

Chemistry Research and Applications

COMBUSTION

*Types of Reactions,
Fundamental
Processes and
Advanced Technologies*

Joseph M. Grier
Editor

NOVA

CHEMISTRY RESEARCH AND APPLICATIONS

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**TYPES OF REACTIONS,
FUNDAMENTAL PROCESSES
AND ADVANCED TECHNOLOGIES**

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JOSEPH M. GRIER
EDITOR

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PREFACE

In this book the authors present current research in the study of different types of reactions, fundamental processes and advanced technologies of combustion. Topics discussed in this compilation include the Lagrangian formulation to treating the turbulent reacting flows; g -equation in white-noise in time turbulent velocity field; deposition of thin functional coatings at atmospheric pressure using combustion chemical vapor deposition; fundamentals of oxy-fuel carbon capture technology for pulverized fuel boilers; combustion of lignocellulosic biomass and marine biomass by means of thermal analyses; methane combustion by electrochemical promotion of catalysis phenomenon; novel nitrate-free acetate- H_2O_2 combustion synthesis; and solution combustion method.

Chapter 1 - In this chapter the authors outline a Lagrangian approach to treating problems of turbulent reacting flows. In order to avoid unnecessary complications, and to highlight the basic issues they limit ourselves to the particular case of a constant density, homogeneous isotropic turbulent flow. The case a passive reactive scalar is considered, i.e. it is assumed that the turbulence is not affected by the combustion.

Chapter 2 - A promising approach to simulating premixed turbulent combustion in gas turbine and spark ignition engines consists of tracking a flame surface in the turbulent velocity field in the framework of so called G – equation, associating the evolution of the flame surface with the evolution of zero (or G_0) level set of a function $G(\mathbf{x}, t)$. The goal of the present chapter is to derive the equation for the probability density function of G straightforwardly from the well-known G -equation for tracking an infinitely

thin flame sheet (flamelet) in a white-noise in time statistically homogeneous isotropic constant density turbulent flow.

Chapter 3 - The deposition of thin functional layers under atmospheric pressure conditions using flame-based techniques is a cost-effective solution for several applications in comparison with the well known vacuum techniques. The basic principles of the flame-based deposition techniques are reviewed and the technical realization is shown by means of selected examples of the current research and development of Innovent e.V.

In the case of combustion chemical vapour deposition (CCVD) a combustible gas-air mixture is ignited in a burner. The temperature of the flame depends on the gas-air ratio and strongly on the zone of the flame. In the simplest case oxidizing and reducing flame are differed. In dependence of both of these main flame-properties, the chemistry of precursor reactions and film-deposition is influenced. The film morphology can also be adjusted for example by the distance of the substrate to the flame. Additionally a specialized remote CCVD system is developed in order to deposit hydrolyzing precursors.

The formation of silicone oxide layers with a wide range of properties is investigated in detail. The most famous applications like adhesive, optical effective, barrier and matrix layers for embedding particles are reviewed. Fundamental investigations were performed to deposit zinc oxide layers with the objective of transparent and conducting coatings. Further coating systems like photocatalytic active (TiO_2), electrochromic (wolfram oxide), silver, aluminium oxide and rare-earth layers are also introduced.

Chapter 4 - Coal is expected to continue to contribute to electricity production in the near future. However, it generates more CO_2 per unit of produced energy than other fossil fuels and its use is associated with the formation of contaminants such as NO_x , SO_x , Hg, etc. In recent years, oxy-fuel combustion has attracted great interest as a promising Carbon Capture and Storage (CCS) technology, since it can be easily adapted to both existing and newly built coal-fired power plants. During oxy-fuel combustion coal is burnt in a mixture of oxygen and recycled flue gas (RFG) (mainly CO_2 and water vapor), that is used to lower the flame temperature and yield a rich stream of CO_2 . However, the successful implementation of oxy-fuel combustion technology depends on having a full understanding of the difficulties that arise as a result of replacing inert N_2 by reactive CO_2 in the oxidizer stream.

Biomass is a renewable fuel which can be used to reduce CO₂ emissions, as it is considered carbon-neutral. The combination of oxy-coal combustion with biomass co-firing could provide an effective method of CO₂ disposal which has only partially been studied. Furthermore, biomass co-firing is presented as an option for increasing capture efficiency, as the costs and efficiency penalties would be reduced. This chapter presents a technical review of the oxy-fuel combustion process, covering the most recent experimental studies at both laboratory and pilot scale. The impact of replacing N₂ by CO₂ upon heat transfer, devolatilization, ignition, combustion kinetics, pollutant formation (mainly NO_x and SO_x) and fly ash and slag formation is also evaluated. Furthermore, the effect of blending coal and biomass under oxy-fuel conditions on combustion properties is assessed.

Chapter 5 - Biomass fuels are gaining particular attention as a potential alternative to increase energy independence of fossil fuels and reduce environmental pollution. The main ones refer to lignocellulosic biomass and marine biomass (especially microalgae). There is a growing interest in the cultivation of lignocellulosic biomass for energy production as they typically have less capital-intensive conversion technologies, attractive opportunity for local and regional self-sufficiency, reduction in greenhouse gas emissions and viable alternative to fossil fuel use. On the other hand, microalgae have received increasing attention due to the fact that they can be cultured in ponds or photobioreactors with supply of nutrients or waste water. Moreover, the production of microalgae does not require of high quality arable land and therefore it does not compete with food crops.

Direct combustion is the oldest and still the most commonly used route for converting biomass to heat, power and combined heat and power. Combustion can be defined as the conversion of biomass fuels to several forms of useful energy in the presence of air or oxygen. Despite its inherent potential as a biofuel resource, the commercial viability of biomass combustion technology has not been achieved yet. In this regard, thermogravimetric analysis is one of the most common techniques used to rapidly investigate and compare thermal events and kinetics during combustion of biomass. TGA provides useful information concerning the temperatures at which combustion or decomposition reactions in the sample start. Biomass characteristics and kinetics of biomass combustion are essential for modeling the combustion in industrial processes. Therefore, from TGA data suitable mathematical models can be derived for a better comprehension of the oxidation behavior of these complex feedstock that allow to perform economic analysis and develop technology for a more efficient biomass conversion.

Additionally, during the combustion of biomass, the composition of the gas emissions should be determined before industrial application. In spite of the environmental advantages, some aspects concerning the release of contaminants during biomass combustion must be taken into account. In this regard, NO_x and SO_x emissions depend on raw biomass composition, which usually is variable. Furthermore, the chloride amount in biomass might turn into operational problems such as corrosion. Other organic compounds such as benzene and toluene are considered to be part of the most dangerous emissions from biomass combustion causing diseases as lung infection and leukemia. Therefore, the knowledge of pollutant release during biomass conversion is truly important in order to reassure the use of biomass from the environmental point of view. In this regard, the coupling of thermogravimetric analysis with mass spectrometry (TGA-MS) stands out as the only experimental technique able to afford real-time and sensitive detection of evolved gases from the thermochemical conversion of a very small sample.

In this chapter, the combustion behavior and the gas evolution analysis of different biomass feedstock (lignocellulosic and microalgae) by means of TGA-MS will be addressed. Finally, the kinetic analysis of the combustion process will be presented.

Chapter 6 - Methane is the main component of natural gas and is probably the most abundant organic compound on Earth. In view of the fact that the world petroleum reserves are on the decline, a great deal of emphasis has been placed on developing alternatives for energy production. Significant efforts have been focused on finding effective processes and technology for the optimum utilization of the abundant natural gas in energy production. During the last decades, the catalytic combustion of methane has been extensively studied as an alternative to conventional thermal combustion. This method allows converting methane at relatively low temperatures and with very high combustion efficiency, thus avoiding emissions. Hence, it is considered an effective route to produce power with low environmental impact and then suitable for gas turbine applications.

On the other hand, one of the latest advances in catalysis is the phenomenon of Electrochemical Promotion Of Catalysis (EPOC), or Non-faradaic Electrochemical Modification of the Catalytic Activity (NEMCA), that has had a strong impact in the fields of electrochemistry, heterogeneous catalysis and surface science. This phenomenon is an important tool to improve the catalytic performance of a metal catalyst interfaced with a solid electrolyte by the application of low current or potentials over the catalytic film. During the last years, it has been demonstrated that it is based on the

change of the work catalytic function due to the electrochemical pumping of ions from the solid electrolyte to the catalyst.

In this chapter, the catalytic combustion of methane by this new phenomenon will be addressed. Finally, the application of this technology to the methane combustion over palladium based catalyst-electrodes will be presented.

Chapter 7 - One of the key challenges in materials science research is the synthesis of ceramic materials with the desired phase purity, morphology, particle size and expected properties for defined applications, while controlling cost. The selection of the synthesis method is vital to regulate the composition, structure, and morphology of a preferred material. Ceramic oxide materials are typically prepared by solid-state reactions, for example simple mechanical mixing of ceramic oxide powders, or by precipitation from solution and following decomposition. Nonetheless, the solid-state route can often lead to the appearance of non-homogeneity in the final products and low phase purity that can deteriorate the desired properties.

A novel nitrate-free acetate- H_2O_2 combustion synthesis method has recently been developed that has been demonstrated for the successful preparation of $\text{Ni-BaZr}_{0.85}\text{Y}_{0.15}\text{O}_{3-\delta}$ cermet anodes and $\text{Ba}(\text{Ce,Zr,Y})\text{O}_{3-\delta}$ electrolytes for Proton Ceramic fuel cell (PCFC) applications. Metal acetates ($\text{M}(\text{OCOCH}_3)_x \cdot y\text{H}_2\text{O}$) and 30% H_2O_2 are employed as starting precursors for this combustion reaction, using microwave heating. The new route contrasts dramatically to traditional nitrate-based combustion processes in that the metal precursors now constitute the fuel rather than the oxidant in the combustion reaction. Another significant distinction of the novel route is that the acetate precursor solution is neutral in contrast to typical nitrate-based combustion routes that involve acidic solutions. This factor has been shown to be highly important for the successful preparation of cermet anodes such as $\text{Ni-BaZr}_{0.85}\text{Y}_{0.15}\text{O}_{3-\delta}$ that contain alkaline earth metals. The novel combustion route produces powders with a fine crystallite size in the nanometric scale. The presence of an intermediate peroxy (-OOH) bond has been identified and is suggested to aid the combustion reaction by harnessing the required oxidant in the form of labile peroxide complexes. This soft chemical method offers homogeneous distribution and stabilization of the metal ions in the solution state and can be applied for the formation of further multi-element ceramic oxide materials, offering economical advantages over more classical nitrate-based combustion routes, as well as significant environmental benefits due to the avoidance of releasing NO_x gases.

Chapter 8 - The development of advanced catalyst synthesis methods to meet the stringent environmental regulations in the production of ultraclean transportation fuels represents a major challenge for catalyst suppliers. In this chapter, the positive impact of solution combustion synthesis (SCS)-based preparation approach in the synthesis of alumina-supported NiMoP and NiMoW hydrotreating catalysts has been examined. The results show that the use of urea as fuel can tune the metal oxide-support interaction, altering the distribution of Mo-oxo species onto alumina support. Furthermore, the hydrodesulphurisation (HDS) activity of alumina-supported NiMoP sulphide catalysts achieved a maximum at Φ ratios between 0.6 and 1.2. This maximum HDS activity is attributed to a higher surface density of polymolybdate relative to molybdate species in the catalyst precursor and the effective interaction of nickel with the edges of MoS₂ that facilitates the formation of NiMoS structure. On the other hand, the sequential deposition of NiMo-urea solution on metal oxide-modified alumina surface produces a reduction of the catalyst bed temperature rate and an increase of the decomposition period of the redox mixture. The addition of Ni and Mo to WO_x-modified alumina assists the segregation of MoO_x and WO_x species on the alumina surface and promotes their reducibility. Furthermore, the NiMoW catalyst prepared impregnation-solution based combustion method showed higher hydrotreating activity than a commercial NiMo catalyst.

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Chapter 1

LAGRANGIAN FORMULATION TO TREATING THE TURBULENT REACTING FLOWS

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ABSTRACT

In this chapter we outline a Lagrangian approach to treating problems of turbulent reacting flows. In order to avoid unnecessary complications, and to highlight the basic issues we limit ourselves to the particular case of a constant density, homogeneous isotropic turbulent flow. The case a passive reactive scalar is considered, i.e. it is assumed that the turbulence is not affected by the combustion.

Keywords: Advection-reaction equation, Eulerian frame, Lagrangian frame, Lagrangian characteristics, Eulerian characteristics, mixed Lagrangian-Eulerian quantities, Premixed turbulent combustion, combustion progress variable, Taylor theory, turbulent diffusion coefficient, G -equation

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1. INTRODUCTION

The impetus for this study stems from two recent publications [1], [2] devoted to the analysis of the Lagrangian properties of turbulent diffusion that, as the authors of [1] wrote, "even if they are ignored in the Eulerian approach used for the description of heat and mass transfer, are important in several applications, in particular in turbulent premixed combustion". The authors [1] derived the equations which illustrate, in particular, the nonequilibrium behavior of the turbulent diffusion coefficient. This effect, as it is well-known, is important for modeling the initial stage of combustion for example, in the spark ignition engine. Unfortunately some conclusions of the paper [1], as will be demonstrated in the present paper, are incorrect.

The main objective of the present paper is to develop a systematic approach to cope with the Lagrangian formulation to treating the turbulent reacting flows. The case a passive reactive scalar is considered, i.e. it is assumed that the turbulence is not affected by the combustion. We revise also the incorrect results in [1]. We begin with, in the section 2, the formulation of an instantaneous advection-reaction equation for reactive scalar. In the section 3 the relations connecting the instantaneous and expected Lagrangian and mixed Lagrangian-Eulerian quantities are derived. In the section 4 the relations connecting the instantaneous Eulerian and Lagrangian quantities, and expected Eulerian and mixed Lagrangian-Eulerian quantities are derived. In the section 5 the equations for the expected mixed Lagrangian-Eulerian quantities are derived. In the section 6 we apply the Taylor theory of the turbulent diffusion to transform the equation for the expected mixed Lagrangian-Eulerian reactive scalar derived in the section 5. The section 7 is devoted to consideration of the turbulent premixed flame employing the equations derived in the section 6. The discussion addresses an asymptotic case of an infinitely thin flame front (flamelet) that separates the reactants and products in a turbulent flow and self-propagates at a speed S_L with respect to the products. When the flame front hits a reactant particle it turns into a product particle. An exact analytical expression for the density probability function of the flame front hitting the reactant particle is derived. To this end we applied the well-known G -equation (the level set method for tracking interfaces). The section 8 continues the analysis of the premixed combustion. An approximate expression connecting expected Eulerian progress variable and the Lagrangian transition probability density function is derived. Then an approximate equation for the mean progress variable is derived. This equation

coincides with well-known in the theory of the premixed combustion Prudnikov equation. In section 9 we summarize the principal results and discuss the relation and an advance to what was previously published. In section 10, the principal results are summarized.

2. THE ADVECTION-REACTION EQUATION

The derivation of the Lagrangian and expected mixed Lagrangian-Eulerian equations follows closely to the approach presented in the book [3]. The main part of the notations is taken also from this book. Boldface notations refer to the three-dimensional (3D), otherwise to one-dimensional (1D) quantities.

Let us consider the initial boundary value problem (IVBP) for an advection-reaction equation

(i.e. the case of zero molecular diffusion)

$$\frac{\partial c}{\partial t} + \mathbf{u} \cdot \nabla_{\mathbf{x}} c = W(c, \mathbf{X}, t), \quad \nabla_{\mathbf{x}} = \frac{\partial}{\partial \mathbf{X}}, \quad (1)$$

$$c(\mathbf{X}, t = 0) = c_0(\mathbf{X}), \quad (2)$$

where $c(\mathbf{X}, t)$ is a reactive scalar, $\nabla_{\mathbf{x}}$ is a nabla symbol (i.e. $\nabla_{\mathbf{x}} c$ and $\nabla_{\mathbf{x}} \cdot \mathbf{u}$ stand for gradient of $c(\mathbf{X}, t)$ and divergence of velocity $\mathbf{u}(\mathbf{X}, t)$, respectively), $\mathbf{u} \cdot \nabla_{\mathbf{x}} c$ stands for the scalar product, $\mathbf{u}(\mathbf{X}, t)$ is an isotropic homogeneous incompressible turbulent (i.e. random) flow field, which is assumed not affected by chemical reaction (passive reactive scalar), i.e.

$$\nabla_{\mathbf{x}} \cdot \mathbf{u} = 0, \quad (3)$$

with zero mean value $\langle \mathbf{u} \rangle = 0$. The density is assumed constant $\rho = \text{const}$. Without loss of generality we assume that an initial scalar field $c_0(\mathbf{X})$ is deterministic. The case of a random initial scalar field $c_0(\mathbf{X})$ is considered in

the Annex A. Eq. (1) is a stochastic partial differential equation (SPDE) with multiplicative noise term $\mathbf{u} \cdot \nabla_{\mathbf{x}} c$.

Eq. (1) can be rewritten in the conservative form

$$\frac{\partial c}{\partial t} + \nabla_{\mathbf{x}} \cdot (\mathbf{u}c) = W(c, \mathbf{X}, t), \quad (4)$$

by virtue of the incompressibility Eq. (3).

In the section 7 the particular case of premixed combustion is studied. In this case the reactive scalar c is called the combustion progress variable. Analysis is conducted in the frame of Bray-Moss-Libby (BML) model [4] (detailed discussion of the BML model can be found, e.g. in [5] and [6]). BML approximation for the turbulent premixed combustion is based on the assumption that the flame front thickness is negligibly small in comparison with the length scales of the turbulent velocity field. In such a limit it is assumed that the infinitely thin flame front separates the products and reactants, i.e. the progress variable c takes only two values $c = 0$, in reactants and $c = 1$, in products. In other words, we neglect the probability of observation of intermediate values $0 < c < 1$ which is proportional to the flame front thickness. The flame front propagates with the normal velocity of flame propagation S_L , supposed below to be constant, without loss of generality. The combustion signifies jump of the progress variable c from $c = 0$ (in the reactants) to $c = 1$ (in the products). This jump takes place when the flame front hits some fluid particle in the reactants.

Accordingly, $\nabla_{\mathbf{x}} c = 0$ everywhere with the exception of the flamelet surface, where $\nabla_{\mathbf{x}} c$ is the Dirac δ function. The source in the frame of BML model reads, e.g. [5], [6]

$$W(c, \mathbf{X}, t) = S_L |\nabla_{\mathbf{x}} c(\mathbf{X}, t)|. \quad (5)$$

A particular case of the source $W(c, \mathbf{X}, t)$ that does not depend on the scalar, i.e. $W(c, \mathbf{X}, t) = q(\mathbf{X}, t)$ is considered in the Annex B.

Averaging (4) yields