1 INTRODUCTION

The most efficient power source among all known types of internal combustion engines is the direct injected diesel engine. Due to its high efficiency, low fuel consumption and longevity, the diesel engine, invented by *Dr. Rudolph Diesel* in the 1890s [1], is also the most common drive system.

However, internal combustion engines are significant contributors to air pollution, which negatively influences human health and the environment [2-4] and are known as a contributor to global warming [5, 6]. Growing concerns about emission of nitrogen oxides (NO_x) and especially diesel particulates lead to a substantial urgency to reduce exhaust gas emissions from diesel engines in terms of a sustainable climate policy. The European Union (EU) aims to introduce stricter limits on pollutant emissions from light road vehicles since 1992 with the EURO I to EURO VI (Sept. 2014) stages [7] and will legislate even stricter terms in the years to come. The necessity of such jurisdiction dates back to the late nineteenth century, in which the demand for crude oil started to accelerate with the invention of the internal combustion engine and became one of the most essential commodities traded worldwide.

Petroleum liquids are non-renewable resources, thus *Hubbert* has developed a method to forecast future production of crude oil. In 1956, *Hubbert* hypothesised that the world oil production follows a “bell-shaped” curve and has already reached its peak in 1970 in the United States [8]. His model gained worldwide popularity and was used to forecast oil production worldwide with a peak before 2010 [9-12]. Henceforth, not only exhaust gas emissions, but also fuel consumption, have been drastically reduced due to a conscious handling of non-renewable resources [13,14].

Besides limited availability due to decreasing fossil resources and growing energy consumption, the pollutant emission represents another problem of fossil fuel. Application of renewable biofuels can overcome both of these problems. Alternative fuels are not from petroleum origin and have a respectively high heating value [15]. 1st generation of alternative fuels such as fatty acid methyl ester (FAME) are based on grain crops, such as rape-seed, grain and maize. The 2nd generation of biogenic fuels is based on biogenic energy such as GtL (Gas-to-Liquid) or BtL (Biomass-to-Liquid). The conversion of coal, natural gas and biomass into liquid hydrocarbons is accessible by the well-known *Fischer-Tropsch* synthesis [16]. Biofuels are already available on the market in the form of bioethanol for gasoline engines and FAME for diesel engines. Small amounts of these components (up to 10 %) are used for blending in gasoline and diesel with an advantage that no modification of the fuel system is necessary [17].

A further approach to overcome the depletion of fossil fuels is to use electric, hybrid electric and fuel-cell powered drive train technologies which are the most promising vehicle solutions in the future. Hybrid technology is commercially available since 1997 and the sales figures are expected to rise considerably until 2023 [18]. Hybrid vehicles add a parallel electric motor with the combination of batteries in the combustion engine. In order to replace combustion engines entirely, fundamental problems like an efficient storage capacity, durability and its lower power output have to be solved [19].

1.1 Motivation

The combustion products of diesel fuel under ideal conditions (complete combustion) are water and carbon dioxide. Residues of incomplete combustion are mainly carbon monoxide, nitrogen oxides, unburnt hydrocarbons and particulate matter. Due to several factors influencing the combustion as the fuel/air ratio of the fuel spray, the short time available for the mixture formation, the temperature during combustion and the increased penetration depth, inefficient combustion with increased emissions is observed.

Development of advanced after-treatments systems and other internal engine modifications has been motivated by the growing interest in reducing the formation of pollutant during combustion. In-cylinder emission control technology and combustion optimisation are the key to reduce emissions and fuel consumption. Suitable combustion chamber geometry [20], favourable fuel injection pressure [21] or optimal fuel/air ratio [22] improve combustion. Another option to achieve maximum power with minimal consumption and exhaust emission lies in the optimisation of the fuel itself. Physical properties of the fuel (*e.g.* viscosity, density and surface tension) affect the evaporation behaviour and the fuel atomisation [23,24]. Due to a changed fuel composition by adding cetane improver or oxygenates [25-27] soot- or NO_x-emissions are reduced. The advantage of a modified fuel composition is not only the reduction of exhaust emissions, but also a decline in CO_2-emission due to the use of biogenic blends: renewable raw materials are characterised by their CO_2-neutral combustion and can therefore be subtracted from the balance [28, 29].

The main pollutants from diesel engines are soot and nitrogen oxides (NO_x). The so-called *soot-NO_x trade-off* describes the contradictory formation of soot and NO_x in the combustion chamber of diesel engines. A simultaneously reduction of both emissions is very difficult as by rising the combustion temperature, the emission of soot declines while the emission of

NO_x increases. In contrast, the emission of NO_x is reduced at the expense of an increased soot-formation at lower combustion temperatures.

One promising, economically efficient and simple way to reduce the emissions and improve the fuel conversion efficiency of diesel engines is the addition of water into the combustion chamber. A number of potential benefits are offered in the combustion of water containing fuel. One effect is based on the volatility difference between water and fuel, which can lead to the so-called microexplosions. The microexplosions of the primary droplet are followed by the secondary atomization producing a number of fine-sized secondary droplets which consequently enhances the fuel/air ratio in the combustion and reduces the flame temperature. Hence, the formation of *Zeldovich* NO is suppressed and an improved combustion efficiency is observed [30]. Due to a changed chemical reaction mechanism by applying water into fuel, a further positive effect is observed. At higher temperatures (> 2000 K) water causes an increased concentration of radicals ($\cdot OH$, $\cdot O$, $\cdot O_2H$) in the combustion chamber, leading to an effective oxidation of soot precursors (C_2H_2, C_2H_4 and unburnt hydrocarbons) [31].

The combination of both effects includes the potential benefit to reduce both hazardous emissions while avoiding the *soot-NO_x trade-off.* Water can be introduced into the combustion chamber in various ways. The University of Applied Science in Trier developed a stratified injection of water and different blending systems in order to improve the response time [32,33]. The recent generated *in injector*-blending allows the generation of appropriate water/fuel-mixing ratios with an even reduced response time due to direct injection of water into the fuel-channel of the injector [34]. The addition of water may also happen in the form of microemulsions or nanoemulsions. Due to finer dispersed water droplets during combustion, an increased positive effect occurs [35]. Ordinary emulsions and microemulsions differ mainly in their thermodynamic stability and surfactant concentration. Thermodynamically stable microemulsions are translucent in appearance and show a homogenous, nanoscale structure of order 10 nm. Thermodynamically unstable emulsions appear white because of their droplet sizes of order 1 μm [36,37]. Generally, more surfactant is required to formulate thermodynamically stable microemulsions (including ultralow interfacial tension [38]) and is thus favoured regarding storage due to its long-term stability. A relatively new, special kind of emulsions can appear transparent with droplet sizes of order 100 nm. They are called nanoemulsions and, interestingly, require a reduced amount of surfactant compared to thermodynamically stable microemulsions.

Both types show different combustion characteristics even if the initial water content is the same [35]. This effect is based upon different size distribution of the dispersed water droplets in a fuel droplet as schematically shown in figure 1-1.

10 µm

with ~ 100 nm dispersed water droplets
Nanoemulsions

10 µm

with ~ 10 nm dispersed water droplets
Microemulsion

Figure 1-1: Schematic illustration of the dispersed water droplets inside a typical fuel droplet of the spray. Nanoemulsions feature larger-scaled dispersed water droplets (~ 100 nm) with a lower number density of water droplets in a fuel droplet (left). Smaller-scaled size distribution of the dispersed water droplets (~ 10 nm) are generated by microemulsions with a accordingly higher number density of water droplets in a fuel droplet (right).

The evaporation of the water droplets in water containing fuels may be accompanied by microexplosions which are not observed in the combustion of pure diesel droplet. Due to volatility difference between the water and the fuel, this phenomenon depends on the size of the dispersed water droplets [39].

1.2 Water containing fuels

The first investigation on water containing fuels started in the 1940s by the NACA during the Second World War by spraying a mixture of water/ethanol/methanol into the air intake of aircraft engines in order to cool the engines while decreasing the combustion temperature [40].

Cornet and *Nero* published in 1954 the systematic investigations of emulsified diesel fuel and observed an improved efficiency with a simultaneous slight reduction of fuel specific consumption [41]. *Feuermann* formulated and patented the first gasoline-water emulsion in 1979 by mixing gasoline, water and non-ionic surfactants and observed a reduction of pollutants during combustion [42]. *Velji et al.* showed a reduction of NO_x-, CO- and soot-emissions by increasing the water content [43]. *Kadota et al.* studied the microexplosion phenomena during combustion while using water fuel emulsions [30]. A lowered combustion temperature was observed which leads to a reduced NO_x-emission. 2005 *Mathis et al.* studied the influence of water on primary soot particle diameter and particle number size distribution in the exhaust of a diesel engine. The diameter of soot particles from the water-diesel emulsion were determined using scanning electron microscopy and were slighter larger than from diesel fuel [44]. The investigations described were related to emulsion-fuels which contained a small proportion of surface active agents in order to provide a kinetically stable mixture.

Despite decades of research activity indicating positive results, and the intense need to improve emissions due to tightening regulatory requirements, no widespread application of water-in-fuel emulsions exists today. Aquazole^{TM} (Lubrizol Corp.) and PuriNOx^{TM} (Elf Aquitaine) water-in-diesel emulsion formulations were commercially available in the mid-2000's, but eventually removed from the market [45]. Most likely the inherent limited stability of emulsions and corrosion effects in the fuel injection system critically hampers application of water-in-fuel emulsions.

Microemulsions containing gasoline, kerosene, diesel and fuel oil with water-solube additives and surfactant-blends of fatty acid derivates, poly-alkanolamine, sorbitan esters and nonylphenol were patented in 1975 by *McCoy* [46]. *Schwab et al.* formulated cryogenic stable water-diesel fuel microemulsion with a combination of dimethylethanolamine and long-chained fatty acids as surfactants [47]. Additionally, investigations on vegetable oil-microemulsions for use in internal combustion engines were studied in 1984 and 1985 [48-50]. *Huzbun et al.* reported the use of microemulsions in 1986 containing 7 wt.% water, tertiary butyl alcohol as major component and a blend of ionic- and non-ionic surfactants [51].

In 2006, *Davis* studied water-in-fuel microemulsions based on fatty acid amines and observed water domains below 0.1 µm [52].

A wide variety of investigations on microemulsions as fuel were studied in the group of *Prof. Strey*. Temperature invariant microemulsions containing water (up to 45 wt.%), diesel fuel and a blend of ionic- and non-ionic surfactants were formulated by *Nawrath* and *Rottländer* [53, 54]. The potential benefit using water-fuel microemulsions while reducing both the soot- and NO_x-emission was patented by *Strey, Nawrath* and *Sottmann* in 2003 with the title “Microemulsions and their use as fuel” [55]. This patent claims the use of the bicontinuous area in fuel-microemulsions which represents the state with a minimum amount of surfactant forming a single phase microemulsion and an ultra-low interfacial tension. *Bemert* published her dissertation in 2008 with a systematically investigation of the influence of different types of surfactants and additives on the phase behaviour. Combustion experiments showed the positive effect on pollutant emissions while applying water containing fuels [56]. *Lif et al.* compared microemulsions and emulsions in terms of emissions and spray behaviour. Both systems represent a promising approach to reduce emissions of NO_x and particulate matter [57-59]. *Wulff*'s work is also an evidence for overcoming the *soot-*NO_x *trade-off* [60]. *Menger* has recently studied the microemulsified fuels under nearly realistic conditions using the test vehicle of the workgroup of *Prof. Strey.* A reduction of toxic emissions over all loads was concluded to require an adjustment of water content on the engine map and through an on-demand water admixing [61].

Industry shows interest in water containing fuels. In 2006, the *Rheinbahn* in Düsseldorf started a practical test using water-in-fuel emulsions [62]. *MAN, Fuel Emulsions International* and *Nonox Ltd.* are developing effective emulsion fuel system technologies which are already used in diesel engines, cruise liners, and commercial ships [63-65].

All these studies show the potential benefit of water containing fuels in order to reduce the emissions of health hazardous and improve burning efficiency. The application would greatly be facilitated or even made commercially attractive, if certain aim are fulfilled. As such

- the water containing fuel should be mixed right before injection,
- it should contain as less as possible surfactant,
- the surfactant should be of biological origin,
- the fuel system should not be contaminated by water,
- the water content should be adjustable to the engine map.

1.3 Task description

The multiplicity of studies of microemulsified fuels confirmed the presumed positive effects of microemulsions on the exhaust gas emissions in diesel engines [53, 54, 56, 60, 61]. However, an improvement potential exists applying catalyst-free (ash-free), bio-derived surfactants which were not used in previous studies leading to inefficient combustion. Hence, one goal of this thesis was the formulation of an efficient, temperature invariant, practice-oriented fuel microemulsion including fully combustible, ash-free surfactants of biological origin while also considering crucial physical properties.. Here, an interdisciplinary cooperation (FVV-project) with the *University of Applied Sciences in Trier* and the *Rheinisch-Westfälische Technische Hochschule Aachen* (RWTH Aachen) should allow a detailed examination of the influence of these water containing fuels on the exhaust emissions and spray behaviour. To this end, inexpensive, fully combustible and "*green*" surfactants and additives were to be introduced into an initial system of the type water/ammonium nitrate/ethanol - diesel - oleic acid/monoethanolamine/oleic acid diethanolamide. Here, the surfactant mixture was to be optimised to guarantee the one-phase state at storage conditions in winter and during combustion (temperature invariant state). Keeping an eye on the engine requirements, physical characteristics of the microemulsified fuels were to be measured evaluating the spray behaviour in accordance with EN 590. Regarding the microemulsification approaching injection conditions, the formation kinetics of such systems were to be analysed for different temperatures and water-content. Furthermore, the structure of water-in-fuel microemulsions was to be determined using small angle neutron scattering (SANS) and dynamical light scattering (DLS).

The second goal of this thesis was to formulate economically more appealing, low surfactant content nanoemulsion fuels for load point dependent on injector-blending of water and diesel streams milliseconds before injection into the combustion chamber. Here, the surfactant blend was to be optimised in order to utilise the ultra-low interfacial tension to form small-scaled dispersed water droplets. The influence by varying the HLB-value and surfactant was to be studied using dynamic light scattering (DLS). In order to be able to use nanoemulsified fuels for the on injector-blending system, a separate aqueous- and oleic-phase was to be prepared. Based on the formulation of the nanoemulsion, the aqueous phase was to be added with a suitable, efficient anti-corrosion agent and lubricant.

Finally, in industrial combustion tests the influence of water- and surfactant-content on exhaust gas emissions and spray behaviour was to be clarified, thereby also comparing the pollutant emissions of microemulsions and nanoemulsions. In particular, scanning electron microscopy (SEM) was to be applied to characterise the soot-structure and aggregation behaviour.

2 FUNDAMENTALS

A fundamental background is needed to understand the present results and techniques in this work. The first sub-chapter (2.1) provides an introduction in microemulsions and their binary systems. In the following sub-chapter (2.2) the properties and different preparation methods for emulsions are explained. The techniques applied for structural and formation kinetics investigations are introduced in sub-chapter (2.3) A basic knowledge of combustion parameters and emission formation is given in the last sub-chapter (2.4).

2.1 Microemulsions

Microemulsions are thermodynamically stable, macroscopically homogenous, optically isotropic, nanostructured systems of at least three components [66]. Microemulsions are formed spontaneously upon mixing a hydrophilic, a hydrophobic and an amphiphilic component. Two of these three components are immiscible, like water (polar component) and oil (non-polar). The amphiphilic nature of the third component allows adsorbing to the interface between the hydrophilic and hydrophobic component. The amphiphilic component features a hydrophilic and a hydrophobic subsection causing a reduction of the interfacial tension between these two immiscible components by forming an amphiphilic film. As a consequence, a nanodisperse mixture of these components forms a thermodynamically stable microemulsion [67]. The first microemulsion was recognised by *Schulmann* and *Hoar* in 1943 [68]. A classification of microemulsions was denoted by *Winsor* in three types of phase equilibria [69]. The temperature-, pressure and component-dependant phase behaviour of microemulsions is closely related to the evolution of the microstructure. Further fundamental backgrounds were observed by *Kahlweit* and *Strey*, which are described and reviewed in this chapter.

In the following, a brief introduction into the application of microemulsions is given. Due to the unique properties of microemulsions, they have been used in various branches of industry. Intensive research on microemulsions was started by the two oil crises in 1973 and 1979. The use of microemulsions was of high interest in terms of enhanced oil recovery. Oil-wells were pumped with water-surfactant mixtures in order to extract the left over crude oil [70]. Microemulsions gained an important role as drug delivery vehicles in the pharmaceutical industry due to their improved bioavailability. Certain drugs were solubilised in microemulsions and penetrated into the blood circuit while being protected from degradation, hydrolysis and oxidation [71, 72]. A large field of application for microemulsions is the cosmetic industry. Many cosmetic ingredients can be solubilised in the swollen micelles of micremulsions and may enhance diffusion and transport through various barriers [73, 74]. Furthermore, microemulsions can also be used in washing processes in addition to conventional liquid detergents. An enhanced removal of contaminants from solid surfaces by the extremely low interfacial tension in microemulsions is observed [75, 76]. Another possible and important application of microemulsions is the use as *nano insulation materials* in order to save energy by improving thermal insulation of buildings [77]. In textile industry, microemulsions are used in textile finishing and impregnation [78]. Further examples for applications can be found in food and agrochemical industry [79, 80], in chemical reactions *e.g.* to produce ultrafine particles [81], for polymerisation [82] and as solvent for electrochemical reactions [83].

2.1.1 Phase behaviour

In simply ternary systems that contain water (A), an alkane (B) and a non-ionic surfactant (C) the main properties of microemulsions can be observed [84]. The fairly universal phase behaviour of all systems of this type can be presented in a phase prism with the temperature axis as the ordinate and the *Gibbs* phase triangle A-B-C as the base [66, 85]. The complex temperature-dependent phase behaviour of the ternary system can be understood by considering the three independent binary systems water - oil (A - B), water - surfactant (A - C) and oil - surfactant (B - C). The binary systems represent the three sides of the phase prism, as shown in figure 2-1. A miscibility gap over the entire experimental temperature range dominates the binary system water - oil (A - B). The binary oil - surfactant (B - C) mixture shows a lower miscibility gap with a critical point cp_α at a critical temperature T_α which is located below 0 °C. The binary system water - surfactant (A - C) features a lower miscibility gap with an upper critical point which is mostly below the melting point of the mixture. An upper closed miscibility gap with lower critical point cp_β at the critical temperature T_β is found at higher temperatures. The locations of cp_α and cp_β depend on the nature of the components and are related to the behaviour of the ternary system. These two critical points deliver an explanation for the temperature-dependant phase behaviour: with increasing temperature the solubility of non-ionic surfactant in water decreases while the solubility in oil increases.