

The Oxidation Potential Number: An Index to Evaluate Inherent Soot Reduction in D.I. Diesel Spray Plumes

Barbara Graziano, Benedikt Heuser, Florian Kremer, and Stefan Pischinger
RWTH Aachen Univ.

Hans Rohs
FEV GmbH

ABSTRACT

A new index to evaluate the inherent soot reduction in a diesel-like spray plume is proposed in this study. The index is named "Oxidation Potential Number" and was derived with the help of a computational fluid dynamics (CFD) software. C8 - C16 n-alkanes, 1-alcohols and di-n-ethers were studied with the help of this index over four part load engine operating conditions, representative of a C-class diesel vehicle. The CFD modelling results have shown that C8 molecules feature a higher potentiality to reduce the soot. Thus, C8 molecules were tested in a single cylinder diesel engine over the same operating conditions. In conclusion, the proposed index is compared with the soot engine out emission.

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INTRODUCTION

Global energy demand has been continuously rising with scientific and technological progress. In recent years, research in internal combustion engines (ICE) has been focusing on alternative fuels due to the limitation of fossil resources. In addition, the increasingly stringent emission regulations have been demanding a drastic reduction in greenhouse gases and combustion pollutants, posing a difficult challenge in the realization of cleaner compression ignition (CI) combustion. When fossil energy sources are used, the reduction of carbon dioxide (CO₂) emission can only be achieved with an improvement in fuel economy. However, to follow current emission regulations, a drastic reduction of nitrogen oxides (NOx) is necessary by means of high exhaust gas recirculation (EGR) rates. Thus, fuel economy and particulate matter (PM) emission are worsened. According to a report by the Joint Research Center of the European Commission released in 2014, in Europe, biofuels represent the best short-term choice as an alternative for standard gasoline and diesel fuels, allowing more than 50% reduction in the overall well-to-wheel CO₂ emission, while keeping production costs competitive with fossil derived fuels [1].

According to the review of Xue et al., beyond the low aromatic content of biofuels, the oxygen content drastically reduces the PM, carbon monoxide (CO) and unburnt hydrocarbons (HC) emissions in diesel engines. The drawbacks are represented by the increase of NOx emissions and fuel consumption [2]. NOx emission increase is due to the higher premixed burn fraction of the combustion, caused by the carbon saturation level of biofuels' straight chained molecular structure, which acts as a self-ignition enhancer. This is generally true

for high cetane number (CN) oxygenated fuels such as di-n-ethers, but it is not valid for alcoholic fuels which are less prone to self-ignite. The increase in fuel consumption is caused by the heating value, which is lower than that of diesel fuel. Consequently, to achieve the same indicated power, more injected mass is required [3].

Recent studies on diesel engines, fueled with biofuels, have demonstrated that adequate injection timings and EGR rates are valid strategies to meet current norms, while keeping engine performance competitive with those diesel-fueled. Miyamoto et al. investigated the effect of non-alcoholic oxygenates on combustion and emission performance when they are blended with diesel fuel. The authors observed significant improvements in PM, NOx, HC, combustion noise and thermal efficiency when blending sufficient amount of oxygenates with diesel fuel in a direct injection (DI) diesel engine [4]. The work pointed out that the improvement in emission performance was mainly due to the oxygen content included in the molecular structure of the tested fuels, independently of oxygenated type and blending ratios. Mueller and Martin investigated the soot reduction caused by the blending of diesel fuel with non-alcoholic oxygenates in an optically accessible heavy duty diesel engine. In this work, owing to the optical investigations, it was possible to underline that the oxygen content of the fuels caused more than 3 times reduction of soot emissions when compared with diesel fuel. Additionally, it was shown that oxygenated fuels' thermo-physical properties and self-ignitability played a fundamental role in the mixture formation quality [5]. The above studies have indicated that oxygenates reduce raw soot emission, i.e., upstream the after-treatment system (in the present study, soot is considered as a tracer of

PM). The oxygen content in their molecular structure is the main cause for the change in combustion properties, such as the lower heating value (LHV), heat of formation, self-ignitability, and adiabatic flame temperature. Furthermore, it acts as suppressor of soot precursors [6, 7]. Thus, research on biofuels is worthwhile to realize cleaner CI combustions, thus reducing the need for costly after-treatment systems. For this reason, an interdisciplinary research project was established to develop novel biofuels at Rheinisch-Westfälische Technische Hochschule (RWTH) Aachen University, namely the Tailor-Made Fuels from Biomass (TMFB). This project aims to discover novel oxygenated fuels for ICE application from a biomass derived feedstock. In the past five years of research, lignocellulose was established as the starting material to develop new biofuels to prevent competing with food industry production [8, 9]. Recently, focus was given on the definition of combustion performance indicators to be introduced in the design process of biofuels in order to tailor their molecular structure towards cleaner CI combustion. This is the long term goal of the study presented herein.

The aim of the presented work is the development of a model capable of correlating raw soot emissions of different fuels with their molecular structure, in order to give feedback information to the design process of novel biofuels. Detailed soot modelling for all possible biofuel candidates, at varying engine operating conditions, would lead to an extensive experimental and simulative effort. Thus, a model-based approach has been chosen. In the numerical modelling, the influence of the molecular structure on the engine soot emissions is studied under three different aspects: intrinsic fuel tendency to form soot, air/fuel mixture tendency to oxidize soot and fuel self-ignitability.

In a former work, a sensitivity analysis on the influence of fuel thermo-physical properties on the mixture formation process was presented [10]. It was performed with the help of a computational fluid dynamics (CFD) software package in order to study the mixture formation from an in-cylinder point of view in a small bore DI diesel engine. C8 - C16 molecules belonging to n-alkanes, 1-alcohols, and di-n-ethers were analyzed with regards to their mixture formation quality. This study pointed out that thermo-physical properties of a fuel directly influence the local air/fuel equivalence ratios during combustion. C8 straight-chained molecules were suggested as optimal candidates to improve the mixture formation process in a typical diesel spray plume. It was shown that n-octane in general allows a better degree of mixing compared to the C8 oxygenated fuels, but this influence is overcome by the oxygen molecular content. Thanks to this preliminary study, it has been possible to identify a new emission index which is herein proposed as the Oxidation Potential Number (OPN). The OPN is used to evaluate the potential of different fuels to reduce the soot formed during combustion. The fuels under examination are C8 - C16 di-n-ethers, 1-alcohols and n-alkanes. Additionally, the fuels are analyzed with regard to fuel impingement on combustion chamber walls. Next, the results of the C8 fuels, which have been tested on a single-cylinder research engine (SCRE), are presented and the soot emissions are correlated with the OPN. The article ends with conclusions and outlook.

MATERIALS AND METHODS

In this paragraph, the relevant aspects for soot dynamics in CI combustion are presented, followed by a description of the fuels under examination. Afterwards, the CFD modelling approach is described. Here, the main realization steps of the preliminary sensitivity study are briefly recalled, followed by the definition of the OPN. Next, the test bench facility used to investigate the C8 fuels is presented.

Model-Based Approach

Relevant Aspects for Soot Dynamics in CI Combustion

Soot formation and oxidation dynamics result from complex phenomena, which occur simultaneously in the combustion chamber. While for a diesel free jet, the dynamics of formation and oxidation of soot have been explained by Hec [11], in CI combustion the dynamics are not completely understood. In ICEs, the soot emissions are influenced by several engine calibration parameters. According to Oppenauer and Alberer, raw soot emissions are influenced by swirl level, EGR rate, ignition delay, injection timing and rail pressure [12]. The authors delineated that the degree of mixing of the air/fuel mixture has an influence on the soot oxidation process and that it has nearly no impact on the soot formation rates. During the high pressure cycle, i.e., from intake valve closing (IVC) time to exhaust valve opening (EVO) time, the soot formed undergoes a maximum peak that is usually located right after the premixed burn rate region of combustion. Afterwards, the soot formed is reduced during the diffusive burn. During this stage, the spray plume is completely surrounded by the flame; an aspect which influences both formation and oxidation of soot. While the formation process is slowed because of the mixture enleanment, the oxidation process is weakened due to the flame temperature cooling induced by the expansion stroke. However, the soot particles formed can survive the combustion process for two main reasons: the exhaust valve opens and there isn't sufficient time to complete the burnout, or peripheral parts of the flame quench due to heat losses at combustion chamber walls. Thus, good air entrainment helps enhancing soot reduction before EVO.

The exact mechanism of soot oxidation has been the focus of research and is not fully understood. One mechanism that has been proposed in literature attributes the soot oxidation near stoichiometric air/fuel ratios to the attack of hydroxyl radicals (OH) on the soot particles. Thus, the ability to form H-bonds on the surface of the soot particle and the oxygen availability in the combustion environment represent boundary conditions for the soot oxidation process [13, 14, 15]. The first aspect depends on the reactivity of the molecule. The reaction kinetics influences the tendency to form soot as well and it will be the object of future investigations. The second aspect depends on the mass transfer occurring between the liquid injected fuel and the hot compressed air in diesel-like spray plumes. Thus, the degree of air/fuel mixing, which drives the spatial distribution of the vapor mixture inside the combustion chamber and controls the air entrainment, is of utmost importance. At a given engine operating point, the influence of turbulence on the mixture formation can be considered constant with good approximation. Hence, the mixing process is controlled by the thermo-physical properties of a fuel and by the injection strategy.

Engine calibration parameters are not the only cause of soot emissions. The intrinsic soot suppression potential of many oxygenated fuels has been extensively reported also in the literature on smoke point measurements. Pepiot-Desjardins et al. have measured an extended set of different oxygenated fuels in a laminar diffusive flame burner and they have found that the oxygen moieties are the main cause of the inhibition in soot precursors when a hydrocarbon fuel is blended with an oxygenated fuel [6]. The recent work of Barrientos et al. on C5 oxygenated fuels is in good agreement with the above mentioned work, confirming that oxygenated fuels reduce soot formation [7]. Thus, the fuel itself can be seen as a source of soot.

As above mentioned, this study aims to delineate a direct link between the molecular structure of a fuel and soot emissions in CI combustion. In order to investigate the influence of the molecular structure on raw soot emissions, several aspects must be taken into account. These can be subdivided into fuel-dependent and engine-dependent categories. The fuel-dependent aspects are a direct consequence of the fuel molecular structure and can be summarized as follows:

- Fuel intrinsic soot formation (i.e., oxygen content of a fuel, fuel reactivity and adiabatic flame temperature [6, 7])
- Influence of fuel thermo-physical properties on soot oxidation (i.e., fuel's capability to mix with surrounding hot air and to entrain oxygen, in order to oxidize the soot formed during combustion [12, 15])
- Fuel self-ignitability (i.e., molecular structure's influence on physico-chemical ignition delay [16]).

Engine dependent aspects can be summarized as follows:

- Engine operating conditions (e.g., speed, indicated mean effective pressure, rail pressure, EGR rates, and injection timing [12])
- Engine combustion system layout (e.g., piston bowl geometry, injector nozzle layout, and turbulence intensity level [17, 18])
- Engine air path system layout (e.g., air charge motion type and swirl level [12])

Fuels Tested

The fuels analysed in the CFD study were n-alkanes, 1-alcohols, and di-n-ethers. An example of C8 molecules for each family is given in Figure 1.

These families were chosen on the basis of the following assessments:

1. Straight chained molecules are desired due to their carbon atom saturation level. They are more reactive with oxygen than their respective isomers and ring structured molecules; thus, more prone to form radicals and self-ignite [19]. Moreover, the higher reactivity of straight chained molecules is beneficial with regard to soot formation and oxidation, assuming the "H-abstraction-C2H2-addition" (HACA) mechanism for polycyclic aromatics' (PAH) growth [20, 21].

2. The chain length of the molecule must not be shorter than C7 with regard to the n-alkanes because n-heptane meets the minimum ignitability standard for diesel fuel in Europe with a Derived Cetane Number (DCN) of 53.8 [22]. Since n-heptane had been extensively investigated [23, 24, 25] in the previous TMFB research campaign, it was decided to start with a minimum chain length of C8. The maximum range was established considering that n-hexadecane (C16) shows similar thermo-physical properties as diesel fuel and corresponds to a maximum CN of 100.
3. The oxygenated families chosen have the same molecular structure as the respective n-alkanes representatives plus one oxygen atom inside the molecule's chain. As can be seen in Fig. 1, 1-alcohols and di-n-ethers differ from each other only by the oxygen functional group. 1-Alcohols and n-alkanes increase their ignitability when their chain length increases. Di-n-Ethers do not show a clear trend; i.e., Di-ethylene glycol dimethyl ether CN = 126, Di-n-Butyl Ether (DNBE) CN = 100, and Di-Methyl Ether CN of 55 [4]. The 1-alcohols are the least reactive fuels analyzed followed by n-alkanes and di-n-ethers. A reduction in the CN was then included inside the domain of investigation for future studies on the ignitability since it was shown by Janssen et al. that the self-ignitability is not necessarily desirable for CI combustion applications when a partially homogenized combustion should be realized to decrease soot formation [26].

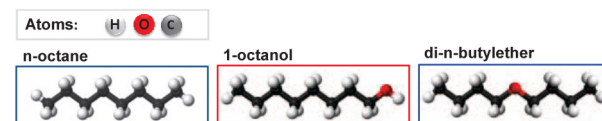


Figure 1. 3D C8 molecules of oxygenated fuel families studied [27].

CFD Modelling

In a previous work, a computer aided engineering methodology was developed to analyze the effect of the thermo-physical properties of a fuel on air/fuel mixing under cold evaporative conditions, this was called Virtual Fuel Approach (VFA) [10]. The analysis was performed in inert conditions in order to only capture the influence of the thermo-physical properties on the mixture formation and evaporation processes. This decision was also motivated by the lack of an available dedicated ignition model for all the different fuels to study. The main implementation steps of the VFA are presented in Figure 2. The VFA is a computer aided engineering method that utilizes a 3D CFD software package. A base CFD model for the combustion system of the SCRE was validated in two different steps. First, the CFD model was validated with regards to spray behavior and afterwards with regard to combustion and emissions for the reference diesel fuel EN590. This two-step model validation was performed for four part load operating points. The details of the CFD modelling validation and of the implementation of the VFA can be found in [10]. The details of the computational domain used to perform the validation of the CFD code are given in Table I in the Appendix. Afterwards, a sensitivity analysis of the local air/fuel ratios at varying thermo-physical properties under examination (viz., density, viscosity, surface tension, vapor pressure and enthalpy of vaporization) was performed. The fuels analyzed in the preliminary study were n-alkanes, 1-alcohol, and di-n-ethers with a range of C8

- C16 carbon atoms in the molecular structure. Each variation in property was performed by increasing the molecular structure of 2 carbon atoms and 4 hydrogen atoms as represented in Fig. 2. The injected mass and injection pressure were kept constant during the property variations to have the same global air/fuel ratio when performing the property variations.

Figure 3 gives an overview of the thermo-physical properties used for the different fuel families. In the top-left plot of Fig. 3, the investigation domain of the liquid density at 20 °C is presented. N-alkanes and di-n-ethers families increase their density with an increase in the molecular chain length. 1-Alcohols show a different trend due to the local polarity caused by the hydroxyl group, which is counteracted by the chain length increase due to the protection of the steric hindrance of adjacent groups [28, 29]. For all the fuels, with the variation of temperature, similar trends were observed in terms of viscosity, vapor pressure and surface tension. Thus, for the sake of brevity, only one family is plotted in Fig. 3; i.e., 1-alcohols for dynamic viscosity, alkanes for vapor pressure, and di-n-ethers for surface tension.

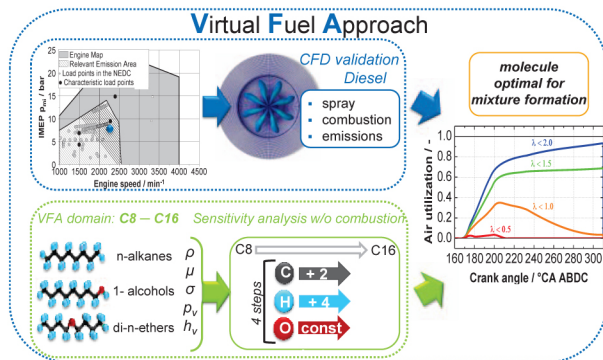


Figure 2. Main implementation steps of the VFA approach [10].

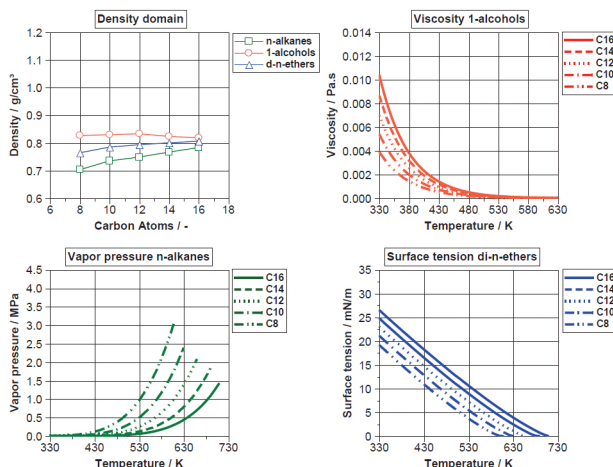


Figure 3. Observation domain of liquid density at 20 °C, viscosity, vapor pressure and surface tension.

The thermo-physical properties were modelled with the help of existing thermo-dynamic models [30, 31]. Linear regression analysis was applied to capture the influence of the carbon content on the different thermodynamic models and on the boiling behavior of a

fuel. The regression analysis was necessary to compensate the lack of data in literature for some of the molecules under examination. The models implemented were:

- Andrade's equation (1923) for the dynamic viscosity;
- Clausius - Clapeyron's (1834) thermodynamic law for the evaporation behavior (i.e., vapor pressure and enthalpy vaporization were varied together since they are linked by this law);
- Brock and Bird (1955) thermodynamic correlation for surface tension.

The influence of the boiling behavior on the liquid density was not modelled, since the software package neglects the temperature influence on the liquid density. All the other properties ranged from the injection temperature of 330 K to the critical temperature. The details of the linear regression models used to perform the fuel properties variation can be found in [10] and the VFA regression models used are presented in Table II in the Appendix.

The monitoring parameter chosen to study the air/fuel mixing process was the "Air Utilization" (AU). Assuming a reaction of complete combustion, the moles necessary to completely burn the fuel in presence of air are derivable by stoichiometry as follows:

$$C_x H_y O_z + \left(x + \frac{y}{4} - \frac{z}{2}\right) O_2 \rightarrow \frac{x}{2} CO_2 + \frac{y}{4} H_2 O; \quad (1)$$

where the term $\left(x + \frac{y}{4} - \frac{z}{2}\right)$ represents the required moles of oxygen to completely burn one mole of fuel.

Air Utilization is a non-dimensional parameter which represents the ratio of effective oxygen volumetric fraction over the stoichiometric one, as shown in Equation 2:

$$AU = \frac{Vol \lambda_i}{Vol_{totalchamber}}; \quad (2)$$

where 'i' stands for the different λ values of 0.5, 1.0, 1.5, and 2.0 as defined in Equation 3.

$$\lambda_i = \frac{O}{2 \cdot C + 0.5 \cdot H}; \quad (3)$$

As explained in Figure 4, the AU monitors the air/fuel equivalence ratios only during the high pressure cycle of the engine, in particular from starting of injection (SOI) to EVO.

In this study simplifications were made in order to consider only two main shares of the air/fuel mixture:

- Rich range ($\lambda < 1$), to monitor the share of mixture involved in the soot formation;
- Lean range ($1 < \lambda < 2$), to monitor the share of mixture involved in the soot oxidation process.

The air/fuel mixture not involved in the soot formation, and oxidation ($\lambda > 2$) was defined as unused air.

The CFD software package KIVA 3V Release 2, with the Engine Research Center (ERC) model extensions, was used to realize the simulations. The code includes a modified Re-Normalization Group (RNG) k- ϵ turbulence model, a Kelvin-Helmholtz (KH) and a Rayleigh-Taylor (RT) spray models, a Shell auto ignition model, a laminar/turbulent Characteristic Timescale Combustion (CTC) model, a crevice flow model and a spray/wall impingement model. The code features a Hiroyasu single-step soot model and uses the Zeldovich formulation for the NO_x emissions [32, 33]. This KIVA code also includes a soot model based on a modified Nagle and Strickland-Constable (NSC) oxidation model [34]. Modifications were implemented into the code to develop a fuel-flexible version, which permitted monitoring the mixture formation from an “in-cylinder” point of view, allowing the evaluation of characteristic numbers such as the Reynold (liquid phase), Weber (liquid and gaseous phase), Ohnesorge number, as well as the spray's physical properties (viz. droplet momentum, total liquid mass, relative velocity between liquid and gaseous phase, droplet radius). All these properties were analyzed and averaged over the injection duration through nine fixed cross sections, in order to capture the influence of the fuel path on the air/fuel mixing process.

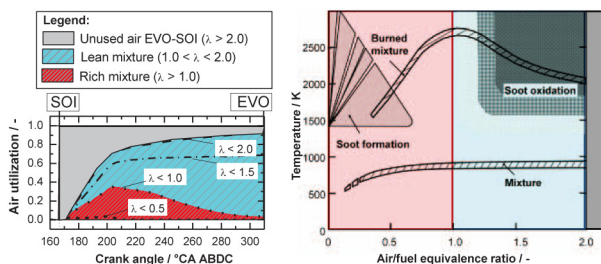


Figure 4. In-cylinder AU versus degrees Crank Angle (°CA) after bottom dead center (ABDC) and its correlation with soot emissions [35].

Figure 5 provides explanation of the nine sections implemented in the computational domain, where the term ‘r’ indicates a fixed section and the subscript number refers to the proximity from the nozzle hole (e.g., 1 is the nearest and 9 is the farthest section). A variable time step refinement was implemented in KIVA in order to increase the model accuracy during the injection event. A methodology to estimate the fuel impingement on the combustion chamber walls was developed owing to the implementation of the nine radial sections. The assumption made in this study, in order to evaluate the impingement, was that the liquid droplet leaving the last section, marked in blue in Fig. 5, will be less likely to evaporate, resulting in impinged mass of liquid fuel on the combustion chamber walls.

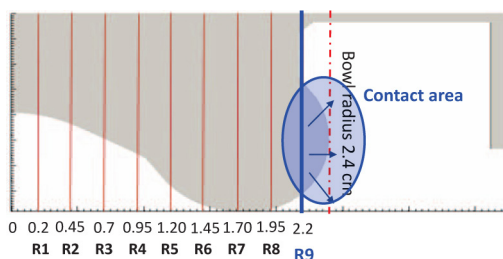


Figure 5. Radial sections implemented in the computational domain and example of the evaluation of the fuel impingement.

Definition of the Oxidation Potential Number

Thanks to the preliminary sensitivity study, it was possible to define a new emission performance index, namely the OPN. Referring to the fuel-dependent aspects discussed above, the OPN establishes a criterion to evaluate the inherent potential of an air/fuel mixture to reduce soot, accounting at the same time the engine-dependent aspects (viz., combustion system layout, air charge motion, injection strategy etc...). The main assumptions made while designing this index, are listed below:

1. In conventional CI combustion, when liquid fuel is injected into the combustion chamber, the formation of soot inside the rich vapour mixture cannot be avoided. Consequently, a good degree of air/fuel mixing is desirable to improve raw soot emissions.
2. The mixture formation process is a consequence of both convective and diffusive mass transfer. An improved mass transfer generates higher gaseous species gradients inside the combustion chamber, promoting oxygen diffusion.
3. The models featured by the software package are accurate enough to screen different fuels candidates for CI combustion.

The OPN was derived from the AU definition as presented by Equation 4:

$$OPN = \frac{\int_{SOI}^{EVO} AU|_{1 < \lambda < 2} \times \int_{SOI}^{EVO} AU|_{total}}{\int_{SOI}^{EVO} AU|_{1 < \lambda} \cdot \int_{SOI}^{EVO} unused\ air} ; \quad (4)$$

The share of the lean mixture was divided by the rich one and by the unused air. The OPN was defined as a non-dimensional number; a higher value of OPN should correlate with a better soot oxidation potential. The OPN with respect to the other stoichiometry-based indices, such as the oxygen equivalence ratio introduced by Chen at al. in [3], monitors the mixture in ranges of equivalence ratios which are relevant for soot emissions in CI combustion.

Comparison of the Different Fuels under Real Engine-Like Operating Conditions

Starting from the above mentioned VFA, a further simulation loop was realized in this study to analyze the OPN of the C8 - C16 fuels in real engine boundary conditions. Here, the fuel properties were varied all together at once and the injected mass was scaled according to the LHV of the fuel. Thus, the fuels were evaluated at a constant injected energy over four different part load engine operating points. This decision was made considering that the mixture formation dominates combustion and emission behaviors in DI diesel small bore engines. Rectangular shaped main injections were implemented in the CFD models. The needle opening and closing times were kept constant to avoid the influence of the needle lift on the nozzle outlet velocities. Thus, only the influence of flow behavior of the fuels was studied. The fuel variations were performed under cold evaporative conditions.