

Simplified Calculation of Chemical Equilibrium and Thermodynamic Properties for Diesel Combustion

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ABSTRACT

Computation of combustion, in particular of emissions over crank angle, relies on chemical oriented models. In some cases, chemical equilibrium can be assumed, as chemical reaction time scales tend to be fast compared to the crank rotation, so the rather complex reaction kinetics can be neglected. For engine process calculation based on the measured cylinder pressure chemical equilibrium concentrations are needed for every crank angle or calculation time step. On the one hand the equilibrium concentrations are necessary for estimating the thermodynamic properties of the working gas (internal energy and specific gas constant) which are needed for deriving the energy release (burn rate) and on the other hand the obtained concentrations are inputs for crank angle based soot and nitric oxygen emission models which depends also on the engine process calculation results. For a common accurate 11 component equilibrium calculation a nonlinear equation system must be solved with an iterative method. To reduce calculation complexity a new explicit method is described in the paper which is especially designed for the typical range of a common Diesel. The main benefit is that it does not need initial values and iteration. Additionally new explicit descriptions for the thermodynamic properties are presented. The development process for both approaches was supported by data based identification methods. Several validation examples are shown to estimate the deviation of the new approaches for chemical equilibrium species and the gas properties compared to the more complicated standard methods in a practical use. In particular the importance of the achieved species accuracy on soot dynamics and nitric oxygen calculation based on published 1- and 2-zone models is presented in detail.

INTRODUCTION

The classical 0-dimensional 1-, 2- or multi zone engine process calculation based on the measured cylinder pressure is still an important topic for analyzing the combustion and emission formation in a given engine. To solve the coupled system of the necessary equations (ideal gas equation, first law of thermodynamics and mass conservation) thermodynamic properties and their partial derivatives are required. For each zone and for each time or crank step, the internal energy (u) and the specific gas constant (R) must be calculated. These specific thermodynamic properties can be derived from chemical equilibrium concentrations analog to [1, 2] with a component based approach. If emission modeling is not in focus of interest chemical equilibrium calculation could be avoided and alternatively direct equations for the thermodynamic properties according to [3] could be used to calculate the burn rate. As already mentioned above equilibrium concentrations are needed as inputs for crank angle based Diesel emission models based on 1- or 2-zone engine process calculations. For instance, many of the published soot models (e.g. [4]) need O_2 -concentration or OH -concentration (e.g. [5]) as input for the oxidation term. Moreover, for the reaction kinetic modeling of nitric oxygen (NO) emissions with the extended Zeldovich mechanism 4 concentrations (N_2 , OH , O , O_2) are necessary as inputs for a nitric oxygen 2-zone model, like it is fully described in [6]. Note that the NO emission time scale is much slower compared to the 4 input concentrations and therefore must be modeled with reaction kinetics. Figure 1 illustrates the described topics and the workflow positions of the new approaches presented in the paper.

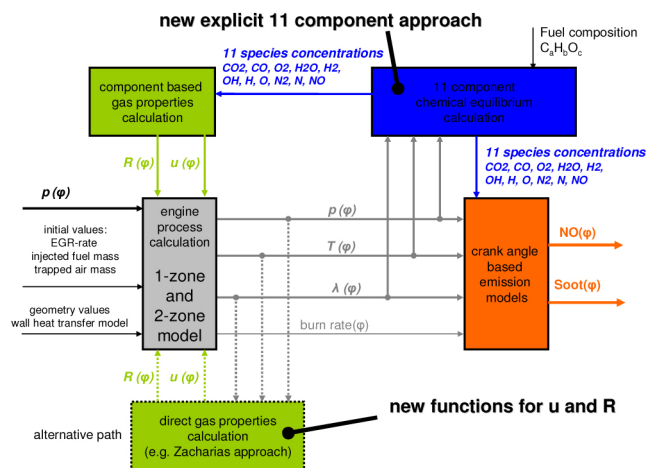


Figure 1. Workflow

For the described chemical equilibrium applications several authors [1, 2, 7,8,9,10] propose an 11 component system. Thus a nonlinear equation system with 11 equations and 11 unknown species which are a function of pressure (p), temperature (T) and relative air/fuel ratio (λ) must be solved numerically, e.g. with a Newton method. The main drawbacks of the numerical solvers are the need for good initial values for the 11 species to achieve convergence and the substantial computational effort. As a consequence, before calculating the target values, several authors (e.g. [10]) initially use a reduced system of equations without dissociation for estimating these initial values.

To avoid the above mentioned efforts like iteration and convergence problems, the concentrations and the thermodynamic parameters could be stored in look up tables. However, due to the many zones of the heterogeneous Diesel combustion and the strong nonlinearity of the chemical equilibrium equation system, large look up tables are required if only a simple interpolation routine is used. Consequently a lot of memory would be necessary. Against this background several authors (e.g. [11] or [12]) presented improved interpolation routines and methods with acceptable results.

As an alternative, the main focus of this paper is to present new simple explicit methods for the calculation of the 11 component concentrations and thermodynamic properties u and R without any necessary memory for tables or interpolation. To solve the 11 component system explicitly, descriptions for oxygen and the sum of nitrogen atoms were developed with data based identification methods - in particular by the application of genetic programming (GP). A fortunate characteristic of the given coupled equation system is, that it is possible to derive the rest of the 11-species without iteration in a top down way based on these 2 new explicit equations. This method is robust in a sense of insensitivity against initial values, i.e. it does not have a convergence problem. Furthermore, no storage in look up

tables is required. Additionally new explicit equations for thermodynamic properties u and R were developed with similar methods and benefits.

First, this paper presents general aspects of the workflow to derive equilibrium concentrations and the gas properties for a Diesel fuel as shown in Figure 1. Afterwards the development of the new explicit approach for the 11 species concentrations with GP is described in detail. Based on these concentrations the thermodynamic properties u and R can be derived. Alternatively a new direct method calculating u and R is presented, which could be used when species are not necessary and only the burn rate or rate of heat release is calculated. In the last chapter a wide evaluation is presented on the accuracy of the new methods compared to the standard iteration methods which is the reference. Engine process calculations based on experimental data in a lot of operating points were analyzed. For the validation also experimental data from operating points is used, where standard ECU calibration is changed by varying swirl level, rail pressure, injection timing and EGR-rate. The prediction of the equilibrium concentrations and the thermodynamic properties over crank angle is beyond the expectations for possible operating range of common passenger car diesel engine, even if the combustion is changed with a changed ECU calibration. The validation results should underline the general accuracy of the new simple method, because these points and changed conditions were not used for the identification process itself and are outside of the identification space.

As one application field the new methods were used for crank angle based emission models and the obtained failure compared to the reference method is not significant, but the authors can not give general recommendation for the use of the new methods. Especially for real time applications it is difficult to say which method is best, because it depends on the available memory, the processor and the necessary accuracy itself. That is why no comparison of the computational expenses is shown in the paper. For sure when enough memory is available also interpolation in tables could be the fastest method. In a computational point of view the mathematical most complicated iteration method could be also efficient if iteration time is low enough for the application. It depends mostly on the application itself which method is sufficient. The new presented simple methods with their specific advantages are suitable for several applications especially when simplified calculations are desired. Note that the presented formulations are specialized only for the possible operating range of a passenger car Diesel engine and Diesel fuel, but the structure may also be used for other fuels and engines if parameters will be adapted to the different fuel properties.

WORKFLOW

ENGINE PROCESS CALCULATION

A classical thermodynamic working cycle or 1-zone process calculation according to [6] is done for every measured operating point, which is mainly based on the measured cylinder pressure. The results are needed as inputs for later emission models. For the identification process the results from a lot of operating points were also used to determine the necessary space conditions.

The engine process calculation is based on 3 equations:

- ideal gas equation
- mass conservation
- energy conservation

After some modifications and simplifications 3 linear explicit coupled differential equations for $\lambda(\varphi)$, $dQ_B/d\varphi(\varphi)$ and $T(\varphi)$ can be obtained. Equation (1) describes the global λ progress in the cylinder during combustion starting from initial conditions which depends on the EGR-rate and results in the λ after combustion which is measureable in the tailpipe. The λ change during combustion depends mainly on the burn rate or the derivative of the burned fuel mass. For a direct injected diesel engine the derivative of the total cylinder mass ($dm/d\varphi$) can be set equal to derivative of the burned fuel mass ($dm_B/d\varphi$) for the high pressure phase (IVC to EVO). The assumption “fuel mass is added to the combustion chamber when it is burned and not when it is injected” is necessary for this simplification.

$$\begin{aligned} \frac{dm(\varphi)}{d\varphi} &= \frac{dm_B(\varphi)}{d\varphi} = \frac{1}{H_U} \cdot \frac{dQ_B(\varphi)}{d\varphi} \\ \rightarrow \frac{d\lambda(\varphi)}{d\varphi} &= -\lambda \cdot \frac{1}{m_B(\varphi = IVC) + m_B(\varphi)} \cdot \frac{dm_B(\varphi)}{d\varphi} \end{aligned} \quad (1)$$

$$\frac{dQ_B(\varphi)}{d\varphi} = \frac{N1 + N2 + \frac{dQ_w(\varphi)}{d\varphi}}{1 + \frac{u(\varphi)}{H_U} + \frac{T(\varphi)}{H_U} \cdot \frac{\delta u}{\delta T}(\varphi) + D1}$$

with

$$\begin{aligned} N1 &= p(\varphi) \cdot \frac{dV(\varphi)}{d\varphi} \cdot \left(1 + \frac{1}{R(\varphi)} \cdot \frac{\delta u}{\delta T}(\varphi) \right) \\ N2 &= \frac{dp(\varphi)}{d\varphi} \cdot \left(\frac{V(\varphi)}{R(\varphi)} \cdot \frac{\delta u}{\delta T}(\varphi) + m(\varphi) \cdot \frac{\delta u}{\delta p}(\varphi) \right) \\ D1 &= \frac{m(\varphi) \cdot \lambda(\varphi)}{H_U(m_B(\varphi = IVC) + m_B(\varphi))} \cdot \frac{\delta u}{\delta \lambda}(\varphi) \end{aligned} \quad (2)$$

$$\frac{dT(\varphi)}{d\varphi} = \frac{N3 - N4}{m(\varphi) \cdot R(\varphi)}$$

with

$$N3 = p(\varphi) \cdot \frac{dV(\varphi)}{d\varphi} + V \cdot \frac{dp(\varphi)}{d\varphi}$$

$$N4 = m(\varphi) \cdot T(\varphi) \cdot \frac{dR(\varphi)}{d\varphi} + R(\varphi) \cdot T(\varphi) \cdot \frac{dm(\varphi)}{d\varphi} \quad (3)$$

Moreover some starting values are required, which are based on measured EGR-rate, injected fuel mass and fresh air mass. The volume and volume changing work calculation is done by crank equations and a heat transfer multiplier according to [13] is used for wall temperature losses.

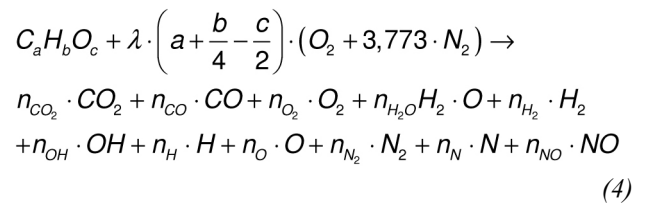
The calculation of the thermodynamic properties specific gas constant (R) and specific internal energy (u) and their derivatives which are necessary for burn rate analysis in equation (2) is described in detail in the next chapters. Essentially the same is done for the burned and unburned zone for 2-zone models and is described in detail in [6], depending on which type of 2-zone model is used.

CHEMICAL EQUILIBRIUM CONCENTRATIONS

Chemical equilibrium could be assumed for several concentrations produced during combustion, because the time scales of the reactions are fast compared to the rotation of the crank. For the above described applications several authors propose an 11 component equilibrium system with the 11 components CO_2 , CO , O_2 , H_2O , H_2 , OH , H , O , N_2 , N and NO . The 11 “exact” or reference concentrations for the data based modeling process were calculated in the same way as it is perfectly described in [1, 2].

C-H-O-N System

A defined fuel ($\text{C}_a\text{H}_b\text{O}_c$) is burned with air which consists of 21 % oxygen and 79 % nitrogen. For this paper the values are set to $a = 8$, $b = 14.51$ and $c = 0$ which is common for a commercial Diesel fuel.



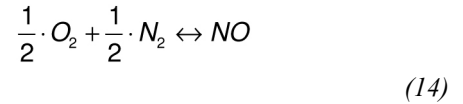
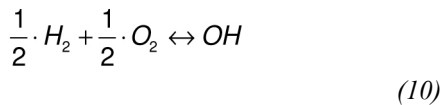
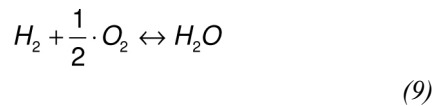
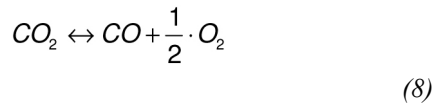
Obviously the ratios of the atoms must stay constant on the right and the left hand side of equation (4). This leads to the following equations (5), (6), (7) for the left hand side of reaction equation (4). N_H , N_N , N_C and N_O describe the number of atoms of H, N, C and O. Further simplification is done by inserting the fuel composition a, b, c-values for the given Diesel fuel. The simplified equations (5), (6), (7) are necessary for the equations (25), (26), (27) in the next chapter, which are based on the right hand side of equation (4).

$$\frac{N_O}{N_N} = \frac{c + 2 \cdot \lambda \cdot (a + \frac{b}{4} - \frac{c}{2})}{3.773 \cdot 2 \cdot \lambda \cdot (a + \frac{b}{4} - \frac{c}{2})} = \frac{1}{3.773} \quad (5)$$

$$\frac{N_C}{N_O} = \frac{a}{c + 2 \cdot \lambda \cdot (a + \frac{b}{4} - \frac{c}{2})} = \frac{0.344}{\lambda} \quad (6)$$

$$\frac{N_H}{N_O} = \frac{b}{c + 2 \cdot \lambda \cdot (a + \frac{b}{4} - \frac{c}{2})} = \frac{1.2479}{\lambda} \quad (7)$$

For the 11 species on the right hand side of equation (4) 7 elementary reaction equations are responsible.



Nonlinear Equation System

To calculate the 11 unknown species concentrations, 11 equations are needed. If the fuel is specified the 11 species concentrations in any operating point are a function of p , T and λ .

The equilibrium reaction coefficients ($K_{p,i}$) for the given 7 reaction equations (18), (19), (20), (21), (22), (23), (24) are derived with a relative new database according to [14]. They are valid for a wide temperature range (1000 - 6000 K) and for each reaction they are continuously valid and do not interpolate between any ranges. The calculation is done with equation (15) for each reaction with the $\Delta a_{i,j}$ parameters from matrix (16) for each reaction (see [1, 2] or the general source [14]).

$$K_{p,i} = e^{\frac{\Delta a_{i,1} \cdot \ln(T-1)}{2} + \frac{\Delta a_{i,2} \cdot T}{6} + \frac{\Delta a_{i,3} \cdot T^2}{12} + \frac{\Delta a_{i,4} \cdot T^3}{20} + \frac{\Delta a_{i,5} \cdot T^4}{T} + \Delta a_{i,6}} \quad (15)$$

$$\Delta a_{i,j} = \begin{bmatrix} 2.424552150E-01 & -1.061546039E-03 & 4.395287975E-07 & -7.124313310E-11 & 3.814344496E-15 & 3.415079838E+04 & 9.659674120E+00 \\ -2.086272015E+00 & 1.818400819E-03 & -5.567935775E-07 & 6.873378010E-11 & -2.930636710E-15 & -2.846484956E+04 & 6.199185480E+00 \\ 4.503603350E-01 & 9.889311185E-04 & -1.502251815E-07 & 2.407306460E-11 & -1.428834585E-15 & 4.712324615E+03 & 4.849423800E+00 \\ 1.033584750E+00 & 4.132980100E-04 & 7.320028500E-08 & -7.704925500E-12 & 3.443980750E-16 & 2.588018791E+04 & 6.547535000E-02 \\ 7.131565500E-01 & -3.554990101E-04 & 6.838444730E-08 & -5.330644500E-12 & 1.700125400E-16 & 2.983400063E+04 & 3.214613600E+00 \\ 9.398547150E-01 & -5.235959500E-04 & 1.272821115E-07 & -9.074985750E-12 & 2.676777200E-16 & 5.636674834E+04 & 1.713966690E+00 \\ -4.605626000E-02 & 1.643783885E-04 & -1.122321020E-07 & 1.985775365E-11 & -1.079614550E-15 & 1.099139429E+04 & 1.725380450E+00 \end{bmatrix} \quad (16)$$

The reaction coefficients are available depending on partial pressures in the unit bar. Thus the equations (8), (9), (10), (11), (12), (13), (14) are modified into partial pressure equations (18), (19), (20), (21), (22), (23), (24). This is possible, because molar concentrations or ratios of moles have the same behavior as the partial pressure ratios.

$$\chi_{species} = \frac{n_{species}}{n} = \frac{p_{species}}{p} \quad (17)$$

$$species = [CO_2, CO, O_2, H_2, H, H_2O, O, OH, N_2, N, NO]$$

The modification to partial pressures leads to the first 7 equations of the 11 equation system.

$$p_{CO_2} = \frac{1}{K_{p,1}} \cdot p_{CO} \cdot \sqrt{p_{O_2}} \quad (18)$$

$$p_{H_2O} = K_{p,2} \cdot p_{H_2} \cdot \sqrt{p_{O_2}} \quad (19)$$

$$p_{OH} = K_{p,3} \cdot \sqrt{p_{O_2}} \cdot \sqrt{p_{H_2}} \quad (20)$$

$$p_H = K_{p,4} \cdot \sqrt{p_{H_2}} \quad (21)$$

$$p_O = K_{p,5} \cdot \sqrt{p_{O_2}} \quad (22)$$

$$p_N = K_{p,6} \cdot \sqrt{p_{N_2}} \quad (23)$$

$$p_{NO} = K_{p,7} \cdot \sqrt{p_{N_2}} \cdot \sqrt{p_{O_2}} \quad (24)$$

The next 3 equations (25), (26), (27) are based on the conservation of the ratios of N-, O-, H- and C- atoms which represents the right hand side conditions of reaction equation (4). The left hand side of the equations (25), (26), (27) is described by the simplified equations (5), (6), (7). The right hand side of equation (4) shows the amount of atoms after reaction of fuel and air - subject to the chemical equilibrium condition. Again partial pressures in the unit bar are used instead of moles. The ratio of atoms must stay constant - even after combustion or reaction.

$$\frac{N_O}{N_N} = \frac{2 \cdot p_{CO_2} + p_{CO} + 2 \cdot p_{O_2} + p_{H_2O} + p_{OH} + p_O + p_{NO}}{2 \cdot p_{N_2} + p_N + p_{NO}} \quad (25)$$

$$\frac{N_C}{N_O} = \frac{p_{CO_2} + p_{CO}}{2 \cdot p_{CO_2} + p_{CO} + 2 \cdot p_{O_2} + p_{H_2O} + p_{OH} + p_O + p_{NO}} \quad (26)$$

$$\frac{N_H}{N_O} = \frac{2 \cdot p_{H_2O} + 2 \cdot p_{H_2} + p_{OH} + p_H}{2 \cdot p_{CO_2} + p_{CO} + 2 \cdot p_{O_2} + p_{H_2O} + p_{OH} + p_O + p_{NO}} \quad (27)$$

The last necessary equation to solve the system is the sum of the partial pressures which is equal to the global pressure.

$$p = p_{CO_2} + p_{CO} + p_{O_2} + p_{H_2O} + p_{H_2} + p_{OH} + p_H + p_O + p_{N_2} + p_N + p_{NO} \quad (28)$$

The 11 equations (18), (19), (20), (21), (22), (23), (24), (25), (26), (27), (28) show a coupled nonlinear equation system with 11 unknown species or partial pressures which are a function of p , T and λ . Due to the fact that the system is implicit and non linear, it must be solved numerically. Therefore, several authors use a Newton method. The main drawbacks of the numerical solvers are the need for good starting or initial values for the 11 species to achieve convergence and the substantial computational effort. Thus, before calculating the target values it is common to initially use a reduced reaction system of equations without dissociation to determine initial values.

The convergence difficulties and the effort for good initial values might be not a problem, if only some points are analyzed. However, the effort increases significant, especially if transients are analyzed in the crank angle domain and the chemical equilibrium is needed for each crank angle step.

The alternative of storing the 11 species concentrations in 4 dimensional tables and interpolating between the grid points is also insufficient, namely a lot of grid points of p , T and λ would be necessary because of the high nonlinearity of the concentrations and the wide range of the necessary inputs during combustion.

Consequently the new explicit approach is developed for a defined Diesel fuel ($C_8H_{14.51}$), especially for analyzing combustion during transients. Only explicit equations are used. However for the identification process (supported by GP) the identification data is calculated with a conventional numerical Newton algorithm described in detail by [2] and [10].

THERMODYNAMIC PROPERTIES CALCULATION

The thermodynamic properties internal energy and specific gas constant are necessary for a 1- or 2-zone engine process calculation for each zone. On the one hand they could be derived based on the above described 11 species concentrations with a component based calculation on the a direct calculation could be used according to [3] or [15].

Component Based Calculation

Component based calculation is again fully described in [2] and only the principle equations are presented in this paper. For the specific gas constant the formulation is quite simple, depending only on the constant molar masses of each species ($M_{species}$), the constant general or molar gas constant (R_m) and the species concentrations which depends as described above on T , p and λ .

$$species = [CO_2, CO, O_2, H_2, H, H_2O, O_2, OH, N_2, N, NO] \quad (29)$$

$$R(T, \lambda, p) = \sum_{species} \frac{R_m}{M_{species}} \cdot \chi_{species}(T, \lambda, p) \quad (30)$$

The calculation of the internal energy is a more complex, because the calculation of the specific enthalpy $h_{species}$ is a polynomial function for each species with a temperature dependency and is calculated according to [16]. The conversion enthalpy to internal energy is done with equation (32).

$$h(T, \lambda, p) = \sum_{species} h_{species} \cdot \chi_{species}(T, \lambda, p) \quad (31)$$

$$u(T, \lambda, p) = h(T, \lambda, p) - T \cdot R(T, \lambda, p) \quad (32)$$

Following the ideas of [2] about freezing the chemical equilibrium a freeze temperature was defined at 1600 K. That means at temperatures below 1600 K the equilibrium concentrations at freeze temperature were used for calculating h and R .

For the component based calculation of the thermodynamic properties both methods could be used as inputs to calculate the species concentrations, the conventional iteration method or the new presented explicit method.

Direct Calculation

If no further crank angle based emission modeling is necessary and only calculating the burn rate would be of interest, the species concentrations are not directly required. To this end some authors Justi [15] or Zacharias [3] defined explicit functions for the internal energy, to avoid interpolating in big tables. The Justi formulation (see equation (33)) is simple and helpful in some cases, if very low computational effort is necessary, but does not have a pressure dependency and is not very accurate compared to the full calculation of the species as described above.

$$u(T, \lambda) = 0.1445 \cdot \left(1356.8 + \left(489.6 + \frac{46.4}{\lambda^{0.93}} \right) \cdot (T - 273.15) \cdot 10^{-2} \right. \\ \left. + \left(7.768 + \frac{3.36}{\lambda^{0.8}} \right) \cdot (T - 273.15)^2 \cdot 10^{-4} \right. \\ \left. - \left(0.0975 + \frac{0.048536}{\lambda^{0.75}} \right) \cdot (T - 273.15)^3 \cdot 10^{-6} \right) \quad (33)$$

The quite more complicated Zacharias formulation (see equation (34)) has a pressure dependency and is more accurate when high pressure is taking place in the engine and ideal gas assumption which is used in Justi correlation is invalid. Some comments on the accuracy on the formulations is done in [2] and [17].

$$u(T, \lambda, p) = R_0 \cdot T \cdot \left(-A \cdot \frac{\pi}{\vartheta^2} \cdot e^{\frac{D}{\vartheta^2}} \cdot \left(1 + 2 \cdot \frac{D}{\vartheta^2} \right) + \sum_{i=0}^6 (FA(i) \cdot \vartheta^i) - 1 \right)$$

with

$$R_0 = \frac{R_m}{28.89758 + 0.06021 \cdot r}$$

$$\pi = \frac{p}{0.980665}$$

$$\vartheta = \frac{T}{1000}$$

$$r = \frac{\lambda - 1}{\lambda + \frac{1}{L_{st}}}$$

$$A = 2.77105 \cdot 10^{-4} - 9.00711 \cdot 10^{-5} \cdot r$$

$$D = 0.008868 - 0.006131 \cdot r$$

$$FA(0) = 3.514956 - 0.005026 \cdot r$$

$$FA(1) = 0.131438 - 0.383504 \cdot r$$

$$FA(2) = 0.477182 - 0.185214 \cdot r$$

$$FA(3) = -0.287367 - 0.0694862 \cdot r$$

$$FA(4) = 0.0742561 + 0.01640411 \cdot r$$

$$FA(5) = -0.00916344 - 0.00204537 \cdot r$$

$$FA(6) = 0.000439896 - 0.00010161 \cdot r$$

(34)

CRANK ANGLE BASED EMISSION MODELS

Crank angle based emission models for NO and soot formation depend on the one hand on the values from the engine process calculation (T, p, λ , burn rate) and on the other hand on the equilibrium concentrations. For NO formation several authors [5,6,7, 18, 19] use a 2-zone model where NO is formed in the burned zone. For the soot dynamics often a 1-zone calculation is used (e.g see [4]). Note that accuracy and general validity of the used emission models itself is not a topic of the paper. The following models are only used to evaluate the deviation, if the results from the new sufficient complexity methods are used as inputs instead of the standard methods.

NO Model

During the combustion process nitrogen (N) from the air is oxidized to nitric oxygen (NO), in zones with high temperature and enough oxygen. These conditions were modeled with the burned zone of a 2-zone model. The NO formation itself must be modeled with reaction kinetics because the slower timescale of the NO formation compared

to combustion itself. The NO model which is used for the validation of the new explicit approach is based on the Zeldovich mechanism [20]. The simplified equation (35) of the Zeldovich mechanism is described in [8].

$$\frac{d[NO]}{dt} = 2 \cdot k_1^f \cdot [N_2] \cdot [O] \frac{1 - \frac{[NO]^2}{k_1^f \cdot k_2^f \cdot [N_2] \cdot [O_2]}}{1 + \frac{k_1^b \cdot [NO]}{k_2^f \cdot [O_2] + k_3^f \cdot [OH]}} \quad (35)$$

Reaction rates according to [8] are used and they mainly depend on the temperature in the burned zone. See equations (36). The burned zone temperature is calculated with a 2-zone model according to [6].

$$\begin{aligned} k_1^f &= 13 \cdot 10^{13} \cdot e^{\frac{-38230}{T_{burned}}} \\ k_1^b &= 2.8 \cdot 10^{13} \\ k_2^f &= 6.4 \cdot 10^9 \cdot T \cdot e^{\frac{-3145}{T_{burned}}} \\ k_1^b &= 1.5 \cdot 10^9 \cdot T \cdot e^{\frac{-19635}{T_{burned}}} \\ k_3^f &= 4.2 \cdot 10^{13} \\ k_3^b &= 1.3 \cdot 10^{14} \cdot e^{\frac{-22865}{T_{burned}}} \end{aligned} \quad (36)$$

The unknown concentrations [O₂], [O], [OH], [N₂] in (35) can be described by the equilibrium concentrations. The simplification is possible, because the timescale for NO formation is slower than burning fuel and their components. Hence [O₂], [O], [OH], [N₂] is set to the equilibrium values.

$$\begin{aligned} [O] &= [O]_{Equilibrium} \\ [O_2] &= [O_2]_{Equilibrium} \\ [OH] &= [OH]_{Equilibrium} \\ [N_2] &= [N_2]_{Equilibrium} \end{aligned} \quad (37)$$

Soot Model

Modeling the soot dynamics is more complicated than the NO formation, because the amount of soot we can measure in the tailpipe depends mainly on two controversial effects which is described in detail in [21]. One effect is the formation process which is most relevant for the actual soot concentration in the first phase of combustion. The second effect, the oxidation, starts a bit later and is still present after combustion, but it is slowed down in the late combustion phase.

The very complex chemistry behind the soot kinetics is not fully understood until today, but there are several approaches to model it phenomenologically. One way to explain the main mechanism are the empirical equations according to [22] which could be called “mother equations” of a lot of other later published models. One of these models is described in [4] and is based on a one zone calculation and should illustrate the validity of the new approach. The soot dynamics in equation (38) are described by two controversial equations, the formation- (39) and oxidation-equation (40) which depend on the results of a 1-zone calculation and the equilibrium for oxygen is needed for equation (40), because it characterizes the oxidation.

$$\frac{dm_{Soot}}{dt} = \frac{dm_{SootForm}}{dt} - \frac{dm_{SootOxi}}{dt} \quad (38)$$

$$\frac{dm_{SootForm}}{dt} = A_{Form} \cdot \frac{dm_{B,Diff}}{dt} \cdot \left(\frac{p}{p_{ref}}\right)^{n_1} \cdot e^{\frac{-T_{AForm}}{T}} \quad (39)$$

$$\frac{dm_{SootOxi}}{dt} = A_{Oxi} \cdot \frac{1}{\tau_{char}} \cdot m_{Soot}^{n_2} \cdot \chi_{O_2}^{n_3} \cdot e^{\frac{-T_{AOxi}}{T}} \quad (40)$$

IDENTIFICATION - DATA BASED METHODS

GENETIC PROGRAMMING

Genetic programming (GP) is an extension of genetic algorithms and essentially a data based method. GP uses starting populations and is based on modifying them by the Darwinian principles selection, crossover and mutation to find an optimal solution for a given problem data set. See [23] for further details.

For this work the GP-software HeuristicLab (HL) was used (see [24]). The software package heuristic lab allows choosing different specialized algorithms and solvers. For finding the formulations the specific “Offspring Selection Genetic Algorithm” solver was used which allows specifying several parameters, especially input candidates, mutation ratio, initial population size, maximum depth, maximum length and structure of the final formulation. As input candidates all inputs which are also necessary in the physical equations were selected and the GP algorithm chooses the most relevant ones. The best results were performed with mutation ratios between 11-13 % and initial populations from 500-1500. Further information about the used solver is available in [24]. Alternatively the software package is described in the internet at <http://dev.heuristiclab.com> and the solver is especially described at <http://dev.heuristiclab.com/trac/hl/core/wiki/OSGA>. An advantage of GP compared to