

Modeling Soot Size Distribution Evolution and Pollutant Formation Inside Diesel Engine Using a 0D Multi-zone Gas Parcel Model with Detailed Chemistry and Soot Microphysics

Chowdhury G. Moniruzzaman and Fangqun Yu
State University of New York at Albany

ABSTRACT

Diesel engine emits soot which causes harm to human health, air quality and climate. It is important to understand the formation and time evolution of soot and its size distribution evolution inside engines to design strategies for emission reduction. We have developed a 0D multi-zone model for diesel fuel spray and coupled it with detailed surrogate diesel fuel chemistry and a sectional aerosol dynamics model for soot nucleation, surface growth and coagulation. Variable equivalence ratios in different zones are created by fixed fuel injection rates and variable air entrainment rates by a normal distribution function in different zones which ensures the existences of different pollutant forming zones having different equivalence ratios. Engine exit measured data of total soot mass and NOx for one operating condition are used to optimize the three model parameters. Model simulation of soot size distribution is consistent with typical measured data. Other than soot, the model also calculates the concentration of a wide range of combustion products (NOx, CO, SO₂, SO₃, NO, NO₂, N₂O, OH, HO₂ etc.) which may help to study engine exhaust chemistry of pollutant reduction. Sulfur oxidation efficiency $([SO_3]+[H_2SO_4])/([Total\ S])$ is found to be 2% at end of the expansion stroke. The model simulation produces the typical trend that late injection increase soot but decrease NOx. The model may enable us to test the predicting capability of any existing or newly developed chemical kinetic mechanism of surrogate fuel oxidation and soot formation inside the engine.

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INTRODUCTION

Diesel engines emit more soot and NOx (NO+NO₂) despite having a higher thermal efficiency relative to gasoline engines. Soot and particulate matter (PM) from diesel engine contribute to local air pollution which causes respiratory and cardiovascular health problems [1, 2] and neurodegenerative disorders [3]. NOx and hydrocarbon (HC) emissions contribute to formation of ozone which causes decreased lung function, inflammation of the airways [4, 5] and increased respiratory symptoms and mortality [6]. Diesel soot emissions also lead to climate change [7, 8]. Hence, soot and NOx emissions are major concerns to regulating agencies and engine manufacturers. Controlling soot emission is one of the major research goals of engine manufacturers in order to comply with the constantly evolving stringent emission standards [9] of the US EPA and Europe. The new EURO 5b/6 regulation limits PM number concentration emission by diesel fueled vehicles to 6×10^{11} #/km in addition to the total PM mass emission limit [9, 10]. To reduce soot or to increase diesel particulate filter (DPF) efficiency [11], it is important to understand the soot size distribution evolution and pollutant formation inside the engine.

Modeling of soot size distribution evolution and pollutant formation inside a diesel engine, combined with measurements, is an important approach to advance such an understanding. A sectional aerosol dynamics model coupled with detailed diesel fuel chemistry inside a diesel engine can determine in-cylinder soot size distribution evolution.

Although there are some modeling studies for soot size distribution in flames [12, 13, 14, 15, 16, 17], in perfectly-stirred reactors(PSR)-plug flow reactors (PFR) [18, 19, 20], in homogeneously charged compression ignition (HCCI) engines [21] and in aircraft engines [22], none of these was applied for studying soot size distribution evolution inside a diesel engine. To model the soot size distribution evolution and other pollutants formation and evolution in the diesel fuel spray, an engine model needs to be developed for cylinder pressure and temperature changes, heat transfer, fuel injection, droplet break-up, fuel evaporation and air entrainment. Available engine models in the literature can be categorized in three groups. One group is zero dimensional (0D) single zone models [23, 24]. The second group is computational fluid dynamics (CFD) based three dimensional (3D) models [25, 26].

[27](#), [28](#), [29](#), [30](#), [31](#), [32](#), [33](#)] and the third group is the 0D multi-zone (quasi-dimensional) or two-zone models [[34](#), [35](#), [36](#), [37](#)].

The 0D model is efficient enough to yield cylinder pressure and heat release rate but does not characterize the spatial variability of temperature, equivalence ratio (ER) (which is the ratio of the fuel-air mass ratio over the fuel-air stoichiometric mass ratio) and pollutant formation in the spray. The 3D CFD model includes fluid advection, diffusion and turbulence. The main output variables of the 3D model are temperature, fluid velocity, and concentrations of very limited number of pollutant species and uniform-sized soot particles in 3D spatial coordinates. Most of the 3D models use the widely used CFD software KIVA-3 [[38](#)] to determine these output variables. However, the CFD model is primarily used for engine design, its main limitation is that it cannot consider detailed chemistry and soot microphysics because of excessive computation time. The 0D multi-zone (quasi-dimensional) model is a trade-off between 0D single zone model and 3D CFD based model which has the option to model the spatial variability of temperature, ER, and concentration of pollutants without using the 3D CFD model and thus is simpler and more computationally efficient. The simplicity and computational efficiency of this model gives an opportunity to include as many chemical reactions as possible and as many soot size bins as required to determine soot size distribution evolution and pollutant formation. Although, efforts have been made to model combustion and soot formation by this type of 0D multi-zone models [[34](#), [35](#), [36](#), [37](#)], no models, based on our knowledge, include detailed combustion chemistry and size-resolved soot microphysics. Although one previous model has used detailed soot chemistry and size resolved soot microphysics in an HCCI engine [[21](#)] and found qualitative agreements between model simulated soot size distribution and measurements in the cylinders, modeling soot size distribution evolution in a diesel fuel spray inside a diesel engine remains to be achieved. Moreover, fuel and air are premixed in HCCI engines which are different than diesel engines where fuel is injected into the air creating a local fuel rich zone which favors soot formation.

The main objective of this paper is to develop a 0D multi-zone (quasi-dimensional) gas parcel model for diesel fuel spray including sub-models of cylinder pressure, temperature, heat transfer, fuel injection, fuel droplet break-up, fuel evaporation and air entrainment coupled with a sectional aerosol dynamics model [[39](#), [40](#)] for soot nucleation, growth, coagulation and detailed combustion chemistry of a surrogate diesel fuel. The present model is based on a quasi-dimensional multi-zone spray model [[34](#)] updated by including major types of reaction chemistry such as HC, polyaromatic hydrocarbon (PAH), oxides of sulfur, nitrogen species, and soot with size distribution. The developed model is then used to study the influences of engine operating condition such as fuel injection timing (FIT) on emissions which is a widely used tool to control soot and NOx emission [[25](#), [41](#), [42](#)].

MODEL DESCRIPTION

The details of the physics and chemistry based 0D multi-zone diesel engine emission model developed in this study are described in this section. The reference measurement conditions for model comparison are discussed briefly in 1st subsection, reaction chemistry is summarized in 2nd subsection, and the sectional aerosol dynamics model for soot microphysics is discussed briefly in 3rd sub section. The fourth sub section describes in detail the 0D multi-zone gas-parcel combustion model and governing equations, while the 5th sub section outlines the model's three input parameters and the 6th sub section discusses the steps to optimize the input parameters.

Engine Information and Measurements for Model Comparisons

The model is applied to a single cylinder version of the Caterpillar 3406 research engine [[43](#)] and model calculations were compared with measurements from Nehmer et al., [[43](#)] and Jung and Assanis [[34](#)]. The operating conditions and engine details are given in [Table 1](#). Model results of the soot size distribution at the end of the expansion stroke are compared with the measurements at the engine exhaust [[44](#)] for the same engine.

Table 1. Engine specifications [[43](#), [25](#), [34](#)].

Engine	Caterpillar 3406 engine
Bore	137.19 mm
Stroke	165.1 mm
Connecting rod length	261.62 mm
Displacement	2.44 L
Compression ratio	15.0
Engine speed	1600 rpm
Fuel injected per cycle	0.1622 g
Nozzle hole diameter	0.259 mm
Number of nozzles	6
Fuel injection timing (degree)	-11 ATDC (Baseline)
Intake air temperature (K)	310
Intake pressure (kPa)	184

Chemical Kinetic Model

A n-heptane mechanism, widely used for diesel engine simulations, from Lawrence Livermore National Laboratory (LLNL) [[45](#)] is chosen for fuel chemistry, and n-heptane is assumed as the diesel fuel. The n-heptane chemistry is coupled with PAH [[46](#), [47](#)] and soot formation mechanisms [[48](#), [47](#), [49](#)]. The NOx reactions are taken from the University of Leeds mechanism [[50](#), [51](#)] and LLNL mechanism [[52](#), [53](#)]. Sulfur chemistry has been taken from the University of Leeds mechanism [[51](#)]. The combined chemistry mechanism has 280 chemical species and 2137 reversible reactions which are

given in Table S1 and S2 in the supplementary materials. The ignition delay of n-heptane with the coupled PAH, sulfur and nitrogen chemistry was same as the ignition delay for the n-heptane chemistry alone as shown in Fig. 1. All of these reactions are coupled in Chemkin [54] code to determine the rates of change of concentrations of chemical species and temperature (heat release) by chemical reactions in a gas parcel (a zone). The differential equations are solved by the ordinary differential equation (ODE) solver VODE [55].

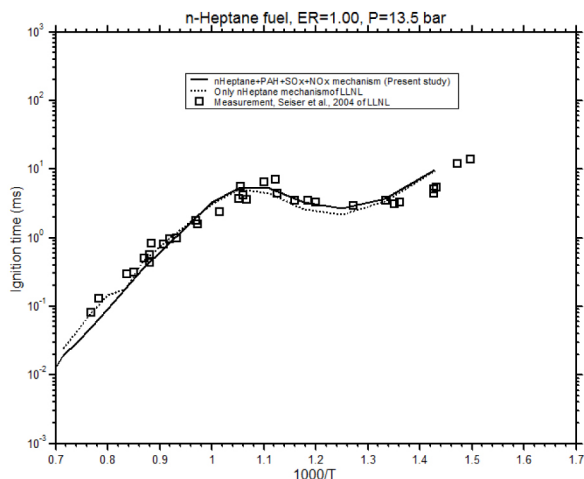


Figure 1. Ignition delay of reduced n-heptane mechanism [45, 53] coupled with mechanism of PAH [48, 46], nitrogen chemistry [50, 51] and sulfur chemistry [51].

Sectional Aerosol Dynamics Model for Soot Size Distribution Evolution

A sectional aerosol dynamics model for aerosol nucleation, growth and coagulation [39, 40] is used to simulate soot size distribution evolution. The aerosol dynamics model employed in this study is modified from an advanced multi-component, size-resolved microphysics code which has been used and is being continuously developed and improved for a wide range of application in the past several decades [56, 57, 39, 58, 40]. In contrast to the simple mono-disperse soot model which assumes the same size (at a given time) for all soot particles, the sectional model divides the entire particle size regime (from the size of the soot nucleus to several micrometers) into a number of volume bins. The section spacing factor (i.e., the ratio of the volume of two consecutive bins) used in this study is 1.45. Soot is assumed to be nucleated by coagulation of 2 pyrene (a 4-ring aromatic compound) molecules in this study [47]. The nucleated particles then grow (positive growth by adding mass or negative growth by losing mass) through surface reactions by hydrogen-abstraction/carbon-addition (HACA) of acetylene (C_2H_2), hydrogen gas (H_2), hydrogen atom (H), oxidation by oxygen molecule (O_2) and hydroxyl

radical (OH) [49], and condensation (surface deposition) of 19 PAH molecules [19]. The soot particle size distribution change by coagulation and surface growth/oxidation is modeled with a sectional particle microphysics model [39, 40]. The details of soot nucleation and surface growth can be found in widely used soot papers [48, 47, 49]. The details of the sectional aerosol dynamics model for soot size distribution evolution which includes soot nucleation, coagulation, and surface growth can be found elsewhere [59]. The simulation conditions are given in Table 2.

Table 2. Simulation conditions of the gas parcel model.

Model Fuel : n-Heptane	
Fuel composition (sulfur free)	n-heptane (C_7H_{16})
Fuel sulfur content (H_2S)	15 ppm (mass/mass)
Combustion chemistry	
Number of reactions	2137
Number of chemical species	280
Sectional aerosol dynamics model	
Number of size bins of particle	75
Particle size range	0.2 nm to 3000 nm
Ratio of 2 consecutive bin volume	1.45
Multi-zone gas parcel model	
Number of entrained zone	15
Number of un-entrained zone	1

0D Multi-zone Gas Parcel Model for a Fuel Spray Inside Diesel Engine

A diesel engine is a cylinder where intake air enters into the cylinder during the intake stroke, and is then compressed adiabatically by the momentum of the piston from the previous cycle. The engine has multiple fuel nozzles at the top center of the cylinder through which fuel is injected at the timing near the end of the compression stroke. It is assumed that the present engine has n_s number of (6 in the model engine) fuel nozzles which create n_s number of uniform fuel sprays simultaneously. The main feature of the present model is that the model divides a fuel spray into n_z entrained co-centric annular zones (gas parcels) shown in Fig. 2 and one additional zone (gas parcel) for un-entrained air. The properties (mass, volume, temperature and concentration of gas and soot) of zones (gas parcels) are not fixed which vary with crank angle. At any time (or crank angle), the total mass of gas in the cylinder is the summation of masses of n_z entrained gas parcels (zones) in all n_s fuel sprays and the air mass of the un-entrained zone. Before fuel injection starts, the total mass of air in the un-entrained zone is equal to the total mass of gas in the cylinder. How the mass of gas in different zones change with time are discussed in this section.

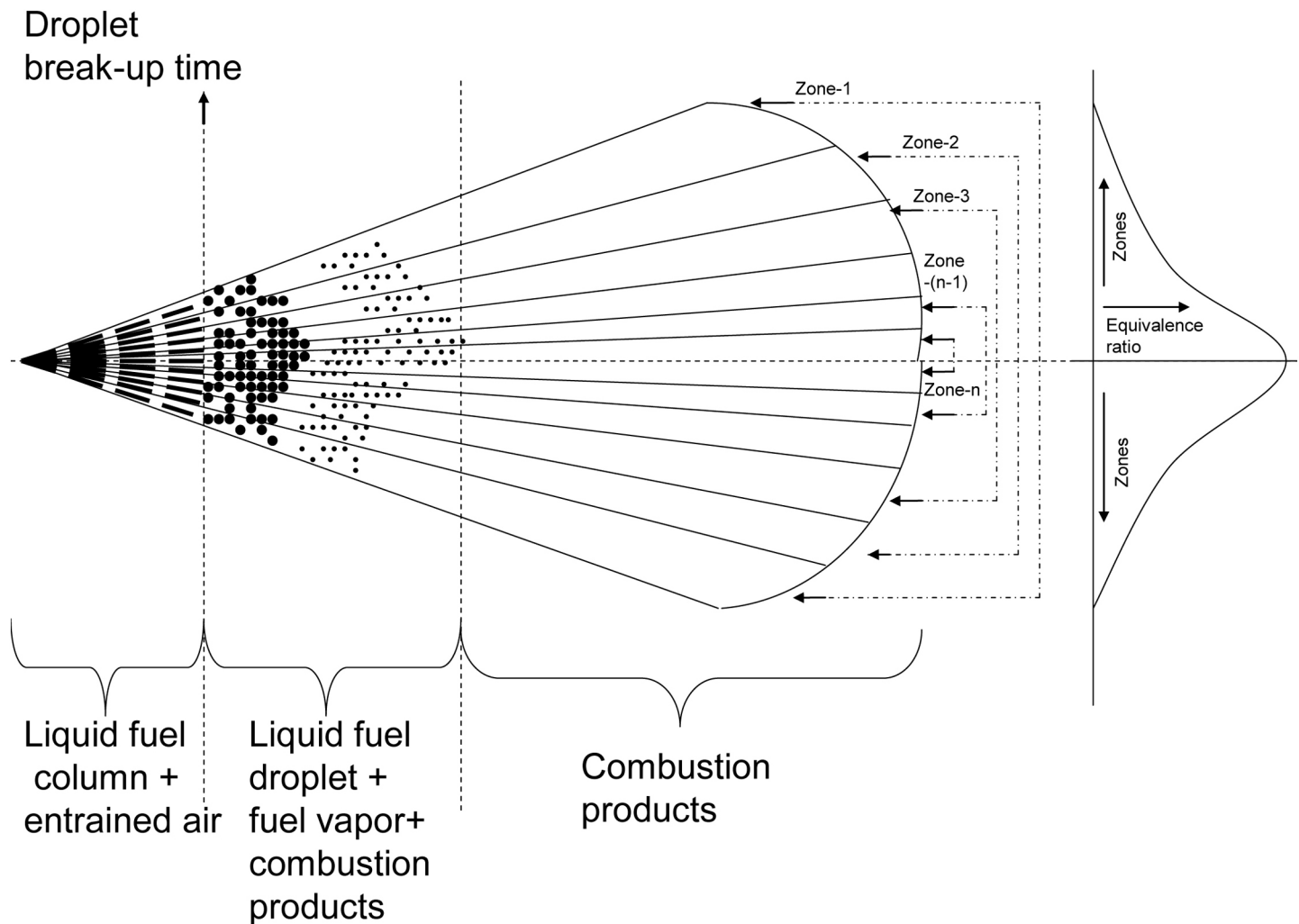


Figure 2. Schematic (side cross-sectional view) of a fuel spray inside diesel engine. Black columns are liquid fuel columns before droplet breakup, black dots are liquid fuel droplets after break-up and white empty space is fuel vapor + entrained air + combustion products.

Mass Distribution in Different Zones in a Fuel Spray and in Un-entrained Air Zone

The schematic (side cross sectional view) of a fuel spray inside a diesel engine is shown in Fig. 2. Fuel is injected through the nozzle. Black columns are liquid fuel columns before droplet break-up, black dots are liquid fuel droplets after break-up and white space is combustion products. The zones are annular and are assumed to be symmetrical along the axis of the spray. If the spray is sliced by a plane, the side cross sectional view of the spray should look like Fig. 2 where two symmetric zones in either side of the axis make one zone. It is assumed that the engine has n_s spray nozzles and fuel is injected in equal rate through these n_s nozzles (sprays). The air entrainment rate of the whole spray is distributed in the $2n_z$ number of zones (2 symmetric zones make a single zone, see Figs. 2 and 3) by a normal distribution. The model calculation of the overall (i.e.,

the sum of all the zones) changes of fuel injection rate and air entrainment rate with time in a spray are shown in Fig. 3a. To create the variable ER in the spray, air addition rates (i.e., entrainment rates) in different zones have been varied according to a normal distribution function (Figs. 3b-3c) but fuel addition rates in different zones have been assumed to be constant (Fig. 3c). The variable ER calculated by the model is given in Fig. 3d. More details are given in Section A3 in Appendix A.

At any time, there are three types of materials present in any zone (gas parcel) of a spray which are liquid fuel columns, liquid fuel droplets, combustion products (gases and soot particles). The mass of these three types of materials are tracked separately by solving their respective differential equations which are given in the following sections.

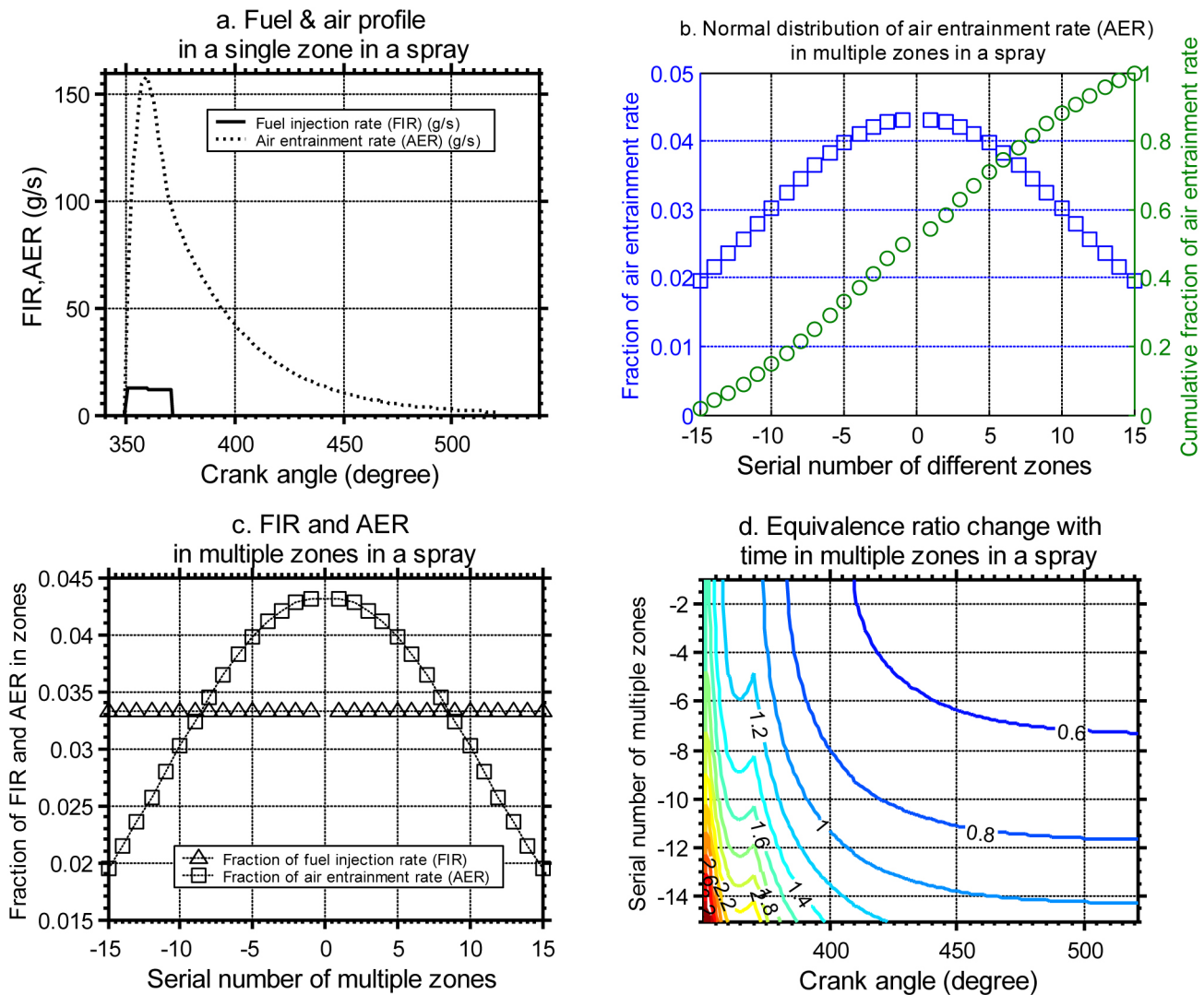


Figure 3. a) Fuel injection rate and air entrainment rate in two zone model, b) how the single zone air entrainment rate is distributed in multiple zones by a normal distribution function, c) fuel injection rates and air entrainment rates in multiple zones, d) model simulation of overall equivalence ratio (without chemical reaction) change with time in multiple zones.

The rate of change of mass (g) of the liquid fuel column, $m_{lfc,j}$, liquid fuel droplet, $m_{lfd,j}$, and fuel vapor + entrained air (equal to the mass of combustion products), $m_{vfa,j}$, in the j^{th} zone in a spray can be

$$\frac{dm_{lfc,j}}{dt} = R_{fir,j} - R_{dgr,j} \quad (1)$$

$$\frac{dm_{lfd,j}}{dt} = R_{dgr,j} - R_{der,j} \quad (2)$$

$$\frac{dm_{vfa,j}}{dt} = R_{der,j} + R_{aer,j} \quad (3)$$

Where t is residence time (s), $R_{fir,j}$, $R_{dgr,j}$, $R_{der,j}$ and $R_{aer,j}$ are the fuel injection rate (g/s), droplet generation rate (g/s), droplet evaporation rate (g/s) and air entrainment rate (g/s) in the j^{th} zone respectively whose values are determined by equations (A4, A17, A45 and A13) of Appendix A respectively.

The rate of change of total liquid fuel mass (both liquid fuel droplet + liquid fuel column) in the j^{th} zone in a spray (g/s) can be written from equations (1) and (2) as

$$\frac{dm_{lfc,j}}{dt} = R_{fir,j} - R_{der,j} \quad (4)$$

The decrease rate of un-entrained air (g/s) in the cylinder is the increase rate of entrained air in all the entrained zones in all the sprays which can be written as

$$\frac{dm_{uea}}{dt} = -n_s \sum_{i=1}^{j=n_z} R_{der,i} \quad (5)$$

Where n_s is the number of fuel sprays in the engine.

After solving equations (1, 2, 3, 4, 5) at each time step, the cumulative overall mass fraction of liquid fuel column, $\alpha_{lfc,j}$, liquid fuel droplets, $\alpha_{lfd,j}$, sum of fuel vapor and entrained air (cumulative evaporated fuel vapor + cumulative entrained air), $\alpha_{vfa,j}$, total liquid fuel, $\alpha_{lf,j}$, in the j^{th} zone in a spray and un-entrained air, α_{uea} , in the cylinder can be calculated in the following equations respectively as

$$\alpha_{lfc,j} = \frac{m_{lfc,j}}{n_s \sum_{j=1}^{j=n_z} m_{vfa,j} + n_s \sum_{j=1}^{j=n_z} m_{lf,j} + m_{uea}} \quad (6)$$

$$\alpha_{lfd,j} = \frac{m_{lfd,j}}{n_s \sum_{j=1}^{j=n_z} m_{vfa,j} + n_s \sum_{j=1}^{j=n_z} m_{lf,j} + m_{uea}} \quad (7)$$

$$\alpha_{vfa,j} = \frac{m_{vfa,j}}{n_s \sum_{j=1}^{j=n_z} m_{vfa,j} + n_s \sum_{j=1}^{j=n_z} m_{lf,j} + m_{uea}} \quad (8)$$

$$\alpha_{lf,j} = \frac{m_{lf,j}}{n_s \sum_{j=1}^{j=n_z} m_{vfa,j} + n_s \sum_{j=1}^{j=n_z} m_{lf,j} + m_{uea}} \quad (9)$$

$$\alpha_{uea} = \frac{m_{uea}}{n_s \sum_{j=1}^{j=n_z} m_{vfa,j} + n_s \sum_{j=1}^{j=n_z} m_{lf,j} + m_{uea}} \quad (10)$$

Concentration of Gas, Soot and Temperature in Different Zones of a Spray and in Un-entrained Air Zone

The rate of change of mass fraction of the i^{th} gas species $Z_{vfa,j,i}$, the soot particle number concentration $N_{vfa,j,k}$ (#/g-gas) in the k^{th} aerosol size bin, the temperature $T_{vfa,j}$ (K) in the j^{th} gas parcel and the temperature of the un-entrained air T_{uea} (K), in the cylinder by different physical and chemical mechanisms can be expressed in the following equations

$$\begin{aligned} \frac{dZ_{vfa,j,i}}{dt} = & \frac{dZ_{vfa,j,i}}{dt} \Big|_{\text{droplet-evaporation}} \\ & + \frac{dZ_{vfa,j,i}}{dt} \Big|_{\text{by.chemistry}} + \frac{dZ_{vfa,j,i}}{dt} \Big|_{\text{by. soot.formation}} \\ & + \frac{dZ_{vfa,j,i}}{dt} \Big|_{\text{mass-addition-from un-entrained-air-zone}} \end{aligned} \quad (11)$$

$$\begin{aligned} \frac{dN_{vfa,j,k}}{dt} = & \frac{dN_{vfa,j,k}}{dt} \Big|_{\text{by. soot.formation}} \\ & + \frac{dN_{vfa,j,k}}{dt} \Big|_{\text{mass-addition-from un-entrained-air-zone}} \end{aligned} \quad (12)$$

$$\begin{aligned} \frac{dT_{vfa,j}}{dt} = & \frac{dT_{vfa,j}}{dt} \Big|_{\text{mass-addition-from unentrained-air-zone}} \\ & + \frac{dT_{vfa,j}}{dt} \Big|_{\text{fuel-evaporation}} + \frac{dT_{vfa,j}}{dt} \Big|_{\text{chemistry}} \\ & + \frac{dT_{vfa,j}}{dt} \Big|_{\text{work on-piston}} + \frac{dT_{vfa,j}}{dt} \Big|_{\text{heat-transfer through-wall}} \end{aligned} \quad (13)$$

$$\frac{dT_{uea}}{dt} = \frac{dT_{uea}}{dt} \Big|_{\text{work on-piston}} + \frac{dT_{uea}}{dt} \Big|_{\text{heat-transfer through-wall}} \quad (14)$$

Where $j = 1$ to n_z , $i = 1$ to n_{sp} , and $k = 1$ to n_{st} . And n_z , n_{sp} and n_{st} are the total number of zones in a spray, total number of gas species, and total number of soot size bins respectively. Here, $j = 1$ is for the outer most zone (see Fig. 2) having lowest ER (see Figs. 2 and 3d) and $j = n_z$ for the inner most zone having the highest ER in a spray. The subscripts and superscripts of each right hand side (RHS) term of equations (11, 12, 13, 14) represent the physical and chemical mechanisms by which the variable changes. The details of these RHS terms are given in Appendix A in Section A12.

Overall Concentrations of Gases and Soot and Overall Temperature Inside the Cylinder

The concentration of gas species at any time (or at any crank angle) of the cylinder, is the sum of the concentrations in all the zones (gas parcels) in all sprays and in the un-entrained zone at the corresponding time. Hence, by solving equations (1, 2, 3, 4, 5) and (11, 12, 13, 14) using the simulation conditions given in Table 1 and 2, the overall (summation in all entrained zones in all the sprays and in the un-entrained air zone) mass fraction of the i^{th} gas species Z_i , and number concentration of soot particles N_k (#/g-gas) in the k^{th} aerosol-size-bin in the cylinders at any time are determined as

$$Z_i = Z_{i,uea} \alpha_{uea} + n_s \sum_{j=1}^{j=n_z} (Z_{vfa,j,i} \alpha_{vfa,j} + Z_{lf,j,i} \alpha_{lf,j}) \quad (15)$$

$$N_k = N_{k,uea} \alpha_{uea} + n_s \sum_{j=1}^{j=n_z} N_{vfa,j,k} \alpha_{vfa,j} \quad (16)$$

Where $Z_{i,uea}$ is the mass fraction of the i^{th} gas species in the un-entrained air zone whose value does not change with time. And $N_{k,uea}$ (#/g-gas) is the soot particle number concentration (whose value is assumed to be zero) in the k^{th} aerosol size bin in the un-entrained air zone,

The overall temperature of mixture of liquid fuel, entrained gas and un-entrained air can be determined (assuming all the liquid fuel columns, liquid fuel droplets and combustion products in the n_z number of entrained gas parcels in the n_s number of sprays and air in the un-entrained air, are mixed hypothetically to form a gas mixture of uniform temperature) by energy balance as

$$T = \frac{T_{uea}\alpha_{uea}c_{p,uea} + n_s \sum_{j=1}^{j=n_z} T_{vfa,j}\alpha_{vfa,j}c_{p,vfa,j} + n_s \sum_{j=1}^{j=n_z} T_{lf,j}\alpha_{lf,j}c_{p,lf,j}}{\alpha_{uea}c_{p,uea} + n_s \sum_{j=1}^{j=n_z} \alpha_{vfa,j}c_{p,vfa,j} + n_s \sum_{j=1}^{j=n_z} \alpha_{lf,j}c_{p,lf,j}} \quad (17)$$

Where c_p is the heat capacity (erg/g-K). The average temperature, $T_{lf,j}$ (K) of liquid fuel (liquid fuel columns and liquid fuel droplets) is approximated by [equation A41](#) in [Appendix A](#).

Model's Three Input Parameters

The model has three important optimizing parameters which are discussed here. The values of these three parameters need to be varied to reach the final solution point at which the model-calculated NOx and soot concentration at the engine exit are consistent with available measurements. The ranges of values used in the simulation are given in [Table 3](#). The three parameters are briefly discussed here. The sensitivity analysis of these parameters is presented in a later section.

Table 3. Three model input parameters.

Parameters	Value used in final solution run	Value range varied for trial and error
σ_{nd}	6.95	6.85-7.05
$f_{exp,aer}$	0.85	0.75-0.95
$f_{hrr,max}$	0.75	0.60-0.90
σ_{nd} is the standard deviation of a normal distribution function of air entrainment rate in different zones (details are given in next section and in equation (A13) in Section A3 in Appendix A). $f_{exp,aer}$ is a decay constant of the exponential decay function $R_{aer,s} = R_{aer,s,fi} \exp(-f_{exp,aer}/t)$ of air entrainment rate for the time regimes after fuel injection ends (details are given in next section and in equation (A12) in Section A3 in Appendix A). $f_{hrr,max}$ is a maximum heat release factor by which the chemical reaction rate of any chemical species is slowed down during ignition in PSR simulation to approximate mixing effects so that overall heat release rate in the cylinder does not exceed a certain maximum input value during ignition (details are given in next section and in Section A11 in Appendix A).		

Equivalence Ratio Distribution in Different Zones

Variable ER is present in the fuel spray inside the engine having the higher ER inside the spray and the lower ER near the outside wall of the spray. Soot is formed in fuel rich zones having ER greater than 2 and NOx is formed in the lower ER zone. To model the all types of pollutant formation, variable ER zone needs to be present in the model.

To create the variable ER in the spray in different gas parcels (zones), air addition rates (i.e., entrainment rates) in different zones have been varied according to a normal distribution function ([Figs. 3b-3c](#)) but fuel addition rates in different zones have been assumed to be constant ([Fig. 3c](#)). The air entrainment rate of the whole spray (obtained from [equation \(A12\)](#) in [Appendix A](#)) is distributed in different zones by a normal distribution function having the standard deviation σ_{nd} by the [equation \(A13\)](#) in [Appendix A](#). This standard deviation σ_{nd} of the normal distribution function is the user input parameter in this model. The range of values of this parameter, σ_{nd} , are given in [Table 3](#). The sensitivities of this parameter are discussed in a later section.

Air Entrainment Rate After Fuel Injection Ends

The air entrainment rate in a fuel spray is inversely proportional to the spray velocity. The spray velocity can be determined by differentiating the spray penetration equation ([equation \(A6\)](#) in [Appendix A](#)). Spray penetration equation is an empirical equation which is a function of pressure drop between fuel injection nozzle and the cylinder. As long as there is fuel injection, the air entrainment rate can be calculated via momentum balance equation by differentiating [equation \(A11\)](#) in [Appendix A](#). However, for the time regime after fuel injection ends, the air entrainment rate cannot be calculated by the momentum balance equation as there is no fuel injection rate (and no initial fuel injection velocity) in [equation \(A11\)](#) in [Appendix A](#) and spray velocity cannot be calculated by [equation \(A6, A8\)](#) in [Appendix A](#). In the real condition, the fuel spray gas parcel continuously slows down even after the fuel injection ends. The physics behind this slowdown is the air entrainment rate. We tried to model this air entrainment rate in this time regime (time after fuel injection ends) by an exponential decay function of un-entrained air mass which will continuously decrease (entrained air mass will continuously increase) exponentially to zero (making all the unmixed or un-entrained air mass becomes mixed or entrained). The decrease rate of un-entrained air mass is equal to the increase rate of entrained air mass in the gas parcel. Here, the input variables, $f_{exp,aer}$ is the decay constant of the exponential decay function (see [equation \(A12\)](#) in [Appendix A](#)). Hence, air entrainment rate has been modeled in two time regimes: one for during fuel injection and another for time after fuel injection ends. The air entrainment rate in the 1st time regime (fuel injection duration time) is modeled by momentum balance (by differentiating [equation \(A11\)](#) in [Appendix A](#)), and in the 2nd time regime (time regime after fuel injection ends) by the exponential decay function (see [Section A3](#) in [Appendix A](#)) having the exponential decay constant $f_{exp,aer}$. The sensitivities of this parameter are discussed in a later section.

Approximation of Mixing effects in Determination of Overall Reaction Rates During Ignition

In the present study, the turbulent mixing in reaction chemistry is not considered because of the 0D nature of the model. The model depends on perfectly stirred reactor (PSR) simulation in

determining the reaction rates of chemical species without considering turbulent mixing in a gas parcel. One problem of PSR simulation of fuel spray is that evaporated fuel and entrained air are instantaneously mixed which abnormally increases the reaction rates of chemical species than the actual rates (where all the fuel vapor and entrained air are not mixed instantaneously) during ignition. These abnormally high reaction rates of chemical species during ignition increase the total heat release rate in the cylinder which increases the cylinder pressure during ignition. Hence, to get the realistic heat release rate (and then realistic cylinder pressure) during ignition, the reaction rates of chemical species during ignition are slowed down using this input parameter, $f_{hrr,max}$, by a method discussed in Section A11 in Appendix A. The input parameter, $f_{hrr,max}$, is defined as the maximum heat release factor by which the chemical reaction rate of any chemical species is slowed down during ignition so that overall heat release rate in the cylinder does not exceed a fixed input value (fuel injection rate multiplied by higher heating value of fuel and the factor $f_{hrr,max}$ in equation (A75) in Appendix A) during ignition. The range of values of the input parameter, $f_{hrr,max}$, used to reach final solution point are given in Table 3. The sensitivities of this parameter are discussed in a later section.

Steps to Optimize the Three Input Parameters

The values of the three input parameters (discussed in previous section) need to be optimized against measured data of concentration of soot and NOx. The three parameters given in Table 3 are varied and equations (1, 2, 3, 4, 5, 11, 12, 13, 14) are solved multiple times to get the final solution point when model calculated NOx and soot concentrations at the engine exit are consistent with the measurements at engine exit.

RESULTS AND DISCUSSION

Concentration, Equivalence Ratio and Temperature Change in Different Zones of a Spray

The model tracks the concentration change of gas, soot in different size bins, temperature and cumulative ER (ER without chemical reaction of fuel) of each zone by equations (1, 2, 3, 4, 5 and 11, 12, 13, 14). Results can be seen in Fig. 4.

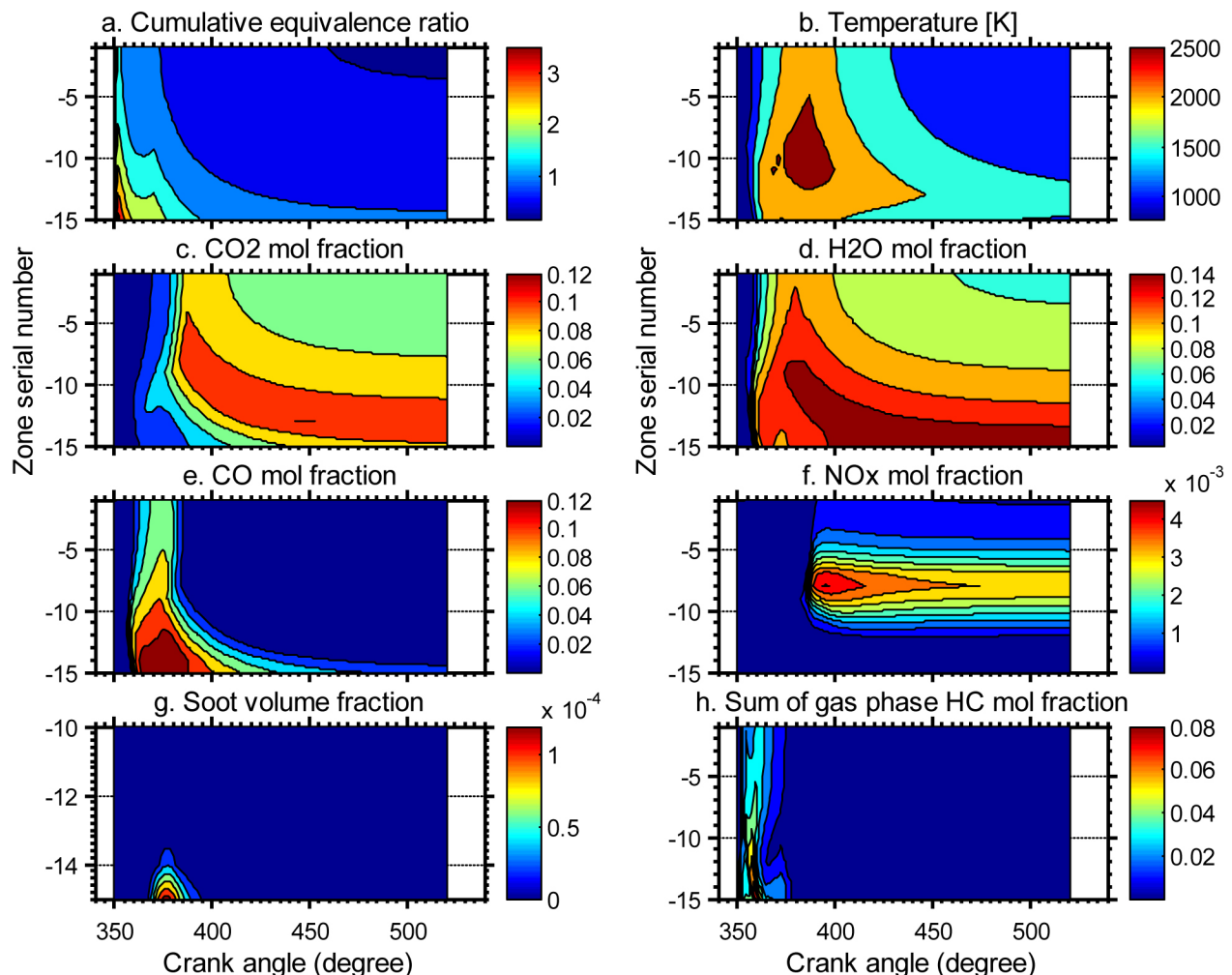


Figure 4. Time (crank angle) evolution of a) overall equivalence ratio (without chemical reaction), b) temperature, concentration of c) CO₂, d) H₂O, e) CO, f) NOx, g) soot volume fraction and h) concentration of HC in multiple zones in a spray inside a diesel engine calculated by the model.

The cumulative ER, shown in Fig. 4a, increases from outer side (lower zone serial number) to the inner side (higher zone serial number) of the spray which actually happens in a real spray where entrained air enters the spray from outer side to inner side making the ER higher in the inner side of the spray. The ER decreases with time by entrained air in all zones shown in Fig. 4a. The temperature change in different zones can be seen in Fig. 4b. The temperature, shown in Fig. 3b, is the highest in the zones where local ER close to 1 (see also Fig. 4a) and at crank angle around 370 to 400 degree. Temperature decreases with time by entrained air and adiabatic expansion. The carbon dioxide (CO_2) and water vapor (H_2O) concentration change can be seen in Fig. 4c and 4d respectively where the highest concentration are along the ER ~1 (see Fig. 4a) trajectory. In the present model, shown in Fig. 4e, most of the carbon monoxide (CO) is produced in fuel rich zones (higher ER, see Fig. 4a) although, in real engines,

some CO forms near the wall zone where HC is typically formed (one thing to note here is that the model's main goal is to simulate soot size distribution, hence, wall zone producing HC has not been considered). The NOx formation zones are clearly visible in Fig. 4f where highest NOx formation occurs in high temperature zones (Fig. 4b) having local ER~1 (see Fig. 4a) at crank angle around 390 to 410 degree inside the spray and then decreases by dilution air (entrained air) with time. Soot is formed in the last 2 zones, where ER is initially greater than 2, and quickly oxidizes with time as shown in Fig. 4g. The evolution of soot size distribution will be discussed in the following section. The time evolution of HC (the survived un-burnt fuel vapor) can be seen in Fig. 4h which shows that HC burns rapidly. No HC is present after ~385 degree as present model does not have option to model the HC survival (avoid oxidation) mechanism in the cylinder.

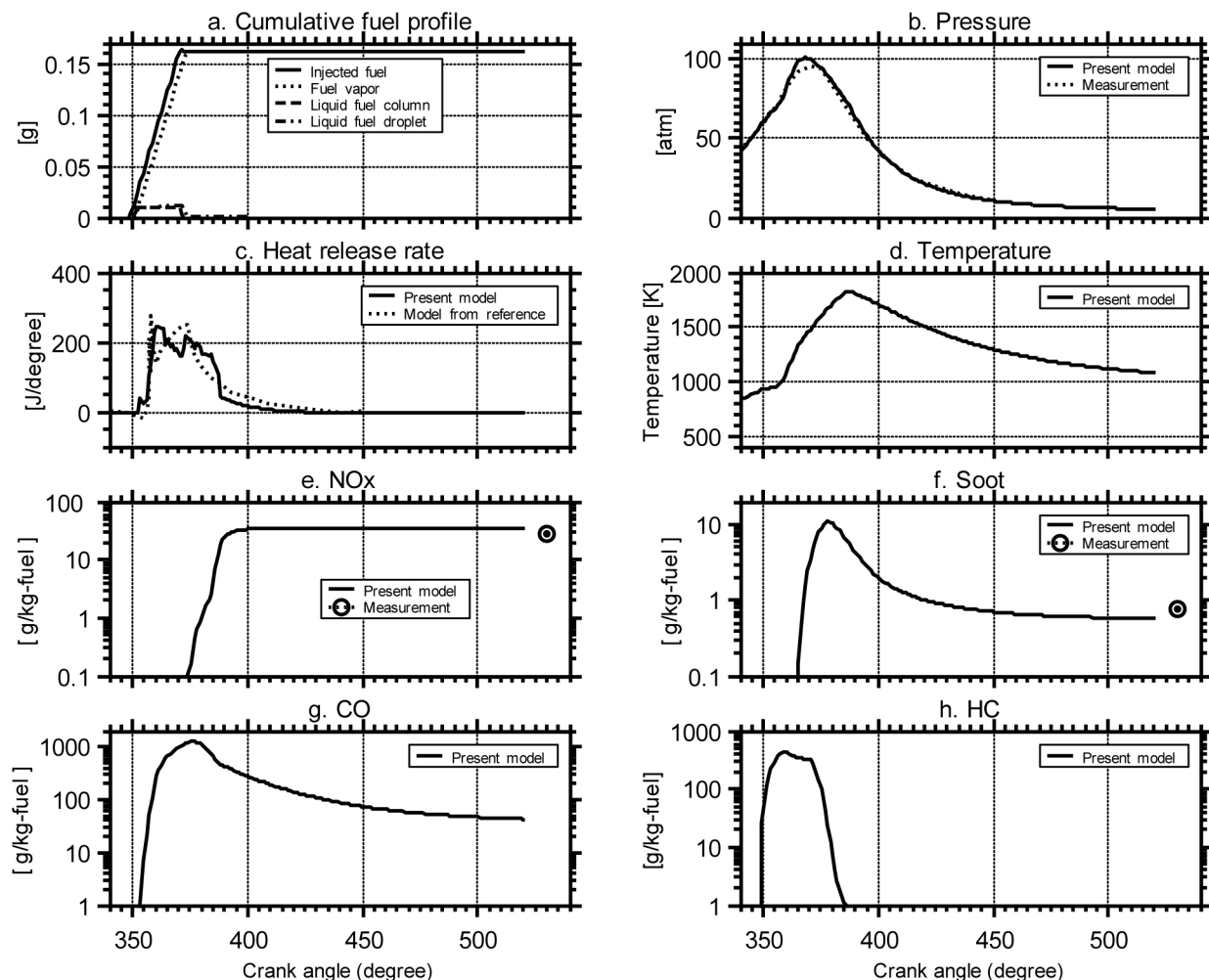


Figure 5. Time (crank angle) evolution of a) cumulative fuel profiles, b) cylinder pressure (measurements [34]), c) heat release rate (reference model data [34]), d) overall cylinder temperature, e) NOx (measurements [43]), f) soot (measurements [43]), g) CO and h) HC inside a diesel engine.

Overall Injected Fuel Profile, Concentration of Gas and Soot and Temperature Change in the Engine

The cumulative injected fuel profile, cumulative liquid fuel column, cumulative liquid fuel droplets, and cumulative vaporized fuel are shown in Fig. 5a. The pressure profile determined by the present model can be seen in Fig. 5b which is overall consistent with measurements [34] but over predicts near the peak which might be caused by the model uncertainties in modeling heat release rate during ignition (discussed earlier in a section, see also Table 3). Model-simulated heat release rate can be seen in Fig. 5c which is consistent with an empirical model [34] although peak heat release rate is forced to be within the typical measured value by an input parameter (discussed earlier in a section, see also Table 3). The overall cylinder temperature calculated by the model can be seen in Fig. 5d.

The time evolution of NO_x inside the engine can be seen in Fig. 5e. The time evolution of the normalized soot mass concentration can be seen in Fig. 5f. It should be noted that the engine exit measurements of NO_x and soot for the chosen operating condition of the chosen engine are user input parameters in this study which are shown discussed in Table 3. The NO_x concentration, shown in Fig. 5e, increases more than 2 orders of magnitude from ~375 degree to ~395 degree and remains constant in the rest of the expansion stroke (from ~400 degree to ~520 degree). The soot mass concentration, shown in Fig. 5f, increases by nucleation and surface growth, reaches maximum, and then decreases by oxidation in the rest of the expansion stroke. The CO time evolution and engine exit value can be seen in Fig. 5g. The concentration reaches as high as 1100 g/kg-fuel at ~ 375 degree and then continuously decreases in the rest of the expansion stroke by oxidation. The model result of CO time evolution inside the engine is similar with other in-cylinder measurement for another engine [60]. The hydrocarbon time evolution can be seen in Fig. 5h. All the HC is burnt in the cylinder. However, substantial amount of HC is typically observed in engine exhausts, ~5 g/kg-fuel [61]. Sources of the HC measured in the engine exhaust are the un-burnt lubricating oil and un-burnt fuel vapor inside the engine. During combustion, some fuel and lubricating oil avoid the oxidation by the inhomogeneous mixing and being in low temperature region near the wall. Present model does not have option to model the HC survival (avoid oxidation) mechanism. Inclusion of a low temperature wall zone in the present scheme may help to determine HC concentration.

Soot Formation and Size Distribution Evolution Inside the Engine

The Normalized concentrations of total soot number (number EI, #/kg-fuel) and total mass (EI, g/kg-fuel), are shown in Figs. 6a, b respectively. The soot number concentration, shown in Fig. 6a, increases initially due to the dominance of nucleation

over coagulation and oxidation-loss (complete burnout) of the smallest size soot particles. The number concentration reaches a peak when the soot nucleation rate is equal to the soot particle number loss rate by coagulation and oxidation. Thereafter, the soot number concentration decreases continuously in the rest of the expansion stroke by coagulation and by oxidation (oxidation-loss of smallest size soot particle by complete burnout). Soot number concentration decreases by ~ 98% from its peak near the ignition to the end of the expansion stroke. The change of soot mass concentration is consistent with the typical trend seen in in-cylinder measurements [60, 62, 63] and modeling studies [25, 34] which show that soot mass increases initially, reaches peak and then decreases by oxidation in the later stage of combustion. The soot mass decreases from its peak value by ~95% at the end of the expansion stroke. Evolution of the soot size distribution can be seen in Fig. 6c. The size distribution at the end of the expansion stroke is consistent with measurement at typical engine exhaust [44]. The measured particles around 10 nm shown in Fig. 6c are the volatile nucleation-mode particles formed during the mixing of exhaust with ambient air [44]. Present model simulation is limited to inside engine and thus doesn't calculate the formation of this nucleation-mode particles. Figure 6c shows that the mode diameter of soot particle size distribution moves towards the larger diameter particles initially by nucleation and surface growth, then moves towards a smaller diameter particles through the dominance of oxidation over coagulation in the rest of the expansion stroke.

Model Prediction of All Types of Combustion Products Inside the Engine

The present model has the capability of determining the concentrations of several combustion products including nitrogen species, sulfur species and species of hydrogen and oxygen inside the engine. Engine exit value of concentration of these species may help to study the exhaust chemistry of pollutant reduction.

Time Evolution of Major Nitrogen Species Inside Diesel Engine

The time evolution of NO, and NO₂ can be seen in Fig. 7a, b respectively. The emission indices of non-NO_x species such as HONO, N₂O are calculated to be ~ 0.01 g/kg-fuel at the end of the expansion stroke shown in Fig. 7c, d respectively. The N₂O is a greenhouse gas whose emission index information is helpful in climate study. The model simulated emission index, ~0.01 g/kg-fuel, of N₂O at the end of the expansion stroke is in the same order of magnitude of the typical reported value ~0.02 g/kg-fuel [63]. The model simulation finds, shown in Fig. 7d, that HNO₃ emission index at the end of the expansion stroke is negligible (~1e-5 g/kg-fuel).

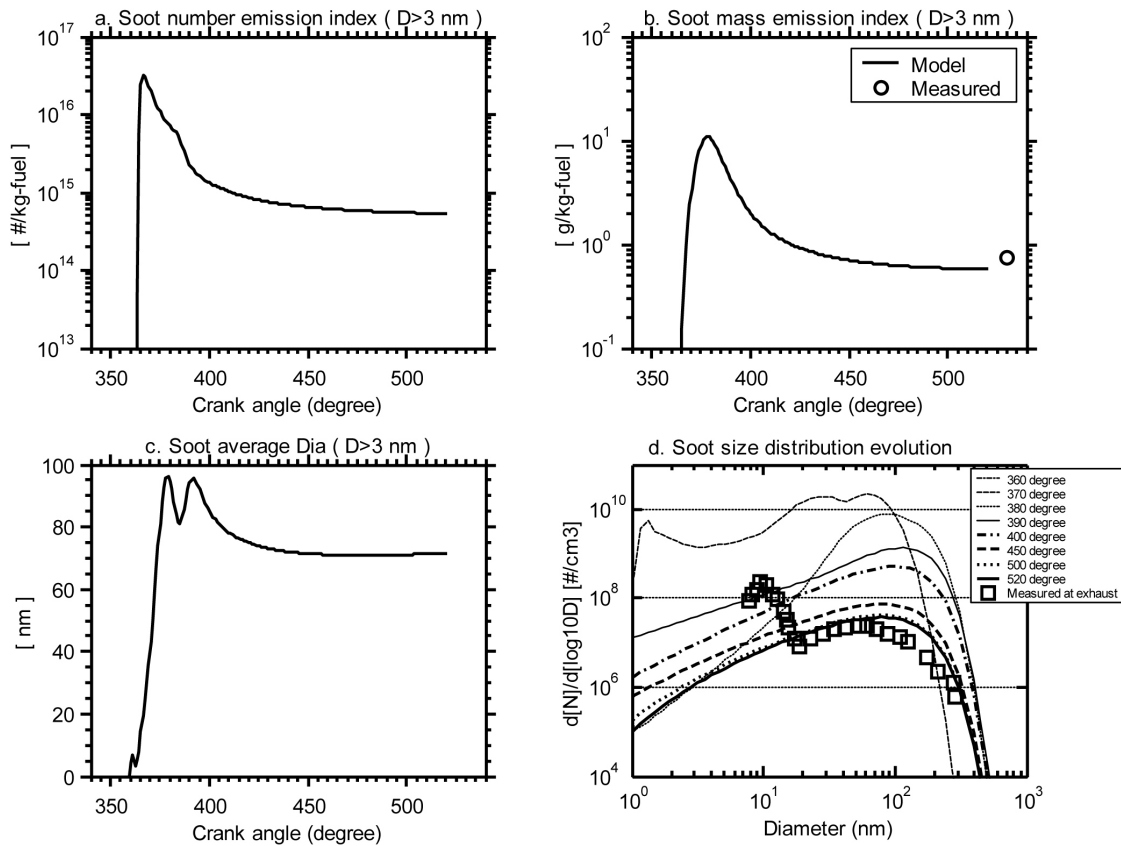


Figure 6. Time (crank angle) evolution of soot properties: a) normalized number concentration, b) normalized total soot mass concentration (measurements [43]), and c) size distribution (measurements at the engine exhaust [44]) inside a diesel engine.

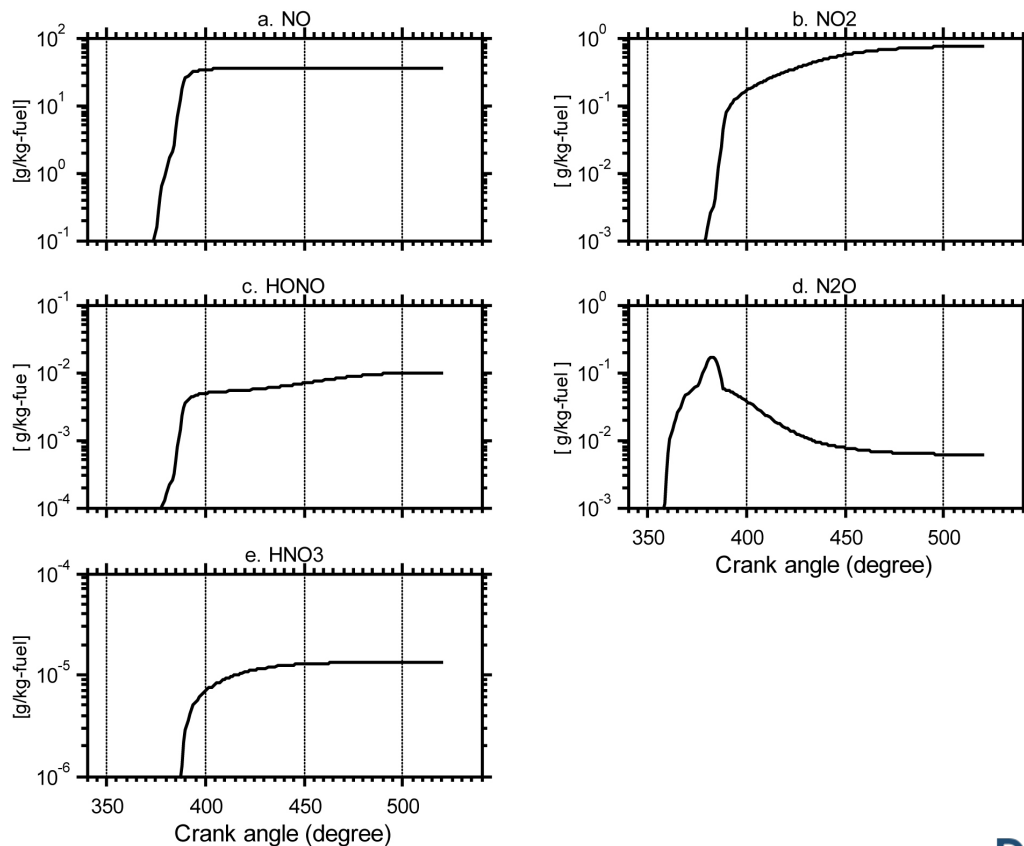


Figure 7. Time (crank angle) evolution of concentrations of nitrogen species: a) NO, b) NO₂, c) HONO, d) N₂O, and e) HNO₃ inside a diesel engine.