

The Relative Importance of Fuel Oxidation Chemistry and Physical Properties to Spray Ignition

Doohyun Kim, Jason Martz, and Angela Violi
University of Michigan-Ann Arbor

ABSTRACT

The ignition delay time for direct injection compression ignition engines is determined by complex physical and chemical phenomena that prepare the injected liquid fuel for gas phase ignition. In this work, Computational Fluid Dynamics (CFD) simulations of a reacting spray within a constant volume spray chamber are conducted to investigate the relative importance of liquid fuel physical properties and oxidation chemistry on the ignition delay time. The simulations use multi-component surrogates that emulate the physical and chemical properties of petroleum-derived (Jet-A) and natural-gas-derived (S-8) jet fuels. Results from numerical experiments isolating the fuel physical property and chemistry effects show that fuel chemistry is significantly more important to ignition delay than fuel physical properties under the conditions studied. In addition, as the air charge temperature increases, the effects of physical properties and oxidation chemistry decrease, indicating that the effect of variation in fuel properties on ignition timing may be mitigated through increased pre-ignition charge temperatures.

CITATION: Kim, D., Martz, J., and Violi, A., "The Relative Importance of Fuel Oxidation Chemistry and Physical Properties to Spray Ignition," *SAE Int. J. Fuels Lubr.* 10(1):2017, doi:10.4271/2017-01-0269.

INTRODUCTION

The diesel combustion process within direct injected (DI) compression ignition engines is composed of several phases, including the ignition delay period, the premixed combustion phase, the mixing-controlled combustion or diffusion burning phase, and the late combustion phase [1]. The ignition delay period, which is defined as the time between the start of injection (SOI) and the start of combustion (SOC), is quite important for diesel engine calibration. The onset of combustion in diesel engines is controlled through the fuel injection timing, and the ignition delay period changes drastically depending on the operating conditions and the properties of the fuel. Since optimal combustion phasing is critical for achieving high efficiency, understanding the ignition delay phenomena is essential for the engine control scheme.

It is well known that the ignition delay period is governed by complex fuel dependent physical and chemical phenomena, which prepare the injected fuel for combustion [1,2]. Figure 1 conceptually illustrates some of the major physical and chemical phenomena that occur during the ignition delay period of DI diesel engines. Initially, the liquid fuel is injected and starts to break down, generating smaller liquid droplets (breakup/atomization). These liquid droplets are decelerated (drag) and deformed (distortion) by the ambient charge; the droplets also collide and merge (collision/coalescence). At the same time, liquid fuel droplets are heated up by the hotter ambient charge and are eventually vaporized (evaporation). Air entrained into the fuel jet is mixed with the vaporized fuel to within combustible limits (fuel/air mixing). These are the physical processes required for fuel ignition, which are influenced by the temperature-dependent

liquid physical properties of the fuel, in addition to injection parameters (injection pressure, orifice diameter, etc.), air charge state during injection and geometric factors (combustion chamber/piston bowl design, etc.).

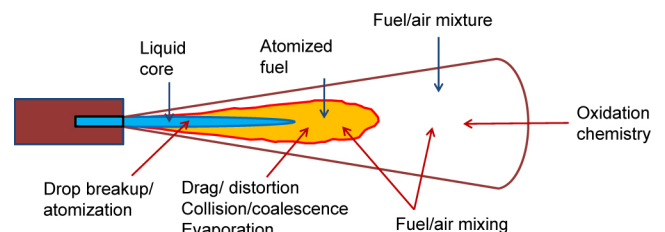


Figure 1. Conceptual schematic of the physical and chemical processes occurring during the DI diesel ignition delay period.

As soon as the liquid fuel is vaporized and the gas phase fuel meets oxygen, oxidation chemistry begins to prepare the fuel-air charge for ignition, which is enhanced by high temperature and pressure within the combustion chamber. Decomposition of the fuel molecules into smaller hydrocarbons and active radicals initiates the spontaneous ignition of the properly mixed air/fuel charge, leading to the premixed combustion phase.

Thus, the ignition phenomena of DI diesel engine present both physical and chemical aspects that are affected by the physical properties of fuel and its oxidation chemistry. Previously, these effects have been experimentally investigated using spray bombs. One of the approaches was to differentiate the physical and chemical processes by comparing the pressure trace from a reacting case with

fuel injection into air against the pressure trace from a non-reacting case with fuel injection into inert nitrogen. The instance when the two pressure traces diverge as a result of heat release was defined as the end of the physical delay period and the start of the chemical delay [3,4]. While this methodology attempted to isolate the closely-coupled physical and chemical processes, it inherently over-estimates the physical delay, since the time needed for the properly mixed charge to achieve noticeable heat release is regarded as the physical delay by this method. However, in principle, that period should be the chemical delay. A similar study using a constant volume spray chamber with optical access called Cetane Ignition Delay (CID) has been also reported [5,6], where the end of the physical delay and the start of the chemical delay is defined when excited CH_2O^* chemiluminescence, a low temperature heat release indicator, is first observed. Experimental studies using Ignition Quality Tester (IQT) with isomeric fuels [7, 8, 9] concluded that the differences in oxidation chemistry, and not physical property differences, were the dominating factor for the change in ignition delay time at the normal IQT operating condition (ambient charge of ~ 818 K at ~ 2.1 MPa). Bogin et al. [8] also observed that the change in liquid phase physical processes, which were perturbed by changing either the orifice diameter, injection pressure, or injected fuel mass, only caused small changes in ignition delay times (maximum 14%), while changes in the fuel auto-ignition quality resulted in a more than doubling of the ignition delay time relative to the baseline case.

While these studies provide valuable insights, these experiments were conducted at the nominal operating temperature of the spray chamber or in a narrow temperature range close to the nominal operating point. In diesel engines, the charge temperature at the start of injection has been estimated to range from approximately 850 to 1100 K [10]. The relative importance of physical and chemical processes to the ignition delay time may be therefore different from those previously investigated.

In this study, a series of numerical experiments under engine-relevant pressures and temperatures is performed to expand the current understanding on the relative importance of the fuel physical properties and oxidation chemistry to ignition within the fuel spray. 3-D CFD simulations of reacting fuel spray in a constant volume chamber are utilized for the numerical experiments. Multi-component fuel surrogates that capture the variations in the physical properties and oxidation chemistry of conventional and alternative jet fuels are used with a 360 species skeletal mechanism to understand the importance of these properties to diesel ignition.

COMPUTATIONAL MODEL

Spray CFD Model

CFD simulations of reacting sprays within the Sandia National Laboratories' constant volume optical spray chamber were conducted using the CFD package CONVERGE [11]. The turbulence in the gas-phase flow field was modeled with the RANS RNG k - ϵ model. The processes in the liquid phase were described with spray submodels, which are summarized in Table 1. The blob injection method [12] was used, which injects parcels of liquid fuel with the diameter equal to the effective nozzle diameter. The modified

Kelvin-Helmholtz – Rayleigh-Taylor (KH-RT) model, without the ad hoc breakup length definition, was used to predict the breakup and atomization of the liquid fuel [11]. Droplet evaporation was modeled with the Frossling correlation [13]. These spray submodels include liquid physical properties (density, viscosity, surface tension, vapor pressure, etc.) as model parameters, which is required for the fuel property perturbations in the current study. Also, previous computational studies have shown that these spray submodels are capable of capturing the spray characteristics of fuels with drastically different physical properties, such as DME, large alkanes, diesel fuel, and biodiesel [14, 15, 16, 17]. For the Sandia National Laboratories' spray chamber, a computational mesh of 0.25 mm minimum grid size was used; the base mesh size of 2 mm was refined with an automatic mesh refinement algorithm; fixed embedding was used near the nozzle to increase the grid spatial resolution. The minimum grid size was determined following the recommendations in Senecal et al. [21] which showed asymptotic convergence of spray characteristics with grid refinement.

Table 1. List of spray submodels used in the CFD simulations.

Phenomena	Model	Ref.
Liquid injection	Blob injection model	[12]
Breakup/atomization	Modified KH-RT model	[11]
Collision/coalescence	No Time Counter model	[18]
Collision outcome	Post outcome model	[19]
Drop drag	Dynamic drop drag model	[20]
Drop dispersion	O'Rourke turbulent dispersion model	[13]
Evaporation	Frossling correlation	[13]

Fuels and Their Surrogates

Three types of jet fuels, Jet-A POSF-4658, S-8 POSF-4734, and a JP-8 batch with unknown POSF identification number were considered for the current study. Jet-A POSF-4658 is a blend of several petroleum-derived conventional Jet-A batches, which represents the properties of a nominal Jet-A. S-8 POSF-4734 is a natural-gas-derived alternative jet fuel. These fuels were chosen since they have been extensively studied and have a wide range of property measurements and experimental data available. More importantly, these two fuels have significantly different properties due to the difference in the hydrocarbon class composition, which makes them suitable for the current study investigating the effect of fuel physical properties and oxidation chemistry on the spray ignition process. Jet-A POSF-4658 has Derived Cetane Number (DCN) of 47.3, while S-8 POSF-4734 has much higher ignition quality indicated by its DCN of 60.4. Also, Jet-A POSF-4658 has higher density compared to S-8 POSF-4634, which mainly stems from the absence of aromatics in S-8, compared to the approximately 19% liquid volume of aromatics in Jet-A [22]. In order to include more validation cases for the CFD

model, an additional petroleum-derived JP-8 was considered, which was extensively tested in a wide range of conditions in the Sandia National Laboratories' constant volume spray chamber [23].

Surrogates for Jet-A, S-8, and JP-8 were developed using the surrogate formulation methodology presented in [24,25]. The surrogate optimizer and the six-component surrogate palette (n-dodecane, n-decane, iso-cetane, iso-octane, decalin, toluene) for conventional and alternative jet fuels were utilized to emulate the various physical and chemical properties of the target fuels. Target properties include DCN, Lower Heating Value (LHV), Hydrogen-Carbon Ratio (H/C), Molecular Weight (MW), temperature-dependent liquid density, viscosity, specific heat, and the distillation curve. For JP-8, a smaller number of target properties was considered, which were cetane number, LHV, H/C, density at 15°C, viscosity at -20°C and 40°C, and distillation curve, due to a limited number of measured properties for the specific JP-8 batch. The surrogate compositions for Jet-A, S-8, and JP-8 are summarized in Table 2.

Table 2. Compositions of jet fuel surrogates in liquid volume fraction.

Vol Frac.	Jet-A surrogate	S-8 surrogate	JP-8 surrogate
n-dodecane	0.4784	0.3073	0.1417
n-decane	0	0.4234	0.1699
iso-cetane	0.1129	0.2309	0.2989
iso-octane	0	0.0384	0
decalin	0.2821	0	0.2487
toluene	0.1266	0	0.1408

Skeletal Mechanism Development

A comprehensive detailed chemical mechanism with 4236 species and 18000 reactions from the Model Fuel Consortium (MFC) [26] is used for kinetic modeling of the three jet fuel surrogates. A reduced version of the detailed mechanism is necessary to achieve feasible computational times for the CFD simulations. Therefore, a skeletal version of the MFC detailed mechanism was generated using Directed Relation Graph with Error Propagation and Sensitivity Analysis (DRGEPSA) [27], an automated reduction algorithm implemented in CONVERGE [28]. The original DRG algorithm [29,30] and its various derivatives including DRGEPSA [27,31,32] generates skeletal versions of detailed mechanisms for large hydrocarbons by identifying and removing unimportant species. For the current study, the DRGEPSA reduction algorithm was configured to exclude species from the detailed mechanism that had minor impact on homogeneous reactor ignition delay. The ignition delay calculations for the mechanism reduction were for the Jet-A and S-8 surrogates in the low to high temperature regime (700 K ~ 1100 K), with equivalence ratios from 1 to 2, and pressures from 20 atm to 40 atm for consistency with the conditions expected for ignition within the spray chamber [2]. The resulting skeletal mechanism includes 360 species and 1851 reactions.

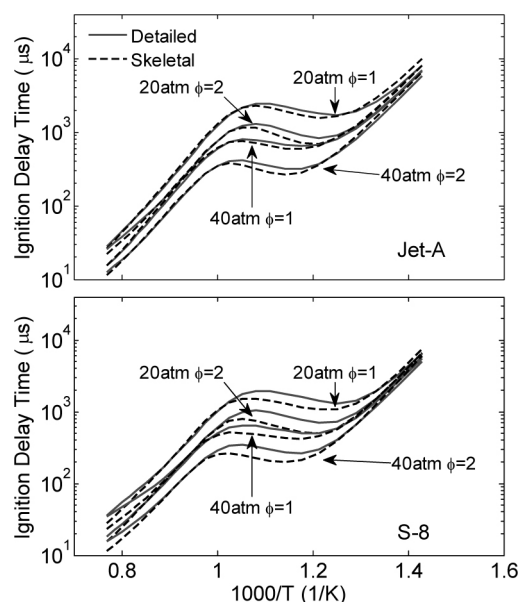


Figure 2. Comparisons of ignition delay predictions from the 360 species skeletal mechanism against the detailed MFC mechanism for the Jet-A and S-8 surrogates.

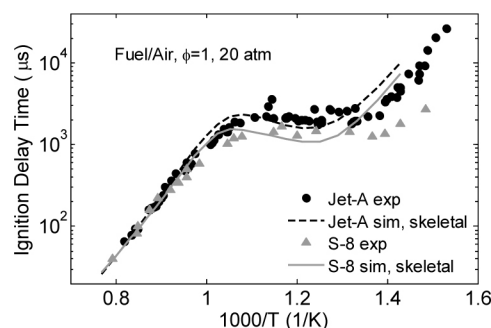


Figure 3. Comparisons of ignition delay predictions from the skeletal mechanism against the measured ignition delay times for stoichiometric Jet-A POSF-4658 and S-8 POSF-4734 air mixtures at 20 atm [33,34].

Figure 2 compares the ignition delay times calculated by the skeletal mechanism against those from the detailed mechanism. Overall, the skeletal mechanism maintains the ignition delay characteristics of the surrogates predicted by the detailed MFC mechanism. Among the 100 simulated points for each surrogate, the average relative deviation from the parent detailed mechanism was 8.0 % for Jet-A, and 13.6 % for S-8, while the maximum deviation was +23.2 % for Jet-A, -33.8 % for S-8. The most notable discrepancy for the S-8 surrogate was within the NTC regime, where the skeletal mechanism underpredicts ignition delay. Figure 3 compares the calculated ignition delay times of the Jet-A and S-8 surrogates using the skeletal mechanism against the measured ignition delay times from stoichiometric shock tube experiments at 20 atm [33], where the experimental data is available for the target jet fuels. It is shown that the predicted ignition delay times of the Jet-A and S-8 surrogates still captures the ignition delay trends observed in the shock tube experiments.

The reduction in computational expense with the skeletal mechanism was drastic. For example, while the parent detailed mechanism took approximately 3 to 5 hours to complete a single homogeneous reactor simulation, the 360 species mechanism required less than one minute.

to run the identical case. This 360 species skeletal mechanism was used for the remaining reacting CFD simulations of this study for the three jet fuel surrogates.

Spray Model Validation

Reacting spray simulations were compared against Sandia's reacting spray experiments [23,35,36] for the validation of the CFD model and the chemical mechanism. Details of the experiments are summarized in Table 3. In addition to reacting spray experiments using Jet-A POSF-4658 and S-8 POSF-4734, experimental data using a conventional JP-8 batch with cetane number of 38 [23] was also used for model validation. As mentioned in previous section, the surrogate for this specific JP-8 batch was formulated and used in CFD simulations for the validation purpose. Boundary conditions of the CFD simulations, including the injector specifications and the injection rate profile, were taken from the experiments. In the CFD simulations, the liquid penetration length was defined as the axial distance from the nozzle to the region that includes 95 % of the total liquid fuel mass at a given time. The vapor penetration length was defined as the maximum axial distance from the injector to where the fuel mass fraction is 0.1 %. The ignition timing was defined as the time when the maximum rise rate of the peak temperature in the entire domain was observed.

Table 3. Details of the Sandia National Laboratories' spray chamber experiments.

Fuel	Jet-A	S-8	JP-8
Cetane Number	47.3 ^a	60.4 ^a	38
Temperature	900, 1000 K		850, 1000, 1200 K
Density	22.8 kg/m ³		14.8, 30 kg/m ³
Pressure	6.1, 6.7 MPa		3.58 ~ 10.34 MPa
Orifice Diameter	0.09 mm		0.18 mm
Injection Pressure	150 MPa		110, 138 MPa
Oxygen Content	15 mol%		21 mol%
Reference	[35,36]		[23]
^a Derived Cetane Number from IQT (ASTM D6890)			

Table 4 compares the calculated and experimental liquid penetration lengths and ignition delay times of Jet-A and S-8. For the Jet-A and S-8 simulations, the model constant B_1 of the KH-RT spray breakup model was set at 8.5, which is identical to the value used in a previous CFD study [37] where the same injector (0.09 orifice diameter) and spray breakup models were used. Note that B_1 varies from one injector to another [38]. The predicted liquid penetration

lengths in Table 4 are in good agreement compared to the experimental stabilized liquid penetration lengths from [35]. Table 4 also shows the calculated ignition delay times of Jet-A and S-8 in comparison with experimentally measured values at 900 K and 1000 K at 22.8 kg/m³ ambient density. When the ambient temperatures corresponding to the experiments were used in the simulations, the ignition delay times were considerably longer than measured values. To achieve reasonable agreement with the experimental ignition delay times, the ambient temperatures were increased by 80 K for the 900 K case, and 30 K for the 1000 K case. Ignition delay times from the spray simulations with RANS turbulence models have often been reported to be longer than experiments [39, 40, 41]. Utilizing LES turbulence models may be an option to improve the agreement with experimental ignition delay times, as suggested by previous studies comparing RANS vs LES models [39,40]. Another aspect of possible model improvement is the chemical mechanism. As shown in Figure 3, the ignition delay predictions in the low temperature regime are longer than experiments in general, indicating the low temperature chemistry of current mechanism is slow. Thus, further advances in the low temperature chemistry within the parent detailed mechanism may be required. Alternatively, optimization of the reaction rate parameters in the reduced mechanism may improve the quantitative agreement with the experimental data.

Table 4. Comparison of the calculated liquid penetration lengths and ignition delay times with Jet-A and S-8 experiments [35,36].

	Experiment	Simulation
Stabilized Liquid Penetration Length		
Jet-A @ 900 K, 22.8 kg/m ³	10.5 mm	10.7 mm
S-8 @ 900 K, 22.8 kg/m ³	10.4 mm	9.9 mm
Ignition Delay Time		
Jet-A @ 900 K, 22.8 kg/m ³	0.7 ms	0.931 ms ^a
S-8 @ 900 K, 22.8 kg/m ³	0.58 ms	0.608 ms ^a
Jet-A @ 1000 K, 22.8 kg/m ³	0.47 ms	0.549 ms ^b
S-8 @ 1000 K, 22.8 kg/m ³	0.4 ms	0.428 ms ^b
^a ambient temperature increased by 80 K		
^b ambient temperature increased by 30 K		

Figure 4 compares the calculated liquid/vapor penetration of the JP-8 surrogate from a non-reacting simulation at the 850 K 14.8 kg/m³ ambient condition against experimental data. The JP-8 spray experiments used injectors with 0.180 mm orifice diameter. For these injectors, the model constant B_1 in the KH-RT spray breakup model was set at 10.5. In general, the model captured the overall shape of