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## INTRODUCTION

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Human activities are increasingly becoming factors in influencing global rather than local changes in Earth's troposphere. Oxidation of fossil fuels in power plants, transportation vehicles, and chemical factories results in atmospheric and terrestrial contamination. Release of pollutants — carbon and nitrogen oxides, hydrocarbons, dioxins, sulfur compounds, heavy metals, and various particulates, to list a few — attains levels that threaten natural habitat and ecology. In view of this, there is an urgent need for the development of environmentally clean and friendly fuel oxidation and burning technologies, on the one hand, and a better understanding of the effects pollutants exert on the environment, on the other hand. The goal of the International Symposium on Combustion and Atmospheric Pollution was to provide a forum to address these issues through dialogue among world-renown experts in combustion and in physical chemistry of atmospheric pollution. The two schools of thought of the research community was the topic of Panel Discussion at the Symposium: “Clean combustion or exhaust aftertreatment? Perspectives of the approaches.”

This book is presented to better understand the complex and interrelated combustion–pollution issues. The contents of the book are organized in:

Part I: Combustion Science and Technology, and

Part II: Pollutants and Environment.

The theme and significance of the articles included in each Part are briefly outlined below.

### Combustion Science and Technology

*Warnatz* (p. 3) presents an overview on oxidation chemistry of aviation kerosene relevant to combustion in gas-turbine engines. Kerosene is represented by simple two- or three-component mixtures (consisting of aliphatic hydrocarbons like decane and of aromatic hydrocarbons like benzene derivatives) which are tuned to have the same flame velocity and ignition behavior and the same soot formation tendency as kerosene. The assumption of intrinsic low-dimensional manifolds (ILDm) adopted in the author's studies leads to a substantial simplification of chemical reaction systems and is a promising approach to describe reactive flows in a relatively easier way. As an application example, decane oxidation in a laminar flat flame is considered. In this system, three-dimensional ILDM proved to be sufficient to describe the chemical reactions.

*Azatyán et al.* (p. 17) study the effect of small quantities of propylene and iso-propanol additives on the burning velocity of hydrogen–air mixtures in various combustion regimes, including transient processes preceding detonation and combustion in a constant-volume reactor. It is shown that the efficiencies of these inhibiting additives are different. The authors have proved that the difference in the efficiency is due, in the first place, to dissimilar ability of the additives to terminate reaction chains. Reaction of the additives with highly reactive species arising in the course of hydrogen oxidation produces less reactive radicals that slow down the overall combustion reaction and thereby inhibit the flame propagation.

*Starik et al.* (p. 31) consider, theoretically, the possibility of using laser-induced excitation of vibrational states of molecules to produce highly reactive radicals and atoms in chemical reactions for controlling combustion processes. Different target molecules are used for initiating chain-branching reactions in gaseous combustible mixtures. The computations, based on the extended physicochemical model involving vibrationally excited molecules, have shown that excitation of the asymmetric mode of  $\text{H}_2\text{O}$  or  $\text{O}_3$  molecules admixed in small amounts to  $\text{H}_2\text{--O}_2$  mixture by infrared laser radiation would make it possible to reduce significantly the induction time and ignition threshold. The laser-induced excitation of asymmetric vibrations of  $\text{O}_3$  and  $\text{H}_2\text{O}$  molecules also provides the possibility to ignite the  $\text{H}_2\text{--O}_2$  mixture in a supersonic flow behind the oblique shock wave at very short distances from the front, at extremely low temperatures, and at a feasible laser energy flux.

*El-Rabii & Rolon* (p. 51) report the results of their experimental study of the mechanisms occurring during the earliest stages of flame kernel development during laser-induced ignition. Using planar laser-induced fluorescence (PLIF), the evolution of the flame kernel in methane–air mixtures was recorded. A clear anisotropy in the kernel shape was detected. At early stage, a pear-shape kernel undergoing axial contraction was observed. Then, the contracted kernel split into two parts and became similar to a structure observed in electrode spark ignition. Later, a tendency of the flame kernel to move back towards the laser source was found, until the kernel splits again, leading to three separate reactive zones.

*Buriko & Goltsev* (p. 69) study the capabilities of two-staged hydrocarbon-fuel combustion in an attempt to decrease  $\text{NO}_x$  emission in a combustor. Optimum air distribution between two combustion stages, providing minimum  $\text{NO}_x$  emission, is found when fuel is injected only at the first stage. The benefits of lean-lean combustion of hydrocarbon fuel are demonstrated. The technology ensures an increased combustion stability and decreased  $\text{NO}_x$  emission compared to a conventional single-stage premixed lean combustion of fuel mixture.

*Packan et al.* (p. 79) present preliminary results of their experimental study of the interaction between a nanosecond pulsed plasma discharge and hydrocarbon diffusion flame. A coaxial burner made of electrically nonconductive material,

allowing the use of high-voltage discharges in its vicinity, was designed and built. Different electrodes and electrode/flame configurations were tested. The pulsed discharge plasma was able to successfully attach a lifted turbulent methane diffusion flame. The creation of carbonaceous species ( $C_2$ , CH,  $C_n$ ) by the discharge was evidenced on emission spectra from a pulsed discharge operated in a cold propane flow.

*Borisov et al.* (p. 87) study both theoretically and experimentally the combustion of super-rich methane mixtures with air and oxygen. The composition of the mixtures and initial conditions most favorable for synthesis of syn-gas to be used in producing liquid motor fuels are ascertained based on thermodynamic and kinetic calculations. The effect of increased pressures and temperatures on flammability limits of rich methane-air mixtures is investigated experimentally. The burning velocities are measured and the effect of turbulence on the burning times and yield of desired products are ascertained. The composition of combustion products is close to its thermodynamic counterpart; kinetic modeling also provides similar results. The results of measurements and computations are used in designing and testing chemical reactors based on pilot industrial power-producing units adapted for synthesizing syn-gas.

*Soulard et al.* (p. 105) propose a new probability density function (pdf) approach for modeling scalar micromixing. The approach is aimed at accounting for the influence of turbulence intermittency on molecular mixing. Two models are derived: the Extended Interaction by Exchange with the Mean model and the Extended Langevin model. These models are described and tested against direct numerical simulation (DNS) results in the case of the decay of a homogeneous scalar field in homogeneous turbulence. The asymptotic behavior of the pdf is also discussed. Vaporizing droplets are represented by analogy with a partially stirred reactor. The influence of intermittency effects on droplet dynamics is shown to be significant.

*Frolov et al.* (p. 117) computationally study hydrocarbon drop vaporization, ignition, and combustion with relatively extended kinetics of fuel oxidation and pollutant (CO, NO, and soot) formation, transient heating, and multicomponent diffusion, as well as with spray effects taken into account. Based on the detailed simulation of drop behavior in a uniform monodisperse suspension, the authors demonstrate that (1) drops in suspension vaporize slower than isolated drops, (2) quasistationary  $d^2$ -law is, in general, not valid for drops in suspension, (3) at suspension densities exceeding a certain limiting value, drops vaporize only partly or virtually do not vaporize, (4) drop autoignition delay depends on the drop diameter and suspension density and is strongly affected by the amount of prevaporized fuel, (5) individual drop flame structure and parameters depend on suspension density, (6) individual drop flame exists within a limited range of suspension densities, and (7) emission indices of pollutants (CO, NO, and soot) depend considerably on suspension density. Results of calculations have been compared with available experimental data.

*Atthasit et al.* (p. 133) present the results of their experimental studies on vaporization of a monosized ethanol droplet stream to understand the effects of droplet interaction on the drag coefficient and vaporization process. A continuous droplet stream was injected into a free convective thermal boundary layer of a vertical heated plate. An electrostatic deviator is installed to vary the spacing parameter between droplets. Standard Rainbow Thermometry is used to measure droplet size and temperature. The experimental results on the drag coefficient and the evaporation rate are analyzed and compared with the previous correlation obtained in the combustion regime.

*Manzhalei* (p. 151) reports the results of his experimental studies on transitioning explosion from one volume to another through a long channel. Three near-limit detonation modes in stoichiometric acetylene-oxygen and propane-oxygen mixtures, namely, normal, galloping, and low-velocity detonations, are considered. The acetylene-oxygen mixture in the acceptor volume is ignited by any type of a detonation wave in a channel. The propane-oxygen mixture in the acceptor volume is not always ignited. Low-velocity detonation of this mixture in the channel does not ignite gas in the acceptor volume at any initial pressure. Galloping detonations ignite the mixture in the acceptor volume only when specific conditions are met. Based on the qualitative analysis of the problem, the criterion of gas ignition in the acceptor volume has been suggested.

## Pollutants and Environment

*Naydenova et al.* (p. 161) present the results of calculations based on the detailed kinetic model of soot formation. The model incorporates the mechanisms of gas-phase acetylene pyrolysis, formation of polyaromatic hydrocarbons, polyene molecules, and pure carbon clusters. It combines the H-abstraction-C<sub>2</sub>H<sub>2</sub>-addition and polyene pathways of soot formation. The formation, growth, and coagulation of soot precursors and soot particles are described within the framework of a discrete Galerkin technique. The authors compare predicted results with experimental data on the soot yield, the apparent rate of soot particle growth, and the induction time of soot formation process obtained by the extinction technique during pyrolysis of ethylene, acetylene, and methane. Also presented are the soot yield and the mean diameter of soot particles determined by the extinction-scattering technique during *n*-heptane rich oxidation behind reflected shock waves. The comparison of the calculations with the experimental measurements shows a quantitatively good correlation for all main parameters of soot formation.

*Toennies et al.* (p. 181) study biomass gasification with air in a laboratory-scale gasifier with fluidized bed. The objective of the research is to generate a tar-free combustible gas from wood gasification through catalytic treatment of the gas. The generated tar-like substances of low volatility (mainly, aromatic

hydrocarbons with high boiling points: polycyclic aromatic hydrocarbons, phenols, furans, and aromatic compounds like benzene, toluene, xylene, and styrene) are undesirable by-products, which have to be reduced through the use of optimal process parameters, and, where necessary, gas aftertreatment. The precise knowledge of segregation characteristics and their dependence on the process parameters is essential. For this purpose, online measurements are taken before and after the catalytic gas cleaning step downstream of the gasifier. Laser mass spectrometry is used to allow quick and continuous determination of a multitude of tar compounds in the gas probes.

*Bilera et al.* (p. 191) demonstrate potentials and benefits of nonpolluting burning of toxic organic waste from chemical factories, and reaction products from installations for destroying toxic agents. General requirements imposed on the apparatus and the technology used to destroy toxic products by incineration are formulated, and the methods for minimizing dioxin yield are discussed. A specialized reactor based on a liquid-propellant combustion chamber is proposed to destroy toxic species. Experiments on burning imitators of phosphorus-containing toxic materials and of products of their chemical detoxication support high efficiency of the proposed method.

*Karasev et al.* (p. 207) study soot,  $\text{Al}_2\text{O}_3$ , and  $\text{TiO}_2$  aerosol aggregates of nanoparticles by means of transmission electron microscopy and video microscopy. Soot was formed in both benzene pyrolysis and propane combustion roots. Alumina and titania aggregates were formed by combustion of metallized pyrotechnical mixtures. By observation of the aggregate movement in the electric field, it was found that the aggregates are charged. Roughly symmetric bipolar charge distributions were measured for all types of aggregates. The typical charge per aggregate is a few elementary charge units. In case of soot, the charge distribution was above equilibrium being wider than the room temperature equilibrium distribution. The fractal-like dimension of aggregates was determined by different methods.

*Laskin et al.* (p. 229) demonstrate the utility of single particle analysis to investigate the chemistry of individual atmospheric particles using state-of-the-art scanning electron microscopy and time-of-flight secondary ionization mass spectrometry techniques. The paper gives a brief review of a number of the research projects carried out in the authors' laboratory on the heterogeneous chemistry of atmospheric particles. The data provided by these techniques offers a rich set of qualitative and quantitative information on the mechanisms of gas-particle interactions which are of high importance to atmospheric processes involving particulate matter and air pollution.

*Alcala-Jornod et al.* (p. 245) apply the novel technique of molecular diffusion tube experiment to the measurement of the adsorption of water vapor on different types of flame soot generated in the laboratory. From the kinetic data for surface residence times as a function of temperature, the enthalpy of  $\text{H}_2\text{O}$  adsorption on soot was determined. The results obtained correspond to the initial chemical

kinetic processes of ice nucleation on soot from a molecular point of view. Nitrous acid, HONO, strongly interacts with all surfaces examined such as KNO<sub>2</sub>, FEP Teflon, toluene, and decane soot, usually leading to a mixture of NO and NO<sub>2</sub>. Nitric acid reacts with soot to HONO that either desorbs on decane flame soot from rich combustion or decomposes on soot from lean combustion. The observed products NO and NO<sub>2</sub> are therefore the secondary decomposition products of HONO.

*Behr et al.* (p. 261) investigate adsorption of acetone and acetic acid on ice surfaces at temperatures between 190 and 223 K. The gas-surface interaction was analyzed from adsorption isotherms and hence from temperature-dependent Langmuir constants. Adsorption enthalpy of  $-43.7 \pm 7.9$  kJ/mol and adsorption entropy of  $-65.6 \pm 11.8$  J/(mol·K) were obtained for acetone. For acetic acid on ice, the corresponding value of adsorption enthalpy is  $-54.8 \pm 10$  kJ/mol. Dissociation and recombination with D<sup>+</sup>-ions of intermediately adsorbed acetic acid molecules have been confirmed from proton exchange experiments using D<sub>2</sub>O-ice surfaces. The thermodynamic data derived for acetone and acetic acid were used to estimate the equilibrium partitioning of these trace gases to ice surfaces under conditions relevant to the upper troposphere.

*Gershenzon et al.* (p. 275) propose a heterogeneous-homogeneous autocatalytic process to accelerate the rate of chlorine activation in the coastal NO<sub>x</sub>-enriched zones. The “explosion-like” chain branching mechanism contains reactions of night-time initiation and chain propagation, morning and daytime photobranching, and chain termination. In addition to regular gas-phase photochemistry in marine boundary layer, the mechanism includes two heterogeneous reactions of NO<sub>3</sub> and ClONO<sub>2</sub> with NaCl. Additional vertical flux of NO<sub>2</sub> is introduced to imitate enrichment of NO<sub>x</sub>. The results of model simulation show that the limit of fast autocatalytic chlorine generation exists. It depends on aerosol particles specific volume and on NO<sub>2</sub>, O<sub>3</sub>, and CH<sub>4</sub> concentrations. Under real tropospheric conditions, concentrations of ClONO<sub>2</sub> and Cl reach 10<sup>9</sup> cm<sup>-3</sup> and 10<sup>5</sup> cm<sup>-3</sup>, respectively. The rate of C<sub>2</sub>H<sub>6</sub> consumption over the limit of fast reaction is higher by a factor of 3.5 than under NO<sub>x</sub>-poor conditions.

It is evident that a great deal of research is going on around the world focusing on combustion-generated pollutants and their environmental effects. It is our hope that this book will help promote further investigations in these research areas and foster further dialogue among the experts in combustion and in physical chemistry of atmospheric pollution.

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