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Water-in-diesel emulsions and related systems

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Abstract

Water-in-diesel emulsions are fuels for regular diesel engines. The advantages of an emulsion fuel are reductions in the emissions of nitrogen oxides and particulate matters, which are both health hazardous, and reduction in fuel consumption due to better burning efficiency. An important aspect is that diesel emulsions can be used without engine modifications. This review presents the influence of water on the emissions and on the combustion efficiency. Whereas there is a decrease in emissions of nitrogen oxides and particulate matters, there is an increase in the emissions of hydrocarbons and carbon monoxide with increasing water content of the emulsion. The combustion efficiency is improved when water is emulsified with diesel. This is a consequence of the microexplosions, which facilitate atomization of the fuel. The review also covers related fuels, such as diesel-in-water-in-diesel emulsions, i.e., double emulsions, water-in-diesel microemulsions, and water-in-vegetable oil emulsions, i.e., biodiesel emulsions. A brief overview of other types of alternative fuels is also included.

Keywords: Emulsion; Diesel; Emission; NO_x; Particulate matter; Hydrocarbon; Carbon monoxide; Engine; Combustion

Contents

1. Introduction

Emulsions of water in diesel for use in internal combustion engines are easily applicable alternative fuels for the existing vehicle fleet. The emulsion fuel is defined as an emulsion of water in standard diesel fuel with specific additives, surfactants, to stabilise the system.

There is a growing interest in the use of diesel emulsions and environmental aspects are the main driving force. As is discussed in some detail below the presence of water has a significant effect on several emission constituents: exhaust gases such as nitrogen oxides (both NO and NO_2, which are collectively referred to as NO_x) and carbon monoxide (CO), as well as black smoke and particulate matter. There may be a certain loss

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in engine performance due to the presence of water, but the diesel consumption is often reduced. A typical water content of the diesel emulsions is between 10 and 20%.

Both the global and the local effects of the emissions on the environment are of concern for the use of alternative fuels for vehicles. The global effect due to the gradual increase of CO_2 in the atmosphere was the decisive factor behind the Kyoto protocol of 1997. In the transport sector the use of renewable fuels is the most effective way of limiting the net increase of CO_2 in the atmosphere. Also replacement of diesel and gasoline by natural gas will reduce the CO_2 emissions due to its lower carbon-to-hydrogen ratio, although the gain will be much less than for a renewable fuel. For the local effect of the emissions most focus is placed on the health hazardous NO_x and particulate matter emissions. For new engines these emissions are strictly regulated by legislation. In the so-called Euro 4, effective from 2005, and in the coming Euro 5, which will be in force from 2008, the emissions of NO_x, particulate matter, hydrocarbons and carbon monoxide are clearly regulated. For existing vehicles other rules apply.

Large scale use of emulsion fuels is of considerable interest also to the surface chemistry community. Considering the enormous volume of diesel fuel that is being consumed today, a replacement of just a fraction of regular diesel by water-in-diesel emulsion would mean that a new and very large application for surfactants had been created. The stability requirements on such emulsions are obvious: they need to stay stable for a specific time and over a wide temperature span. The surfactants used, i.e., the emulsifiers, must burn readily without soot formation and should not contain sulphur and nitrogen. Thus, they should contain only carbon, hydrogen and oxygen and they should preferably not have aromatic rings in their structure. Nonionic surfactants based on aliphatic hydrocarbon tails, such as alcohol ethoxylates, fatty acid ethoxylates and sugar esters of fatty acids, are typical candidates. This review will present the current status of water-in-diesel emulsions and also comment on the development in some related areas.

2. Water-in-diesel emulsions

The interest in water-in-diesel emulsions derives from the fact that water in the form of micrometer-sized droplets exerts some positive effects on the combustion of the fuel. Water-in-oil emulsions have been formulated and evaluated for most types of fuels, ranging from light hydrocarbons to triglycerides. However, the main interest in the concept lies in water-in-diesel emulsions. The main reason for a stronger interest in incorporating water in diesel than in gasoline is that the high combustion temperature and the high pressure that exist in diesel engines is particularly suitable for the concept. This was found experimentally [1] and verified by theory [2] almost 30 years ago. Use of diesel emulsions has been shown to give several interesting effects, such as (i) reduced nitrogen oxides (NO_x) emission and also lower soot and particulate contents in the exhaust, and (ii) improved combustion efficiency. These aspects on the use of water-in-diesel emulsions will be discussed below.

2.1. Reduced emissions

The presence of water in diesel fuels brings about a considerable reduction in NO_x and in particulate matters (PM) emission [3–8]. It is probably true to say that the effect on the emissions is the main reason for the large interest in diesel emulsions today. It has been reported that 15% water in the diesel can give a reduction in nitrogen oxide (NO_x) emission of up to 35% under regular conditions [9]. Such level of NO_x reduction has also been reported by other authors [6,10–13]. However, it relates to diesel and other lighter hydrocarbon fractions with very low nitrogen content. For fuels with high nitrogen contents, such as some residual oils, the NO_x in the exhaust comes mainly from oxidation of the nitrogen-containing fuel components and in such cases emulsified water has only a small effect on the NO_x level [14]. For diesel fuels there may be a concomitant increase in emission of carbon monoxide (CO) as well as in hydrocarbons [9]. The amount of PM in the exhaust from fuels with high nitrogen contents is normally significantly reduced [14].

Experimental studies have been made on the effect of water in the form of water-in-diesel emulsion on the formation of polycyclic aromatic hydrocarbons, some of which are known to be mutagenic [15]. Emulsion fuels were found to give lower amounts of polycyclic aromatic hydrocarbons in the flame, as well as reduced emission to the atmosphere. A more specific analysis showed a decrease of two substances, pyrene and fluorene, when the fuel was an emulsion. It is believed that the microexplosions, see below, promote oxidation of the hydrocarbons, possibly involving attack by hydroxyl radicals. The reduced amount of formed polycyclic aromatic hydrocarbons is probably one of the reasons for the lower amount of soot obtained with emulsion fuels because these hydrocarbons can be seen as precursors for soot particles.

The reduction in soot formation has been demonstrated in several ways. Using a CCD camera with an image intensifier synchronized with a laser pulse it has been shown that the highly sooting region of the spray flame exists along the central axis of the flame and that the soot concentration profile is very heterogeneous. Fig. 1 shows how the amount of water in a water-in-dodecane emulsion affects the soot formation [16]. As can be seen, there is a very large decrease in soot content by mixing in 5% water. Further addition of water gives only a small extra reduction. It can also be seen that increased water content gives an increase in the time between fuel injection and the peak in soot formation. The time effect is most likely due to either better mixing of air and fuel as a result of the microexplosion phenomenon, or decrease in flame temperature caused by the water, or a combination of the two.

The size of the water drops in the emulsion, i.e., the degree of dispersion of the water, is probably an important factor for the emissions. This issue does not seem to have been studied in a systematic way for diesel fuels. However, for combustion of emulsified heavy fuel oil it was found that the finer the water dispersion, i.e., the smaller the droplets of the water-in-fuel emulsion, the smaller the amount of water was needed to obtain good results in terms of reduced coke emission [17]. Thus, it is the oil–water interfacial area, not the amount of water incorporated in

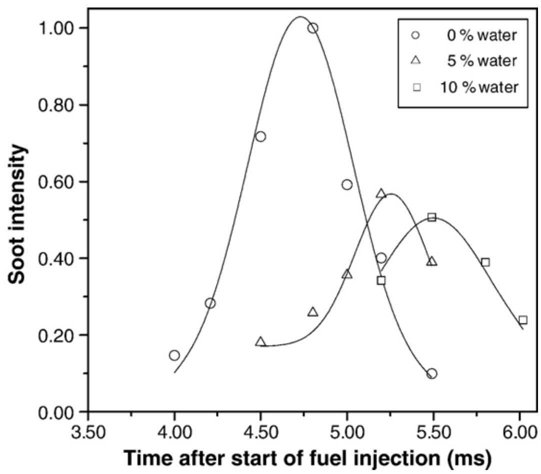

Fig. 1. Effect of water content of water-in-dodecane emulsions as a function of time on the total amount of soot yielded in the diesel spray flame. (Redrawn after Ref. [16].)

the fuel per se, that governs the efficiency in reducing the emissions. Obviously, good surfactants are needed to formulate emulsions with small water droplets.

A recent report from the Texas diesel fuels project, where emissions of NO_x, CO, PM and hydrocarbons have been monitored together with fuel efficiency, showed a considerable reduction in both NO_x and PM along with a decrease in fuel efficiency (calculated based on total fuel, i.e., on diesel + water in the case of the emulsion). The emulsion fuel, named PuriNOx produced increased levels of specific oxidation products such as formaldehyde, acetaldehyde, acrolein and methyl ethyl ketone [18].

Schlitt and Exner have compared water-in-diesel emulsions with humidified intake air, i.e., water in the form of an aerosol [19]. It was found that both systems reduced the NO_x level compared to traditional diesel fuel. Only the emulsion was effective in reducing also the soot level, however.

The water level in the studies on diesel emulsions varies. Most authors use a water content of 5–10% but higher percentages have also been investigated. It has been claimed that the optimum water content for PM reduction is between 10 and 20% [1]. Samec et al. studied the effect of 10 and 15% water in the diesel on emission levels of NO_x, hydrocarbons and soot, as well as on the specific fuel consumption. The values obtained, relative to the values for neat diesel, are shown in Fig. 2a–c [20]. As can be seen, there is a considerable reduction in both hydrocarbons and soot already at 10% water. The NO_x reduction seems to be more water dependent and a 15% level is needed in order to obtain a significant effect. However, also the 15% water level did not produce the very high values of NO_x reduction that had been reported in earlier work [9].

In one study up to 40% water was used in combustion tests and the general picture of considerably reduced NO_x and smoke reduction and of small effects on CO and hydrocarbon emissions was maintained over the entire composition range [10]. Another study on the use of emulsions with high water content showed a slightly different picture [11]. The NO_x and soot levels were significantly reduced at water contents between 15–45% but there was an increase in the CO and hydrocarbon emissions with increasing water content. The latter increase could, at least partly, be overcome by preheating the intake air. Very high water content is hardly economic, however, since it requires high amounts of emulsifier. In addition, one can anticipate stability problems with emulsions of high water-to-hydrocarbon ratios.

The Aquazole formulation from TOTAL S.A., which is a water-in-diesel emulsion, has been claimed to bring about a reduction in NO_x emission of up to 30% together with a reduction in black smoke of up to 80% [12,13]. Aquazole also reduces hydrocarbon

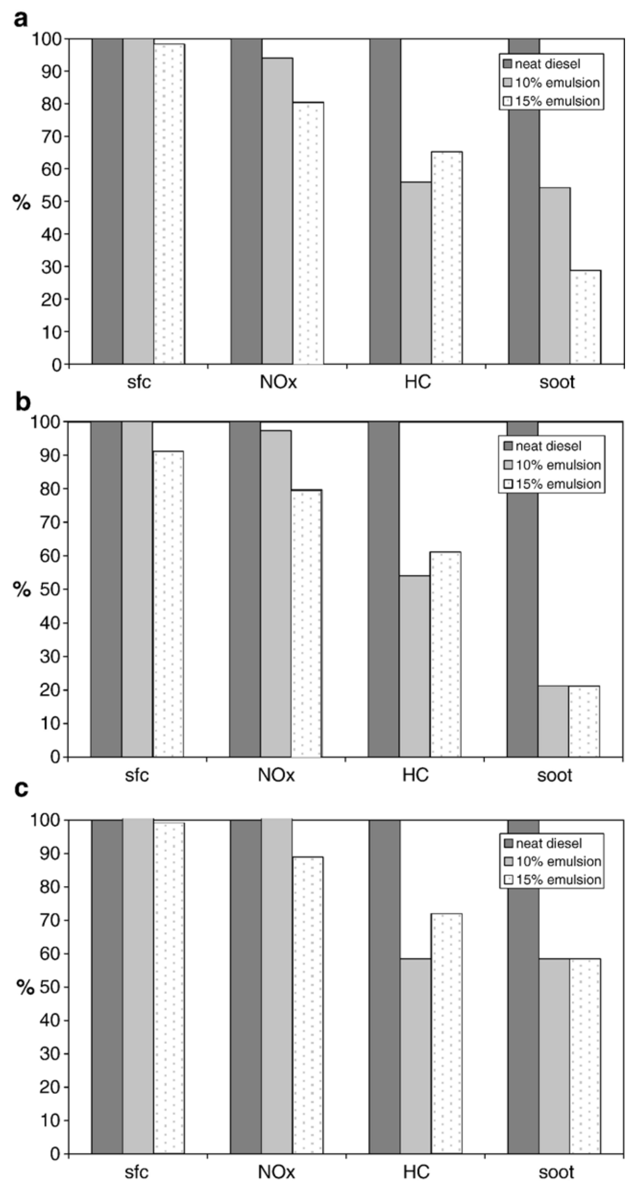

Fig. 2. a. Relative reductions of specific fuel consumption (sfc) and of exhaust emissions of nitrogen oxides (NO_x), hydrocarbons (HC) and soot. Engine-operating regime: exhaust pressure (p_e) = 10 bar, engine speed (n) = 1700 rpm. (Redrawn after Ref. [20].) b. Relative reductions of specific fuel consumption (sfc) and of exhaust emissions of nitrogen oxides (NO_x), hydrocarbons (HC) and soot. Engine-operating regime: p_e = 8 bar, n = 1700 rpm. (Redrawn after Ref. [20].) c. Relative reductions of specific fuel consumption (sfc) and of exhaust emissions of nitrogen oxides (NO_x), hydrocarbons (HC) and soot. Engine-operating regime: p_e = 5 bar, n = 1700 rpm. (Redrawn after Ref. [20].)

consumption, although only marginally. By using an oxidation catalyst the emission level of CO, as well as of hydrocarbon, is also reduced and so is the amount of PM. Aquazole is in use today on a large number of vehicles in France and other countries in Southern Europe.

2.2. Improved combustion efficiency

By investigating emulsion fuels with varying amounts of water Abu-Zaid showed that the presence of water had a positive effect on the combustion efficiency of a single cylinder, direct injection diesel engine [21]. Fig. 3 shows how water in the form of an emulsion affects the engine torque output for various speeds. The emulsions are made using a mixture of two nonionic surfactants, Span 80 and Tween 80, as emulsifiers. The surfactants are used in a combined amount of 2 vol.%. Span 80 is sorbitan monooleate and Tween 80 is ethoxylated (20 oxyethylene units) sorbitan monooleate. Span 80 is a very hydrophobic surfactant and Tween 80 is a very hydrophilic surfactant. When used alone none of them is a good emulsifier but a mixture of the two is known to be efficient and is widely used for various emulsification purposes. It is a generally established fact that a mixture of two surfactants, one more hydrophobic and one more hydrophilic, often gives better emulsification result than a single surfactant with intermediate hydrophilic–lipophilic balance [22,23].

The general appearance of the curves should be interpreted as follows. At low speed, the torque increases as the engine speed increases. At around 1500 rpm the torque starts to decrease because the engine is unable to ingest full charge of air. This effect becomes very pronounced at high speeds (above 3000 rpm in the figure).

It can be clearly seen from the figure that addition of water in the form of an emulsion has a positive effect on the combustion efficiency. The torque increases with water content over the entire rpm range. When the charge is fired in the cylinder, the water will turn to steam with high pressure.

Another likely reason for the improved combustion efficiency is that the presence of water and, in particular, the presence of the oil–water interface with very low interfacial tension, leads to a finer atomization of the fuel during injection [24]. A finer dispersion of the fuel drops leads to higher contact with the air during the burning process, which is obviously advantageous for the combustion. It has been postulated that water in the fuel improves the combustion process owing to the simultaneous additional rupture of the drops, to the increase in evaporation surface of the drops, and to better mixing of the burning fuel in air [25].

Fig. 4 shows the brake specific fuel consumption as a function of engine speed for various contents of water in diesel [21]. Again the water is in the form of a water-in-diesel emulsion using a mixture of Span 80 and Tween 80 as emulsifier. The fuel is here calculated as the hydrocarbon only, i.e., the water in the diesel is not included in the fuel.

As can be seen from the figure, the brake specific fuel consumption decreases with increasing engine speed up to around 2100 rpm, after which it increases. The high consumption at low engine speed is believed to be due to heat loss to the combustion chamber walls and the high consumption at high engine speed is claimed to be caused by high friction [21]. The fuel consumption decreases with increasing water content over the investigated rpm range. Similar results have been obtained by other workers [26,27]. The influence of the water may be attributed to an influence on the atomization process, as well as on the ignition temperature [28,29].

When a water-in-diesel emulsion is heated, the water in the droplets is vaporized first because water is more volatile than diesel. The vaporization will cause the continuous hydrocarbon phase to “explode”. This occurs at a temperature much above the boiling point of water, around 270 °C, which is referred to as the superheat limit temperature. It is a general phenomenon that in order to make systems of a lower-boiling liquid immersed as droplets in a higher-boiling liquid “explode” one must reach a temperature far above that of the lower-boiling component. This

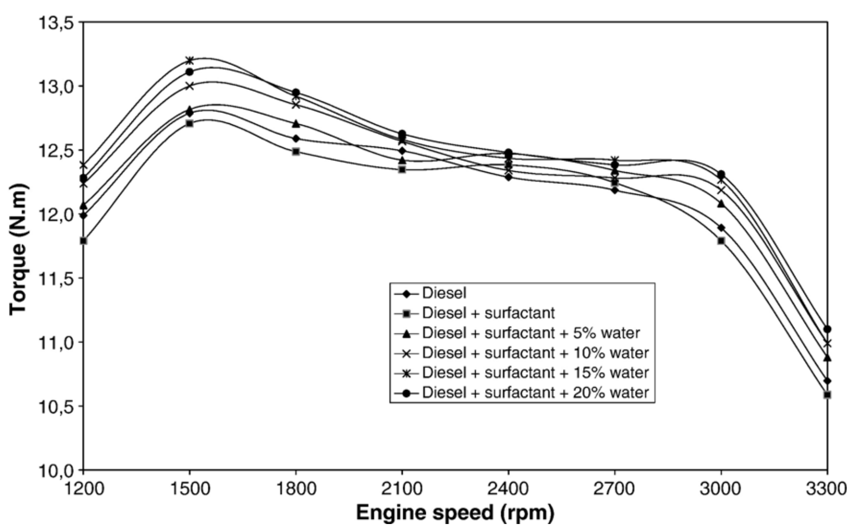

Fig. 3. Engine torque output versus engine speed using water-in-diesel emulsions as fuel. (Redrawn after Ref. [21].)

phenomenon, known under the name microexplosion, helps in the atomization of the fuel. The violent disintegration is beneficial for the mixing of fuel and air because the air–fuel interfacial layer will be larger than in the corresponding process without microexplosions. The net result will be that the combustion reaction and the burning efficiency will be improved; thus, the fuel consumption will be reduced. The microexplosion also helps in suppressing the formation of soot and unburned hydrocarbons, as was discussed in the section "Reduced emissions" above. There is a vast literature dealing with microexplosion of fuel emulsions [16,30–45] and some of the results reported will be commented on below.

Wang and co-workers have investigated the combustion characteristics of drops of a number of alkanes (*n*-heptane, *n*-decane, *n*-dodecane, *n*-hexadecane, and isooctane) emulsified with various amounts of water and freely falling in a furnace of controlled temperature [30–32]. The objective was to evaluate how the water of the emulsion affected the combustion. It was found that the burning time was significantly reduced for the emulsions compared to water-free alkanes. The effect is believed to be due to reduction of the ignition delay and to advancement of the onset of the microexplosion.

Different methods have been employed to study the microexplosions. Sheng et al. used holography and high-speed photography to study drop combustion in emulsion fuels [33]. A Schlieren optical system together with a high-speed camera has also been used [34]. Hang et al. employed a so-called Fraunhofer holographic system and high-speed Schlieren photographic technique to study the atomization and vaporization of a spray of a diesel emulsion in a high temperature combustion bomb [35]. They showed that the emulsion was better atomized than the neat hydrocarbon. A high-speed video camera with laser illumination has also been used to document the microexplosions of fuel drops consisting of water in light oil [36].

Water may be introduced into the fuel either as an emulsion or as a microemulsion. (Water-in-diesel microemulsions are treated in a separate section below.) A comparison of the atomization characteristics between macro- and microemulsions has been made [37]. It was found that macroemulsions produced smaller drops in the flame.

The microexplosion characteristics of the emulsion drops over a hot plate have been studied and so has the effect of pressure on this drop-plate system [38]. The drop gasification over a hot plate is called the Leidenfrost phenomenon [39,40] and the evaporation characteristics of drops consisting of water-in-hydrocarbon emulsions have been thoroughly investigated by Avedisian [41,42]. The secondary atomization process has been studied by laser light scattering and a beneficial effect of water on soot formation was detected [43]. Based on systematic work on microexplosions of water-in-hydrocarbon emulsions, using a range of hydrocarbons from hexane to hexadecane, also including gasoline and diesel fractions, a mathematical model of the microexplosion phenomenon has been constructed that takes into account variables such as temperature, drop size and parent fuel properties [44].

In a relatively recent work various aspects of microexplosions of water-in-diesel fuels have been studied and a model to predict the occurrence and the strength of microexplosions has been put forward [45]. The authors postulate that the drops formed in the atomization process, which consist of emulsified microdroplets of water in the surrounding diesel fuel, first change their internal structure so that an oil membrane is formed at the boundary. The reason for this is that the water in the microdroplets close to the boundary vaporizes more easily than water confined in microdroplets in the interior of the droplet, leaving a layer, or membrane, of neat oil surrounding the remaining water-in-diesel emulsion. The thickness of the oil membrane has been calculated to be of the order of 10–20 μm. It is these core-shell drops, see Fig. 5, that burst when the temperature is high enough. The thickness of the oil membrane dictates the strength of the microexplosion. If the membrane is too thin, due to incomplete evaporation of water from the outer water microdroplets, the drops become too unstable. If the membrane has become too thick, there is not enough water left to cause a strong burst.

It was further demonstrated that the oil–water interfacial tension in the system (which is low due to the presence of surfactants) is not decisive for the superheat limit temperature,

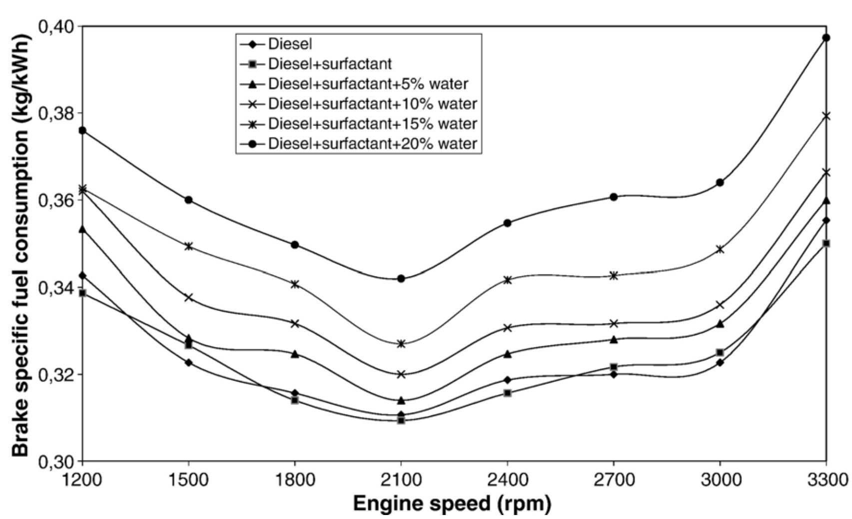

Fig. 4. Brake specific fuel consumption versus engine speed using water-in-diesel emulsions as fuel. (Redrawn after Ref. [21].)

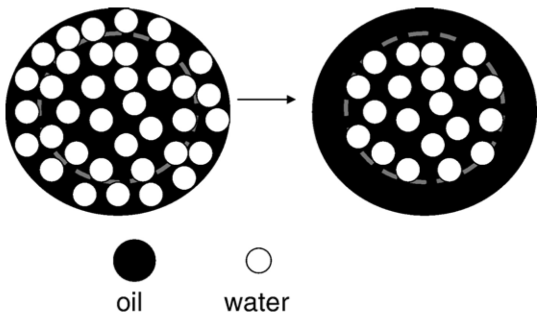

Fig. 5. Formation of the oil membrane in the atomization process after fuel injection in the cylinder. Evaporation of water microdroplets in the periphery gives a membrane of oil. (Redrawn after Ref. [45].)

i.e., the microexplosion occurs at approximately the same temperature regardless of the choice of emulsifier [45]. The microexplosion phenomenon was also found to be independent of the viscosity of the emulsion. Degassing the emulsion can slow down the microexplosion because dissolved gas can reduce the superheat temperature of water.

3. Diesel-in-water-in-diesel emulsions

Double emulsions of the type oil/water/oil (O/W/O), where oil is diesel, have been investigated by Lin and Wang [28,46–49]. It was found that the viscosity of the double emulsions was higher than for the normal emulsions but the higher viscosity was not a problem in the use of the formulation as a fuel [46]. The benefits in terms of reduced emissions obtained with water-in-diesel emulsions were obtained also with the O/W/O formulations. The double emulsions seemed to give even lower levels of NO_x and CO than the regular emulsions although the differences were relatively small. With regard to engine performance and combustion characteristics the double emulsions gave a higher exhaust gas temperature. Studies were made on the use of diglyme (diethylene glycol dimethyl ether) as an additive [47]. Diglyme is sometimes used to improve combustion characteristics in diesel engines. It was found that addition of diglyme caused stability problems for the double emulsions. Most likely, the diglyme dissolves in the water phase and makes this a better solvent for the surfactant, causing desorption of the surfactant from the oil–water interface. Addition of diglyme also caused stability problems for normal water-in-diesel emulsion but the effect on stability was less pronounced in this case.

4. Water-in-diesel microemulsions

Microemulsions are alternatives to emulsions as a means to incorporate water in a fuel. The terms "microemulsion" and "emulsion" seem to imply that such systems are very similar, differing just in the size of the dispersed component, but that is not the case. There are several fundamental differences between a microemulsion and an emulsion and the most important characteristics of the two types of systems are summarized in Fig. 6 [50].

Microemulsion-based fuel formulations date back to 1976 when Gillberg and Friberg published a paper on the use of water-in-diesel microemulsions as fuel [51]. Since microemulsions consist of much smaller domain sizes than emulsions, one may anticipate that they are superior to emulsions with regard to the atomization process but there are indications that the opposite holds true. As mentioned above, Qingguo and Gollahalli have reported that macroemulsions, i.e., normal emulsions, produced smaller drops in the flame than microemulsions [37]. In the experiments they used 10% water in so-called Jet-A fuel in both types of formulations. The general characteristics of emulsions

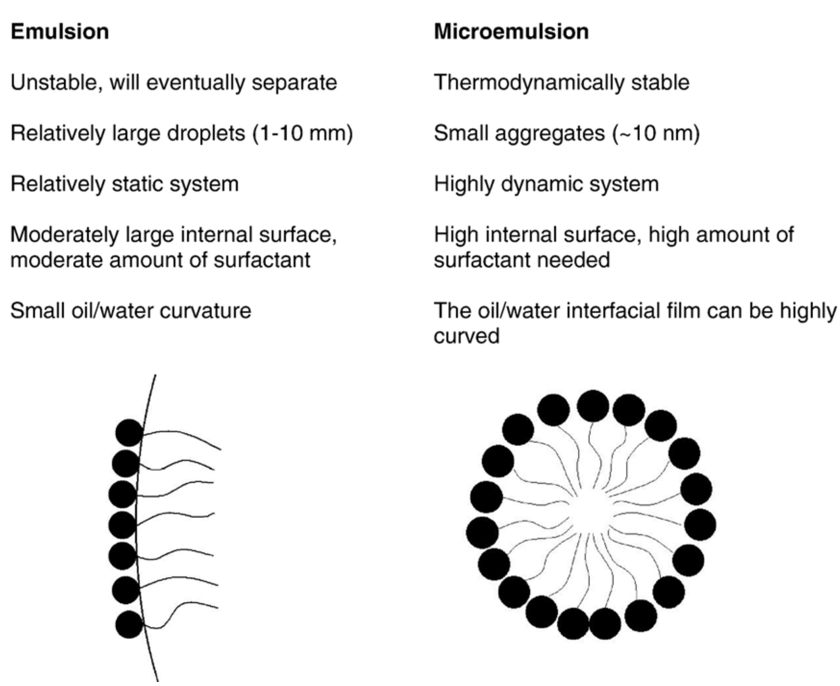

Fig. 6. Characteristic differences between emulsions and microemulsions. (Redrawn after Ref. [50].)

with regard to emission levels seem to hold true also for microemulsions, i.e., NO_x and CO emissions are reduced compared to neat diesel as fuel [52]. Attempts have also been made to add vegetable oils into water-in-diesel microemulsions, thus combining two approaches: replacement of hydrocarbons by triglyceride oils and introducing water into the fuel [53].

Systematic studies have been made on combustion of microemulsions based on hydrocarbons of varying chain lengths [54,55]. Special attention was paid to the vaporization behaviour under dynamic heating conditions. The results indicated that the microstructure of the microemulsion played a role in the physical effects related to the microexplosion, and, thus, to the combustion process.

Not much has been published on water-in-diesel microemulsions in recent years. It is probably true to say that the advantages of the microemulsion approach, in particular the thermodynamic stability, do not compensate for the drawback of the much higher loading of surfactants needed in a microemulsion formulation compared to an emulsion formulation. The microemulsion route is probably too costly for a very large scale application, such as fuels for vehicles.

5. Water-in-vegetable oil (water-in-biodiesel) emulsions

The majority of water-in-fuel emulsions relate to diesel and other hydrocarbon fuels, but there are also a few papers that deal with the combustion characteristics and the emissions from emulsions of water-in-triglycerides, i.e., water-in-biodiesel. In a study where palm oil emulsions were compared with diesel emulsions it was shown that engine performance, fuel consumption and wear resistance were all comparable for the two types of fuels [56]. It was found that water-in-biodiesel fuel, containing 15% water, gave lower NO_x and smoke emissions than plain biodiesel, which is in line with comparisons of emissions from water-in-diesel emulsions and neat diesel, see above [57]. In a series of papers Crookes and co-workers have investigated water-in-biodiesel emulsions and they compared the effect of the water in both diesel and biodiesel on the emission levels [58–62]. It was found that NO_x emissions were generally lower for vegetable oils than for regular diesel and the values were reduced for both fuels when water was included in the form of an emulsion. CO emissions were higher for the vegetable oil emulsions than for the diesel emulsions although both values were low.

6. Other trends in fuels

There is a wide variety of alternative fuels in use or at various stages of introduction today. Apart from water-in-fuel emulsions, which is the main topic of this review, the term alternative fuels comprises hydrogen, natural gas, biogas, dimethylether (DME), alcohols such as methanol and ethanol, liquefied petroleum gas (LPG), vegetable oils and fatty acid methyl esters, and blends of these with gasoline or diesel. The list can be extended further. Biofuel is the generic term for all alternative fuels based on renewable raw material. As a consequence of the Kyoto protocol of 1997 and the European Parliament Directive 2003/30/EC, the search for renewable alternative fuels is extensive. Among all different kinds of fuels based on biomass the most accessible ones today are biodiesel and ethanol.

All major oil companies, as well as all major automotive companies, have research programs today related to alternative fuels. There is a general belief that the upcoming shortage of oil, with concomitant rise in oil prices, will accelerate the switch from plain diesel and gasoline to alternative fuels but there are different opinions about which type of products will dominate the market for vehicle fuels in the future. The issue is very complicated because not only cost and performance, but also political considerations, will influence the outcome. For this reason many of the big players in the field have decided to carry on research and field tests on more than one fuel type in order to leave several options open.

The legislation is pushing the issue both in Europe and the US. The European legislation regulates the motor vehicle emissions by Directive 70/220/EEC (light vehicles) and Directive 88/77/EC (heavy vehicles) and amendments to these directives. In the amendments the limits for emissions have been tightened. The current Euro 4 and the coming Euro 5 in the European Directive 1999/96/EC (amendment to 88/77/EC) set the emission limits for heavy-duty diesel engines, see Table 1.

For the use of alternative fuels the European Commission's Green Paper "Towards a European strategy for the security of energy supply" of 2001 sets a target for the transport sector at 20% by 2020. To further strengthen the transition to alternative fuels the directive 2003/30/EC of the European Parliament on "The promotion of the use of biofuels or other renewable fuels for transport" sets indicative targets on renewable fuels at 2% and 5.75% for 2005 and 2010, respectively.

In the US, the Environmental Protection Agency (EPA) regulates the emissions. The so-called Tier 2, valid during 2002–2009, regulates the emissions from cars and light duty vehicles. For heavy-duty vehicles the emission regulation of 2004 limits NMHCs (non-methane hydrocarbons) and NO_x further. From 2007, the emission levels will be reduced even further, see Tables 2 and 3. The California Air Resources Board (CARB) adopted the world's most stringent low emission vehicle program in 1990 and the federal emission levels for 2007 were already in force in 2001. The unit g/bhph is gram per brake horse power per hour. The conversion factor is 1 g/bhph = 1.3410 g/kWh.

Below is a short description of the more important alternative fuels.

Natural gas is a versatile fuel. It can be used directly in compressed or liquefied form (CNG and LNG, respectively), but it can also be converted to methanol, dimethyl ether (DME),

Table 1
The European heavy vehicle emission legislation

	HC (g/kWh)	CO (g/kWh)	NO_x (g/kWh)	PM (g/kWh)
Euro 3 (2000)	0.66	2.1	5.0	0.1
Euro 4 (2005)	0.46	1.5	3.5	0.02
Euro 5 (2008)	0.46	1.5	2.0	0.02

HC, CO, NO_x, and PM stand for hydrocarbons, carbon monoxide, nitrogen oxides, and particulate matters, respectively.

gas-to-liquid (GTL) fuel or Fischer–Tropsch diesel, which are all useful fuels. Natural gas is used in modified spark-ignition engines or in dedicated engines. Both PM and NO_x emissions from natural gas and natural gas-derived fuels are very low and sulphur emissions are virtually non-existent.

Today much attention is paid to *dimethyl ether* (*DME*). Neat DME has good ignition properties; its initial use in fuel was as an ignition improver in methanol [63] but it was found that using neat DME was favourable since methanol had a negative effect on the ignition of DME. DME can be made from either natural gas or biogas.

Liquefied petroleum gas (*LPG*) is the liquefied form of petroleum gases released during the extraction of crude oil and natural gas or during the refining of crude oil. The hydrocarbons in LPG are mainly propane and butane and these gases are liquefied under moderate pressure (800 kPa). As with all fuels based on light and relatively pure components, the combustion of LPG gives low emissions due to its clean burning properties. LPG can be used in both converted gasoline engines and in dedicated LPG engines, and also in heavy-duty diesel engines converted to spark-ignition.

Hydrogen can be used as a fuel in internal combustion engines and also in fuel cells. It has very clean burning characteristics with zero emission. Today hydrogen is mainly produced from natural gas but it can also be produced by electrolysis of water. Using electrolysis to generate hydrogen is the reverse of the process that takes place in the fuel cell and the same amount of energy released in the fuel cell is needed in the electrolysis. Thus, hydrogen produced through electrolysis is a viable alternative only at places where there is cheap energy, based on renewable sources such as hydroelectric power, available [64]. There are currently several large scale trials with vehicle fleets using fuel cells or internal combustion engines, demonstrating the advantage of the clean fuel. Apart from issues related to production of hydrogen, the distribution chain, as well as the storage and handling at gas stations and in the vehicles, is a major concern.

Biodiesel refers to a diesel fuel from a renewable base. Fatty acid methyl ester (FAME), made by transesterification of a triglyceride with methanol, is the dominant type. Biodiesel is the most easily applicable renewable fuel of all the alternatives. It can be used either as blends with regular diesel or as 100% pure in the existing diesel vehicle fleets. It is widely accepted by the market. Different raw materials are used; in Europe the most common is rape seed oil giving rape methyl ester (RME), or waste vegetable oils. The use of sun flower oil is increasing. In the US market soy oil is mostly used. Biodiesel increases NO_x emissions by about 10% but considerable reductions in hydrocarbon, CO and PM (50%) are achieved. Neste oil has developed a specific diesel fuel, called NExBTL, based on triglycerides of any origin. The production involves two catalytic processes: the first to eliminate oxygen from the triglyceride and the second to branch the linear alkyl chains formed in the first process. Branching leads to improved low temperature properties. The fuel can be used neat or in blends with standard fossil diesel. It is claimed to have superior properties compared to FAME.

Table 2
The US federal heavy vehicle emission legislation

	HC (g/bhph)	CO (g/bhph)	NO_x (g/bhph)	PM (g/bhph)
1998	1.3	15.5	4.0	0.1
2004	1.3	15.5	See Table 3	0.1
2007	1.3 [a]	15.5	0.14	0.01

[a] The NMHC level at 0.14 g/bhph.

Table 3
Emission levels of NMHC and NO_x were tightened in the US federal regulations as of 2004

Option	NMHC+NO_x (g/bhph)	NMHC (g/bhph)
1	2.4	n/a
2	2.5	0.5

One of the options must be fulfilled.

Ethanol (*bioethanol*) is another widely accepted renewable fuel. Like FAME it can be used as a blend with a regular diesel or as neat ethanol. Scania AB has developed special engines dedicated for bioethanol as fuel. The emission improvements compared to regular diesel are large. PM is reduced by 80% and NO_x by 28%, and also reductions in CO and HC emissions are achieved (80 and 50% respectively). Ethanol can also be used in blends with gasoline. A well-known concept is the flexi-fuel vehicles that can run on 85% ethanol (E85). In Brazil the majority of the cars are run on neat ethanol, produced from sugar cane. Also low-level blends of ethanol are used; in the United States blends of 10% ethanol and 90% gasoline, known as E10, are available and in Europe blends of 5% ethanol and 95% gasoline, called E5 are used. All car manufactures have approved the use of E5/E10 in the ordinary gasoline cars. The gasoline oxygenating additive, ETBE, ethyl *tert*-butyl ether, is made from ethanol and isobutylene and can be used as a replacement for MTBE, methyl *tert*-butyl ether. Ethanol as such is also an oxygenating additive. These additives act as octane enhancer and thus suppress knocking, which is the uncontrolled self-ignition. Ethanol is mainly produced from sugar cane, wheat or wine. Intensive research is being conducted on lignocellulosics as raw material [65,66].

Gasification processes of biomass will give *biogas-to-liquid fuels* (*BtL fuels*). The biomass can have various origins, such as black liqueur, forestry residues, or municipal or industrial waste products. The resulting fuels are methanol, DME and Fischer–Tropsch diesel.

7. Summary

Alternative fuels cover a broad range of fuels, some of which, including water-in-diesel emulsions are readily available, while other types require further investigations, are produced in very limited amounts or require specially designed, i.e., dedicated, engines. Even if the water-in-diesel emulsion fuel has only a limited effect on the reduction of fossil CO_2, it is still beneficial from an environmental point of view because it brings about a reduction in the levels of both NO_x and particulate matters (PM). Up to 30% reduction in NO_x and 60% reduction in PM can be achieved by emulsifying up to 15% water in diesel. The water content affects the combustion mainly on two accounts. The first is the reduced peak temperature in the cylinder, resulting in a lower level of NO_x formed. The second is the microexplosion phenomenon, which is due to the volatility difference between water and diesel. Water contents ranging from 5% to 45% have been studied. There is, however, only limited amount of information about the emulsifiers used in the emulsions and there are no reports dealing with the emulsion stability.

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