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Innovative Energetic Materials: Properties, Combustion Performance and Application

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Preface

In recent years, significant advancements have been made in the exploitation, combustion, ignition, and application of innovative energetic materials, including solid fuels, energetic binders, metal particles, energetic composites, *etc*. One of the main reasons for utilizing innovative energetic materials and their composites in various chemical propulsion systems is due to the high heat of formation and high energy density. Although innovative energetic materials have the very attractive feature of producing high energy in their combustion processes, their ignition and efficient combustion presents a great challenge to many engineers and scientists. Various techniques have recently been developed to overcome the intrinsic difficulties. Many fundamental research investigations have also been conducted to explore detailed physicochemical processes associated with innovative energetic materials combustion and industry application. Propellants, explosives, and pyrotechnics, which are grouped as high-energy materials (HEMs) or innovative energetic materials (IEMs) have made a significant contribution to modern industry and economy. In particular, state-of-the-art rocket propulsion systems have greatly benefited from innovative energetic materials development in recent years, especially in terms of future prospective energetic materials for rocket fuels and fabrication of propellants, explosives, and pyrotechnics. The organization of this book was initiated in early 2018, and the outline was first reviewed and discussed by four co-editors and several Springer press editors, who provided invaluable suggestions which are greatly appreciated. This book is organized as a milestone of advanced research on energetic materials as used in chemical rocket propulsion technologies.

The book presents compiled results of the most recent development of innovative energetic materials and combustion, especially applications technology in chemical rocket propulsion systems. On the one hand, considerable effort is being spent on the improvement and perfecting of the propulsion systems themselves which are designed exclusively for the ingredients they work with. On the other hand, the research for new ingredients for rocket propulsion is a challenge for chemistry. This effort focuses on the design and investigation of novel high-tech energetic materials for fuels, oxidizers, polymer matrices, plasticizers, and further additives for liquid, solid, gelled, and hybrid propellant systems. In recent years, for energetic materials ingredients for chemical propellants, great progress has been made in the development of propellants for rockets, guns, and mortars. Similar milestones were reached in the field of explosives and pyrotechnics which are essential parts of any system that uses propellants and explosives. Many major breakthroughs in the field of propellants, explosives, and pyrotechnics using high-energy materials (HEMs) were possible in recent years. This development area particularly concerns the energetic ingredient families that are known to be toxic or harmful and also the conventional non-energetic ingredients that need to be replaced to achieve more energy, safe and environment friendly. Despite the impressive progress witnessed in the field of HEMs during the last century, it must be admitted that the rate of progress is much slower when compared to other fields such as polymer chemistry, electronics, and computers owing to a number of constraints and restrictions that an HEMs scientist has to encounter in developing a new HEM. These include safety, stability (thermal, mechanical, storage, *etc.*), cost, and other considerations.

This book with 17 chapters summarizes the most recent achievements of the leading research groups working in the field of innovative energetic materials, combustion, and application in chemical rocket propulsion in Russia, UK, Italy, Japan, Israel, Poland, Hong Kong, India, Belgium, Kazakhstan, Morocco, Algeria, and China.

Part I covers the properties of innovative energetic materials, which include 4 chapters. Composite energetic materials such as solid propellants are characterized by a solid fuel, typically a polymeric binder matrix, containing solid oxidizer particles. Chapter 1 presents the novel concept of an energetic material consisting of a solid fuel matrix containing liquid oxidizer units. The oxidizer units may be capsules (filled with a liquid oxidizer) similar to that of typical solid oxidizer particles. It reveals the theoretical energetic performance (specific impulse) of solid propellants containing different liquid oxidizers compared to standard solid propellants consisting of ammonium perchlorate (AP) oxidizer. Chapter 2 presents three types of metal fuels which were prepared for use in hybrid rocket engines, and three for solid rocket motors. Powders were characterized in terms of morphology, metal content, and reactivity at low heating rate. The positive effect exploited by activated powders in diminishing the agglomerate average diameter was observed and discussed. The outcomes from this experimental campaign suggest that mechanically activated Al seems to be a candidate for performance enhancement in both hybrid fuels and solid propellants.

In the past few decades, nanothermites have attracted much attention as a kind of highly reactive nanoenergetic materials (nEMs). Especially, core-shell structured nanothermites is one of the most potential nEMs with adjustable energetic properties. In Chap. 3, the preparation strategies and energetic properties of these core-shell nanothermites are introduced and summarized, respectively. In particular, the advantages of core-shell structured nanothermites in terms of energy density and combustion efficiency are clarified, based on which suggestions regarding the possible future research directions are proposed.

Chapter 4 discussed some basic problems of ignition of energetic materials (EMs) which are able to burn in the absence of an external oxidizer. The attention is paid to theoretical description of transient burning rate behavior of the EMs exothermically reacting in both phases, to formulation of ignition criterion and to experimental methods of measuring transient burning rate. In additional, the problems of correct determination of the EMs high temperature kinetics are discussed as well as the problems of ignition of EMs with shielded reacting surface.

Part II covers the combustion performance of energetic materials, which include 8 chapters. Chapter 5 examines several instances of unsteady combustion regimes of solid rocket propellants when loaded with nano-sized metals, while steady combustion regimes are discussed in a companion paper. Both papers describe the main features in terms of solid propellant performance (ignition, extinction by fast depressurization, self-sustained oscillatory burning, pressure deflagration limit, and other transient burning processes) and aim to emphasize the unique properties or operating conditions made possible by the addition of nano-sized energetic ingredients. Attention is mainly focused on nAl addition to AP/HTPB formulations, the workhorse of solid space launcher motors.

The thermal behavior and combustion of the modern aluminized propellants loaded with nano- and micron-sized metals and oxides as modifiers and catalysts are discussed in Chap. 6. The very fast burning formulations contained Cu nanopowder. The mechanism of new additives effect on the propellants burning and their interaction with nitramines are discussed.

Metal powders (mainly aluminum), due to their high energy density, are important fuels for propulsion systems, material synthesis, and energetic materials. Prospective solution to the problem of increasing the efficiency of metal fuel combustion is the complete or partial replacement of aluminum by energy-intensive components or Al/Mg alloys in energetic materials. The thermal analysis data, the ignition parameters, the combustion and agglomeration characteristics for the propellants based on ammonium perchlorate, butadiene rubber and Alex, Alex/Fe, Alex/B ultra-fine powders were presented in Chap. 7. The reduce of the ignition delay time and increase of the burning rate for the EM sample containing Alex/Fe ultra-fine powder in comparison with the Al-based energetic material was found. The presence of amorphous boron in the bimetal fuel of EM significantly increases the agglomeration of condensed combustion products and practically unchanges the burning rate of propellant.

Chapters 8, 9, and 10 are focused on the combustion performance of energetic materials, which include tetrazole-based energetic materials, hydroxylamine nitrate (HAN), and ammonium perchlorate (AP). Chapter 8 presents the experimental results on the thermal decomposition and combustion of hydroxylammonium nitrate (HAN)-based propellant in the presence of nanoporous activated carbon with a high specific surface area (SSA) up to 3000 m^2/g. Combustion of HAN in the presence of activated carbon (AC) was investigated in a constant-pressure bomb within the initial pressure range of 1–6 MPa. Thermal decomposition of HAN-based propellant admixed with AC was assessed by DTA-TG method, and the volatile products emitted during thermal decomposition of HAN doped with AC were characterized by electron ionization mass spectrometry analysis.

Chapter 9 discusses the combustion characteristics of ammomium perchlorate (AP) monopropellant from the experimental and computational viewpoints. Three different methods were used to determine low pressure deflagaration limit (LPDL) of AP monopropellant. The combustion parameters of the model established are suitably updated and a good match is obtained with the experimentally observed burn rate, pressure index, and temperature sensitivity.

Based on the studies performed in Chap. 10 on numerical investigation of AP-based propellants in recent and future development, it was shown that the combustion of composites could be described by various combustion models that depend on considering of reaction zones and complexity, nature of ingredients, and parameters of simulations. Recent models allow to calculate the burning rate, flame structure, thermal parameters of AP combustion and are in good agreement comparing with experimental results.

As a further supplement, Chap. 11 presents the topic of low-burn-rate composite solid rocket propellants. Focus is given to the means of obtaining low regression rates. Challenges in the development of low-burn-rate propellants are discussed. Moreover, the impacts of several low regression rate propellants on solid rocket motor design are described, which includes material oxidation, nozzle erosion, and expected heat loads. Finally, an outlook on further low-burn-rate propellant development and utilization is given.

As we know, combustion of solid propellant, especially burning rate and pressure exponent, is much important for researchers worldwide. Another supplement of Chap. 12 is to assess two different methods used to determine the burning rates of solid rocket propellants and to find a convenient correlation of the measured data. The well-known strand burner test (Crawford test) and the closed vessel test were employed. One composite propellant containing polyvinyl chloride (PVC) as matrix and ammonium perchlorate (AP) as an oxidizer is used to clarify the relation between the two techniques. The obtained results show an acceptable correlation between the two techniques in the range of pressures between 5 and 25 MPa.

Part III covers the application of energetic materials in chemical propulsion, which include 5 chapters. Chapter 13 discusses the approach, which cover all aspects from conception to disposal and includes performance optimization, to solve the problem of matching formulation to desired characteristics in a systematic manner, beginning with the use of predictive modeling, based on known properties, both of ingredients and of the required output, and also considers its use for the design of novel ingredients to support synthesis research. The options for the physical nature of the ingredients, size, shape, crystal habit, polymorph, etc. and the ways of treating these for use were also discussed. Finally, the approaches to processing were considered. The aim is to argue that such an integrated approach is the most cost effective and productive method of formulating for the future.

In order to study the metal particle combustion behavior, based on the "method of model agglomerates" approach, Chap. 14 reported the valuable information on the combustion mechanisms of Al, Ti, and Al+B agglomerates at atmospheric and elevated pressures.

Chapter 15 experimentally studied the thermal properties of metallized propellant matrices with composite nanoparticles of aluminum, nickel, and iron. Thermal, thermodynamic, and kinetic effects of the oxidation of microencapsulated aluminum and bimetallic nanopowders were determined. It is shown that use of micro-encapsulated aluminum powders in high-energy material (HEMs) compositions changes the characteristics of HEM components. In particular, the microencapsulation of aluminum particles with both active and passive binders leads to an increase in the resistance of particles to the oxidation, improving their combination with HEM components and increasing their mixing rate.

Chapter 16 analyzes the microstructural physicochemical properties of 1,1-diamino-2,2- dinitroethylene (FOX-7) and the probable formation of FOX-7/CL-20 and FOX-7/HMX co-crystals. Hydroxyl terminated polybutadiene (HTPB), nitrate ester plasticized polyether (NEPE) solid propellants, and composite modified double-based (CMDB) propellants containing different mass fractions of FOX-7 were experimentally prepared. The effects of FOX-7 on the burning rate, pressure exponent, and hazard properties as well as the associated thermal decomposition were investigated, and are compared with those of the propellant without FOX-7.

Chapter 17 considers the mathematical simulation of the condensed products formation process near the burning surface of solid propellant. These products include agglomerates and smoke oxide particles (SOP). The developed models are used to determine (estimate) the relations between the two main fractions, size of the agglomerates and SOP, parameters of the chemical composition and structure of the agglomerates for these types of propellants. Validity of the approaches used is confirmed by comparing the calculation results and experimental data.

To improve the quality of this book, many other experts were involved as external reviewers of the chapters in addition to us as the editors. It is our great pleasure to thank the following international reviewers for their substantial help in raising the quality of the book. Without their efforts, the publication of this volume would have been impossible. Those experts include: Prof. *Vladimir E. Zarko* from Voevodsky Institute of Chemical Kinetics and Combustion, Tomsk State University, Russia; Prof. *Luigi T. DeLuca*, Prof. *Luciano Gafetti,* Prof. *Filippo Maggi, Dr. Christian Paravan* from Space Propulsion Laboratory (SPLab), Politecnico di Milano, Italy; Prof. *Adam S. Cumming* from University of Edinburgh, UK; Prof. *Niklas Wingborg* from FOI, Department of Energetic Materials, Sweden; Prof. *Valery A. Babuk* from Baltic State Technical University, Russia; Prof. *Igor Assovskii* from Semenov Institute of Chemical Physics, Moscow, Russian Federation; Prof. *Alexander A. Gromov* from National University of Science and Technology "MISiS", Russia; Prof. *Jiri Pachman* from University of Pardubice, Czech Republic; Prof. *Helen Stenmark* from Eurenco Bofors AB, Sweden; Prof. *Daniele Pavarin*, Center of Studied and Activities for Space CISAS G.Colombo, University of Padua, Padova, Italy; Prof. *Adam Okninski* from Lukasiewicz Research Network - Institute of Aviation Center of Space Technologies, Poland; Prof. *Benny Natan*, Dr. *Danny Michanel* from Faculty of Aerospace Engineering, Technion-Israel Institute of Technology, Haifa, Israel; Dr. *Yinon Yavor*, Afeka Academic Colleage, Tel Aviv, Israel; Prof. *Djalal Trache* from the Ecole Militaire Polytechnique University in Algeria; Dr. *Francisco Barato* from Padova University; Prof. *RuiQi Shen. Dr. Wei Zhang* from the Nanjing University of Science and Technology, China; Prof. *QiLong Yan* from Northwestern Polytechnical University, China; Prof. *GuangCheng Yang*, Dr. *Long Zhang* from Institute of Chemical Mateirals, China Academy of Engineering Physics, China; Dr. *Rui Liu* from Beijing Institute of Technology, China; Prof. *FengQi Zhao*, Prof. *XueZhong Fan*, Prof. *BoZhou Wang,* Associate Prof. *YanJing Yang*, and the colleagues from Xi'an Modern Chemistry Research Institute, China. Finally, we especially thank the managing editors of this book from Springer Press, Dr. *Yin Hu*, Mrs. *Kavitha Palanisamy*, and *Muruga Prashanth Rajendran* for their patience and kind support. Without their work, this book would not be organized and published. The editors sincerely hope that the research efforts described in this book will continue to exhibit fast growth and lead to maturation of advanced technologies, which will improve the quality of chemical rocket propulsion for better defense and space exploration. We also sincerely wish that this joint international effort will help all readers to gain a better understanding of the puzzling intricacies and appealing secrets of innovative energetic materials as well as of the perplexing difficulties but also fascinating horizons of space propulsion!

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March 2020

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Part I
Properties of Innovative Energetic Materials

Chapter 1
Study of a Concept of Energetic Materials Consisting of a Solid Fuel Matrix Containing Liquid Oxidizer

Avishag Deborah Pelosi and Alon Gany

Abstract Composite energetic materials such as solid propellants are characterized by a solid fuel, typically a polymeric binder matrix, containing solid oxidizer particles. The energetic performance of solid propellants is inferior to that of liquid or hybrid propellants. The main reason is that the available practical solid oxidizers are less energetic than the available liquid oxidizers. This article presents and studies the novel concept of an energetic material consisting of a solid fuel matrix containing liquid oxidizer units. The oxidizer units may be capsules filled with a liquid oxidizer. The size of the capsules may be similar to that of typical solid oxidizer particles. In this way, one maintains the structural characteristics of a solid material (e.g., solid propellant), yet benefiting from the superior energy of a liquid oxidizer. The study reveals the theoretical energetic performance (specific impulse) of solid propellants containing different liquid oxidizers compared to standard solid propellants consisting of ammonium perchlorate (AP) oxidizer. It is shown that the combination of certain liquid oxidizers such as hydrogen peroxide or nitrogen tetroxide with a hydroxyl-terminated polybutadiene (HTPB) matrix can increase the overall energy by about 20%, implying about 12% increase in the specific impulse. The combustion processes are discussed as well.

1.1 Introduction

The main advantage of solid propellant motors is their simple structure and operation. It results from the absence of flow and control systems, having the propellant grain within the combustion chamber ready for operation without special preparation. However, solid propellants exhibit inferior energetic performance

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(characteristic velocity, specific impulse) compared to that of liquid propellants. In fact, in the last three decades there has been only little progress with respect to improvement of the energetic performance of solid propellants. Different solid energetic ingredients have been developed (e.g., glycidyl azide polymer (GAP), ammonium dinitramide (ADN)) [4, 10], but they failed to replace the commonly used solid propellant components, namely, hydroxyl-terminated polybutadiene (HTPB), ammonium perchlorate (AP), aluminum (Al), and nitramines in any major system due to either incompatibility, sensitivity, cost, or poor physical properties. The fact that solid propellants are less energetic than liquid propellants stems from the inferior energetic characteristics of available solid oxidizers (particularly ammonium perchlorate, AP) compared to liquid oxidizers.

The objective of this work is to present a novel concept for a new class of high-energy propellants: propellants consisting of a solid fuel matrix containing encapsulated liquid oxidizer units. The liquid capsules are introduced and distributed within the solid matrix in a way, which is similar to the distribution of solid AP particles within the propellant binder in conventional solid propellants (Fig. 1.1).

The capsules can replace a part of the solid oxidizer particles or the entire amount of the solid oxidizer. In this way, the simple structure of the solid propellant motor is maintained, while substantially increasing its energetic performance. Elaboration on the concept described here can be found in a number of articles of these authors and colleagues [5–7, 9].

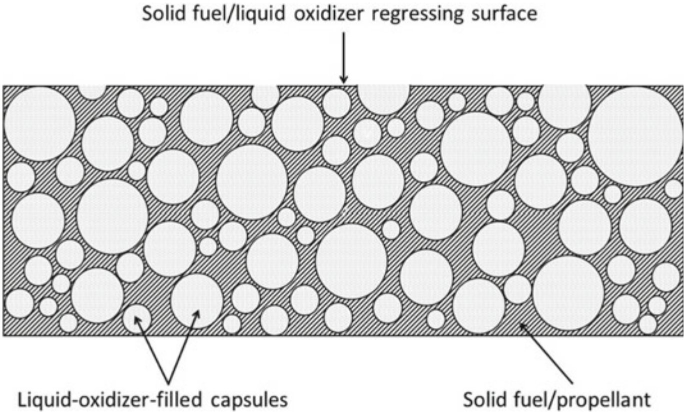

Fig. 1.1 Schematic description of the concept of a solid propellant augmented by liquid oxidizer droplets/capsules

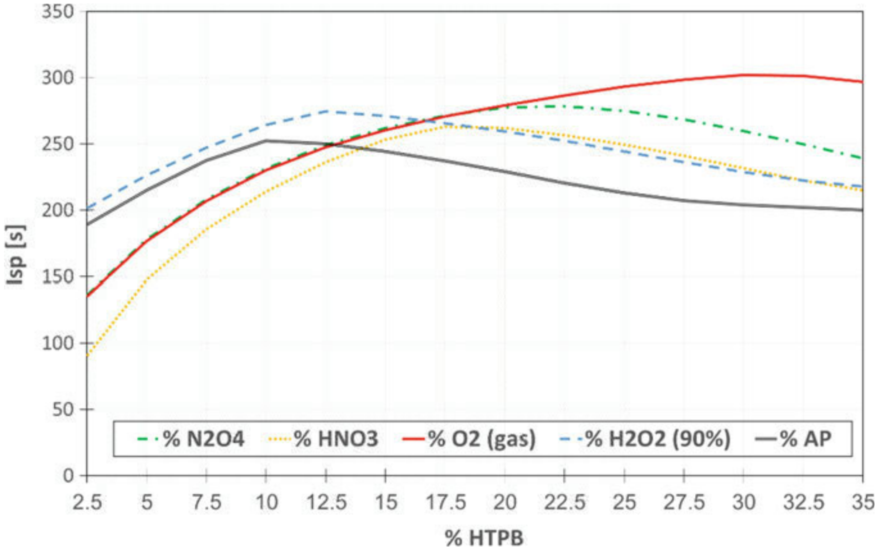

Fig. 1.2 Specific impulse versus HTPB fraction in non-aluminized propellants consisting of HTPB and different liquid oxidizers as well as AP solid oxidizer

1.2 Theoretical Performance

Theoretical predictions of the energetic performance of different formulations of solid propellants enhanced by a liquid oxidizer have been made using a thermochemical code ([3], Fig. 1.2). The calculations reveal that the inclusion of a storable liquid oxidizer such as hydrogen peroxide or nitrogen tetroxide within a non-aluminized solid propellant may theoretically increase the heat of reaction by as much as 20%. It implies enhancement of the specific impulse by up to 12% compared to that of AP-based propellants. The theoretical increase in specific impulse when adding oxygen as the oxidizer can be as high as 20%. Nevertheless, liquid oxygen is a non-storable oxidizer and can be maintained only at cryogenic temperatures.

1.3 Combustion Model

For the combustion process, a simplified one-dimensional combustion model of a liquid oxidizer droplet burning with an adjacent solid fuel has been formulated [9]. The liquid oxidizer is an endothermically vaporizing/decomposing material such as nitric acid (HNO_3). The surrounding solid fuel is typically a polymeric matrix such as hydroxyl-terminated polybutadiene (HTPB). The model resembles certain features of the BDP model of Beckstead et al. [1] for the combustion of composite solid propellants with AP oxidizer. Similarly to the BDP model, it is assumed that the single oxidizer droplet and surrounding fuel unit combustion characteristics represent the combustion behavior of such propellants.

However, the present work takes into consideration the basic transient nature of the combustion process, resulting from the considerable difference in instantaneous oxidizer and fuel fluxes. In the AP/HTPB composite propellant model, both AP and HTPB vaporize according to Arrhenius pyrolysis/vaporization law. In the case of a liquid oxidizer droplet, the process involves a heating time followed by a relatively rapid evaporation phase. For subcritical pressure operation described herein, the surface temperature of the vaporizing droplet is the saturation (boiling) temperature of the liquid, which is substantially lower than the fuel surface temperature. A more comprehensive model is presented by Pelosi [7] and Pelosi and Gany [8], taking into consideration liquid-oxidizer-filled capsule shell material, capsule heating and rupture mechanisms and the combustion of a liquid oxidizer droplet with adjacent solid fuel at both subcritical and supercritical pressure conditions. A somewhat different approach is demonstrated by Livne and Gany [6], presenting a quasi-two-dimensional process; the model assumes variable fuel and oxidizer fluxes with three combustion stages: initial heating, vaporization/gasification and combustion of both fuel and oxidizer, and gasification of fuel into oxidizer-rich environment and rapid consumption. Both model approaches give similar overall results. A description of the heat fluxes, temperature, and one-dimensional flame development over the oxidizer and fuel surface is presented in Fig. 1.3. The model makes use of mass conservation, fuel steady-state energy conservation, and steady-state oxidizer energy conservation during oxidizer vaporization, to predict oxidizer and fuel mass fluxes, flame height and

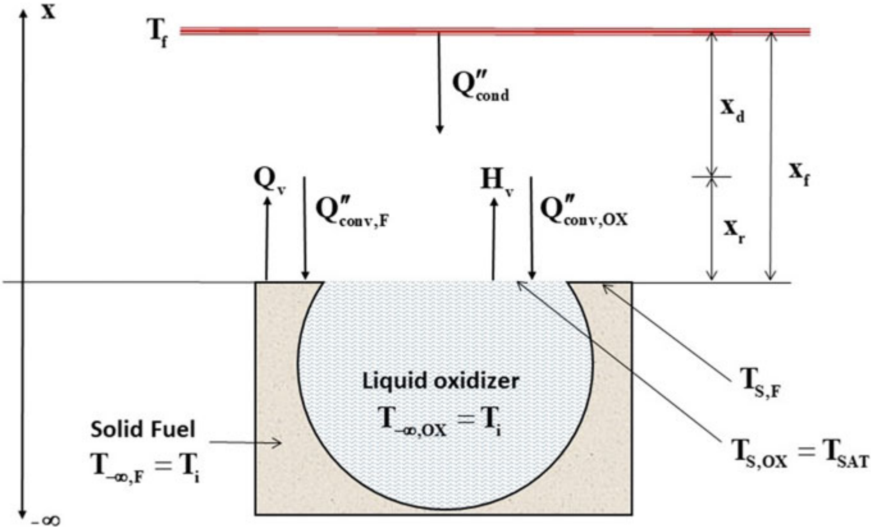

Fig. 1.3 Illustration of the heat fluxes, temperature, and one-dimensional flame development over the oxidizer and fuel surface combustion cycle unit

propellant regression rate, as well as characteristic times involved in the combustion process. Radiant heat transfer is neglected.

1.4 Mass Conservation

The total mass flux emerging from the propellant surface is

$$m'' = \overline{m''_{OX}}\left(\frac{S_{OX}}{S}\right) + m''_F\left(\frac{S_F}{S}\right) \tag{1.1}$$

where the oxidizer mass flux $\overline{m''_{OX}}$ is the average oxidizer flux over a cycle and m''_F is the fuel flux. S stands for the surface area. The subscripts OX and F represent oxidizer and fuel, respectively. The oxidizer-to-fuel mass ratio is

$$\frac{O}{F} = \frac{\overline{m''_{OX}}}{m''_F}\left(\frac{S_{OX}}{S_F}\right) \tag{1.2}$$

It is assumed that over a combustion cycle of a single oxidizer droplet, the ratio between the amount of oxidizer and the surrounding fuel is stoichiometric, in accordance with the overall oxidizer-to-fuel *(O/F)* ratio. Schematic of the oxidizer droplet and surrounding fuel in a micro-cycle unit is shown in Fig. 1.4. The characteristic oxidizer diameter $d_{OX,av}$ is defined as the diameter of an oxidizer cylinder of height d_{OX}, which is volumetrically equivalent to the original droplet. Following the approach of Pelosi and Gany [9], uniform oxidizer and fuel fluxes into the gas phase, equal to their average values over a cycle, are assumed (Fig. 1.5). Each cycle includes a heating time, t_H of the liquid droplet, a vaporization time, t_v, driven by a constant vaporization rate with maximum oxidizer flux $m''_{OX,\max}$, and a characteristic residual time t_r, when the droplet is completely consumed and leaves a cavity in the solid fuel.

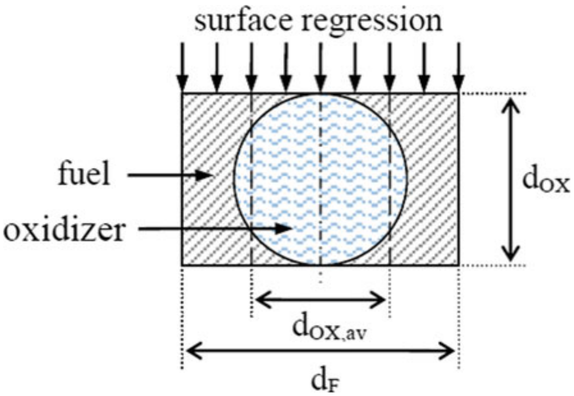

Fig. 1.4 Schematic description of the oxidizer droplet and surrounding solid fuel in a micro-cycle unit

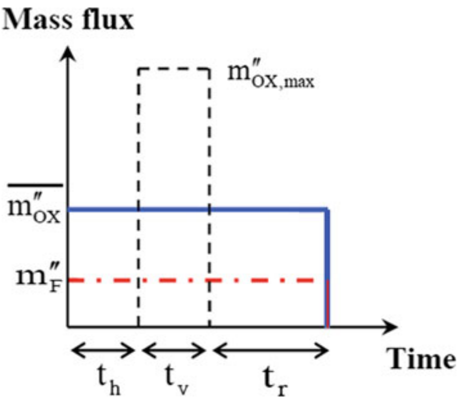

Fig. 1.5 Schematic description of the oxidizer and fuel mass fluxes and characteristic times over a micro-cycle

The fuel-to-oxidizer surface area ratio is such that overall stoichiometric conditions are satisfied, yielding

$$\frac{S_F}{S_{OX}} = \frac{2}{3}\left[\frac{1}{O/F}\frac{\rho_{OX}}{\rho_F} + 1\right] \tag{1.3}$$

ρ_{OX}, ρ_F are the oxidizer and fuel densities, respectively.

The total mass flux can be expressed in terms of the fuel mass flux, or of the time-averaged oxidizer mass flux:

$$m'' = m''_F\frac{S_F}{S}\left(1 + \frac{O}{F}\right) = \overline{m''_{OX}}\frac{S_{OX}}{S}\left(\frac{O/F}{1 + O/F}\right) \tag{1.4}$$

Both oxidizer and fuel mass fluxes can be expressed in terms of the surface temperatures $T_{s,OX}$ and $T_{s,F}$, respectively. At the fuel burning surface, Arrhenius pyrolysis law (with fuel-appropriate pre-exponential factor A_F and energy of activation, E_F) gives a good approximation for the mass flux of the binder:

$$m''_F = A_F\exp\left(-E_F/\Re T_{s,F}\right). \tag{1.5}$$

1.5 Fuel/Oxidizer Energy Balances

A separate fuel and oxidizer energy balance from deep within the fuel or oxidizer to just above the condensed layer (fuel or oxidizer surface) is formulated. A steady-state energy conservation equation for the fuel provides an expression for the fuel surface temperature:

$$m''_F C_{p,F} \left(T_{s,F} - T_i \right) + m''_F Q_v = Q''_{cond} \tag{1.6}$$

where Q''_{cond} is the heat feedback flux from the flame to oxidizer or fuel surfaces. It is calculated by solving the steady-state energy equation of the gas phase, which enables to find an appropriate temperature profile above the fuel/oxidizer surfaces. Q_v is the fuel specific heat of pyrolysis and vaporization, Q''_{conv} represents the heat needed to increase the temperature of the fuel from T_i (the initial fuel temperature) to the surface temperature $T_{S,F}$, $C_{p,F}$ is the solid fuel's specific heat at constant pressure.

A steady-state energy balance for the oxidizer describes the vaporization phase, yielding the actual peak oxidizer flux:

$$m''_{OX,\max} H_v = Q''_{cond} \tag{1.7}$$

H_v is the oxidizer-specific latent heat of vaporization. The oxidizer surface temperature is assumed to be the saturation temperature.

Equation (1.6) provides an implicit solution for the fuel surface temperature, whereas Eq. (1.7) determines the actual oxidizer vaporization flux. The flame temperature, needed to quantify Q''_{cond}, is calculated for a diffusion flame at stoichiometric conditions. In addition, it is assumed that the flame height is a result of the diffusion distance x_d and the reaction distance x_r, namely,

$$x_f = x_r + x_d \tag{1.8}$$

Flame height resulting from reaction is calculated, taking into account the reaction rate of the final (slow) reaction step of the oxygen-hydrocarbons reaction at the flame temperature. The diffusion flame height is approximated making use of the inverted Burke–Schumann solution approach for diffusion flames [2].

Detailed description of the solution procedure and physical values is given in Pelosi [7] and Pelosi and Gany [9].

1.6 Characteristic Cycle Times

The characteristic time of the cycle, t_c is defined as the time it takes the fuel to regress a droplet diameter unit. This time is determined by the fuel regression rate, $\dot{r}_F$:

$$t_c = \frac{d_{OX}}{\dot{r}_F} \tag{1.9}$$

Heating of the oxidizer droplet results from the heat feedback from the flame to the surface, Q''_{cond}. An unsteady energy balance, based on temperature uniformity in the droplet, enables to approximate the heating time of the oxidizer:

$$t_h = \frac{4m_{OX}C_{p,OX}\left(T_{S,OX} - T_i\right)}{Q''_{cond}\pi d^2_{OX,av}} \tag{1.10}$$

Heat transfer from the droplet to the surrounding is neglected, m_{OX} is the oxidizer droplet mass, $C_{p,OX}$ is the liquid oxidizer's specific heat at constant pressure.

The oxidizer vaporization time is calculated, based on the droplet mass and the peak oxidizer flux obtained from Eq. (1.7):

$$t_v = \frac{m_{OX}}{m''_{OX,\max} S_{OX,av}} \tag{1.11}$$

The average surface area, $S_{OX,av}$, corresponds to the area of an oxidizer droplet with average diameter, $d_{OX,av}$.

The droplet lifetime is then:

$$t_{drop} = t_h + t_v \tag{1.12}$$

The model predicts surface fuel and oxidizer temperatures, fluxes, and flame height as a function of pressure and droplet size. In addition, the fuel regression rate and the characteristic times of the combustion cycle are calculated.

1.7 Results

Flame standoff distance (height) as a function of pressure is presented in Figs. 1.6 and 1.7 for nitric acid (HNO_3) oxidizer droplets of different diameters: 20 and 100 μm, respectively.

One can observe that with the increase in pressure, the overall flame height decreases both for small and large droplets. As may be expected, the smaller the oxidizer droplet, the smaller the flame standoff distance. Yet another conclusion is that the reaction distance decreases substantially with pressure, while the diffusion distance exhibits the opposite trend.

Characteristic droplet life time for a micro-cycle of 20- and 100-μm-diameter oxidizer droplets versus pressure is presented in Figs. 1.8 and 1.9, respectively. In general, all the characteristic times (heating, vaporization, and fuel regression) decrease with increasing the pressure. Furthermore, for the fuel and oxidizer combination analyzed here (HTPB and nitric acid), the overall droplet lifetime is shorter than the fuel regression time throughout the pressure and droplet diameter ranges under consideration. One notes that smaller droplets are heated and evaporated in shorter time.

The difference in characteristic times between the cases of 20- and 100-μm-diameter droplets is almost by an order of magnitude. In general, droplets in the range of the solid oxidizer particles in solid propellants (tens to hundreds of μm size) seem to imply efficient and stable combustion. Droplets of the range of millimeter