

Mechanisms of Soot Reduction in Diesel Pool Fire by Ferrocene

V. Weiser*, N. Eisenreich, E. Roth, A. Pfeil

Fraunhofer-Institut Chemische Technologie (ICT)

Abstract

Ferrocene is widely used to reduce soot production in combustion engines. A study of the influence of ferrocene to small diesel pool fires gives new insights to mechanisms of soot reduction in evaporating fuels e.g. fuel sprays. Laminar pulsating pool fires of pure diesel oil and a solution of 1% ferrocene in diesel were investigated using fast scanning IR emission spectroscopy, 2-colour-pyrometry, laser absorption, thermocouples and fast movie camera. Soot was measured gravimetrically at different distances above the fuel level and analysed with TGA, XRD and SEM. 1% ferrocene reduced the soot volume fraction of the smoke gases by a factor of three. Significant observations were detected in the temperature characteristic of short time flame structures. Soot samples taken from the lower part of the fires and analysed in a DSC show that the soot from flames with ferrocene reacts at 480°C that is 150 K lower than soot from pure diesel flames. Ferrocene evaporates conjointly with the diesel fuel and decomposes at about 470°C inside the flame. When soot is formed, iron oxide is inserted homogeneously inside the soot particles that catalyses the combustion at lower temperature. So the flame structures burn out more completely when the smoke gases cool down but simultaneously enrich with ambient air.

Introduction

Ferrocene is a well-known additive to reduce soot formation in combustion processes [1], [2]. Ferrocene was also discussed as an additive to crude oil and fuel storages in scope to reduce smoke in the case of hazardous fire. The effect of ferrocene to pool fires was investigated previously [3], [4]. Both authors found a positive effect on soot reduction in the smoke but Kim also stated that the fire got more intensive by adding ferrocene [4]. Even several investigations on the mechanism of soot reduction were presented not all details are solved. This study was performed to get more insights of the effect of ferrocene to the combustion process inside the flame zone and the soot reduction mechanism at self-organized diffusion flames [5]-[7].

Pool fires are buoyancy controlled diffusion flames generated over plain liquid fuel surfaces. Often they are used for phenomenological investigations of hazardous fires [8]. Typically they show a characteristic periodic flickering with uprising flame structures [9], [10] (Figure 1). The frequency depends only marginal to the type of organic fuel but mainly to the burning area [11]-[13].



Figure 1. Diesel pool fire (40 mm diameter) with periodic ascending flame structures received with 50 fps.

Experimentals

Ferrocene (PLUTO) was solved in commercial diesel oil. The prepared concentrations are listed in Table 1. In most experiments sample 4 with 1% ferrocene was compared to pure diesel (sample 1).

Table 1
Investigated samples

Sample #	unit	1	2	3	4	5
Ferrocene in diesel	Ma%	0	0,0016	0.5	1	2
Test 1	ppm	0,314	0,314	0,162	0,093	0,062
Test 2	ppm	0,333	0,245	0,240	0,092	0,082
Test 3	ppm	0,342	0,295	0,179	0,089	0,048
Average	ppm	0,330	0,285	0,194	0,091	0,064

Pool fire investigations were performed in a porcelain pan with 40 mm diameter and 40 mm height. At the beginning of each experiment the pan was filled up to 2 mm below the upper rim. Fuel temperature was about room temperature (18 to 25°C) at the beginning. During the experiment it heated up to 50 to 80°C over a time period of 5 minutes. Most measurements were taken about 1 minute after ignition when the flame burned stable.

Measurement techniques and analysis

To measure the mass loss rate the burning fuel was placed on a digital balance with an accuracy of 10 mg connected to a PC as data logger. Weight was read out every second. Mass loss per second and pool area was determined from the gradient calculated by a linear regression to the data received over 5 minutes after ignition.

To investigate the change of ferrocene concentration in the fuel during the combustion period of 8 minutes a small sample of the fuel was taken from the pool each minute and analysed in a FTIR spectrometer. The mixtures show significant peaks at 1005 and 1107 cm^{-1} that responds very sensitive to concentration changes and allowed an analysis with an accuracy of <0.05% (Figure 2 left).

Soot concentration in the exhaust gas above the illuminating flame ($x = 300 \text{ mm}$) was detected by the

* Corresponding author: vw@ict.fraunhofer.de

absorption of a laser beam using a method described in [11].

Inside the flame soot samples have been taken using aluminium and glass plates that have been put horizontal into the flame for one second at different flame zones and were analysed with optical and electronic microscopy (SEM).

To receive larger soot samples a simple probe was devised consisting of a cylindrical container (5 mm diameter) made of tin foil like it is used for TGA or DSC measurement. For sampling the probe was filled with a large water drop to cool the tin foil and allowing a sampling time of 60 s. After collecting soot out of the flame the probe was dried in an oven and the amount of attached soot was determined gravimetrically. Some of this samples were analysed thermo analytically (TGA) and by X-ray diffraction.

Mean concentration of main combustion products CO, CO₂, NO/NO₂, hydrocarbon as CH₄ and O₂ was analysed with a gas analyser (AFRISO Infralyt) at axial distances $x = 10, 80, 130$ and 200 mm above the fuel level.

The flickering flame shape was observed with a DV camera (Panasonic) with an exposure time of $1/250$ s and a fixed aperture providing 50 de-interlaced frames per second. The movies were transferred to PC in raw AVI format and could be analysed using the picture analysing code AVICOR especially developed for statistic analysis of transient flames [15].

Spectral flame emission was measured with two MMS-spectrometers (Zeiss) in the range of 0.45 to 0.90 and 0.90 to 2.25 μm and a filter wheel spectrometer produced at Fraunhofer ICT in the range of 2.4 to 14 μm with a sampling rate of 100 spectra per second [16], [21]. Both systems were calibrated on intensity per wavelength with a technical black body radiator.

To measure radiation temperatures of the flame a fast scanning 2-colour-pyrometer also developed at Fraunhofer ICT with a sampling rate up to 1 MHz was used [18], [16]. The system presumes grey body radiation with constant emissivity. The detector consists in a Si/Ge-sandwich detector with nominal sensitivities at 0.85 and 1.55 μm . The quotient of the diode voltage that is proportional to the emission intensity is calibrated to temperature using a black body radiator. For the recent application a sampling rate of 10 kHz proved as adequate.

All spectrometers and the pyrometer were focused to various locations in different flame zones using a lens system. The resolution of the detected area was estimated to about 100 mm^2 .

The temperature of the comparatively cold and non-lighting pyrolysis zone in the centre of lower flame was measured with Pt-RhPt thermo-couples.

Results

The addition of ferrocene has a significant effect to the soot volume fraction in the smoke that is presented in Table 1. 1% ferrocene reduces the soot volume fraction to a quarter of that evolved from pure burning

diesel fuel. With the investigated pool fire types this appears to be an optimum. So it was chosen as reference value for the comparison to pure diesel.

During the test period of 300 s the mass loss showed strongly linear regression behaviour. The data analysis yield to 12.0 $\text{g m}^{-2}\text{s}^{-1}$ of pure diesel and 11.7 $\text{g m}^{-2}\text{s}^{-1}$ with diesel added with 1% ferrocene. The difference seemed not to be significant so that it was concluded that the mass loss was not affected by ferrocene.

During the measurement period the ferrocene concentration in the fuel kept constant that is indicated by FTIR absorption measurements presented in Figure 2 (right). So it can be presumed that ferrocene was neither decomposed during the examined combustion period nor accumulated or depleted by a distillation effect but it evaporates simultaneously with the diesel fuel.

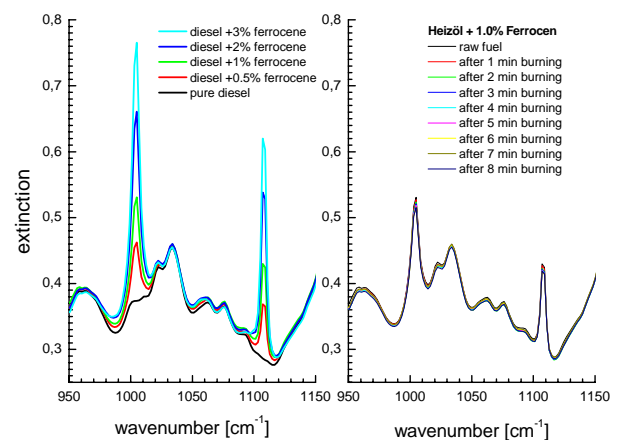


Figure 2. FTIR absorption spectra from diesel with different amount of ferrocene (left) and samples of diesel with 1% ferrocene from 0 to 8 minutes combustion time (right)

The video exposures of both fuels show the characteristic pulsing given in Figure 1. The mean light emission over the total flame size calculated by statistic average of all pictures received from the first two minutes after ignition is given in Figure 3. The pool fire of the pure diesel shows a higher intensity about 20 to 60 mm above the fuel level. The flame of diesel pool fire with 1% ferrocene is significant longer.

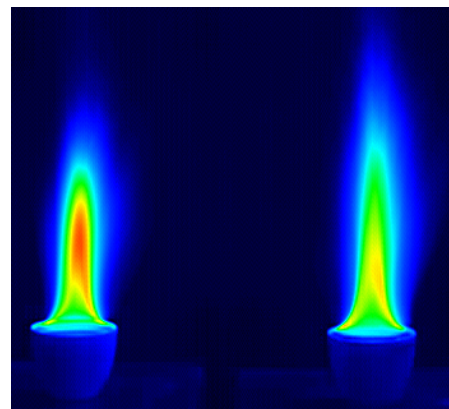


Figure 3. Mean light emission of the investigated pool fires of pure diesel (left) and diesel with 1% ferrocene (right)

A characteristic single screenshot presented in Figure 4 indicates that the short time structures of both flames were identical. But the flame with ferrocene shows an additional bright light emission at the flame tip. This was significant for the majority of screenshots of the investigated movies.



Figure 4. Screenshot of synchrony pulsing diesel pool fires: pure (left) and with 1% ferrocene (right)

Downstream no significant differences of the mean concentrations inside the flame or smoke gases were analysed. The gravimetric measured soot concentrations are illustrated in Figure 5. The pool fire with 1% ferrocene shows inside the pyrolysis zone at the base of the flame ($x = 10$ mm) a slightly higher amount of soot than the pure diesel flame. At high positions the flame with ferrocene exhibits less soot.

In SEM all soot samples taken from different positions and samples did not show any significant variations. Micron sized soot particles were composed of agglomerations of spherical particles of about $100 \mu\text{m}$. Optical microscopy showed that in the lower part of the flame the soot particles of about $1 \mu\text{m}$ taken from the pool fires with 1% ferrocene have a minor tendency to agglomerate than from pure diesel. The same result was observed in soot samples taken from the exhaust gas of the pool fires featuring with less and smaller soot flakes.

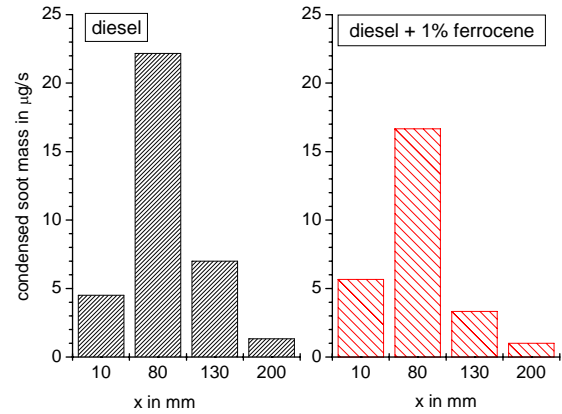


Figure 5. Gravimetrically determined soot received from the diesel pool fires without and with 1% ferrocene at different axial positions x .

XRD spectra taken from soot samples of pool fires with 1% ferrocene show reflections from iron oxide (wüstite and hematite) but no residues of ferrocene could be detected.

DSC measurements could only be performed up to 600°C . Two resulting curves are presented in Figure 6. At this temperature soot samples taken from the flame zone of the pure diesel pool fires show an onset of exothermic reaction in air atmosphere (thin line). The soot samples taken from the same position in the pool fire with 1% ferrocene react (thick line) at lower temperatures of 400 to 500°C .

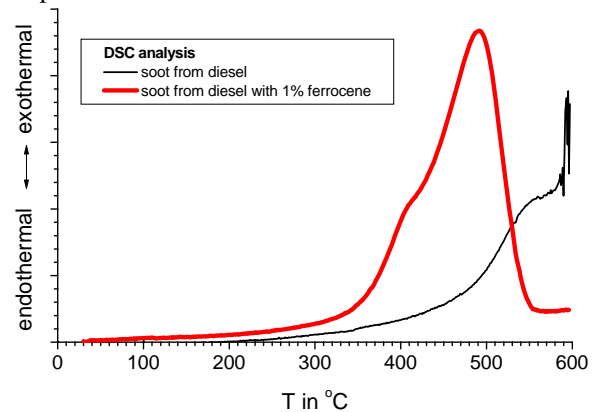


Figure 6. DSC-analysis in air of soot received from the pool fires at the axial position of $x=80$ mm.

IR measurements of the spectral emission from the flame approve this tendency like presented in Figure 7. The continuum radiation evoked from glowing soot particles at the base of the pure diesel flame was lower compared to emission of CO_2 and water bands. At this position the fire of diesel doped with ferrocene showed significant emission of C-H stretch band at $3.4 \mu\text{m}$ pointing to hot reacting hydrocarbons.

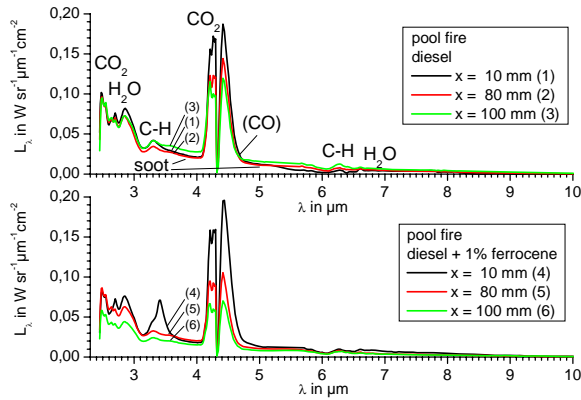


Figure 7. IR-spectra of pool fires from different axial position; pure diesel (top); diesel with 1% ferrocene (bottom)

In the centre of the non radiating pyrolysis zone of the pool fire temperature rises very fast from evaporation temperature of the fuel (about 300 to 400°C) to 700°C. A thin combustion zone with high radiation that surrounds this zone has considerable higher temperature as presented Figure 8. But both samples show no significant differences in the absolute values.

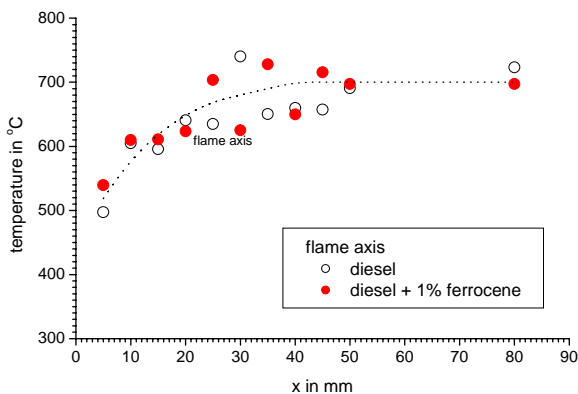


Figure 8. Temperature profiles in the centre of the lower part of the pool fires measured with thermo-couples.

In the visible and NIR spectral range the flame emission that covers the detector sensitivity of the 2-colour spectrometer is dominated by a smooth continuum radiation evoked from soot. At 1.4 μm a weak water band overlays this continuum that has no important contribution to the emission intensity. So the assumption to use a 2-colour pyrometer for temperature measurements from flame radiation was proved to be valid. One has to consider that soot radiation deviate from grey body emission, but it can be demonstrated by radiation model calculations performed with ICT-BaM-Code [19] that within the sensitivity bands of the detectors the measured flame temperatures are at most about 100 K higher than the real ones. At 1800 K that is about 5% of the absolute radiation temperature of the flame. It was not corrected therefore only the tendency of temperature characteristics was in the scope of interest. Such detected mean flame temperature combined with the mean NIR-emission intensity

measured in voltage of the Ge-diode of the 2-colour pyrometer are presented in Figure 9 as function of the axial distance from the fuel level x. The temperature, mainly based on soot emission, of both flames is nearly constant at 1800 K. It has to be considered that the 2-colour pyrometer only measures when an emitting flame zones is present and does not include time periods with no emission that are frequently in the upper part of the flame (compare Figure 10). So this temperature distribution differs from intrusive measurement techniques like e.g. thermo couples (Figure 8) (see also [20]).

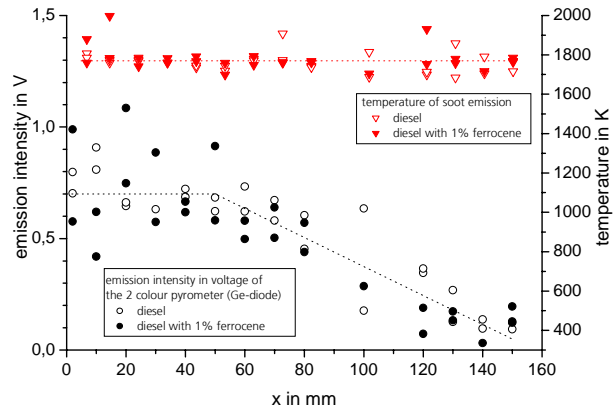


Figure 9. Mean values of flame emission intensity and emission temperature of soot radiation of pure diesel (open dots) and diesel with 1% ferrocene (filled dots) measured with a 2-colour pyrometer.

Chronological intensity and temperature measurements dissolve the periodic fluctuations of the pulsing pool fire. The maxima of the intensity signal correspondent to centre of each ascending flame structure. In the lower part of the flame temperature correlates with the intensity signal varying from 1600 to 2000 K. This characteristic behaviour of small pool fires is described in detail in [21], [22]. An interesting particularity of the comparison of diesel fires with and without ferrocene was observed in the upper part of the flame like demonstrated in Figure 10 and Figure 11. The diesel pool fires with 1% ferrocene show high temperatures at the border of each flame structure like apparent in Figure 11. This behaviour does not appear in each measurement but was found in the majority of several hundred measurements from different experiments that were reviewed.

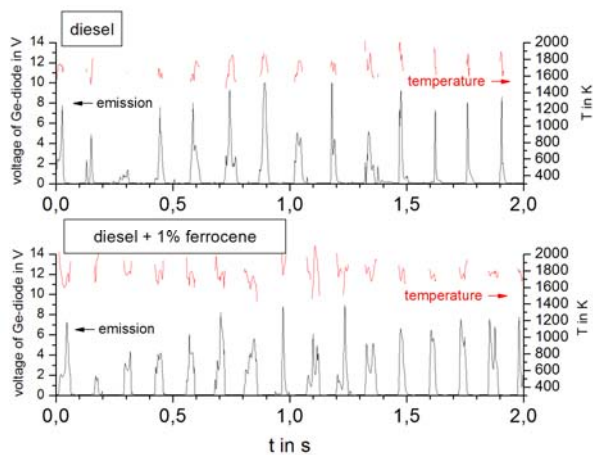


Figure 10. Flame emission and correlated temperature of several flame structures passing the detected area of the pyrometer. Diesel pool fire (top); diesel pool fire with 1% ferrocene (below) at $x=130$ mm.

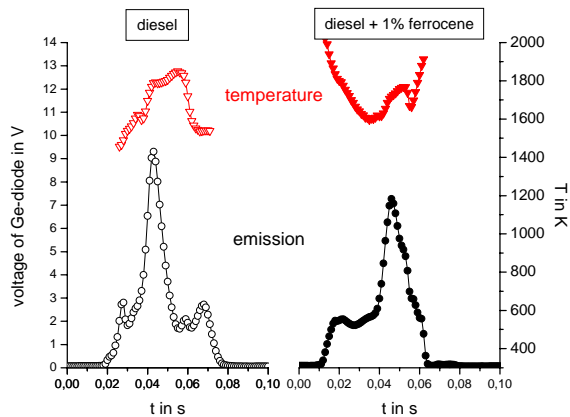


Figure 11. Flame emission and correlated temperature of a single flame structure passing the detected area of the pyrometer. Diesel pool fire (left); diesel pool fire with 1% ferrocene (right) at $x=130$ mm.

Discussion

The investigated pool fire possesses a pyrolysis zone or a fuel rich flame zone inside the lower part of the flame with under-stoichiometric air supply. Here a high amount of soot is generated. Ferrocene evaporates conjointly with diesel fuel controlled by the heat feedback from the flame. In the pyrolysis zone with temperatures up to 700°C the molecules decompose. Decomposition temperature of ferrocene is 460 to 470°C (e.g. [21]). Depending from the air supply the Fe^{2+} -ion oxidises to iron oxide that might acting as seed crystal for formation of primary soot particles. This would explain the higher amount of soot measured in this region. So iron oxide that is known to act as catalyst for soot oxidation [24] is homogeneous dispersed inside the soot particles that follow the stream of the buoyancy driven flame gases forming the macroscopic flame structures. In the upper part of the flame the structures enrich in oxygen entrained from surrounding air by convection and diffusion processes and burn out steadily. Gaseous flame reactions are known to be faster than soot particle oxidation. So soot particles remain inside the flame structures that enrich in inert combustion products like CO_2 , water and nitrogen. By

radiation and conductive heat loss the structures cool out faster than enough fresh oxygen may be infiltrated to burn the soot. At temperatures lower than 600°C that will first appear at the exterior zone of the flame structures. Regular soot does not ignite any more even enough air is available. But soot including catalytic iron oxide ignites at lower temperatures particular inside this colder zone with its higher air concentration and burn out completely. This explains the measured temperature profiles of Figure 10 and Figure 11. This also explains that much less soot is evolved to the cold smoke gases.

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