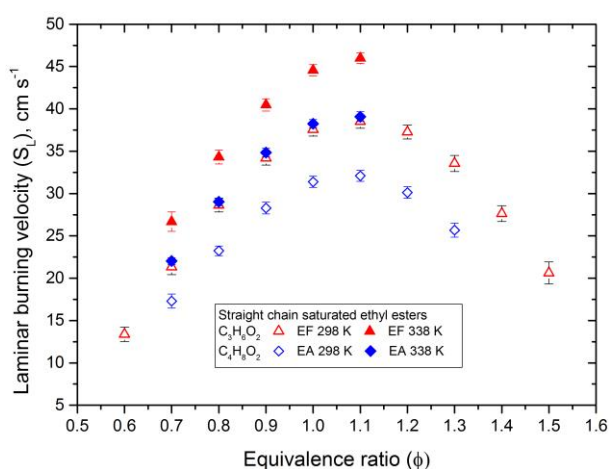

Fig. 5. Laminar burning velocities of ethyl esters (C2 at R_1) at 1 atm, 298 and 338 K.

Laminar burning velocities are mainly governed by the high temperature chemistry of the small species in the H_2/CO subset of reactions, including important radicals such as OH, H and CH_3. Trends in ester laminar burning velocities identified in previous studies have mainly been explained by the production of these small species in the fuel breakdown process. High production of H promote the important chain branching reaction $H+O_2=O+OH$, increasing the laminar burning velocity. When large amount of CH_3 is produced the opposite trend is commonly seen since CH_3 mainly participates in chain termination reactions.

The acetates has a carbon in the R_2 chain and in Fig. 3 results are presented for acetates with total carbon number up to 7, meaning up to C5 in the R_1 chain. The acetates all have similar laminar burning velocities, the difference is at the most 5 cm/s at the lean side. The three smallest that were measured at 298 K are very close, within overlapping errorbars at the lean side, while at equivalence ratios above the maximum, reached at 1.1, they start to diverge with the smallest one (MA) burning fastest and the longest one (PA) slowest.

The methyl esters (C1 in R_1) show identical results, within errorbars for the ones with total carbons 2, 5 and 6, while MA is standing out with lower laminar burning velocity. The ethyl isomer to MA is EF and in Fig. 5 it is plotted together with the longer EA. EF burns significantly faster than EA, over the whole range of equivalence ratios. EF indeed has the highest laminar burning velocity of all the esters presented here. As a further example of this, EF is plotted together with the isomer MA in Fig. 6, and also here the difference is significant. The question rises whether the high reactivity is a result of chemistry related to the ethyl group or the lone carbon in the acid chain, the characteristic of a formate. By comparing peak velocities in Figs. 1 and 2 it is clearly seen that the formates has a generally higher laminar burning velocity. Interesting to note from Fig. 6 is that the
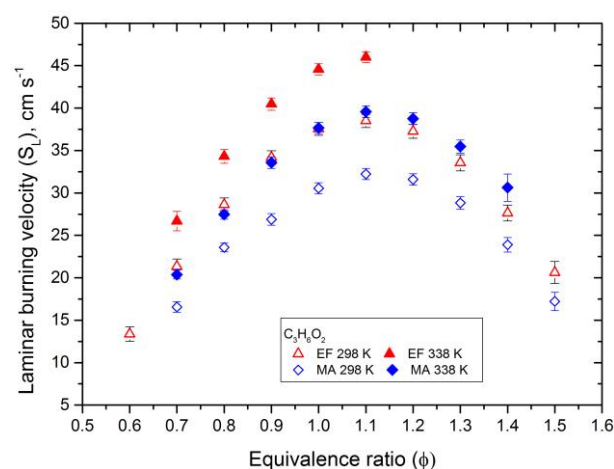

Fig. 6. Laminar burning velocities of C3 esters, at 1 atm, 298 and 338 K.
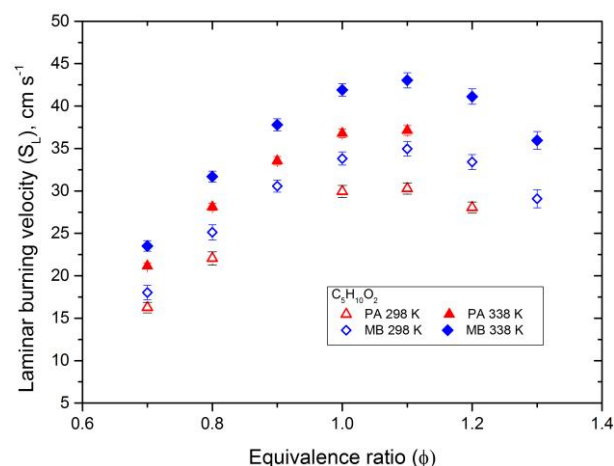

Fig. 7. Laminar burning velocities of C5 esters, at 1 atm, 298 and 338 K.

difference between EF and MA is largest around peak velocities, decreasing towards rich as well as lean conditions.

Comparison of two C5 esters in Fig. 7 again show a trend where the laminar burning velocities are rather close at lean conditions, while the difference increase

towards peak velocities. The structure of these two esters is shown in Fig. 1. The faster burning one, MB, has only one carbon in the alkyl chain and might possibly be more effective in generating small reactive intermediates. For long chained esters, and C5 in particular, a kinetic effect that can be of importance for the reactivity is the formation of relatively stable six-centered intermediates. This has been identified as an important factor for methyl butanoate combustion under some conditions [1].

Conclusions

Experimentally determined laminar burning velocities of C2 to C7 esters with saturated, unbranched hydrocarbon chains have been presented and compared. The aim was to identify trends in laminar burning velocity using datasets generated with the same setup at identical conditions. The present comparative study extends available analysis of trends presented earlier [3-6]. Laminar burning velocities of the esters MF, MA, EF, EA and MB, investigated within the present study, have been determined previously using spherical flames or counterflow methods. Unfortunately the initial gas mixture temperature vary between the different studies and therefore the results are difficult to compare. For the esters PF, PA, BA, MV and AA no measurements of laminar burning velocities have been published previously.

Some trends in laminar burning velocities:
- Formates generally have higher laminar burning velocities than acetates
- The C3 esters MA and EF both stand out, MA for burning slower than other acetates, EF for burning faster than other formates
- For formates as well as acetates the laminar burning velocities of species with different chain lengths are similar at lean conditions, while at rich conditions they diverge
- Maximum in laminar burning velocity is at $\phi=1.1$ for all esters in the present study

One major value of the present study is that large datasets at the same conditions are presented. Further studies of esters at the same conditions, 1 atm, 298 K and 338 K will be of importance in validation of kinetic models with the aim at several esters.

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