The influence of oxygenated fuels on the soot production potential – experiments and modelling

S. Kunte and K. Boulouchos

A survey on the influence of fuel structure and fuel oxygen content on the sooting behaviour of a laminar diffusion flame is given. Gaseous fuels under investigation had been ethylene, ethane and dimethylether (DME). Basic soot characterising measuring techniques like laser-induced incandescence (LII), time resolved laser-induced incandescence (TIRE-LII) and two-color pyrometry had been applied in order to gain basic insight into the soot formation and soot oxidation processes. All received data can provide a basic data set for soot modelling.

Introduction

Many serious studies state that nanoparticles derived from combustion systems do have adverse health effects. In the meanwhile politics have reacted with tighter legislations, forcing manufacturer to improve their combustion related products. To face the basic soot problematic one can in general distinguish between two passable paths or even a teamwork between them. One is the total or partly avoidance of soot formation through reasonable combustion management and the other the effective removal of once formed particles for example with filters or particle traps. Following the path of avoidance, the chemical structure of the fuel is one major parameter. Combustion borne particles show lots of aromatic compounds which are build through obscure chemical pathway. It can be shown, that the chemical structure has an influence on the soot formation tendency. Further is has to be mentioned that soot formation arises as long combustion takes place within rich regions under oxygen deficiency. A possible solution could be the delivery of oxygen with the fuel molecules. The impact of the fuel structure and oxygen content has been investigated within an extensive study.

Experiments

The object under investigation has been an overventilated, non smoking, laminar co-flow diffusion flame, which was stabilised on a Wolfhard-Parker burner (see fig. 3). On this type of slit burner the gaseous fuel stream is sandwiched in between two parallel airflows. The air duct exit velocity should be higher than the fuel flow itself. This ensures a consistant oxygen supply for all possible flame modulations. Three different fuels have been compared concerning their soot formation potential and the subsequent oxidation process. The common properties of the gases are the aliphatic structure and they consist of two “C”-atoms bound within the molecule. They differ solely in the type of bound and in the oxygen content. Figure 4 shows the basic properties of the fuels. Ethylene is a strongly sooting fuel which was taken as base fuel. It has an olefinic structure, i.e. a double bound in between the carbon atoms. As second fuel served ethane as a representative for parafinic structure or single bounded carbon atoms. Dimethylether (DME) is an oxygenated fuel with a etherial structure. The oxygen demand of all three fuels is similar and ranges beween 3.0 and 3.5. Further the calculated adiabatic flame temperature of ethane and DME is similar and close to that of ethylene. This is important in order to minimize temperature effects on the soot formation. For optimum comparison a mixture strategy for the fuels had to be found. Fig. 5 shows a sketch of the principle procedure. Essentially the mixing concept consists of two test series: ethylene <-> ethane and ethylene <-> DME. Both follow the same rules. Ethylene acts as strongly sooting
basic fuel and has a volume flux of 0.13 l/min. This fuel flow is substituted in steps of 10% by volume (or mole) with the corresponding low sooting test fuel. With this proceeding the total molar fuel flux stays constant and also the “C”-flux. In addition nitrogen was admixed in order to study the dilution influence.

Nitrogen flux and fuel flux produce a total volume flux, whereas the amount of fuel is given by the mole fraction of fuel.

**Experimental set-up**

In order to characterize the soot formation process and the accompanying oxidation, four different measuring techniques have been applied and improved. Laser induced incandescence (LII) has been used to measure the soot volume fraction $f_v$ which is a measure of the soot concentration. The corresponding primary particle diameter $d_p$ could be measured with the slightly different time-resolved laser induced incandescence (TIRE-LII). A further possibility to determine the soot volume fraction offers the two color pyrometry. But the main purpose of this technique is the determination of the soot temperature. The results of the two color pyrometry and LII in terms of soot volume fraction show very good agreement and verify the data. The OH-radical which has a strong soot oxidation potential was localized using OH-LIF. Figure 3 illustrates the principle experimental set-up.

**Laser induced incandescence (LII)**

With LII the soot particles within the flame are heated with an intense laser pulse from a frequency doubled Nd:YAG laser (532nm, 7ns) which is prepared to a very thin (0.5mm) light sheet by a combination of a cylindrical lens and a collimating lens. Due to absorption the soot particles reach their evaporation temperature around 3950K and radiate according to Planck’s law. The intensity of the soot particles radiation is a measure of the soot volume fraction. The emitted intensity is recorded by an ICCD-camera DiCam Pro through a 105mm UV-Nikkor Telescope coupled with a 650nm band pass filter (10nm FWHM). Mie-scattered light is rejected with a notch filter at the laser wavelength. The gating time was set to 25ns and overlaps with the laser pulse. Due to the laminar character of the flame an average of 16 pictures has been taken for each setting.

The LII-signal has been calibrated with an extinction experiment performed with a HeNe-Laser.

**Time-resolved laser induced incandescence (TIRE-LII)**

Time-resolved LII uses the same experimental set-up than LII but the timing differs. The signal is taken at two different times (100ns and 500ns) after the laser pulse. The intensity ratio between those two intensity distributions is a measure for the primary particle size. This is possible because different sized particles show a different cooling behaviour. Larger particles cool down slower than small particles. The calculated particle size is an average value of all polydisperse particles situated within the measuring volume (97µm x 97µm x 500µm; (pixel size x pixel size x laser sheet thickness)). This measuring technique is based on calculations for the cooling behaviour of different sized particles and in principle does not need a calibration. The assumptions for the calculations influence the accuracy of this method.

**Two color pyrometry**

The two color pyrometry within flames measures the emission of soot particles within and through a certain volume in the flame. The calculation of the soot particle temperature is based on Planck’s radiation law for solid blackbody surfaces ($\varepsilon = 1$). Within flames it has to be taken into account that the extinction by a collection of particles within the observed optical volume cannot be assumed as unity but smaller. *Hottel and Broughton* [1] have proposed a formulation which describes the emissivity in dependance of the soot volume fraction. They correlated the apparent
emissivity to the extinction efficiency $K_{\text{ext}}$ and the line of sight $L$. The optical absorption for the line of sight is per definition the same for all wavelength. With this definition it is possible to calculate the temperature of the flame by measuring the absolute intensity at two different wavelength. The wavelength has to be chosen carefully to avoid an overlap of the particle radiation and any gas band radiation. In our experiments the wavelengths of choice were 540nm and 700nm, respectively.

The system had to be calibrated by a calibration lamb, were the temperature of the tungsten filament was measured with a industrial two color pyrometer.

The result of this measuring technique is the soot field temperature, as well as the KL-factor which can under certain conditions be recalculated to the soot volume fraction.

Figure 6 shows the experimental arrangement, which was used. All measurements for one flame condition (fuel mixture, dilution) could be performed serial due to the stationarity of the flame. First the LII measurement were done with the frequency doubled Nd:YAG laser and a 650nm filter in front of the ICCD camera. By changing the timing the TIRE-LII measurements could be performed with the same optical setup. The two-color pyrometry was installed 90° to the optical path of the LII experiment. A 45° mirror allowed the same view for the two-color pyrometry set-up. The two filters set in the optical path were interchangeable and a series of 500 pictures was shot added on the chip of a SensiCam (PCO) CCD camera.

**Results**

The following results show the soot characteristics within a set of ethylene flames, where the basic fuel was substituted in steps of 10%-volume flux by the two low sooting test fuels ethane and DME.

Figure 8 illustrates the two dimensional soot volume fraction distribution existing in the 500µm measuring sheet within the flame. On the first left picture the soot distribution for the pure Ethylene flame is shown, whereas the basic fuel is more and more substituted by Ethane or DME respectively towards the right hand side.

For both test gases an overall reduction in the flame soot content can be ascertained but with different efficiencies. With a high proportion of DME the soot vanishes completely. As a side remark one should attract attention to the fact that small amounts of substituent, around 10-20% slightly increase the sooting tendency in both cases.

Considering the whole flame “soot wings” are formed in the vicinity of the flame front under highly sooting conditions. In those wings, the biggest particles can be found like it is shown in figure 9, where TIRE-LII measurements of the primary particle size $d_p$ are representend. As well as the soot amount within the flame the primary particle size is decreasing more and more with the substitution of less sooting fuels.

A further important parameter, which was determined is the soot field temperature $T_S$. All resulting temperatures are pictured in Figure 10 with again the same set of flames as described before.

Remarkable is the strong cooling of the flame obviously by the radiation at high soot load in the ethylene dominated flames. With further replacement of the fuel by low sooting gases the soot content is reduced and the heat realease within the reaction zone is the temperature determining parameter.

Foregoing representation gives at least an overview and an impression what is changing with different fuels. In order to gain a better insight and due to lack of knowledge of the flow field it is of advantage to extract the parameters along the axis of the flow. The interaction with the reaction zone is nonrecurring at the tip of the flame and under these conditions the results are comparable with among all flames.

The sooting behaviour with ethane is totally different compared to the DME case (figure 13). The maximum of soot volume fraction, i.e. the switch from net soot production to net soot reduction located higher with increasing amount of ethylene, whereas this is not observable for DME.
Further an increase of soot production is recognisable as well for ethane as for DME at low proportions (<20%). Generally the soot production is reduced with increasing proportion of test fuel in all cases. DME has a clearly stronger soot reducing effect.

Regarding the primary particle sizes along the flame axis it is striking that 25nm are the maximum values reached. This is around half of the diameter compared to the maximum particle sizes in the flame, which are situated in the strong sooting wings near the reaction zone.

The particle size distribution does not change dramatically with little amount of admixtures of low sooting fuels. The substitution by ethane shows effect from 60% upwards whereas with DME this is reached already with 40%. Considering the DME as a substitute, soot reduction begins before OH-radicals are detectable, whereas this is not the case with ethane.

Of further importance for modelling work is the soot temperature field. It can be shown, that high soot loads cool down the flame drastic by radiation.

All soot characterizing values can be taken to adjust existing or new soot models.

Acknowledgement

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Literature

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motivation / basic approach

• fundamental analysis of the *soot formation* and *oxidation* processes

• survey on the influence of *fuel structure* and *fuel oxygen content* on the sooting behaviour of laminar diffusion flames

• providing a *basic data set for soot modelling*

• design of an appropriate experiment

• application of modern optical soot diagnostics
test facility

Wolfhard-Parker burner

overventilated laminar diffusion flame

fuel + N₂

air

front view

side view
test fuel properties

<table>
<thead>
<tr>
<th>fuel</th>
<th>chemical structure</th>
<th>structure type</th>
<th>molar mass $M$ [g/mol]</th>
<th>stochiometric $O_2$-demand</th>
<th>$H_u^*$ [kJ/mol]</th>
<th>$T_{ad}^{**}$ [K]</th>
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</thead>
<tbody>
<tr>
<td>Ethylene (basic fuel) $C_2H_4$</td>
<td></td>
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<td>Ethane $C_2H_6$</td>
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<td>1428</td>
<td>2276</td>
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<tr>
<td>Dimethylether $C_2H_6O$</td>
<td></td>
<td>etherial</td>
<td>46,07</td>
<td>3</td>
<td>1280</td>
<td>2307</td>
</tr>
</tbody>
</table>

* upper heating value  ** adiabatic flame temperature (undiluted)
mixture strategy fuels

Test series  | Sooting base fuel  | Low sooting test fuel  | Dilution
---|---|---|---
1) Ethane  | H₂C=CH₂  | H₃C-CH₃  | + N₂
2) DME  | H₃C-O-CH₃  |  | + Vₙ₂ = var, addition 0...500%

\[ \dot{V}_{\text{fuel}} = \text{const}, \text{substitution 0...100\%} \]
\[ \dot{V}_{\text{total}}, X_{\text{fuel}} \]

\[ \dot{V}_{\text{N₂}} = \text{var}, \text{addition 0...500\%} \]

\( X_{\text{fuel}} \)

measuring array
measuring set-up

- Beam dump
- DiCam Pro ICCD
- SensiCam CCD
- Delay-Generator
- Beam dump
- Dye-Laser pulse 308, 609nm
- ND:YAG Laser pulse 532nm 13MW/cm²
- 540nm 620nm 700nm
- Mirror
- OH-LIF: OH-presence f_v
- LII: T, KL, f_v
- TIRE-LII: d_p
- 2λ Pyrometry: T, KL, f_v
overview determined flame parameters

<table>
<thead>
<tr>
<th>OH-LIF</th>
<th>LII, TIRE-LII</th>
<th>Two color pyrometry</th>
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<tr>
<td><img src="image1" alt="OH-LIF Image" /></td>
<td><img src="image2" alt="LII, TIRE-LII Image" /></td>
<td><img src="image3" alt="Two color pyrometry Image" /></td>
</tr>
</tbody>
</table>

- **OH**
- **d_p**
- **N_p**
- **f_v**
- **f_v**
- **T_{soot}**
soot volume fraction $f_V$

Ethylene

Ethane

Ethylene

DME

0 %  10 %  20 %  30 %  40 %  50 %  60 %  70 %  80 %  90 %  100 %

initial OH-radical detection by OH-LIF

$f_V = 10^4 [\text{mm}^3/\text{mm}^3]$
primary particle diameter $d_p$

- Ethylene
- Ethane
- DME

Initial OH-radical detection by OH-LIF
soot particle temperature $T_S$

![Diagram showing temperature changes for different gases and reactions.](image-url)
flame soot content in dependance of fuel mixture

Ethylene/Ethane flame (different N₂-dilutions)

Ethylene/DME flame (different N₂-dilutions)
flame soot content in dependence of dilution

Ethylene/Ethane flame
(different fuel mixtures)

Ethylene/DME flame
(different fuel mixtures)
soot volume fraction $f_V$ along the flame axis

Ethylene/Ethane flame (different fuel mixtures)

Ethylene/DME flame (different fuel mixtures)

| OH-concentration rise |

Substitution of Ethylene by

Ethane $X_{\text{fuel}}=1.0$

Substitution of Ethylene by

DME $X_{\text{fuel}}=1.0$
primary particle diameter $d_P$ along the flame axis

Ethylene/Ethane flame
(different fuel mixtures)

Ethylene/DME flame
(different fuel mixtures)

| OH-concentration rise

Substitution of Ethylene by

- 0% Ethane
- 10% Ethane
- 20% Ethane
- 30% Ethane
- 40% Ethane
- 50% Ethane
- 60% Ethane
- 70% Ethane
- 80% Ethane
- 90% Ethane
- 100% Ethane

Substitution of DME by

- 0% DME
- 10% DME
- 20% DME
- 30% DME
- 40% DME
- 50% DME
- 60% DME
- 70% DME
- 80% DME
soot temperature $T_S$ along the flame axis

- **Ethylene/Ethane flame**
  - (different fuel mixtures)

- **Ethylene/DME flame**
  - (different fuel mixtures)

| OH-concentration rise |

Substitution of Ethylen by
- 0% Ethane
- 10% Ethane
- 20% Ethane
- 30% Ethane
- 40% Ethane
- 50% Ethane
- 60% Ethane
- 70% Ethane
- 80% Ethane
- 90% Ethane
- 100% Ethane

Substitution of DME by
- 0% DME
- 10% DME
- 20% DME
- 30% DME
- 40% DME
- 50% DME
- 60% DME
- 70% DME
- 80% DME

Ethane $X_{\text{fuel}}=1.0$

DME $X_{\text{fuel}}=1.0$
conclusions

• oxygenated fuels act chemically and their influence on sooting behaviour is stronger than the structural influence

• with oxygenated fuels, the oxidation starts before OH is present

• particle size seems to be independant of mixture over wide fields

• temperature field is strongly dependant on the soot load
  -> radiation plays a key role which has to be considered in modeling
acknowledgement

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