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WATER-IN-DIESEL EMULSIONS AS ALTERNATIVE FUEL FOR DIESEL ENGINES. PART I: WATER-IN-DIESEL EMULSIONS. A LITERATURE REVIEW

Vlad VRABIE*, Dan SCARPETE, Bianca Elena CHIOSA
„Dunarea de Jos” University of Galati, Faculty of Engineering, Domnească Street, 47, RO-800008, Galati, Romania
e-mail: vlad.vrabie@ugal.ro

ABSTRACT

Although emulsions have found numerous and various applications in chemical, pharmaceutical and food industries, emulsions of water in diesel fuel are applicable alternative fuels for the existing diesel engines.

Water-in-diesel emulsion fuel can improve the combustion efficiency of a diesel engine and reduce harmful exhaust emission, especially nitrogen oxides and particulate matter.

In general, due to the lower heating values of water-in-diesel emulsion fuels, torque and power produced by diesel engines fueled with emulsified fuels are lower as compared to the neat diesel fuel.

The heterogeneous results regarding the use of water-in-diesel emulsions as fuel for diesel engines suggest that more experimental work for optimizing the emulsion formulation is recommended.

KEYWORDS: water-in-diesel emulsion, diesel engines, combustion, emissions

1. Introduction

The technique concerned with introducing water into the engine combustion chamber was proposed by Prof. B. Hopkinson in 1913, to make better internal cooling of the gas engine and to increase the engine output. Furthermore, the technique was developed to improve the thermal efficiency and reduce exhaust emissions, or used as safety fuel [1].

More and more attention is paid to diesel engines which can be used in transportation, industrial and agricultural applications due to their high efficiency and reliability [2].

The main pollutants produced from the exhaust of diesel engines are nitrogen oxides (NOx), particulate matter, black smoke, carbon monoxide and carbon dioxide. The presence of these pollutants in atmosphere will cause serious damage to the environment such as the greenhouse effect, acid rain, and the destruction of the ozone layer [3].

Water-in-diesel emulsion fuel (W/D) is a promising alternative fuel that could fulfill such requests in that it can improve the combustion efficiency of a diesel engine and reduce harmful exhaust emission, especially nitrogen oxides (NOx) and particulate matter (PM). Up to date, there have been many W/D emulsion fuel studies, especially regarding performance, emissions and micro-explosion phenomena [4].

Four major approaches for introducing water into the combustion zone have been reported in the literature [5]:

(i) Fumigating the water into the engine intake air;
(ii) Direct injection into the engine through separate injectors;
(iii) In-line mixing of water and fuel prior to injection (unstabilized emulsion);
(iv) Mixtures of stabilized emulsions treatable as a single-phase drop-in replacement fuel.

The intake manifold fumigation and direct water injection methods lead to an increase in the formation of hydrocarbon (HC) and emission of carbon monoxide (CO). Furthermore, as the water is introduced into the combustion chamber, it tends to be in direct contact with the fuel feed system and cylinder piston group, thus resulting in oil contamination and increasing wear. In addition, both methods require highly complex engine modification in order to integrate the water addition device into the engine. Thus, they require high additional cost [4].

Of all the methods proposed to introduce water into the combustion chamber, diesel oil emulsions appear to be the most appropriate, because they require no engine retrofitting [6].

The main reason for a stronger interest in incorporating water in diesel rather than in gasoline is that the high combustion temperature and the high pressure that exist in diesel engines are particularly suitable for the concept. This was found experimentally and verified by theory almost 30 years ago. The use of diesel emulsions has been shown to give several interesting effects, such as (i) reduced nitrogen oxides (NOx) emission and also lower soot and particulate contents in the exhaust, and (ii) improved combustion efficiency [7].

There is a special occurrence in W/D ignition called the micro-explosion phenomenon that intrigues researchers worldwide, as it is non-existent in other normal diesel combustion. It is a secondary atomization of the primary spray as a result of the rapid evaporation process of water that is initially contained in the oil drop, making the combustion more efficient [8].

All the reviewed studies on the preparation and use of water-in-diesel emulsions have been focused on different aspects of the effects of this fuel on the engine performance and emissions [9].

This paper presents a literature review of the current status of water-in-diesel emulsions and their influence as alternative fuel for diesel engines.

2. Water-in-diesel emulsion fuel

An emulsion is a blend of two or more liquids which are unblended in nature, one present in continuous phase and others in dispersed phase [10]. Emulsions consist of at least one immiscible liquid intimately dispersed in another under the form of droplets, whose diameters, in general, exceed 0.1 μm [11].

The emulsion is formed with the help of mechanical agitation together with the chemical additives called surfactants to keep the immiscible liquids mixed together, forming one solution. Generally, emulsions are divided into two types: oil-in-water emulsions (O/W) and water-in-oil emulsions (W/O) [4, 12].

2.1. Surfactants used in water-in-diesel emulsions

Surfactants or surface-active agents are amphipathic substances with lyophobic and lyophilic groups, making them capable of adsorbing, at the interfaces between liquids, solids and gases. They are capable of forming self-associated clusters, which normally lead to organized molecular assemblies / aggregates, monolayers, micelles, vesicles, liposomes and membranes. Apart from traditional applications such as detergents, emulsifiers, dispersants, wetting and flotation agents, they have tremendous and not yet fully appreciated potential for engineering functional interfaces and surface coatings [12].

The surfactants possess a polar or hydrophilic head, and a nonpolar or hydrophobic tail. The surfactant is incorporated to weaken the surface tension of the medium in which it dissolves. When it is placed in an oil-water mixture, the polar groups orient towards the water and the nonpolar group orients towards the oil as it lowers the interfacial tension between the oil and water phases. They are classified into cationic, anionic, amphoteric, and nonionic, based on the type of polar group of the surfactant [10, 13]. Figure 1 [14] shows the molecular structure of some surfactants such as Span 80, Tween 80, Span 85 and OP 10.

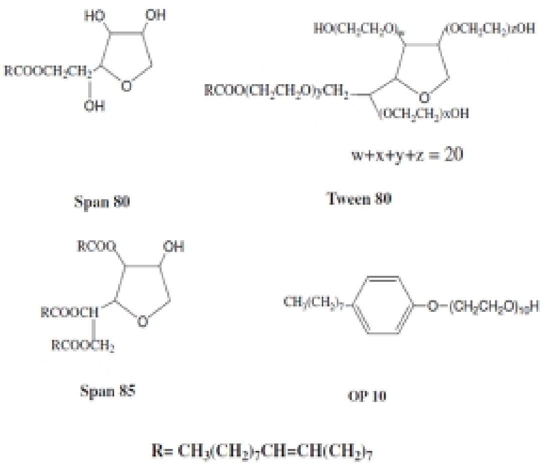


Fig. 1. *Molecular structure of Span 80, Tween 80, Span 85 and OP 10* [14]

A frequently used method for selecting surfactants as emulsifying agents is known as the HLB (hydrophilic–lipophilic balance) method. In this method, a number (0–40) indicative of emulsification behavior and related to the balance between the hydrophilic and hydrophobic portions of the molecule has been assigned to many commercial emulsifying agents [14].

This dimensionless scale ranges from 0–20 for non-ionic surfactants. A low HLB (<9) refers to a lipophilic surfactant (oil soluble) and a high HLB (>11) to a hydrophilic (water soluble) surfactant. Most ionic surfactants have HLB values greater than 20, for example, sodium dodecyl sulfate has an HLB of 40. Some examples of surfactant HLBs are given in Table 1. In general, water-in-oil (W/O) emulsifiers exhibit HLB values in the range 3-8, while oil-in-water (O/W) emulsifiers have HLB values of about 8–18. If the value is not known, then lab emulsification tests are required, using a series of emulsifying agents of known HLB values [15].

Emulsion is formed by mechanical agitation. The mechanical agitation can be generated by ultrasonic vibration machine, magnetic stirrer and centrifugal type mixer [13].

Table 1. *Approximate surfactant HLB values** [15]

Surfactant	HLB
Oleic acid	1
Sorbitan tristearate (SPAN 65)	2
Sorbitan monooleate (SPAN 80)	4
Diethylene glycol monolaureate	6
Sorbitan monolaurate (SPAN 20)	9
Glycerol monostearate	11
Polyoxyethylene (10) cetyl ether (BRIJ 56)	13
Polyoxyethylene sorbitan monooleate (TWEEN 80)	15
Sodium octadecanoate	18
Sodium dodecanoate	21
Sodium octanoate	23
Dioctyl sodium sulfosuccinate	32
Sodium heptadecyl sulfate	38
Sodium dodecyl sulfate	40
Sodium octyl sulfate	42

*SPAN, BRIJ and TWEEN are trademarks of ICI Americas Inc.

The surfactant works as a surface active agent that is a typical chemical additive to attract both immiscible liquids (water and oil) into forming one stable solution. The surfactant functions by reducing the surface tension of the water, by adsorbing at the liquid-gas interface. It also reduces the interfacial tension between oil and water by adsorbing at the liquid-liquid inter phase [4, 16].

The most common surfactants used in the water-in-diesel emulsion are sorbitan monooleate, which is called Span 80 [4, 13], and polyethylene glycol sorbitan monooleate mixture [13], polyoxyethylene nonylphenyl ether [4, 13, 16], called Span 80 and Tween 80 [4], polyethylene lycol sorbitan monooleate (polysorbate 80) and sorbitol sesquioleate (SSO) mixture, sorbitan monolaurate [13], gemini [12], octylphenoxy polyethoxy ethanol, called Triton X-100, dai-ichi kogyo seiyaku (solgen and noigen TDS-30) [4, 16], polysorbate 20 (commercially know as tween 20) [17], sorbitan trioleate (Span 85) andisooctylphenol poly(ethylene glycol) ether (OP 10) [14] and liquid soap or glycerin [4, 13]. The percentage of the surfactant being added in the mixture of the unblended fluids is generally between 0.1 and 2% [4].

2.2. Types of water-diesel emulsions

Emulsions are colloidal dispersions in which a liquid is dispersed in a continuous liquid phase of different composition. The dispersed phase is sometimes referred to as the internal (disperse) phase and the continuous phase as the external phase [15].

A system that consists of water droplets dispersed in an oil phase is called a water-in-oil or W/O emulsion (Figure 2, left [13]), and a system that consists of oil droplets dispersed in an aqueous phase is called an oil-in-water or O/W emulsion (Figure 2, right [13]) [4, 15].

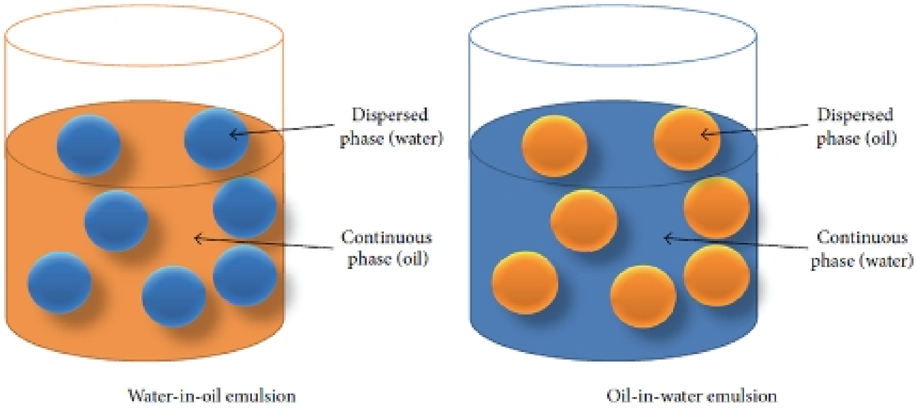


Fig. 2. *Concept of two-phase water-in-oil and oil-in-water emulsions* [13]

The O/W emulsion is not suitable to be an alternative fuel. This is due to the large amount of water that might come into direct contact with the cylinder-piston group and fuel feed system, which will result in failure of the fuel combustion. The W/O emulsion fuel is the most suitable and widely used as the alternative fuel for fueling compression ignition engines by researchers and experts [4]. The two-phase emulsion constitutes one continuous phase and one-dispersed phase liquids while the three-phase emulsion constitutes one continuous phase and two or more dispersed phase liquids [13].

Multiple emulsions consist of three phases: an inner and an outer phase separated by a dispersed phase [15]. In Figure 3 [13] are presented the three-phase emulsions or double emulsions which are denoted as: O/W/O (oil-in-water-in-oil) and W/O/W (water-in-oil-in-water) [15].

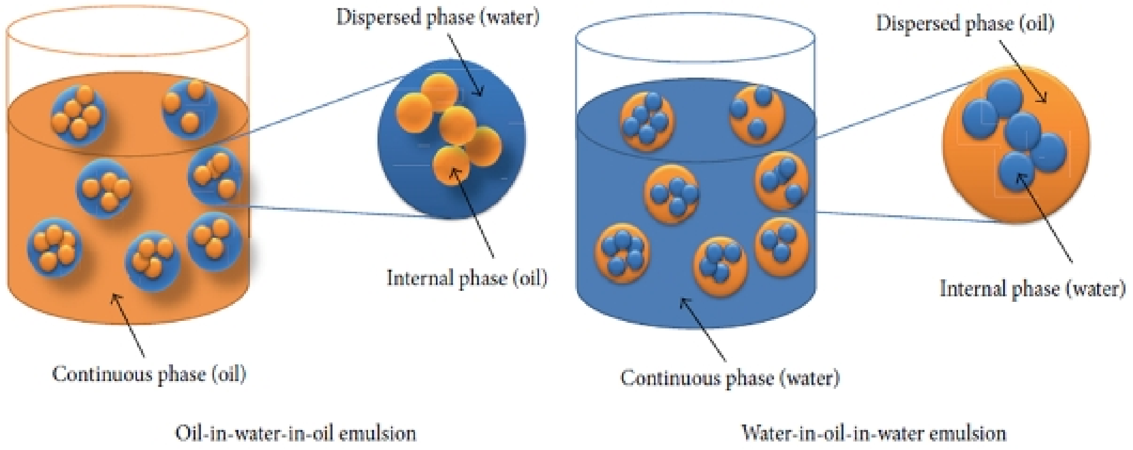


Fig. 3. *Concept of three-phase oil-in-water-in-oil and water-in-oil-in-water emulsions* [13]

Multiple emulsions are complex liquid multiphase systems. They are also called „emulsions of emulsions” because the dispersed phase of these emulsions consists of an emulsion itself. In water-in-oil-in-water (W/O/W) emulsions, water droplets are dispersed in an oil phase which itself forms drops in a continuous waterphase. This complex structure enables their use for different applications ranging from separation processes and encapsulation of specific molecules for cosmetic, pharmaceutical, agrochemical and food products to fat reduction in food [18].

Three-phase emulsions can be prepared by three techniques, namely, phase inversion, mechanical agitation, and two-stage emulsion. A two stage emulsification technique has been used for the preparation of three-phase oil-in-water-in-oil emulsion by many researchers. This technique, which is the most common technique in three-phase emulsions, uses both lipophilic and hydrophilic types of surfactants. First, a two-phase oil-in-water emulsion is prepared by using a hydrophilic type surfactant and a mechanical homogenizer machine. A lipophilic type of surfactant is then used to further emulsify the two-phase oil-in-water emulsion in oil and form three-phase oil-in-water-in-oil emulsion [13].

Nano-emulsions consist of very small emulsion droplets, commonly oil droplets in water, exhibiting sizes lower than 300 nm.

Like conventional emulsions (with sizes > µm), nano-emulsions are, from a thermodynamic point of view, in a non-equilibrium state [19].

The confusion between nano-emulsions and micro-emulsions is, in fact, as much a result of their formulation processes as of their structural (macroscopical and molecular) aspects, both being to some extent very close. Nano-emulsions are only formed if surfactants are first mixed with the oily phase. If they are first mixed with water before adding the oily phase, only a “macroscopic” emulsion will be generated. Micro-emulsions, on the other hand, will be strictly identical whatever the order in which the compounds are mixed (after equilibration time) [19].

Microemulsion based fuel formulations date back to 1976 when Gillberg and Friberg published a paper on the use of water-in-diesel micro-emulsions as fuel [4, 7]. In Figure 4 [7] are shown the characteristic differences between emulsions and micro-emulsions.

The size of the drops in an emulsion are in the range of 1-10 µm, while in a micro-emulsion they are much smaller, e.g. 5-20 nm [20].

Micro-emulsions are thermodynamically stable, while 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 [20].

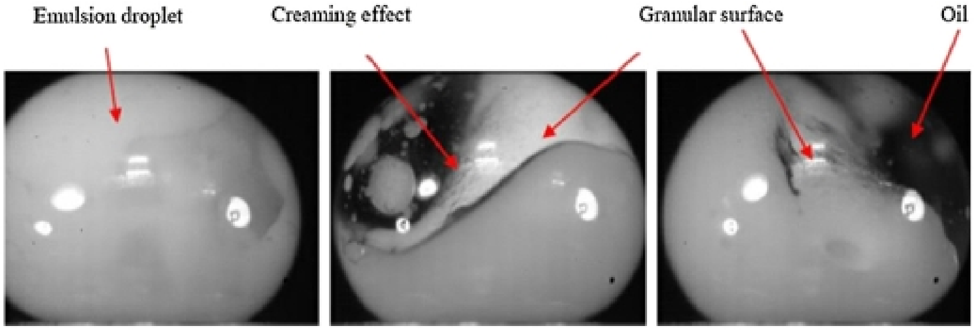
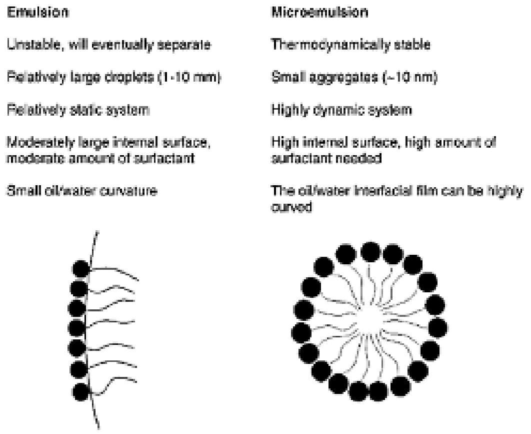


Fig. 5. Sequence of creaming process [4]



Emulsion	Microemulsion
Unstable, will eventually separate	Thermodynamically stable
Relatively large droplets (1-10 mm)	Small aggregates (~10 nm)
Relatively static system	Highly dynamic system
Moderately large internal surface, moderate amount of surfactant	High internal surface, high amount of surfactant needed
Small oil/water curvature	The oil/water interfacial film can be highly curved

Fig. 4. Characteristic differences between emulsions and microemulsions [7]

The thermodynamic stability of the micro-emulsion does not compensate for the drawback of the much higher loading of surfactants needed in a micro-emulsion formulation compared to an emulsion formulation. The microemulsion route is probably too costly for a very large scale application, such as fuels for vehicles [7].

2.3. Emulsion fuel stability

The stability of the diesel emulsion is affected mainly by the emulsification technique, emulsification duration, volume fraction of water (dispersed phase), viscosity of the continuous phase (diesel oil), stirring speed (or ultrasonic frequency) and concentration of surfactants (it is the most important factor) [13].

If the emulsion is destabilized during the engine running time, the probability of the engine failure to operate is high. It may damage the parts inside the engine [4].

In paper [21] it has been demonstrated that the stability of the emulsion fuel is tested under various environmental temperatures for 1 year, and no significant separation is noticed. It is better than normal emulsion fuel which can only maintain the state for up to 3 months.

The destabilization process of W/D emulsion fuel will occur after it goes through several phenomena: creaming, aggregation and coalescence. For the case of the W/D emulsion fuel, the internal phase, which is the water, will sink to the bottom. Figure 5 shows the sequence of the creaming phenomena. The aggregation process is where the droplets in the internal phase attract each other [4].

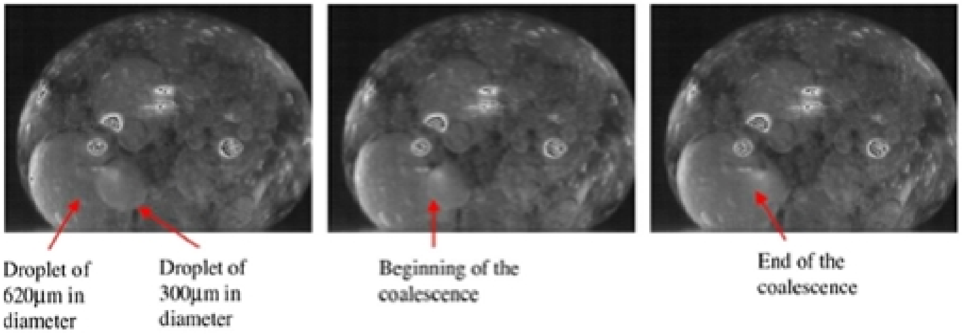


Fig. 6. Sequence of coalescence process [4]

The sequence of the coalescence process is presented in Figure 6. All of these processes will continually destabilize the emulsion until the water and the diesel fuel are fully separated. In addition, the W/D emulsion fuel separation can be initiated by these following cases [4]:

- low speed environment (the phases after a long period will be separated by the gravity effect),
- increase in temperature (lower viscosity),
- external electric field,
- high shear stress in the emulsion,
- the addition of a chemical that influences the emulsifier or liquids, and
- the addition of a diluting liquid.

A colloidal dispersion can be kinetically stable with respect to coalescence, but unstable with respect to aggregation. Or, a system could be kinetically stable with respect to aggregation but unstable with respect to sedimentation. In summary, although lyophobic colloids are thermodynamically unstable, they may be relatively stable in a kinetic sense, and it is crucial that stability be understood in terms of a clearly defined process [15].

2.4. Emulsion fuel viscosity

In general, water-fuel emulsions exhibit greater viscosity than pure liquid fuels, and both water content and size of the droplets dispersed in the emulsion significantly influence its viscosity (Figure 7 [22]) [23].

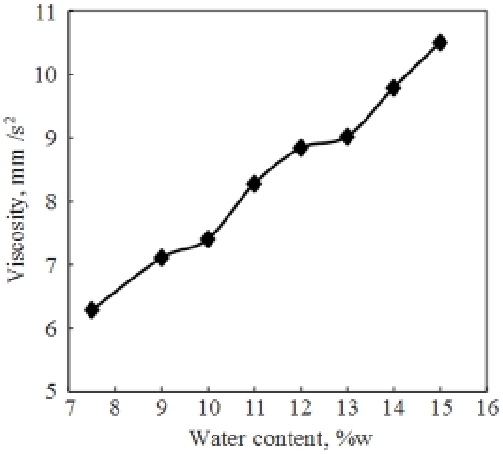


Fig. 7. *Effect of the water content on the viscosity of a micro-emulsion diesel oil* [22]

Ochoterena et al. [20] present an experiment where they compared the performance of EUD (European ultra-low sulphur diesel), water-in-diesel emulsion (88% diesel, 10% water and 2% additives) and micro-emulsion (80%, 10% water and 10% additives). They found that the viscosity of the water-containing fuels is higher than the viscosity of EUD as displayed in Figure 8, but the surface tension of the emulsion fuel across the studied temperature range was similar to that of the regular diesel.

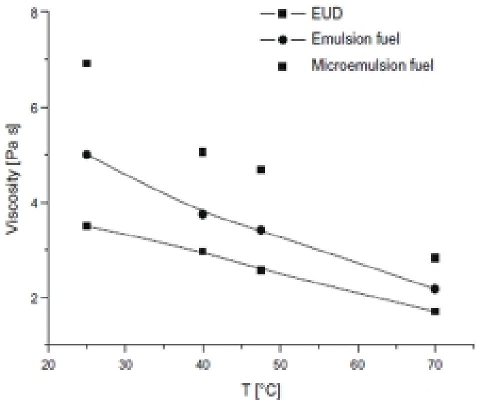


Fig. 8. *Viscosity of the three fuels vs. temperature from 25 to 70 °C, showing the higher viscosity of the water-containing fuels* [20]

The size distribution also has an important influence on the viscosity. For electrostatically or sterically interacting species, the dispersion viscosity will be higher, for a given mass or volume concentration when the species are smaller. The viscosity of all dispersions will tend to be higher when the dispersed species sizes are relatively homogeneous, that is, when the particle size distribution is narrow rather than wide [15].

In Figure 9 from [24], the viscosity of diesel fuel emulsion increases with water content up to the value of 43 centi-poise at 15% water, due to more complex micellar structures formed and it shows the water in oil (O/W) phase at this condition.

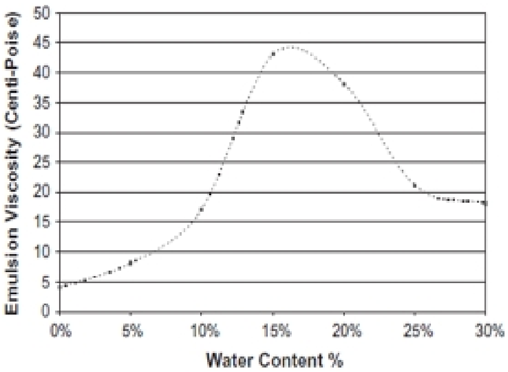


Fig. 9. *Viscosity of emulsion diesel fuel versus water content* [24]

Further addition of water changes the phase to the oil in water (W/O) and leads to the decrease of the viscosity. Therefore, increasing the viscosity of emulsified fuel tends to advance injection timing in some injection systems.

3. Conclusions

The technique concerned with introducing water into the engine combustion chamber was proposed by Prof. B. Hopkinson in 1913.

The main pollutants produced from the exhaust of diesel engines are nitrogen oxides (NOx), particulate matter, black smoke, carbon monoxide and carbon dioxide.

Water-in-diesel emulsion fuel (W/D) is a promising alternative fuel that could fulfill such requests in that it can improve the combustion efficiency of a diesel engine and reduce harmful exhaust emission, especially nitrogen oxides (NOx) and particulate matter (PM).

Of all the methods proposed to introduce water into the combustion chamber, diesel oil emulsions appear to be the most appropriate, because they require no engine retrofitting.

The emulsion is formed with the help of mechanical agitation together with the chemical additives called surfactant to keep the immiscible liquids mixed together, forming one solution. Generally, emulsions are divided into two types: oil-in-water emulsions (O/W) and water-in-oil emulsions (W/O). Multiple emulsions are complex liquid multi-phase systems.

Surfactants or surface-active agents are amphipathic substances with lyophobic and lyophilic groups, making them capable of adsorbing solids and gases at the interfaces between liquids.

A frequently used method for selection of surfactants as emulsifying agents is known as the HLB (hydrophilic–lipophilic balance) method.

The stability of the diesel emulsion is affected mainly by the emulsification technique, emulsification duration, volume fraction of water, viscosity of the continuous phase, stirring speed and concentration of surfactants.

In general, water-fuel emulsions exhibit greater viscosity than pure liquid fuels, and both water content and size of the droplets dispersed in the emulsion significantly influence their viscosity.

With the advantage of energy saving and less environmental pollution for W/D emulsion, together with the newly developed emulsion fuel making device, it will provide a great contribution to the industries, and, at the same time, reduce the consumption of energy and ensure less pollution to the environment.

The obstacles that slow down the commercialization of emulsion fuel are the high production cost involved and the fuel stability issues. In order to eliminate the barriers to the commercialization of W/D emulsion fuel, simplification and optimization of the fuel production device can be investigated.

Some characteristics, such as water percentage, dispersed droplet size and viscosity depending on the engine working conditions, such as engine load and speed would be an interesting research area that can be explored fundamentally and practically in the near future.

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