

# Discrete Reaction Model for Sooting Flames

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## ABSTRACT

A predictive analysis of combustion product composition is provided. Discrete reaction model of sooting combustion is proposed on the grounds of multi-stage representation of oxidation chemistry. By the restrictions on the number of product species involved, and the assumption of fast reaction rates the set of algebraic equations is deduced for the mass fraction of product species. The solutions obtained are shown to be linked to the elemental mass composition with associated limiting requirements. An advanced conserved-scalar approach has then emerged, for which, it is shown that the product mass fractions, including sooting intermediates, can be obtained as a conditional functions of the global mixture fraction. The application of the methodology is illustrated using the example of an industrial carbon black furnace. It is demonstrated that the predictions are in fair agreement to the measured data, and show the correct trends without making any adjustments to the soot modeling concept. The algebraic nature of the model relationships makes it easy bringing them into the computational loops of available predictive tools, so that it is believed the present model has the potential to supplant or complement the similar methods in the engineering computational analysis of combustion.

*Keywords:* Soot formation, combustion, reaction model, elemental balances, mixture fraction.

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## EXTENDED ABSTRACT

### 1 Introduction

Calculating the composition of the sooting flames presents a challenging problem. It is currently solved by the number of demanding and sophisticated numerical techniques. The simplest of them uses empirically based correlations. Thus, it has very limited range of applicability [1]. At the other end, the most popular research methods employ a family of the conservation equations along with PDF, probability density functions, in an attempt to address the detailed stochastic mechanism of soot formation and oxidation [2]. The resulting computing and intellectual requirements may far exceed what is generally

available to the combustion and fire safety engineering communities. We shall refer to such methods as the “detailed approaches” in the remainder of the text.

The engineering practice, however, is in permanent need of affordable, easy for use and reasonably accurate modeling tool to handle the diversity of the combustion problems arising from soot-forming under-ventilated environment, and/or fuel-enriched operating conditions of many real-life fires and flames.

In a response to this demand, some authors [3, 4] have attempted to find the reaction-model-based alternative to the detailed methods of soot-forming combustion. They have argued [3] that sooting effects of combustion may be modeled using an extended form of chemical reaction for complete combustion. Their model uses the soot conversion factor, which is defined as a fraction of carbon, originally presented in the fuel that is converted to the soot during combustion. It is then assumed that the factor is a constant specific to the particular fuel. As a consequence, the soot content by mass becomes proportional to the total product mass fraction which is, in turn, made related to the local value of mixture fraction by fast reaction approximation. The success of the method depends crucially on the value of soot conversion factor; with the latter being empirically increased by more than one order of magnitude for heavily sooting fuels to get the agreement with experimental observations.

A recent attempt [4] to design more realistically simplified reaction model has lead to bringing into the picture the carbon monoxide as another product of incomplete oxidation. The calculation procedure has then required two conversion factors, governing the rates of molar production for both the soot and carbon monoxide. The factors have been computed by making them proportional to the molar production of carbon dioxide. Using the fast reactions assumption the mixture fraction concept has again been employed. This model also makes use of experimental data to adjust the proportionality coefficients of conversion factors to predict the quantities of interest.

While practically attractive because of their simplicity, both foregoing types of analysis are not recommended by the present writer for a number of reasons: (i) The conversion factors are usually a function of local mixture composition, and not constant; (ii) For the simulation to be reliable, its conditions must be close to those of gauge experiments; and (iii) The types of fuel and oxidizer should be similar to the ones on which the calibration was based. These methods will be referred to as the “simplified approaches” in the remainder of the text.

The purpose of this paper is to provide the reader with reasonably simple yet realistic and comprehensive method by which he or she may mathematically predict the composition of flames with special emphasis on sooting effects.

## **2 Foundation**

The theoretical foundation for the present text follows the approach based on the mass fractions of mixture components, as well as on the one that based on the mass fractions of elements. A justification for the use of these, widely-adapted mixture characteristics, is that, historically, the former is well rooted in the engineering practice, while the latter successfully exploits the fact that in the chemical reactions the elements are individually conserved, and, thus, their respective mass fractions can be most easily calculated from the balance equations which do not require any specific sources/sinks.

Component-based and element-based approaches are easily inter-converted. For the element mass fractions known from their balance equations, inter-conversion equations can be viewed as a set of “number of element”-equations in “number of component”-unknowns.

The purpose of this paper is to reduce the product composition problem to the form of closed sets of inter-conversion equations, and then solve them for the mass fraction of product components with associated limiting requirements.

### 3 Multi-stage reaction mechanism

The useful solutions for the product composition are obtained here by (a) discretization of oxidation chemistry followed by (b) the restrictions on the number of product species involved, and (c) the assumption of fast reaction rates.

#### 3.1 Discrete chemical reactions

It is assumed that oxidation of the hydrocarbon fuel in the presence of oxygen from atmospheric air proceeds in four reaction stages, namely:

1. To create complete combustion products when the air is in excess, and as more fuel is added,
2. To create carbon monoxide, and then as even more fuel is added,
3. To create carbon soot, and thereafter, as the fuel becomes in a large excess, the combustion reaction is extinguished, and
4. The unburned fuel coexists with reacted substance, the latter consisting of water vapour, and carbon soot.

In terms of chemical elements involved, the above oxidation stages are represented by four-zone discretization of oxygen, (O), element-space as follows:

1. The lean-mixture zone, in which free oxygen mass fraction exceeds its stoichiometric limiting value;
2. The intermediate zone, in which free oxygen mass fraction lies in between the stoichiometric and rich limits;
3. The sooting zone, in which the free oxygen mass fraction lies in between the rich and soot limits; and
4. The fuel-rich zone, where the free oxygen mass fraction is below the soot limit.

#### 3.2 Flame limits

From discrete chemical reactions, the equations for the mass fractions of elements in the mixture are first obtained. The stoichiometric limit is characterised by the absence of fuel, molecular oxygen, carbon monoxide and carbon soot; the limiting value of oxygen element is then readily calculated. The rich limit is obtained on the grounds that no fuel exists, and neither molecular oxygen, nor carbon dioxide, and never carbon soot are present in the products. It is believed reasonable to assume that at the soot limit only nitrogen, water vapor and carbon soot can be found in the mixture.

The above limiting requirements are expressed as algebraic relations, and can be viewed as problem specific parameters of grid adaptation in (O)-element variable space.

### 3.3 Product composition

If the mass fraction of (O)-element becomes larger than its stoichiometric limit, there is an excess of oxygen. The fast chemistry implies that neither of combustible components (no fuel, no carbon monoxide, no soot) can exist. The element mass fraction expressions are there reduced to a set of three equations in three unknown component mass fractions.

The similar reductions are performed for each of the three other zones guided by the product composition defined by discrete chemical equations and fast chemistry assumptions. Thus, in either zone there will be the closed set of three linear equations for three component mass fractions. The exact solutions are easy to obtain, from which the unknown component mass fractions can readily be found. The resulting algebraic equations for each reaction zone are defined here as DRM, Discrete Reaction Model, formulations. It is the recommended method for computing the composition of sooting flames, which is referred to below as the “present method”.

### 3.4 Mixture-fraction-based formulations of DRM

The coefficients of discrete chemical equations are easily expanded by applying the atomic conservations. The chemical equations at the flame limits are just the special cases of discrete reactions under the limiting conditions listed in 3.2. The limiting equivalence ratios are then readily obtained. The latter are used to convert the present method into the expressions based on widely used definition of mixture fraction as follows.

Through the calculation of limiting values for inert nitrogen mass fractions, and corresponding mass fraction of total products, the individual mass fractions for all product components at the mixture fraction limits are first computed. The local mass fraction formulations are then derived, in a piecewise linear manner, from mixture fraction values.

This, linear-in-mixture-fraction technique, is referred to below simply as a “linear approach”, and may only be applied to the situations within the limitations of mixture-fraction-based methods [1].

## 4 Example: Performance of a carbon black furnace

The methodology based on DRM will be presented below by way of quantitative practical example. The case of an industrial carbon black reactor [5] is considered.

### 4.1 Problem

In the furnace black process fuel (usually natural gas) is burnt under fuel lean conditions in the primary stage (zone). In a secondary stage a feedstock, usually aromatic oil is injected through an atomizer into the hot exhaust from the primary stage. After the reaction mixture is quenched with water and cooled in heat exchangers, the carbon black is collected from the product (tail) gas using a filter system.

The task of the validation exercise is to simulate the industrial production of carbon black by the furnace process, and to study the effect of some operating parameters on the furnace productivity.

## 4.2 Solution

In the case study, the field distributions of gas composition is predicted from which the averaged exit values of the carbon soot mass fraction and yield (kg of carbon soot per kg of feedstock) are computed. The simulation tests the model against industrial data of Philips Petroleum Company as reported by Lockwood, van Niekerk [6].

## 4.3 Discussion

The results suggest that the present method is in agreement with the experimental observations. The soot mass fraction and yield are over predicted by about 30%. Indeed it can be expected that the present prediction will give larger values of soot mass fractions, because mixing is presumed to be perfect. The validation exercises also suggest that results of detailed approach taken from [7], even augmented there by experimental mixing rate, is in no better agreement with experiment; for the detailed calculations under predict the soot contents by about the same percentage.

The application of linear approach has appeared to be possible for the simulation of the primary stage only. There, the mixture is highly fuel lean, and the inlet streams are made up entirely from fuel and oxidizer; the situation that is not to be found in secondary zone, in which one of the inlet streams is formed by the first stage flue gas and feedstock composition is different from primary fuel.

The effects of feedstock on the composition of the product gas have been investigated. The performances of the furnace with both diesel fuel and heptanes as a feedstock are found to be far from being acceptable; for almost the same amount of feedstock as the blacks produced is thrown away with exhaust gases. Even highly sooting toluene can not compete with aromatic oil in terms of feedstock consumption; for it is also unable to react completely under given operating conditions. The aromatic oil as a feedstock solves the problem of reaction incompleteness. Variation of feedstock type has also revealed that the present model predicts the decrease in propensity to soot with the level of hydrocarbon saturation. Aliphatic feedstock such as methane and ethane were much less sooting than aromatics.

The effects of varying equivalence ratio in the primary stage have also been studied. It was predicted that the yield increases in linear manner with the increase in primary equivalence ratio. For the fuel-rich state of the base product mixture a small increase in the oxygen contents of air increases the yield, but a large increase in oxygen fraction significantly decreased soot tendency.

All these trends are in accord with existing technological experience [5]. The similar observations have also been reported in the simulations performed elsewhere [6, 7]. Given the number of assumptions made in the formulation of the present model and in the representation of the furnace, and also the fact that no changes have been made to any of the reaction modeling equations, the present model predictions look fair and versatile.

In contrast, the simplified analysis could not be uniformly applicable at the reactor operating conditions; for the user should always perform sample calculations to obtain trial values of conversion factors prior to using the simplified methods. For many situations the linear approach will suffice; but this will not be the case here as the streams have the different compositions. The present analysis does generate meaningful results

for non-similar inlet streams, and for all specified states of product mixture: lean, intermediate, sooting, and rich. It is therefore recommended.

While it is possible to construct more complex problems, this simple example has served to validate and illustrate the typical performance of the present model.

## 5 General discussions

As developed, the DRM represents the global chemistry of hydrocarbon oxidation by finite number of chemical reaction each associated with certain range of O-element mass fraction. The element-based formulations of present DRM are, by and large, well adapted to different uses arising from industrial combustion applications. The current author's position is that present element-based and linear mixture-fraction-based formulations should be entirely equivalent, provided that the limitations of the latter are not compromised.

In this paper, the example of simulations for the product composition produced in a black carbon furnace fueled and fed by different hydrocarbons was given. The predictions have demonstrated a fair agreement to the experimental observations. It has been achieved without making any adjustments to the original concept of the present approach; the present theory is sufficient to adequately describe the variety of possible scenarios.

The present method may readily be used in the calculation procedures involving thermal effects of heat releases and radiation, heterogeneous reactions, etc. The formulations developed are of algebraic nature, and, therefore, very easy to import, on cell-by-cell basis, into one- or multi-phase CFD solvers. The model framework is flexible enough to readily accommodate the modeling techniques for the turbulence-chemistry interactions, such as presumed PDF [10], or multi-fluid population balance [11].

It might be argued, that there are the situations for which the present analysis does not hold. In those circumstances there might be no other recourse than to solve eddy dissipation type of soot formation model [8], or the two-step Tesner's model [9], or even the joint PDF transport equation [2] to combine the detailed soot modeling with a stochastic mixing.

There are also a number of other important factors to consider when analyzing composition of sooting flames. For example, the present approach must be modified if larger number of product species is to be taken into account. The non-equilibrium effects may be important, and soot particle size distributions should be used to describe the kinetics of soot formation. While the importance of turbulence-chemistry interaction, finite rates of reactions, and the stochastic nature of soot particle formation, agglomeration, and oxidation is not to be understated, there is clearly range of applications, where the present, pragmatic and practically-oriented, method would give reasonable estimate of sooting flame composition.

## 6 Conclusions

An analysis based on the well-established concept of chemical element conservation was adapted to the novel reaction model developed to predict the composition of sooting flames. The model is designed as a discrete reaction set for multi-stage approximation of hydrocarbon oxidation taking place in a seven-species mixture of reactants and products obtained on the grounds of fast reaction chemistry.

It was demonstrated that the predictions by present approach are in fair agreement to the measured data without making any adjustments to the soot-forming reactions. The trends predicted are also seemed correct. A linear approach based on mixture fraction provides identical results, although it does not appear to offer any major advantages over the present analysis, which is working well beyond the limitations of the former. The model developed has an advantage of being in a form fully compatible with methods widely used in CFD practice, and, therefore, has a potential to supplant or complement the latter in the computational analysis of combustion phenomena in engineering equipment.

The full paper details the DRM equations, lists its formulations, and provides currently available testing, validation and some further application cases relevant to sooting flame systems. The results are presented in terms of tables and plots of mass fractions, fuel, feedstock and air utilisation, and also temperature and flow field topology.

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