Optical studies of spray development and combustion of water-in-diesel emulsion and microemulsion fuels

Raúl Ochoterena a,*, Anna Lidf, Magnus Nydén b, Sven Andersson a, Ingemar Denbratta

a Department of Applied Mechanics, Chalmers University of Technology, SE-412 96 Göteborg, Sweden
b Department of Chemical and Biological Engineering, Applied Surface Chemistry, Chalmers University of Technology, SE-412 96 Göteborg, Sweden
c AkzoNobel Surface Chemistry AB, SE-444 85 Stenungsund, Sweden

A R T I C L E   I N F O

Article history:
Received 21 October 2008
Accepted 30 June 2009
Available online 30 July 2009

Keywords:
Spray behaviour
Water-in-diesel emulsion
Spray combustion

A B S T R A C T

Physical properties, spray behaviour and combustion characteristics of a water-in-diesel emulsion, a water-in-diesel microemulsion and a conventional diesel fuel were investigated. The size of the drops, in the water-containing fuels, was measured by NMR diffusometry. Spray development and combustion were studied by optical methods in an optically accessed combustion vessel at conditions similar to those in a diesel engine. High speed shadowgraphs were employed to measure break-up, droplets penetration, vapour penetration and start of combustion. Combustion duration, flame temperature and relative soot concentration were determined by emission-based methods. Differences in spray behaviour suggest an enhanced atomisation for the water-containing fuels compared to regular diesel fuel. Moreover, reduced soot concentrations and flame temperature with increased combustion duration were noticed for the water-in-diesel fuels than for the regular diesel fuel.

1. Introduction

Water has been used as an additional component to the air–fuel mixture in internal combustion engines for several reasons, for instance cooling the charge and increasing its density. Furthermore, the addition of water restrains the onset of knock and can reduce the formation of nitrogen oxides (NOx) inside the combustion chamber [1].

One way to add water to air–fuel mixtures is to use water-in-diesel fuels. These fuels, which may be either emulsions or microemulsions, have aroused the interest of researchers and consumers because emissions of nitrogen oxides and soot can be reduced by combusting them rather than conventional diesel fuels under similar conditions [2–5]. Further, although water can also be introduced into the combustion chamber by direct injection [6], incorporating water into the fuel as an emulsion or microemulsion provides opportunity to use water-in-diesel fuels in the current fleet of diesel engine vehicles with no major modifications of the engines. On top of that it allows regular diesel to be easily replaced by an environmentally preferable alternative without changing the existing fuel supply infrastructure.

In general, water-in-diesel emulsions and microemulsions are generated by mixing vigorously the two main components and stabilising them by adding relatively small amounts of emulsifiers, i.e. surfactants and polymers. The two main components are blend into a system consisting of fine, or ultra fine, water drops dispersed in diesel forming either an emulsion or a microemulsion, respectively. Emulsions and microemulsions differ not only in the size of the drops of the dispersed phase, but also in terms of their thermodynamic stability [7]. Microemulsions are thermodynamically stable, meanwhile emulsions are thermodynamically unstable and will separate into two phases in due time, although this separation can be delayed by a careful choice of surfactants and polymers. The size of the drops in an emulsion are in the range of 1–10 μm, while in a microemulsion are much smaller, e.g. 5–20 nm [8].

Using water-in-diesel fuels in direct injected compression ignition engines has been found to reduce exhaust emissions of both nitrogen oxides and particulate matter. The decrease in nitrogen oxides emissions is explained by the reduction in the combustion temperature caused by the presence of water in the mixture [9,10]. In addition, the reduction in soot emissions is attributed to improved atomisation caused by the rapid evaporation of the water drops [10] and to the formation of hydroxyl radicals by water dissociation, enhancing thus, the oxidation of soot [11]. The enhanced atomisation may be caused by “micro-explosions”, resulting from differences in the volatility of water and diesel [11–15].

This paper presents a study of the physical properties, spray behaviour and combustion characteristics of a water-in-diesel...
emulsion, a water-in-diesel microemulsion and a conventional fuel. The size of the water drops in the emulsion and microemulsion were determined by NMR diffusometry. The spray studies were carried out using the Chalmers High Pressure and High Temperature (HP/HT) Spray Rig in conditions similar to those prevailing in a diesel engine prior to ignition; measuring spray cone angle, liquid phase penetration, droplet penetration, and vapour penetration. Indications of the occurrence of micro-explosions are documented in this study. Flame temperature, relative soot concentration and ignition delay were also measured. These results are used to explain previous engine tests results published by Lif et al. [16], in which large reductions in soot emissions without reductions in nitrogen oxides were observed when water-containing fuels were used, relative to those observed when standard fuel was combusted.

2. Method

2.1. Fuel characterisation

An emulsion fuel and a microemulsion fuel were generated based on European ultra-low sulphur diesel (EUD). Specifications of EUD, according to EN590, are presented in Table 1, while the composition, density and heat of combustion of the three studied fuels are given in Table 2.

The emulsion fuel was prepared using a SEPO.3R Emulsion Research Plant manufactured by AkzoNobel. The additives were dissolved in the diesel, then the water was continuously added under high shear mixing. The additives used were a blend of penta(ethylene glycol)monohexadecyl ether (40%), sorbitan monooleate (30%), and a polymer of polyisobutylene succinic anhydride type (30%). The mixing resulted in an emulsion that was stable for three months. The microemulsion fuel was prepared by dissolving the additives in the diesel, adding the water and then mixing with a propeller agitator. In this formulation the additives consisted of penta(ethylene glycol)monoundecyl ether and sorbitan monooleate. No polymer was included since a microemulsion consisted of penta(ethylene glycol)monoundecylic ether and sorbitan monooleate. No polymer was included since a microemulsion is by definition stable, requiring no extra stabiliser. Deionised water was used for both the emulsion and microemulsion formulation.

### Table 1: European ultra-low sulphur diesel (EUD) specifications.

<table>
<thead>
<tr>
<th>Property</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aromatic content</td>
<td>18.9 vol.%</td>
</tr>
<tr>
<td>Flash point</td>
<td>78.0 °C</td>
</tr>
<tr>
<td>Distillation initial boiling point</td>
<td>192.5 °C</td>
</tr>
<tr>
<td>Distillation final boiling point</td>
<td>358.0 °C</td>
</tr>
<tr>
<td>Hydrogen:carbon (H:C) mass ratio</td>
<td>0.15</td>
</tr>
<tr>
<td>Net heat of combustion</td>
<td>42.86 MJ/kg</td>
</tr>
<tr>
<td>Cetane number</td>
<td>52.0</td>
</tr>
<tr>
<td>Cloud point</td>
<td>−7 °C</td>
</tr>
<tr>
<td>Cold filter plugging point</td>
<td>−15 °C</td>
</tr>
<tr>
<td>Lubricity (WSD 1.4) at 60 °C</td>
<td>372 µm</td>
</tr>
<tr>
<td>Sulphur content</td>
<td>7 ppm (wt.)</td>
</tr>
</tbody>
</table>

### Table 2: Composition, density and heat of combustion of the fuels.

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Component (wt.%)</th>
<th>Heat of combustion [MJ/kg]</th>
<th>Density [kg/m³]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diesel</td>
<td>100</td>
<td>–</td>
<td>42.86</td>
</tr>
<tr>
<td>Water</td>
<td>–</td>
<td>4.28</td>
<td>852</td>
</tr>
<tr>
<td>Additives</td>
<td>–</td>
<td>4.02</td>
<td>866</td>
</tr>
<tr>
<td>EUD</td>
<td>88</td>
<td>10</td>
<td>41.00</td>
</tr>
<tr>
<td>Emulsion</td>
<td>10</td>
<td>10</td>
<td>40.02</td>
</tr>
<tr>
<td>Microemulsion</td>
<td>10</td>
<td>10</td>
<td>40.02</td>
</tr>
</tbody>
</table>

2.2. Physical properties

The viscosity, surface tension, and density of the fuels were all measured at 25, 40, 48, and 70 °C. The viscosity measurements were performed with a controlled stress rheometer (StressTech from Reologica Instruments, Sweden) with an applied shear rate ranging from 0.01 to 1.0 Pa. The measuring unit had a concentric geometry with a 2 mm gap between the bob and the cup. The surface tension and density of the fuels were measured using a Sigma 70 tensiometer (KSV Instruments, Helsinki, Finland) with a Pt–du Noüy ring and a Mettler Toledo DA-100 M density meter, respectively.

2.3. Dispersed phase drop sizing by NMR diffusometry

The water drop sizes of the dispersed phases of the water-containing fuels were measured by NMR diffusometry, using a 500 MHz Varian Unity Inova spectrometer equipped with a diffusion probe supplied by Doty Sci. Inc. The experiments were performed at 25 °C, the observation time Δ, i.e. the time between the leading edges of the gradients, was held constant at 100 ms for the microemulsion fuel and at 300 ms for the emulsion fuel, the gradient length δ was 4 ms and the gradient strength g was varied in 64 steps from 0.06 to 3.84 T m⁻¹. A stimulated echo pulse sequence with a first magnetic field gradient pulse inserted between two 90° radio frequency (r.f.) pulses and a second gradient immediately after a third 90° r.f. pulse was used. All samples were measured in NMR tubes from Shigemi with only 3 mm outer diameter to minimize convective flow due to temperature gradients.

The stimulated spin echo pulses spin gradient magnetic resonance (STE-PFG NMR) technique was used to determine the self-diffusion coefficients of water in the emulsion and microemulsion fuels. A detailed description of this technique can be found elsewhere [17], and only a brief introduction is given here. In an STE-PFG NMR experiment the displacement of water molecules is measured during the time Δ between two gradient pulses, when the water molecules diffuse randomly according to Brownian motion. In a heterogeneous system, such as an emulsion or a microemulsion, the diffusion of the molecules is influenced by the internal structure of the system. In an emulsion the diffusion of water is restricted to the water drops but in a microemulsion the water droplets are much smaller and their diffusion can be treated essentially as the diffusion of water [18]. The mean square displacement (z²) in Eq. (1) describes the average distance a molecule can diffuse during the time t. The diffusion coefficient D₀ refers to free diffusion. In an emulsion the diffusion is restricted to the drops so the mean square displacement is described by Eq. (2) [17], where R is the radius of the water drop.

\[
\langle z^2 \rangle = 2 D_0 t \tag{1}
\]

\[
\langle z^2 \rangle = R^2 \left( \frac{2}{5} \right) \tag{2}
\]

In an STE-PFG NMR experiment, with sine-shaped gradient pulses, the echo-decay from the NMR signal is given by Eq. (3).

\[
I/I_0 = \exp(-kD) \tag{3}
\]

I is the observed signal intensity, I₀ the signal intensity in the absence of field gradient pulses, and \( k = \gamma^2 g^2 (A - \delta) \pi^2 \) the slope being the diffusion coefficient D. From the Stokes–Einstein equation (Eq. (4)) the radius of the water drops...
can be calculated. In this equation \( D_0 \) is the diffusion coefficient for a spherical particle, \( R_p \) the drop radius, \( k_B \) the Boltzmann’s constant, \( T \) the absolute temperature, and \( \eta \) the solution viscosity.

\[
R = \frac{k_B T}{6\pi \eta D_0}
\]

In an emulsion, diffusion is restricted since the molecules are affected by the presence of the walls. The diffusion time, \( \tau \) i.e. the time between the gradient pulses, must be \( \tau \gg R^2/D \). With short \( \tau \) times the water molecules will not diffuse for a sufficiently long time to be subject to the restriction and the obtained value of \( D \) will be smaller than the true \( D \) [19]. For diffusion in a sphere, the echo-decay is described by Eq. (5), which is based on the Gaussian phase distribution approximation [18], where \( x_n \) is the \( nth \) root of Eq. (6) and \( J_n \) is the Bessel coefficient. The mean radius of the water drops is then calculated taking the log-normal distribution function into account.

\[
\ln \left( \frac{1}{T_0} \right) = \left( -\frac{2\pi^2 \gamma^2}{D} \right) \sum_{n=1}^{\infty} \left( \frac{x_n^4}{\pi^2 n^2 - 2} \right)
\]

\[
\times \left\{ 2 + e^{-\left( \frac{4\pi^2 \gamma^2}{x_n^4} \right)} - 2e^{-\left( \frac{2\pi^2 \gamma^2}{x_n^4} \right)} - 2e^{-\left( \frac{\pi^2 \gamma^2}{x_n^4} \right)} + e^{-\left( \frac{4\pi^2 \gamma^2}{x_n^4} \right)} \right\} \quad (5)
\]

\[
(x_n R)^{-1/2} J_{1/2}(x_n R) - 1/2 J_{1/2}(x_n R) = 0 \quad (6)
\]

3. Spray and combustion studies

Spray development and combustion characterisation were studied by optical methods in the Chalmers High Pressure and High Temperature (HP/HT) Spray Rig. The conditions inside the chamber were controlled to achieve conditions similar to those prevailing in a direct injection compression ignition engine prior combustion occurs. The chamber has a relative large volume of 2 l, in which pressurised, preheated air flows at a low velocity (~0.1 m/s). The conditions inside the combustion chamber are quiescent before the injection of fuel and isobaric throughout. Fuel was injected into the combustion chamber by a common rail system using a solenoid injector with a vertically aligned single-hole nozzle with diameter \( \Omega = 0.14 \) mm. The injection pressure was maintained at a constant 50 bar and 830 K during all of the studies reported here. A schematic drawing of the HP/HT Spray Rig is presented in Fig. 1.

3.1. Spray studies

The behaviour and evolution of the sprays were studied using high speed shadowgraphs and a derivative edge detection algorithm. The use of this technique was motivated against elastic scattering because of the difficulties involved in discriminating the border between of vaporised fuel and surrounding air in reacting environments. The difficulty of using elastic light scattering resides in the reduction of the scattering optical cross section caused by the degradation of fuel by pyrolysis into alkenes and other unsaturated hydrocarbons [20,21]. Thus, it is advantageous to use techniques based on diffraction index variations and light extinction for vapour–air interface localisation, such as schlieren or shadowgraph techniques, especially on diesel sprays injected into chambers at very high gas pressures where light scattering by the gas is important.

Shadowgraphs were generated using a collimated light beam and captured by a monochromatic, non-intensified CCD, high speed camera. The camera’s optical objective was slightly back-focused, capturing shadowgraphs and images of flame radiation simultaneously at a rate of 30,000 frames per second. A schematic drawing of the experimental set-up is shown in Fig. 2. The acquired images were digitally post-processed and used to measure the spray cone angle \( \alpha \) and the penetration of the continuous liquid phase, droplets and vapour of the spray. Spray breakup, spray penetration and the half-cone angle \( \alpha/2 \) are schematically illustrated in Fig. 3.

Images of each complete injection sequence were normalised relative to the first image of the respective sequence, which was captured prior to fuel injection commenced. In addition, histogram equalization was performed to enhance the contrast of each image. This procedure minimizes the effect of the attenuation caused by optical vignetting and variations in illumination intensity attributable to misalignment of the optical systems due to temperature variations and lamp degradation. It also simplifies the image processing algorithm.

Fig. 4 shows three graphs. The upper row \( p \), depicts a shadowgraph of a fuel being injected into the combustion chamber at a given instant, the middle row \( s \), plots an intensity profile of the former shadowgraph along the injection axis, i.e. line between \( i_s \) and \( i_r \); meanwhile the bottom row \( d \) depicts a plot of the derivative of the intensity profile along the injection axis, \( t \). The three figures are divided by five vertical lines into six zones with variations of light intensity to indicate the following spray zones: liquid core, droplets, vapour and flame. The “a” zone corresponds to a continuous liquid phase, in which there is almost constant light attenuation. At the border between the end of this zone and the zone marked “b” there is a sharp drop in light extinction, indicating a
this zone ("c") the intensity profile plot reaches unity indicating that droplets are no longer present. However, the minor attenuation of light perceptible in zone "d" is caused by a slab of droplets that had a longer lifetime, which may become a rich lump of fuel vapour. Zone "e" represents a region in which flames and vapor coexist. The frontiers of this zone can be identified by the variations in the texture, diffraction index and, most notably, the emission of light from some spots in this zone manifested in the intensity profile as intensity values greater than unity. Vapour borders are identified by a similar algorithm. After combustion it is assumed that combustion is governed by diffusion thus vapour and flame have the same borders, hence same translational velocities. There are no vapour or combustion events in zone "h".

3.2. Combustion studies

Flame temperature and soot concentration were measured by emission-based, line of sight optical methods in the middle section of the combustion chamber. The interrogation area had a height of 50 nm. An optical arrangement of mirrors, lenses, beam splitters, and filters was coupled to a pair of photodiodes, with a spectral response between 190 nm and 1000 nm and a rise time of 1 μs. Measurements were performed using interference filters with a transmission centred at 450 nm, 532 nm, and 650 nm with a full width, half maximum (FWHM) of 40 nm. The bands monitored using these filters are referred to hereafter, for convenience, as 450 nm, 532 nm and 650 nm bands, respectively. Measurements at 650 nm were not used for flame temperature or soot concentration calculations. Each of the optical detectors was coupled to a positive singlet quartz lens with a focal length \( f = 100 \text{ mm} \). A schematic drawing of the experimental set-up used for these measurements is shown in Fig. 5. The experimental set-up for soot and flame temperature measurements was calibrated by measuring the transmission and reflection of the optical components with the aid of a commercial spectrometer. The detectors’ response was obtained from the manufacturer.

Flame temperature was measured assuming that soot particles and flame are in thermal equilibrium by the aid of the two-colour method to measure the temperature of incandescent soot particles. This method estimates soot temperature by comparing its spectral radiation at two separated wavelength intervals. The total spectral radiation, \( Q_{\text{rad}} \), from a body of emissivity \( e_i \), included in the wavelength interval between \( \lambda_1 \) and \( \lambda_2 \), can be calculated according to Planck [22] (Eq. (7)), where \( h \) is Planck's constant, \( c \) the speed of light, \( \lambda \) the light wavelength, \( k_B \) Boltzmann’s constant and \( T \) is the particle temperature.

\[
Q_{\text{rad}_{\lambda_1-\lambda_2}} = \int_{\lambda_1}^{\lambda_2} e_i \frac{2\pi h c^2}{\lambda^5} \left( \frac{1}{e^{h c / (\lambda k_B T)} - 1} \right) d\lambda
\]  

(7)

The emissivity, \( e_i \), of flames containing incandescent soot particles such as DI diesel sprays [23–26] can be calculated from Eq. (8), where \( k_i \) is an absorption coefficient related to the amount of soot, \( s \) the geometric thickness of the flame along the detection system, and \( x \) a specific coefficient that depends on the wavelength, particle size and flame structure [27]. Variations of \( x \) in the visible region are small and often neglected, thus allowing \( x \) to be treated as a constant [28,29]. Combining Eq. (7) with Eq. (8) leads to Eq. (9), which relates the total radiation from soot particles to the abovementioned parameters.

\[
e_i = 1 - e^{(-x s)}
\]

(8)

\[
Q_{\text{rad}_{\lambda_1-\lambda_2}} = \int_{\lambda_1}^{\lambda_2} \left( 1 - e^{(-x s)} \right) \frac{2\pi h c^2}{\lambda^5} \left( \frac{1}{e^{h c / (\lambda k_B T)} - 1} \right) d\lambda
\]

(9)
The flame temperature is calculated using the ratio between the intensity of electromagnetic radiation at two separated wavelength intervals. The ratio between emission amplitudes $R(T, \lambda, m)$, at these two different wavelengths intervals corresponds to a given temperature. Using this approach, temperature calculations are independent of particle size and particle concentration. The ratio between emission amplitudes at these two different wavelengths intervals corresponds to a given temperature. Using this approach, temperature calculations are independent of particle size and particle concentration.

$$R(T, \lambda, m) = \frac{Q_{rad}(\lambda, N)}{Q_{rad}(\lambda, N)} \frac{I_{bf}(\lambda, N)}{I_{af}(\lambda, N)} \frac{D_{bf}(\lambda, N)}{D_{af}(\lambda, N)}$$

(10)

The ignition delay, i.e. the time until ignition commences, was measured with the aid of the shadowgraph images by detecting variations in the refractive index in the spray region. A sudden variation in the refractive index serves as an indicator of an increase in the gas temperature. Electromagnetic emission was measured in the spray region. A sudden variation in the refractive index serves as an indicator of an increase in the gas temperature. Electromagnetic emission was measured in the spray region. A sudden variation in the refractive index serves as an indicator of an increase in the gas temperature.

### 3.3. Engine studies

The single cylinder research engine used in the experiments consists of a basic AVL Type 501 with a cylinder head from a production Volvo 12-l engine (D12C). The engine is equipped with a unit-injector and a remote injection control system. Details of the engine and the emission analysis equipment used in the experiments are given in Tables 3 and 4. The regulated emissions NOx and HC were measured in ppm (vol.) in wet conditions, while CO and CO2 were measured in dry conditions. Soot emissions were measured in filter smoke number (FSN) units, converted to mg/m³ [30] then further converted to g/kWh [16].

Steady state emission measurements were performed according to the ECE R49 13-mode cycle, in which the engine speed and the load are varied stepwise. To calculate total emissions, appropriate weighting factors for each of the 13 modes were used.

### 4. Results

#### 4.1. Fuel characterisation

There is a marked difference in the appearance of the emulsion and microemulsion fuels due to the differences in the sizes of the water drops in them. The relatively large water drops in the emulsion fuel across the studied temperature range was similar to that of the regular diesel (Fig. 7). The high apparent surface tension of the water-containing fuels is higher than the viscosity of EUD as displayed in Fig. 6, but the surface tension of the emulsion fuel across the studied temperature range was similar to that of the regular diesel (Fig. 7). The high apparent surface tension of the microemulsion fuel provide further indications of its internal structure, and thus were also determined (Table 5).

The viscosity of the water-containing fuels is higher than the viscosity of EUD as displayed in Fig. 6, but the surface tension of the emulsion fuel across the studied temperature range was similar to that of the regular diesel (Fig. 7). The high apparent surface tension of the microemulsion fuel provide further indications of its internal structure, and thus were also determined (Table 5).

<table>
<thead>
<tr>
<th>Component</th>
<th>Diffusion coefficients</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_{diesel}$</td>
<td>$6.5 \times 10^{-10}$</td>
</tr>
<tr>
<td>$D_{water}$</td>
<td>$9.9 \times 10^{-12}$</td>
</tr>
<tr>
<td>$D_{1185}$</td>
<td>$6.2 \times 10^{-12}$</td>
</tr>
<tr>
<td>$D_{SMD}$</td>
<td>$12 \times 10^{-12}$</td>
</tr>
</tbody>
</table>

---

**Fig. 5.** Experimental configuration used for flame temperature and soot measurement. (BS1) Broadband mirror; (BS2) beam splitter; (F1) interference filter 1; (F2) interference filter 2; (D1) photodiode 1; (D2) photodiode 2.
4.2. Spray and combustion studies

4.2.1. Penetration and lift-off

The penetration length of the continuous liquid phase, i.e. break-up length, droplets, and vapour were determined, together with flame lift-off, for sprays of each of the fuels. Fig. 8 shows three series of one in every 10 images captured along the course of a representative single injection for each fuel showing combustion luminosity superimposed onto the shadowgraph images. The upper, central and bottom rows present images corresponding to the emulsion, microemulsion and regular diesel fuel respectively. The horizontal lines delimit the section of the spray from which electromagnetic emission was detected and utilised for combustion analyses, including flame temperature and soot concentration determinations.

Arithmetic mean values of spray penetration for the continuous liquid phase, droplets, and vapour as a function of time after start of injection (ASOI) are plotted for each fuel in Fig. 9. The arithmetic mean values given correspond to the statistical data obtained for ten consecutive injections.

Figs. 10–12 show filtered-average signals of flame lift-off together with spray penetration of the continuous liquid phase, droplets, and vapour of the emulsion, microemulsion and EUD fuels, respectively. Flame lift-off length is defined as the shortest distance between the injector and flame at a given time.

4.2.2. Cone angle measurements

Spray cone angles were measured at 42 (5.8 mm) and 112 (15.6 mm) nozzle diameters downstream the nozzle in order to measure the cone angle before the break-up and before the droplets were completely evaporated. Spray cone angle measurements at these locations are shown in Figs. 13 and 14, respectively.

4.2.3. Start of combustion measurements

Probability density functions, normalised to unity, for the start of combustion (SOC), start of soot radiation (SO-Soot) and end of combustion (EOC) obtained for sprays of each of the studied fuels are plotted in Fig. 15.
Fig. 9. Arithmetic mean values of spray penetration for the continuous liquid phase, droplets, and vapour of the emulsion fuel, microemulsion fuel and EUD as function of time ASOI.

Fig. 10. Flame lift-off, filtered continuous liquid phase, droplets and vapour penetration of the emulsion fuel as function of time ASOI.

Fig. 11. Flame lift-off, filtered continuous liquid phase, droplets and vapour penetration of the microemulsion fuel as function of time ASOI.

Fig. 12. Flame lift-off, filtered continuous liquid phase, droplets and vapour penetration of the EUD fuel as function of time ASOI.

Fig. 13. Cone angle at 42 nozzle diameters (5.8 mm) downstream of the nozzle.

Fig. 14. Cone angle at 112 nozzle diameters (15.6 mm) downstream of the nozzle.
4.2.4. Singularities regarding atomisation

In the injector the temperature is close to the ambient temperature, but the pressure is high (1200 bar). However, when the fuel is injected into the combustion chamber of an operating engine, it is introduced into a hot, less pressurised environment, in which any water in the fuel is rapidly transformed into superheated steam. The effects of this phenomenon can be observed in Fig. 16, which displays three consecutive images of both a multiple injection and a single injection of each of the studied fuels. Each set of images in the figure shows the fragment of the injection sequence in which this phenomenon was noticed. Thus, the frames of the different sets do not necessarily correspond to the same instant ASOI.

4.2.5. Electromagnetic emission from the combusting sprays

Plots of the electromagnetic emission measured at the wavelength intervals $\lambda_a = 450$ nm and $\lambda_c = 650$ nm, normalised to the maximum value of EUD emission at $\lambda_c = 650$ nm are presented in Fig. 17. Furthermore, plots of the electromagnetic emission measured at $\lambda_a = 450$ nm and $\lambda_b = 532$ nm intervals, normalised to the maximum value of EUD emission at $\lambda_b = 532$ nm, are presented in Fig. 18.

4.2.6. Flame temperature and soot concentration in flames

Flame temperature and in-flame soot concentration plots, calculated from emission measured at two spectral bands ($\lambda_a = 450$ nm and $\lambda_b = 532$ nm), are depicted in Fig. 19.

4.3. Engine studies

Exhaust gas emissions of soot and NOx generated during the combustion of each of the three fuels were studied in tests with a direct injection compression ignition engine operating in the
ECE R49 13-mode cycle [16]. Weighted average results from the emission tests are given in Table 6. Large reductions in soot emissions were observed, but the NOx emissions were barely effected, when the emulsion and microemulsion fuels were combusted compared to those detected when regular diesel fuel was used.

5. Discussion

A microemulsion of oil and water can consist of either drops dispersed in the continuous domain, or continuous, interpenetrated domains of both water and oil. In a water-in-oil structure, water diffuses much more slowly, and thus has a much lower diffusion constant than the oil ($D_{\text{oil}} \gg D_{\text{water}}$). The surfactants are likely to diffuse at approximately the same rate as the water. The diffusion coefficients obtained from NMR densitometry, presented in Table 5, show that $D_{\text{oil}}$ is approximately two orders of magnitude larger than $D_{\text{water}}$, clearly indicating that the microemulsion had a water-in-oil structure.

The water-containing fuels are more viscous than regular diesel fuel (Fig. 6) since a microheterogeneous medium, such as an emulsion or microemulsion, is likely to be more resistant to shear than a homogeneous organic solvent. In accordance with most fuels, the viscosity declines with increases in temperature. A similar behaviour is noticed for the surface tension [31,32]. However, it should be noted that at temperatures higher than ca. 35 °C the microemulsion “breaks” and undergoes a phase separation. Thus, at all measuring points above the microemulsion’s phase separation threshold there are ongoing changes in the structure of the fluid due to the phase separation. Therefore, the viscosity and surface tension curves for the microemulsion in Figs. 6 and 7 are shown without connecting lines, to indicate that these are not physically valid measurements. The viscosity and surface tension values vary somewhat with time and the curves should be regarded as indicative, rather than absolute. However, they are of practical interest for the application of the microemulsion as a fuel, and the curves are therefore included in the diagrams.

Information regarding spray behaviour, flame lift-off length, start of combustion and combustion duration is presented in Figs. 8–15, which show that there were no substantial differences among the fuels in terms of the penetration of either the vapour phase or continuous liquid phase. However, there were variations in terms of the penetration of droplets, combustion duration, ignition delay and the point at which soot starts to emit visible radiation.

Concerning droplets penetration, it is shown that the microemulsion fuel penetrates furthest, followed, in decreasing order, by the emulsion fuel and the regular diesel fuel (EUD). These variations in penetration can be attributed to differences in volatility and also to the droplet size distribution. It is expected thus that the addition of water leads to longer penetration because of the lower volatility of the water as is the case for the water-containing fuels which penetrate longer than compared to the regular diesel fuel. Nevertheless, for the case of comparing the emulsion and the microemulsion the effects caused by the surfactant in atomisation or microemulsion, seem to compete to the consequences of the volatility of the mixture. In spite of the high amount of surfactants contained in the microemulsion, which would lead to a reduction in the surface tension and therefore smaller droplets, it also results in a mixture with lower volatility than the emulsion, having as a final outcome a mixture that penetrates longer.

By comparing Figs. 9–14, it is observed that the penetration of droplets is almost constant before ignition. After ignition takes place the penetration of droplets shortens. This can be attributed to hot gases entering into the spray favouring the vaporisation of droplets. Furthermore, when radiation from soot commences this vaporisation process is enhanced even more.

A minimum lift-off distance (Figs. 10–12) is reached as the flame propagates in the up-stream direction near EOI when either EUD or the microemulsion fuel is combusted. Conversely, for the emulsion fuel the flame lift-off remains almost constant throughout each injection. The flame lift-off increases when injection of all three fuels ceases, but slightly later for the water-containing fuels compared to EUD.

The spray cone angle measured at 42 nozzle diameters downstream the injector (Fig. 13), show that the emulsion fuel yields to the widest cone angle followed by EUD and the microemulsion fuel. The sprays narrow and reach an approximately steady state shortly after SOI (~1 ms). However, the spray cone angle for EUD
continues narrowing faintly but monotonically after the start of combustion \((t \sim 2 \text{ ms ASOI})\). This behaviour can be explained by the influence of flame radiation and hot air entrainment exerted on the spray. EUD is influenced by these phenomena more than the water-in-diesel fuels because of its higher volatility.

The measurements of spray cone angles 112 nozzle diameters downstream of the nozzle (Fig. 14) show that the cone angles of all of the sprayed fuels decline with time, especially briefly after the SOI. Nevertheless, the wideness of the spray from the microemulsion fuel continues almost unaffected because of its low volatility. The constant narrowing of the emulsion fuel and EUD occurs as the radiation from the soot in the flame increases.

The start of combustion (SOC), start of soot radiation (SO-Soot), and end of combustion (EOC) probability density functions are presented in Fig. 15. It is noticed that the water-containing fuels have a slightly longer ignition delay and longer combustion duration than the EUD which can be attributable the lower flame temperature (Fig. 19).

A particular phenomenon, named micro-explosions in the literature, was observed when the water-containing fuels were injected into the combustion chamber (Fig. 16). The presence of glowing spots in their flames, unnoticed for EUD, is believed to be caused by the rapid vaporisation of the water contained in the fuels. It is plausible that water becomes superheated steam rapidly after being introduced into a very hot environment such as the combustion chamber.

Flame temperature and soot concentration were measured by comparing the electromagnetic emission from the flames in different spectral bands. The selection of spectral bands for this purpose must be very meticulous because of the strong interference of chemiluminescence from the additives employed for the preparation of the water-containing fuels in some part of the spectrum. Fig. 17 shows the electromagnetic emission from thecombusting fuels in two spectral bands \((\lambda_a = 450 \text{ nm and } \lambda_c = 650 \text{ nm})\) relative to those from the regular diesel (EUD) emission at \(\lambda_c\). Anomalously high electromagnetic emission centred at \(\lambda_c\) was detected from the water-containing fuels. Further, the emission ratio between the microemulsion fuel and EUD is almost four times larger than the emission ratio between the emulsion fuel and EUD. Coincidently the amount of additives used in the microemulsion fuel is five times more than for the emulsion fuel. Nevertheless, the electromagnetic emission of the water-containing fuels at \(\lambda_a\) and at \(\lambda_b\) \((532 \text{ nm})\) are weaker than those from the radiation from EUD as shown in Fig. 18.

The absence of chemiluminescence at \(\lambda_b\) \((532 \text{ nm})\) from the water-containing fuel additives, allows the flame temperature and soot concentration of the combusting sprays to be measured by comparing their relative emissions at two wavelength bands without interference from the additives. In spite that flame temperature is measured by measuring the temperature of the soot particles in the flames, interference due to chemiluminescence peaks from the fuel additives would have resulted in biased and inaccurate measurements. Therefore the temperature measurements are conducted at \(\lambda_a\) nm and \(\lambda_b\).

If \(\lambda_a\) and \(\lambda_c\) \((450 \text{ and } 650 \text{ nm})\) had been used for the temperature measurements the resulting errors would have led to estimated flame temperatures of ca. 2000 K for the water-containing fuels, with relative soot values exceeding corresponding values for EUD.

Fig. 19 shows the average flame temperature and average soot concentration calculated from measurements at \(\lambda_a\) and \(\lambda_b\) \((450 \text{ and } 532 \text{ nm})\) bands relative to EUD. Less soot is formed and soot levels rapidly reach a plateau when the water-containing fuels are combusted, while soot concentrations continue to increase during the combustion of EUD until close to EOI \((t \sim 3.8 \text{ ms ASOI})\). In addition, the microemulsion fuel produces slightly lower levels of soot than the emulsion fuel. It is presumed that the reduced flame temperature inhibits soot production [10], this supports the measurements presented here in which EUD has the highest flame temperature and highest levels of soot concentration in flames.

The engine results (Fig. 20) show there were corresponding reductions in exhaust soot emissions of 81% and 89% when the emulsion and microemulsion fuels were used, relative to those emitted when EUD was combusted. This is believed to be due to the combined effects of lower flame temperatures, lower concentrations of soot in the flames, rapid evaporation of water and the presence of hydroxyl radicals from water dissociation, all of which promote the oxidation of soot to CO.

The previous engine tests [16] also showed that combustion of water-in-diesel fuels yielded to no reductions in nitrogen oxides \((\text{NO}_x)\) even if the flame temperature of these water-in-diesel fuels is lower than the regular diesel, EUD fuel (Fig. 19), which would normally be expected to reduce levels of NO\(_x\) emissions. However, the cited engine experiments were conducted without correcting for combustion phasing. Furthermore, the prompt presence of radiation from soot and the enhanced atomisation of the water-containing fuels caused by the rapid evaporation of water led to a higher degree of premixed combustion (Fig. 21), with higher...
in-cylinder pressure, temperature (Fig. 22) and hence causing higher levels of NO\textsubscript{x} emissions. Because of the short ignition delays and low soot concentrations measured in the flame using these water-in-diesel fuels (see Figs. 15 and 19), it appears profitable to conduct these engine tests by retarding the start of ignition, achieving thus, a possible reduction in both soot and NO\textsubscript{x} emissions.

6. Conclusions

The combustion studies with the HP/HT Spray Rig showed that the water-in-diesel fuels yielded to flames with lower temperature and lowered soot concentrations than the pure regular diesel fuel. Furthermore, spray behaviour studies demonstrated that droplets of the water-containing fuels penetrated further than droplets of the regular diesel fuel, which is correlated with the relatively low volatility of the water. The combustion of the water-in-diesel fuels resulted in electromagnetic emission with an abnormal peak around $\lambda \sim 650$ nm, attributable to chemiluminescence from the surfactant. This abnormal luminosity prevents measurements of flame temperature or soot concentration based on black body radiation across the entire visible spectrum. Therefore, soot concentration and temperature measurements by the employment of commercial pyrometers with a colour camera detector which principle is based on the two-colour method may produce abnormal and biased results. Nevertheless, it is still possible to measure soot concentration and flame temperature using the two-colour method by a carefully selection of spectral filters.

Ignition delay tests show that the water-in-diesel fuels have a slightly longer ignition delay but exhibit a prompter presence of radiation from soot than the pure regular diesel fuel, furthermore, the enhanced atomisation caused by the rapid evaporation of water may yield to a higher degree of premixed combustion. If such fuels are combusted in a diesel engine, the aforementioned factors will lead to higher in-cylinder pressure and temperature, resulting in higher levels of NO\textsubscript{x} emissions. This explains the findings of previous engine tests, which were carried out without adjusting combustion phasing, resulting in elevated exhaust NO\textsubscript{x} emissions even though the flame temperature of the water-in-diesel flames are lower than those of the regular diesel fuel.

Acknowledgements

The authors would like to express their gratitude to the Combustion Engine Research Centre (CERC) at Chalmers, and both for financial support and also AkzoNobel Surface Chemistry AB and the Knowledge Foundation through its graduate school YPK for financial support. Special thanks are also due to Dr. Savo Gjirja.

References