

Water-Surrogate Fuel Emulsion Combustion Effect on CO and NO_x Emissions

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Abstract

Water emulsified fuel is one of the few promising emission reduction techniques with the potential to reduce NOX in diesel engines. little effort has been directed towards modeling the combustion of water-in-fuel emulsion. This work provides a better understanding of the effects of the existence of water in fuel in the form of emulsion on spray combustion and pollutant emissions namely NOX and carbon monoxide by modeling the relevant processes and focusing on the variables behind the emission reduction criteria and performance. The commercially available software CHEMKIN IV was used to simulate spray combustion at diesel engine-relevant conditions. Surrogate fuel (80 % n-heptane and 20 % toluene) was used due to the available detailed kinetic and thermodynamic data needed for modeling. An emulsified fuel with 3, 5, 8 and 20 % water by volume is used as an engine feed for each run separately and the results are compared with that of the dry surrogate fuel of 0 % water. The modeling results show that water has a significant effect on reducing engine operating temperature, and NOX formation. However the reduction of NOX is at the expense of an increase in carbon monoxide (CO) emissions and elongated ignition delay time, which is disadvantageous for the steady running diesel engines.

Keywords: water-surrogate fuel emulsion, combustion, CO and NOx emissions

1. Introduction

Global warming lousily generated by the increase in CO_2 emission via fossil fuel consumption is serious concern with respect to climate changes in the world. In addition, control of pollutant emissions is a major focus in the design of modern combustion systems. The major task for combustion engineers to pursue is, therefore, to achieve low pollutant emissions as well as reduction of fuel consumption.

Exhaust emission from diesel engines is a serious problem. However; according to the International Energy Agency (IEA) [1], 90% of the world's primary energy comes from combustion of fossil fuels, coal, oil and natural gas. The transportation sector is a major consumer of fossil fuel and additional efforts to cut emissions from road vehicles and airplanes are very important. Further growth of diesel engines in the light-duty and heavy-duty vehicular market has continued to focus attention on emissions reduction technology and the health risks of diesel exhaust. Market penetration of light-duty diesels has the potential for a significant impact on CO_2 emissions and a reduction in demand for imported crude oil due to offsets in overall global warming or thermal efficiency [2,4]. Although over the years significant advances have been made in reducing diesel engine emissions, the new stringent emission standards and legislation and the challenge to protect society, animals and nature against air pollution motivate the scientists to perform further studies and research to comply with the new regulations and reduce diesel engine emissions.

The basic engineering methods used by engine manufacturers to control emissions involve combustor design modifications [2-4], optimizing the in-cylinder operating parameters and exhaust after-treatment techniques. However, redesigning a combustor would be a viable option only for future engine design since retrofit costs would apply in this case. Also optimizing the in-cylinder operating parameters by doing some combustor modifications or changing operating conditions would very often result in reduced particle emissions and increased NO_X [5,6].

Exhaust after-treatment technologies for lean burn systems such as diesels in transportation applications are still in the development phases. Development and application of catalytic exhaust after-treatment technologies are hampered by the inherently high sulfur content in currently available diesel fuel. The high aromatic content and sulfur content of currently available diesel fuel also influences both NO_X and PM emissions [7,8]. For turbine engines, the use of after-treatment

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devices such as particle traps may not be practical as they would increase the engine weight and reduce performance. It is expected to enable after-treatment technologies so that heavy-duty engines can meet 2007 and beyond emission regulations [9,10] after the new significant legislation regarding sulfur content of diesel fuel (<15 ppm) which took place the year 2006.

Fuel reformulation, by altering the physical or chemical composition of fuel, has been used as a pollution control technique and continues to be considered as one of the more preferred avenues for realigning emissions in the future. Technology includes increasing fuel efficiency, wider use of alternative fuels and using fuel additives to improve the fuel quality.

One promising method to enhance this technology is the use of water emulsified fuel which can economically and environmentally accomplish the goals. It is one of the effective solutions to improve combustion, reduce fuel consumption and reduce emissions without enormous costs associated with engine modifications. In this regard, emulsified water-diesel fuel is attractive thus offering future economic and strategic alternatives to fuel oil consumption. There exists a wide range of applications with the potential of utilizing water-in-oil emulsified fuel in liquid-fueled combustors for pollutant reduction and enhanced fuel economy. The present study focuses on two aspects of emulsified water-diesel fuel utilization in diesel engines: first, the effect on engine operating conditions, mainly combustion temperature, and second, the influence of emulsified water-diesel fuel on emission degree of NO_X, and carbon monoxide 'CO'.

Several basic studies on the evaporation and combustion of isolated drops and burning sprays of emulsions have appeared in the literature [11-13]. Also, many researches on the use of emulsions in conventional combustors have been reported. These studies have shown that the effect of using emulsified fuel with the heavier fuels such as residual oils is more obvious where particulate matter emission and flame radiation are generally reduced by emulsification [7-9]. However, the CO, NO and hydrocarbon emissions and the thermal efficiency of combustion devices do not always improve when fuels are emulsified with water.

The effect of single and multi-point water addition systems on the NO_X and soot emissions of a vehicular heavy-duty diesel engine have been investigated by Samec *et.al* and coworkers [14,15]. Their results confess that both systems (single and multi-point) demonstrate practically the same propitious influence on NO_X emission reduction, but rather a poor effect on soot emission. However, the results of several other investigations 'performed recently' using water in fuel emulsion [16,17] have concluded that more promising results on NO_X and soot reduction may be expected.

Several experimental investigations were carried out on industrial furnaces and external combustion systems [18, 19], diesel engines [20,21] and gas turbines [22,23] to discuss some of the benefits of using water in fuel as an approach to improve the engine emission criteria, reduce the specific fuel consumption, control the engine thermal loading, and maximize combustion pressure [24,25]; however the variations in results from one set of experiments to another encouraged researchers to model the combustion of emulsified fuels and compare the modeling results with the actual combustion system results to predict the possible improvement that can be suggested. Schlitt and Exner [26] have compared water-in-diesel emulsions with humidified intake air; i.e., water in the form of aerosol. It was found that both systems reduced the NO_X level compared to traditional diesel fuel. The percentage of water in fuel in the studies of diesel emulsions varies. Most of the investigators used water content of 5–10%; however the use of higher percentages needs to be thoroughly investigated. It has been claimed that the optimum water content for NO_X reduction is between 10 to 20% [27].

Samec *et al.* [28] studied the effect of 10 and 20% water-indiesel on emission levels of NO_X , hydrocarbons and soot, as well as on the specific fuel consumption. The values obtained, compared to those of the neat diesel show considerable reduction in both hydrocarbons and soot at 10 % water; however 'in their work' the NO_X reduction seems to be more water sensitive than the hydrocarbons and soot, therefore the 20 % water in fuel level is needed to be investigated and reviewed thoroughly to clarify the discrepancies in results between the earlier work of Lawson, A, for Heavy-Duty Diesel Emission Control in 1986 [29] and that of Samec [14] in the year 2000.

Many researchers concentrated on the secondary atomization phenomena and emulsified fuel penetration concept. Zhou and Thorp [30, 31] have presented both theoretical and experimental studies on the differences between pure fuel and emulsified fuel atomization and discussed the effect of emulsified fuel atomization on fuel combustion. They measured the spray tip penetration and the spray angle in the combustion chamber of a marine diesel engine (Ruston 6APC) by using a high-speed camera with a micro-lens. In their study they found that the pure fuel spray compared to that of the emulsified fuel has longer spray tip penetration and wider spray angle. Also they proved that the tip penetration increases as the water percentage increases within the range 5-20% water in fuel. The number of countable droplets of emulsion fuel was much greater than that for pure fuel, indicating that the emulsion fuel spray possesses a larger total surface area. In addition, mathematical models for the prediction of spray tip penetration and spray angle were proposed.

A review of literature indicates that one of the significant virtues of applying emulsion fuels to combustion systems may be due to the changes of fuel properties which lead to enhanced atomization characteristics.

Little attention has been drawn in the past to modeling the combustion of emulsified fuels. Most of the work was directed toward modeling the behavior of emulsion droplet progress during the combustion process to thoroughly understand the micro-explosion phenomenon and when it could be established [22, 32]. The ability to predict whether micro-explosions will or will not occur, and when during the droplet lifetime they are likely to take place, though of great value, is not sufficient to clarify the role of water on the combustion process effluent materials formed.

The approach described here aims at providing a model for emulsion spray combustion of different water-in-fuel ratios on emission reduction and engine operating conditions. The modeling procedure conducted through CHEMKIN code modeling software and the fuel used is a surrogate fuel consists of 80% n-heptane and 20% toluene which represent the conventional diesel fuel.

2. Modeling Approach

CHEMKIN IV modeling code [33] was used in this study to investigate the combustion of a mixture of surrogate fuel and water, whereas the surrogate fuel consists of 80% n-heptane and 20% toluene (by volume) and water ratios are 3, 5, 8 and 20% H₂O (by volume). The analysis was carried out using the PaSR model approach; hence PaSR addresses the interaction between chemical reactions and turbulence. One of the basic characteristics of PaSR is that the thermo-chemical properties inside a PaSR which are assumed to be spatially homogeneous are imperfectly mixed at the molecular level. The reactive fluids are not completely diffused into each other at the molecular level but their mean values are uniform throughout the reactor by turbulent stirring, thus PaSR may be used as a stand-alone model for studying turbulent combustion or other reactor systems where mass transport may be a rate-limiting factor.

CHEMKIN computation was performed using 393 species [29], including NO_x and soot precursors species, and 1,925 reactions [34]. The computations were initiated at 900 K and 39 bar with air as the oxidizer and surrogate mixture as the fuel. The temperature and pressure values were chosen to fit the actual parameters of the real engine [35, 36]. The fuel/air equivalence ratios studied were 0.8, 1, 2, 3, and 5. This enabled

exploration of how the product composition change with the amount of fuel from lean and stochiometric ($\emptyset \le 1$) to fuel rich ($\emptyset > 1$) combustion. Table 1 shows the initial composition for the five runs.

3. Results and Discussion

The temperature histories are plotted in Figure 1. First, it can be observed that the final combustion temperature decreases with increasing fuel/air-equivalence ratio. The ignition characteristics also change with fuel/air-equivalence ratio. The ignition delay decreases monotonically with increasing fuel/air equivalence ratio. This might appear unusual but can be explained by the higher concentration of fuel that speeds up the formation of H, O and OH.

These three species are important for the chain-branching reactions leading up to autoignition [34,37,38]. Information about ignition delay acquired from these computations is very important. In diesel spray combustion the temperature increases as the mixture is leaned out by entrained hot ambient air, thus acting in the opposite direction compared to the influence of mixture strength alone. Figure 2 shows how the chemical reactions proceed for a fuel/air-equivalence ratio of 2.

Table 1 Initial gas composition for the Chemkin computations

| | Equivalence Ratio, Ø | | | | | | | |
|---|----------------------|--------|--------|--------|--------|--|--|--|
| Mole fraction[%] | 0.8 | 1 | 2 | 3 | 5 | | | |
| n-heptane, C ₇ H ₁₆ | 0.8823 | 1.1005 | 2.1685 | 3.202 | 5.191 | | | |
| Toluene, C ₇ H ₈ | 0.3027 | 0.3795 | 0.7475 | 1.102 | 1.787 | | | |
| Oxygen, O ₂ | 20.705 | 20.651 | 20.345 | 20.054 | 19.495 | | | |
| Nitrogen, N ₂ | 78.110 | 77.869 | 76.739 | 75.642 | 73.527 | | | |



Figure 1. Calculated temperature for air/ Fuel (80% n-Heptane+20% Toluene) mixtures of different equivalence ratios. Pressure = 39 bar



Figure 2. Major species and OH for auto-ignition and combustion of (80% n-Heptane+20% Toluene), for (fuel/air)equivalence ratio = 2

Shown in Figure 2 are the major species during the combustion: C_7H_{16} , C_7H_8 and O_2 as reactants, CO, H_2O , CH_4 and CO_2 as products. OH is plotted since it plays an important role during autoignition and combustion. The amount of carbon dioxide is very small due to the deficit of oxygen at fuel rich condition. From an emissions point of view, it is interesting to predict the variation of CO values with fuel/air-equivalence ratio. The time-histories for CO are shown in Figure 3.



Figure 3 Mole fraction of carbon monoxide at different equivalence ratios

As expected, the lowest CO-level is found for lean and stoichiometric conditions at equivalent ratio of $\mathcal{Q}=0.8$ and 1. The temperature is, however, high and dissociation of CO_2 keeps the CO level higher than the expected level at normal exhaust temperature. It is interesting to have the peak at 24 ms for $\emptyset = 0.8$ and 1 which coincides with the starting final fuel breakdown and maximum heat-release. This shows that CO is important intermediate species during lean an and stoichiometric combustion. The final CO-level is much higher than the rich combustion cases. The highest CO-level is found for a fuel/air equivalence ratio of 2. However at higher equivalence ratio (i.e. 3&5) CO formation decreases. This can be explained by understanding that CO has to compete for oxygen with the partially oxidized hydrocarbons as shown from Figure 4.



Figure 4 Formation of HCHO from the combustion of surrogate fuel (80% n-heptane and 20% toluene) at different equivalence ratios

Adding water to surrogate fuel (80% n-heptane and 20% toluene) has a significant effect on changing the combustion behavior inside the PaSR reactor. Four different ratios (3, 5, 8 and 20%) of water (by volume) were added to fuel in the form of emulsion at two different air/fuel equivalence ratios (0.8 and 2). Those ratios were chosen to study the effect of water on the fuel-lean and fuel-rich combustion conditions. The real diesel engine only runs on a fuel lean condition, so it is just a matter of curiosity to know how water can affect this assumed situation.

Figure 5 and 6 predict the temperature profiles of fuel lean and fuel rich combustion conditions after adding 3, 5, 8 and 20% water to fuel. It is clear from those figures that the addition of water can eventually reduce the combustion temperature over the time range of the combustion process. Compared to neat surrogate fuel the peak temperature decreases with the increasing water content.



Figure 5. Calculated temperatures for water in surrogate (80% n-heptane+20% toluene) emulsified mixtures at fuel/air-equivalence ratio, Ø=0.8



Figure 6. Calculated temperatures for water in surrogate (80% n-heptane+20% toluene) emulsified mixtures at fuel/air-equivalence ratio, $\mathcal{O}=2$

Table 2 shows the maximum peak temperatures during the combustion of different surrogate emulsions at \emptyset =0.8 and 2. The values from this table were plotted in figure 7 to closely express the effect of water addition to fuel on combustion temperature. This figure clarify the temperature drop for both cases (i.e. fuel lean \emptyset =0.8 and rich \emptyset = 2) at different water ratios. The 20% water in fuel shows the largest temperature drop which suggests a major change in the combustion environment of the PaSR model. This temperature drop which occurs after adding water to fuel is explained by the heat loss taken from the process to evaporate water also the increased specific heat of the combustion gases due to the percent of water vapor involved [39].

Comparably, the effect of adding water to fuel in the case of fuel-rich condition at \emptyset =2 is not different from that of fuel lean condition at \emptyset =0.8. However, the lower temperature at the fuel rich condition reflects a clear change in temperature profile by suppressing ignition and lowering maximum temperature from 2550 K to 1950 K for 20% water in fuel rich condition.

Table 2. Maximum model temperature values at different water in fuel ratios for both fuel lean and fuel rich conditions where $\emptyset = 0.8$ and 2

| Equivalence Ratio | Q = 0.8 | | | | Ø = 2 | | | | | |
|---------------------------|---------|------|------|------|-------|------|------|------|------|------|
| H ₂ O | 0% | 3% | 5% | 8% | 20% | 0% | 3% | 5% | 8% | 20% |
| Maximum Temperature, K | 2750 | 2670 | 2560 | 2550 | 2280 | 2550 | 2450 | 2350 | 2200 | 1950 |



Figure 7. Maximum model temperature change at different water in fuel ratios for fuel lean and fuel rich conditions at Q = 0.8 and 2

Compared to pure fuel, it can be observed that the maximum combustion temperature decreases with the addition of more water to fuel. Also, higher ignition delay can be observed when water is added to fuel; This delay occurs due to lower combustion temperature and it increases monotonically with the increasing water percentage in fuel due to the change in ignition characteristics that occurs after adding water. The formation of carbon monoxide (CO) is considered as one of the major species that could be formed during the combustion process. The mechanism of CO oxidation with hydrogen-containing compounds such as water is usually called wet oxidation. According to Glassman [40], CO oxidation rate substantially increases with the increasing amount of hydrogen containing compounds (i.e. H_2O). In his proposed mechanism, Glassman [40] shows that the effect of small quantities of H_2O on CO oxidation rate are significant because the reaction rates between CO and OH are much greater than the reaction rates between CO and O or CO and O_2 . The water-catalyzed reaction proceeds in the following manner:

$$CO + O_2 = CO_2 + O \tag{1}$$

where k = $2.500E+12 T^{0.0} \exp (-47800.0 \text{ cal/mol} /\text{RT}) \text{ cm}^3/\text{mols} [35]$

$$O + H_2 O = OH + OH$$
 (2)

$$CO + OH = CO_2 + H \tag{3}$$

where $k = 4.76E+7 T^{1.2} \exp(-70 \text{ cal/mol /RT}) \text{ cm}^3/\text{mols}$ [35]

$$H + O_2 = OH + O \tag{4}$$

Reaction (1) is a chain initiating step, but it is slow and does not contribute much to the reduction of CO through the formation of CO₂. Reaction (3) is a chain propagating step, yielding H radicals which react with O₂ to produce the free radicals OH and O through the branching step (4). The formed OH radicals reacts with CO molecules as seen from reaction (3) and the formed O radicals participate in reaction (2) to produce more OH radical. Figures 8 and 9 show how the OH production changes with the amount of water added to fuel. It is obvious from figure 8 that the OH concentration increases with the increasing amount of water in fuel for the fuel-lean condition (\mathcal{O} =0.8).

Also it is depicted from figure 8 that the effect of adding water to fuel results in increase in the concentration of OH to a narrow maximum peak value which then falls down to a nearly constant lower value over the specific time range. Adding more water to fuel did not show significant increase in OH concentration compared to that between 0% and 5% water in fuel. This is possibly related to the imperfect turbulent mixing and temperature reduction inside the PaSR reactor at higher water in fuel ratio which affects autoignition and OH concentration [36].



Figure 8. Concentration change of OH radicals with time at the combustion of Surrogate fuel/water emulsion of 0, 3, 5, 8 and 20% water-in-fuel. \emptyset =0.8

At the fuel-rich condition (\emptyset =2). Markides and coworkers [41,42] in there experimental study, which depends on measuring the OH chemiluminescences from certain spots in the reactor, concluded that the concentration of OH decreases as the fuel ratio increases and they suggested that the combustion reactions are not simply kinetically controlled because of the nonlinear Arrhenius plots they got, and that the turbulence inside the reactor can delay autoignition which further express the effect of mixing.

Figure 9 shows the change of OH concentration at fuel rich condition ($\mathcal{O}=2$) with percent water added to fuel over a certain time period. The addition of 3 and 5 % water to fuel shows an increase in the OH production to a higher value than that of regular fuel; however, when 8 and 20% water were added the results predicted the contrary theme and the production of OH was noticeably decreased, this reflects the intensive dependence of OH formation on air/fuel equivalence ratio, water-in-fuel ratio and the combustion environment inside the PaSR. More water in fuel means lower combustion temperature and lower production of OH radicals.



Figure 9. Concentration change of OH radicals with time at the combustion of Surrogate fuel/water emulsion of 0, 3, 5, 8 and 20% water-in-fuel. \emptyset =2.0

It is also clear that the ignition delay increases with the increasing amount of water added to the fuel and predicts higher values at fuel-rich conditions with higher amount of water-in-fuel, that means CO formation should decrease with the increasing amount of water in fuel, however the formation profile of CO at fuel-lean condition ($\mathcal{O}=0.8$) with the percentage of water added to fuel illustrated in figure 10 shows that the formation of CO increases sharply at the beginning with the increasing amount of water added to fuel a maximum peak point and then decreases to a lower value where it stays constant over the entire time range.



Figure 10. Carbon monoxide (CO) formation change with time at the combustion of surrogate fuel/water emulsion of 0, 3, 5, 8 and 20% water-in-fuel, \emptyset =0.8

It can be seen that due to the fuel-lean condition the concentration of oxygen is high so a substantial amount of CO oxidation occurs which reduces the concentration of CO inside the reactor to a minimum value but remains higher than that of the neat surrogate fuel. Further reduction of CO formation has been expected after adding water to fuel due to the increased OH concentration; whereas more CO is produced through the oxidation reactions of soot precursors with OH radicals from which CO formation is essential, therefore CO compounds continuously compete with the other compounds in the process (i.e. soot precursors and N_2) to react with OH radicals and oxygen to form carbon dioxide which controls the conversion rate of CO to CO₂. Consequently the effect of temperature is important in suppressing the oxidation reactions of CO and N_2 to form CO₂ and NO_X.

A study conducted by Adams and Coworkers [43] proved that CO oxidizes rapidly at high temperatures in the presence of oxygen, but does not oxidize properly at cooler temperatures in turbulent conditions, consequently adding water to fuel in the form of emulsion reduces the temperature as shown in figures 5 and 6 therefore the oxidation rate of CO to CO_2 is expected to be lower.

It was shown before in Figure 3 that CO is an important intermediate species during lean and stoichiometric combustion. The formation level of CO is much higher at the fuel-rich conditions, whereas the highest CO formation level was found at fuel/air equivalence ratio of 2. Therefore, adding water to fuel at this level is expected to affect the CO formation in different way from that of lean and stoichiometric condition.

Figure 11 predicts that change when different ratios of water were added to fuel. It is clear that CO-level increases with the increasing amount of water added to fuel which is similar to the trend at the fuel-lean condition; however, the variation of CO-level at the fuel-rich condition increases sharply at the beginning and then continue increasing monotonically after the maximum peak point in the early combustion stage. The deficits of oxygen in the fuel-rich and the existing low temperature generated after adding water to fuel play an important role in increasing the CO concentration level during the combustion of emulsified fuel at the fuel-rich condition due to the reduced conversion of CO to CO_2 .



Figure 11. Carbon monoxide (CO) formation change with time at the combustion of surrogate fuel/water emulsion of 0, 3, 5, 8 and 20% water-in-fuel, at \emptyset =2

The effect of adding water to fuel on the NO_X formation is presented in Figures 12 and 13. Those figures represent the trend of NO_X formation, inside the PaSR reactor, for 3, 5, 8 and 20 % water added to fuel at fuel lean and fuel rich conditions where \emptyset =0.8 and 2, respectively. Both figures 12 and 13 predict decrease in NO_X formation with the increasing amount of water. However at fuel lean conditions, NO_X formation is higher than that of fuel rich condition for many reasons. First, at fuel rich the overall combustion temperature is lower than that of fuel lean for both neat and emulsified fuel 'as shown in Figures 1, 5 and 6' which negatively affects the formation. Secondly deficit of oxygen at fuel rich conditions makes the nitrogen molecules to compete with the hydrocarbon molecules in the combustion region to form NO_X which has less opportunity to react with oxygen at this lower temperature. Imperfect mixing condition inside the PaSR reactor is another important factor in reducing NO_X formation level due to less opportunity of nitrogen molecules to collide with oxygen or hydroxyl radicals and form NO_X . Also, it can be noticed from Figures 12 and 13 that adding more water to fuel (i.e. >5 %) does not expedite a significant reduction value in the NO_X formation level. That means NO_X formation can be reduced by adding water to fuel up to certain level.



Figure 12. NO Formation during the combustion of surrogate fuel (80 % n-heptane and 20 % toluene)/water emulsion at \emptyset =0.8 for 0, 3, 5, 8 and 20% water-in-fuel



Figure 13. NO Formation during the combustion of surrogate fuel (80 % n-heptane and 20 % toluene)/water emulsion at \emptyset =2.0 for 0, 3, 5, 8 and 20% water-in-fuel

4. Conclusion

Simulation tools provide an opportunity to explore the complex internal processes in the internal combustion engines and emission criteria.

The overall effects of adding water to fuel on diesel engine combustion and pollutants emissions can be summarized as follows.

The combustion peak temperature is reduced by adding water to fuel and this reduction is directly proportional to the amount of water added to fuel. Hence, more water in fuel means more energy is needed to evaporate the mixture droplets. This energy is taken from the system which reduces the temperature, therefore; vaporization of liquid water decreases the internal energy proportionally to the vaporization enthalpy of the liquid water and increases the specific heat capacity of the gas which leads to lowering the combustion temperature [32].

The modeling analysis conducted in this work revealed that the formation level of CO increased with the increasing amount of water added to fuel. Addition of water reduces the average temperature along the engine cylinder pathway to an extent where CO oxidation is substantially reduced and its concentration is increased. The 20% water in fuel shows the highest CO concentration.

Water-emulsified fuel can be successfully used in a percentage up to 5% water to reduce heavy-duty diesel engine exhaust emissions, mainly NO_X . This unconventional technique to reduce NO_X is suitable for on road diesel engine vehicles that can be used for transportation in urban area or for off road stationary engines, when they have to satisfy ultra-low emission standards.

It was interpreted in this work that NO_X formation is decreasing with the increasing amount of water added to fuel. The percentage reduction is related to the amount of water added to fuel. Since the chemical reaction rates are strong exponential functions of temperature which implies that the intensity of reactions in the flame zone decreases exponentially with the increasing amount of water in fuel. As a result, it directly influences the thermal NO_X formation as predicted from Zeldovich reaction mechanisms [44]. However NO concentration is also reduced by reducing the O atoms concentration through the consumption of those atoms to form OH radicals. Adding more water to fuel (i.e >5 %) did not show any significant effect on NO_X reduction level; however a strong relationship between the carbon monoxide concentration and NO_x was noticed. CO concentration increased with the decreased concentration of NO_X that means any decrease in NO_X formation will be followed by more carbon monoxide formation which is one of the most significant threats to the environment.

References

- DOE/EIA (Department of Energy/Energy Information Agency) Annual Energy Outlook, DOE, Washington, DC. (2008).
- [2] Stone, R., "Introduction to internal combustion engines".: Society of Automotive Engineers (SAE), Warrendale, PA, 1999.
- [3] Edwards, S.P., Fränkle, G.R., Binder, K., Wirbeleit, F., "Strategic Analysis of Technologies for Future Truck Engines", SAE paper 2000-01-3458.
- [4] Avinash Kumar Agarwal[,] Biofuels (alcohols and biodiesel) applications as fuels for internal combustion engines[,] Department of Mechanical Engineering, Indian Institute of Technology, Kanpur-208 016, India November 2006.
- [5] Jiafeng Sun, Jerald A. Caton, Timothy J. Jacobs 'Oxides of nitrogen emissions from biodiesel-fuelled diesel engines, Progress in Energy and Combustion Science, 36, 677-695 (2010). http.dx.doi.org/10.1016/j.pecs.2010.02.004
- [6] Xiaoyu Yan and Roy J. Crookes; Energy demand and emissions from road transportation vehicles in

ChinaLow-Carbon Mobility Centre, Progress in Energy and Combustion Science; Elsevier; December 2010.

- [7] C. Allouis, A. L'Insalata, L. Fortunato, A. Saponaro, F. Beretta; 'Study of water-oil emulsion combustion in large Larsen BR.; 'Effect of water/fuel emulsions and a cerium-based combustion improver additive on HD and LD diesel exhaust emissions.' EU Joint Research Centre Ispra, Institute for Environment and Sustainability, Emissions and Health Unit, 21020 Ispra (VA), Italy. Environ Sci Technol. Sep 1;39(17):6792-9; 2005.
- [8] Farfaletti A, Astorga C, Martini G, Manfredi U, Mueller A, Rey M, De Santi G, Krasenbrink A, Larsen BR.; 'Effect of water/fuel emulsions and a cerium-based combustion improver additive on HD and LD diesel exhaust emissions.' EU Joint Research Centre Ispra, Institute for Environment and Sustainability, Emissions and Health Unit, 21020 Ispra (VA), Italy. Environ Sci Technol. Sep 1;39(17):6792-9; 2005.
- [9] Nakicenovic, N., World Energy Outlook 2007: CO₂ Emissions Pathways Compared to Long-term CO2 Stabilisation Scenarios in the Literature and IPCC AR4, OECD/IEA, Paris, available at http://www.worldenergyoutlook.org/docs/weo2007/C O₂_Scenarios.pdf., (2007).
- [10] Walsh, M. P., "Global Trends in Diesel Emissions Regulation - A 2001 Update," SAE 01-01-0183, 2001.
- [11] Gerhard Knothe 'Biodiesel and renewable diesel\: A comparison; Progress in Energy and Combustion Science June 2010.
- [12] Park, J.W., Huh, Y. and Park, K.H., "Experimental study on the combustion characteristics of emulsified diesel in rapid compression and expansion machine Process", Institution of Engreers;214. Part D, ImechE, 2000.
- [13] Isihada, M. and Chen, Z.L., "An analysis of the added water effect on NO_X formation in DI diesel engines", SAE Paper, 941691, 1994.
- [14] Samec, N, Dibble, RW., Chen, JY and Pagon, A., "Reduction of NOx and Soot emission by water injection during combustion in a diesel engine", FISITA 2000, Seoul, Korea; 2000.
- [15] Cernej, A. and Dobovis, ek. Z., Bhattacharya S. and Kegl B., "Experimental study on the effect of the multipoint timed port water injection in a vehicular diesel engine", KONES 93, International Science Conference on IC Engines, Gdansk, Conference, Proceedings; pp. 81–9. 1993.
- [16] Radloff, E. and Gautier, C.,'Diesel Engine NO_X reduction Using Charge Air Water Injection', Transportation Development Centre Transport Canada Proceedings of ICED of ASME: 2005 Fall Technical Conference September 11-14, Ottawa, Canada, ICEF2005-1235, 2005.

- [17] Mello, J.P. and Mello, A..M., "NOx emission from direct injection diesel engines with water/steam dilution", SAE Inc., 01-0836, pp. 15–30.1999.
- [18] Hall, R. E., 'Effect of water/residual oil emulsions on air pollutant emissions and efficiency of commercial boilers', Environmental Protection Agency, Research Triangle Park, NC, ASME J. Eng. Power; Vol/Issue: 98:4; P 425-434, 1976.
- [19] Gunnerman, R.W. and Russell, R. "Emission and Efficiency Benefits of Emulsified fuels to internal combustion engines", SAE Paper, 972009, 1997.
- [20] Storment, J. O. and Coon, C. W., 'Single-cylinder diesel engine tests with unstabilized water-in-fuel emulsions', Department of Transportation, US Coastguard, Report No. CG-D-13-78, 1978.
- [21] Vchniesky, R., Murat, M., Parois, A. and Dujeu, M., 'Employment of fuel-water emulsion in compression ignition engines', CIMAC Conference, Barcelona, Spain, April 28-May 3, 1975.
- [22] M. Arias-Zugasti, D. Rosner 'Multicomponent fuel droplet vaporization and combustion using spectral theory for a continuous mixture' Combustion & Flame, 135, 271-284, 2003. http.dx.doi.org/10.1016/S0010-2180(03)00166-4
- [23] Nageli, D. W. and Moses, C. A., 'A correlation for soot formation in turbine combustion that includes emulsified fuels', in Proc. of Symp. On Water-in-Fuel Emulsions in Combustion, ed. R. Walter and J. White. U.S. Department of Transportation, Report No. CG-D-12-78, 1978.
- [24] Yoshimoto, Y., Tsukahara, M. and Kuramoto, T., "Improvement of BSFC by reducing diesel engine cooling losses with emulsified fuel", SAE Paper, 962022, 1996.
- [25] Tsukahara, M. and Yoshimoto, Y., "W/O emulsion realizes low smoke and efficient operation of DI engines without high pressure injection", SAE Paper, 890449, 1989.
- [26] Schlitt, H-G. and Exner, P., "Emission of diesel motors when run on alternative fuels", Glueckauf-Forschungshefte. Vol. 52, no. 6, pp. 278-282, 1991.
- [27] Bartok, W. and A. F. Sarofim. Eds. Fossil Fuel Combustion: a Source Book. Wiley, New York, 1991.
- [28] Samec, N, Kegl, B and Dibble, RW. 'Numerical and experimental study of water/oil emulsified fuel combustion in a diesel engine' Fuel 81: 2035-2044, 2002.
- [29] Lawson, A, Vergeer, E.C., Mitchell, E.W. and Dainty, E.D., "Heavy-Duty Diesel Emission Control", A Review of Technology, vol. 36. Montreal, Quebec, Canada: CIM; p. 238, 1986.
- [30] Yoshimoto, Y., Tsukahara, M., Murayama, T., 'Studies on the microexplosion of emulsified fuels', Trans. JSME (B) 89-0059 B,1989.

- [31] Lasheras, J, Fernandez-Pello, A, Dryer, F. Experimental observations on the disruptive combustion of free droplets of multicomponent fuels'. Combustion Science Technology. Vol. 22, pp. 195-209. 1980. <u>http:/dx.doi.org/10.1080/00102208008952383</u>
- [32] Wang, Li-Po, Wei-Biao, Fu., 'Analysis of the combustion characters and the mechanism of oilconsumption economy for diesel engines using water-in-oil', Fuel Processing Technology 72(2001).
- [33] Kee, R. J., Rupley, F. M., Miller, J. A., Coltrin, M. E, Grcar, J. F., Meeks, E., Moffat, H. K.,Lutz, A. E., Dixon-Lewis, G., Smooke, M. D., Warnatz, J., Evans, G. H., Larson, R. S., Mitchell, R. E., Petzold, L. R., Reynolds, W. C., Caracotsios, M., Stewart, W. E., Glarborg, P., Wang, C., McLellan, C. L., Adigun, O., Houf, W. G., Chou, C. P., Miller, S. F., Ho, P., Young, P. D., Young, D. J., Hodgson, D. W., Petrova, M. V., and Puduppakkam, K. V., CHEMKIN Release 4.1, Reaction Design, San Diego, CA 2006.
- [34] Curran, H. J., Pitz, W. J., and Westbrook, C. K., 'Extinction and Autoignition of n-Heptane in Counterflow Configuration", Proceedings of the Combustion Institute, Volume 28, p. 2029-2037, 2002 UCRL-WEB-204236 Review and release date: May 19, 2004.
- [35] Canfield, C.A., Effects of Diesel-Water Emulsion Combustion on Diesel Engine NO_X Emissions, a graduate thesis, University of Florida, 1999.
- [36] Akinyemi, O.C. and Cheng, W.K., "A Flame Sheet Model for NO Production in Diesel Combustion Simulation", SAE paper 982586, 1998.
- [37] Heywood, J.B., "Internal Combustion Engine Fundamentals Book", McGraw-Hill, McGraw-Hill Series in Mechanical Engineering, 1988.
- [38] Easley, W.L. and Mellor, A.M., "NO Decomposition in Diesel Engines", SAE paper 01-3546, 1999.
- [39] Siebers, D.L., Higgins, B.S., "Flame Lift-Off on Direct-Injection Diesel Sprays Under Quiescent Conditions", SAE paper 2001-01-0530, 2001.
- [40] Glassman, I., "Combustion (Book)", 3rd edition, Academic, San Diego, Calif., pp 20–29., 1996.
- [41] Markides, C.N. and Mastorakos, E., "Experiments on the Autoignition of Ethylene Injected Concentrically into Confined Annular Jets of Hot Air", European Combustion Meeting, Louvain-la-Neuve, 2005.
- [42] Markides, C.N. and Mastorakos, E., "Turbulent Autoignition of Hydrogen and Acetylene in a Duct", European Combustion Meeting organized by the French Section of the Combustion Institute and CNRS-LCSR, Orleans, 2003.

- [43] Adams, B. R., Cremer, M. A., Wang, D. H. 'Modeling Non-equilibrium CO Oxidation in Combustion Systems', Reaction Engineering International, Salt Lake City, Utah USA. Presented at the International Mechanical Engineering Congress & Exposition, Orlando, Florida, Nov 5-10, 2000
- [44] Mary, F. B, Charles, D. J, William, A. M., "Rate constants for the reaction OH + CO as functions of temperature and water concentration", Chemistry Division, Argonne National Laboratory, Argonne, Illinois 60439, 2000.