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REVIEW PAPER

Surface Pyrolysis of High Energy Materials

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ABSTRACT

The Arrhenius zero-order phenomenological pyrolysis law, commonly used in conjunction with the Vieille ballistic law to study pressure-driven burning of energetic materials, is revisited. Motivated by experimental and theoretical work performed in 1984 in this Laboratory, a relationship among several interplaying parameters is found under steady-state conditions. This relationship corresponds to the Jacobian of the pyrolysis sensitivity parameters used in the Zeldovich-Novozhilov approach. The Arrhenius pyrolysis is still expressed in terms of a global surface activation energy, but consistency with the experimental ballistic law may require an explicit pressure dependence as well. This conclusion is supported by a variety of arguments drawn from different areas. The linear dependence of the pre-exponential factor on surface activation energy (known as kinetic compensation) is proved and extended to the pressure exponent, for any given experimental data set under steady burning. Experimental results are reported for about a dozen solid propellants of different nature. The effects of surface pyrolysis explicit pressure dependence, although modest on steady-state burning, are potentially far-reaching for unsteady regime and/or unstable burning. The paper is mainly focussed on pressure-driven burning and Arrhenius pyrolysis, but the implemented method is believed to apply in general. Thus, enforcing KTSS zero-order phenomenological pyrolysis with the Vieille ballistic law yields similar results and requires an explicit pressure dependence. In case, the Zeldovich ballistic law is enforced instead of the classical Vieille law, no explicit pressure dependence is required. The unifying concept for these different trends is the pyrolysis Jacobian as a consistency requirement between the implemented steady pyrolysis and ballistic laws.

NOMENCLATURE

a,b	Nondimensional stability parameters
$a_p b_p$	Multiplicative factors
$\tilde{A}_s, B_s$	Multiplicative factors
c	Specific heat (cal/g K)
e_m	Average fitting error
$\tilde{E}_{(...)}$	Activation energy (cal/mole)
$E_{(...)}$	$\tilde{E}_{(...)} / \Re / T_{(...)}$, Nondimensional activation energy
E_l	$p_{hig} \ln p_{hig} - p_{low} \ln p_{low} - (p_{hig} - p_{low})$
E_5	$\dfrac{\Re b_p(p_{hig} - p_{low})}{\left[\dfrac{(p_{hig}^{1-n_{T_s}} - p_{low}^{1-n_{T_s}})}{(1-n_{T_s})} + \dfrac{n_{T_s} E_1}{(<\bar{p}>)^{n_{T_s}}}\right]}$
I_s	External radiant flux intensity (cal/cm^{2}s)
j	Running counter, integer
k	ZN steady sensitivity parameter

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m	Mass burning rate (g/cm^{2}s)
m_p	Pre-exponential factor of Zeldovich mass burning rate (g/cm^{2}s)
N	Total number of experimental observations, integer
n	Pressure exponents of ballistic burning rate
n_s	Pressure exponents of pyrolysis law
n_{T_s}	Pressure exponents of surface temperature
p	Pressure (atm)
p_{ref}, T_{ref}	Reference temperature (300 K), reference pressure (68 atm)
Q	Heat release (cal/g) (positive if exothermic)
r	ZN steady sensitivity parameter
r_b	Burning rate (cm/s)
$r_{b,ref}, T_{s,ref}$	Reference burning rate $r_b(p_{ref})$ reference surface temperature $T_s(p_{ref})$
$\Re$	Universal gas constant; 1.987 (cal/mole) K
t	Time coordinate
T	Temperature (K)
T_I	Initial propellant temperature (K)
w_s	Power of KTSS pyrolysis law

Greek Symbols

α	Thermal diffusivity (cm^2/s)
β_g	Overall reaction order of gas-phase chemical reactions
δ	ZN pyrolysis Jacobian
μ, ν	ZN steady sensitivity parameters
ρ	Density (g/cm^3)
σ_p	Steady temperature sensitivity of burning rate (1/K)
ψ	Variable

Subscripts

Arr	Arrhenius pyrolysis law
bal	Ballistic
g	Gas
hig	High
KTSS	KTSS pyrolysis law or flame model
low	Low
min	Minimum
p	Pressure
pyr	Pyrolysis
ref	Reference
s	Burning surface
Vieille	Vieille ballistic law
Ze	Zeldovich ballistic law
$(\ldots)_I$	Cold boundary value

Superscripts

$\overline{(\ldots)}$	Steady-state value
$\widetilde{(\ldots)}$	Dimensional value
$\langle \ldots \rangle$	Average value

1. INTRODUCTION

Following the pioneering work by Zeldovich[1,2] in 1942, two main approaches, known as Zeldovich-Novozhilov (ZN) method and flame modelling (FM) method, have emerged to study unsteady combustion of solid propellants. Both share the basic assumptions of a quasi-steady gas phase, homogeneous condensed phase, and one-dimensional propellant strand (QSHOD framework). Most investigations in the area of solid propellant burning, whether steady or unsteady, have resorted to a one-to-one correspondence between burning rate and surface temperature (no explicit dependence on operating parameters, such as pressure for example, would be considered). Novozhilov[3,5] in 1965 first clearly stated this problem within the ZN framework: In plain words, the burning rate of the pyrolysis law does not necessarily depend on surface temperature only; in technical jargon, the pyrolysis Jacobian is not necessarily zero. Although Denison and Baum[6] in 1961 and Krier[7], *et al.* in 1968 assumed $n_s = 0$ in their intrinsic stability analyses of sharp and distributed flames, respectively, the idea of finite n_s or finite pyrolysis Jacobian is rather old in the FM literature[8-14]. The detailed experimental and theoretical investigation on pressure-driven frequency response, performed by Brown and Muzzy[12] for a generic QSHOD flame, will prove of special interest. Being the Jacobian a mathematical concept, the classical ZN sensitivity parameters are not necessarily needed. In addition, subtle connections may exist with specific flame models. As a matter of fact, although not explicitly stated, the pyrolysis Jacobian[8] already exists yet a satisfactory understanding of this whole matter was never reached. The results obtained for pressure-driven burning with $n_s = 0$, by implementing an exact approach by the FM method and including some effects of volumetrically-distributed chemical reactions, were reported[15]. First results on the surface pyrolysis Jacobian for pressure-driven burning were recently presented[16,17] and a more general theoretical treatment is under preparation.

The critical revision of the Arrhenius pyrolysis law by Brewster[18-21], *et al.* raised questions as to the meaning and relevance of surface gasification processes depending not only implicitly but also explicitly on pressure (in particular). This point has been discussed in detail in this paper. But possible explicit effects from other controlling parameters are excluded; typically, radiation and initial temperature are considered constant parameters (not necessarily zero) acting in the background. The classical QSHOD assumptions are retained for the successive stability predictions, but are not needed for the pyrolysis analysis. The concentrated surface gasification enforced by most investigators is a pure phenomenological approach; and there is no reason to go beyond these phenomenological limits in this paper. Moreover, the paper is not meant to suggest any new pyrolysis model, but simply to point out the need of a consistent implementation of whatever pyrolysis law is considered. Beck and Brill[22-26] have worked on the formidable complexity of pyrolysis processes. An important fraction of our understanding of energetic material burning in general is based on this phenomenological approach. The recent revision of the work of Brewster, Esker and Son[18-21] challenged the validity of this approach and resumed an old dilemma in this technical area. Thus, it would seem that many results well-established in the literature – sometimes of fundamental importance – are jeopardised.

2. SURFACE PYROLYSIS DILEMMA

Gasification processes occur at the burning surface (concentrated pyrolysis) or over a certain thickness of the condensed phase starting from this surface (distributed pyrolysis). Even for the distributed case, the main pyrolysis effects can be reduced to equivalent surface phenomena. In this paper, only concentrated gasification is considered. The burning surface is typically seen as an infinitely thin planar surface subjected to one-step, irreversible, zero-order overall gasification reaction (from which evaporation and/or decomposition products magically appear[20]. Under these circumstances, two global pyrolysis laws of phenomenological nature are commonly used in the literature:

(a) Familiar Arrhenius exponential law

$$r_{b,Arr} = \widetilde{A}_s p^{n_s} \exp\left(-\frac{\widetilde{E}_s}{\Re T_s}\right) \tag{1}$$

where the frequency factor $\widetilde{A}_s$ pressure power, n_s and activation energy, $\widetilde{E}_s$ are in general unknown functions; and

(b) The alternative KTSS power law

$$r_{b,KTSS} = \widetilde{B}_s p^{n_s} (T_s - T_1)^{w_s} \tag{2}$$

where similarly the multiplicative factor, $\widetilde{B}_s$ pressure power, n_s and temperature power, w_s are in general unknown functions; and

The so-called pyrolysis law is meant to provide a direct relationship between burning rate and surface temperature. This is essential to relate burning rate and surface temperature under transient conditions, for which at least in principle no experimental data are available. At any rate, under steady conditions, one can write

$$\bar{r}_{b,Arr} = \widetilde{A}_s \bar{p}^{n_s} \exp\left(-\frac{\widetilde{E}_s}{\Re \bar{T}_s}\right) \tag{3}$$

$$\bar{r}_{b,KTSS} = \widetilde{B}_s \bar{p}^{n_s} (\bar{T}_s - T_1)^{w_s} \tag{4}$$

where $\widetilde{A}_s, n_s, \widetilde{E}_s$ or $\widetilde{B}, n_s, w_s$ are now unknown triplets depending on the enforced set of steady operating conditions.

At the same time, steady-state burning rates can be obtained by a series of experiments where only pressure is varied, while all remaining controlling parameters are held constant. A best fitting procedure by a power law would then provide the familiar empiric relationship involving two coefficients a_p or $r_{b,ref}$ and n:

$$\bar{r}_{b,Vieille} = a_p \bar{p}^n = r_{b,ref}(\bar{p} / p_{ref})^n \tag{5}$$

As an alternative, for some particular compositions the 'normal' exponential ballistic law (first proposed by Zeldovich[1,2] in 1942 and much used in the Russian literature[4,27,28]) can be used:

$$\bar{m}_{Ze} = m_p \exp\left(-\frac{\widetilde{E}_{Ze}}{\Re \bar{T}_s}\right) \tag{6}$$

where $\bar{m} = \rho_c \bar{r}_b$ is the steady mass burning rate, the nondimensional activation temperature, $\widetilde{E}_{Ze} / \Re = 5000$, and the pre-exponential constant, m_p = 1.8 10^3 g/cm^{2}s is the asymptotic (maximum) mass burning rate[28]. This relationship was experimentally shown to hold as an universal law for all known double-base propellants (DBP) and nitrocellulose (NC), over a wide range of pressure and initial temperature. In this work, for convenience, the steady burning rates of Eqns (3) and (4) are called the Arrhenius and KTSS pyrolysis laws, respectively and the steady burning rates of Eqns (5) and (6) obtained from pressure experiments, are called the Vieille (or Saint Robert) and Zeldovich ballistic laws, respectively.

Thus, a simple dilemma arises. While under transient conditions Arrhenius law (or, for that matter, any pyrolysis law) is the only one available, under steady conditions both the Arrhenius law (or, for that matter, any pyrolysis law) of Eqn (3) and the Vieille law (or, for that matter, any ballistic law) of Eqn (5) apply for the burning rate. Are they redundant or in conflict? Since the equations under discussion feature different mathematical trends, difficulties are anyway expected.

In addition, some recent work[18-20] challenged the validity and/or usefulness of the phenomenological approach in general. Yet, there is no contradiction with first principles in using different pyrolysis relationships[29]. In particular, Brewster[18-20], *et al.* re-elaborated a distributed pyrolysis law originated[30] in Russia in 1959, then used for an ablation problem[31], and later extended to radiation sustained burning[32]. This law certainly has a scientific foundation missing in the standard phenomenological laws, but is not necessarily a panacea to all experimental investigations where conflicts with the theoretical expectations arise. Most important, the old phenomenological pyrolysis can still offer a lot at low price.

Under broad terms, it is hoped to offer a clarification of the surface pyrolysis dilemma. In particular, the objective of this paper is to investigate the features of possible explicit pressure-dependent surface gasification under different scenari: the pyrolysis Jacobian is the unifying concept for otherwise apparently contradictory results. The analysis to be performed is of general nature. However, the great importance of the Arrhenius pyrolysis for theoretical (just recall the Zeldovich[29] temperature based on the nondimensional group $\widetilde{E} / \Re / T$) as well as experimental investigations should be recognised; likewise, Vieille law is almost universally employed. Thus, this particular combination for the pyrolysis and ballistic steady burning will more specifically be addressed to. The energetic materials considered in this study include solid propellant components and compositions representative of many kinds (Table 1).

3. STEADY PRESSURE-DEPENDENT PYROLYSIS

The difficulty is to determine the unknown functions $\widetilde{A}, n_s, \widetilde{E}_s$ to be used in Eqn (3) or $\widetilde{B}_s, n_s, w_s$ to be used in Eqn (4). Since first principles are not easily invoked and relevant parameters are strongly dependent on the operating conditions as well as the specific nature of the material under examination, the problem is usually solved by means of experimental information. Let us fix T_l and $\bar{I}_s$ typically (but not necessarily) $T_l = T_{ref}$ and $\bar{I}_s = 0$ as most often done.

Let us enforce the usual definitions

$$n \equiv \frac{d \ln \bar{m}}{d \ln \bar{p}}, \quad n_{T_s} \equiv \frac{d \ln \bar{T}_s}{d \ln \bar{p}} \tag{7}$$

Then, some best fitting procedure can be carried out over the tested pressure interval (p_{low}-p_{hig}) or, at most, over a number of finite sub-intervals obtained by properly dividing p_{low}-p_{hig} and matching both steady-state laws at the breaking points. This would provide the following empiric steady relationships typically by a power law fitting as:

$$\bar{r}_{b,Vieille}(\bar{p}) = a_p \bar{p}^n = r_{b,ref}(\bar{p}/p_{ref})^n \tag{8}$$

$$\bar{T}_s(\bar{p}) = b_p \bar{p}^{n_{T_s}} = T_{s,ref}(\bar{p}/p_{ref})^{n_{T_s}} \tag{9}$$

To a good approximation, the coefficients a_p or $r_{b,ref}$, b_p or $T_{s,ref}$, n, n_{T_s} are now constants quantitatively defined by the implemented regression technique over the proper operating range. The steady laws of Eqn (8) or Eqn (9), being of general validity, are widely used; but when n and /or n_{T_s} continuously vary with the operating conditions, the more general definitions of Eqn (7) should be used.

Table 1. List of examined propellants and measured ambient temperature density

Propellant	Notation	Density (g/cm^3)
AN monopropellant	AN	1.720
AP monopropellant	AP	1.957 ortho
		1.756 cubic
AP/HTPB (86/14)	*AP1*	1.630
AP/CTPB/Al_2O_3(83/16/1)	AP2	1.632
AP/PBAA (80/20) No. 941	AP6	1.540
AP/CTPB (84/16)	AP9	1.600
Uncatalysed double-base	DB2-S	1.632
Catalysed double-base	DB5	1.637
Uncatalysed double-base	N	1.600
Uncatalysed double-base	NB	1.600
HMX	HMX	1.910
RDX or T4 or hexogen	RDX	1.806
RDX/HTPB (84/16)	RDX 1	1.572

AN	Ammonium nitrate
AP	Ammonium perchlorate
CTPB	Carboxyl-terminated polybutadiene
DBP	Double-base propellant
HMX	Cyclotetramethylenetetranitramine
HTPB	Hydroxyl-terminated polybutadiene
N	58 % nitrocellulose + 28 % nitroglycerin + 12 % dinitrotoluence + stabiliser + plasticiser
NB	58 % nitrocellulose + 40 % nitroglycerin + stabiliser + plasticiser
NC	Nitrocellulose
PBAA	Polybutadiene acrylic acid
RDX	Cyclotrimethylenetrinitramine

Notice that Zeldovich ballistic law under steady conditions

$$\bar{r}_{b,Ze}(\bar{T}_s) = (m_p/\rho_c)\exp\left(-\frac{\tilde{E}_{Ze}}{\Re\bar{T}_s}\right) \tag{10}$$

is fully defined; the familiar parameter n related to the independent variables $\bar{p}$ is not needed. This relationship assumes a one-to-one correspondence between burn rate and surface temperature (no explicit contribution from the independent variables or external controlling parameters is allowed).

The two dependent variables, $r_{b,bal}$ and $\bar{T}_s$, are implicitly connected by the steady operating pressure in Eqns (8) or (10) and (9). If in addition, Arrhenius or KTSS pyrolysis laws are accepted, then a direct connection too is provided; hence the need of compatibility. A large body of experimental evidence suggests that the activation energy, $\tilde{E}_s$ or its equivalent, w_s are constant over the same pressure interval for which coefficients a_p or $r_{b,ref}$, b_p or $T_{s,ref}$, n, n_{T_s} are found constant. Under these circumstances and for steady burning, Arrhenius or KTSS pyrolysis laws will depend at most on two functions and one constant (all unknown, for the time being):

Arrhenius	KTSS
$\tilde{A}_s = \tilde{A}_s(\bar{p})$	$\tilde{B}_s = \tilde{B}_s(\bar{p})$
$n_s = n_s(\bar{p})$	$n_s = n_s(\bar{p})$
$\tilde{E}_s$ = *Constant*	w_s = *Constant*

How can these quantities be determined ? The activation energy, $\tilde{E}_s$ or its equivalent, w_s are in principle defined by experiments of physico-chemical nature, providing a clue as to the actual mechanism controlling pyrolysis. The multiplicative factors $\tilde{A}_s$ or $\tilde{B}_s$ are defined by enforcing some kind of compatibility between the ballistic and pyrolysis laws otherwise conflicting. This can be realised either locally (i.e., for a given operating pressure) or globally (i.e., over the whole pressure range under examination or a number of finite sub-intervals):

Local compatibility refers to a given operating condition, i.e., an arbitrary but well identified working point $\bar{p}_x$ (pressure in this instance) inside the tested pressure interval. Local compatibility is flexible and exact, but of limited validity.

- Overall compatibility refers to a finite range of operating conditions. Typically, a suitable regression technique would provide a constant value over the explored pressure range; an alternative analytical approach is discussed in Section 8. At any rate, overall compatibility is approximate but of wide validity.

In either case, the function n_s has yet to be understood. It is believed that for the classical combination of Arrhenius pyrolysis with Vieille ballistic law, finite values of n_s are in general appropriate for surface pyrolysis while $n_s = 0$ is only a particular case. This will be elaborated in this paper by several supporting arguments drawn from a variety of sources on pressure-driven burning: (i) experimental-numerical evidence collected by Oleari[35], (ii) experimental-analytical evidence collected by Lunghi[39] in 1984, (iii) theoretical evidence from pressure-driven linear frequency response of mass burning rate for sharp flames, (iv) theoretical evidence from pressure-driven linear frequency response of surface temperature, (v) an immediate equivalence with the corresponding ZN formalism, (vi) a simple but intuitive mathematical interpretation of the pyrolysis Jacobian and its dependence on burning parameters, and (vii) an analytical proof that the pyrolysis Jacobian minimises the difference between the pyrolysis and ballistic steady burning rates, both locally and over a finite pressure interval.

The Sections 4 to 6 analyse the specific but common combination of Arrhenius pyrolysis with Vieille ballistic law: First, experimental work performed in this Laboratory is recalled (Section 4), second, a linear relationship for the function n_s is obtained by theoretical means (Section 5.2) third, the exact correspondence between the ZN and FM counterparts of the surface pyrolysis Jacobian is verified (Section 6). Next, under more general terms, a simple geometrical interpretation is pointed out (Section 7). Lastly, the pyrolysis Jacobian is shown to provide minimum deviation of the steady Arrhenius pyrolysis [Eqn (3)] from the burning rate ballistic law for $\tilde{E}_s \neq 0$. It was found that implementing KTSS zero-order phenomenological pyrolysis with the Vieille ballistic law yields similar results and requires an explicit pressure dependence, but if the Zeldovich ballistic law is enforced instead of the classical Vieille law, no explicit pressure dependence is required.

4. HISTORICAL NOTE

Evidence for the explicit burning rate dependence of Arrhenius pyrolysis, when used in conjunction with Vieille ballistic law, on both surface temperature and pressure, was provided by Oleari[35] and Lunghi[39].

4.1 Experimental Analysis

About 15 years ago, a rudimentary but combined set of steady burning rates and surface temperatures was collected in this laboratory by students[33,34] preparing their MS theses. Tests were performed in a windoweds-strand burner, for a nonmetallised ammonium perchlorate (AP)-based composite propellant of national production (84 % AP + 16 % carboxyl-terminated polybutadiene (CTPB)), in the pressure range from subatmospheric to 25 atm. A. Oleari[35] in his MS thesis numerically investigated the best fitting conditions of the Arrhenius pyrolysis, assumed of the form in Eqn (3), for the available data. By using desktop computers, the average error between the pyrolysis and ballistic-computed steady burning rates was evaluated as

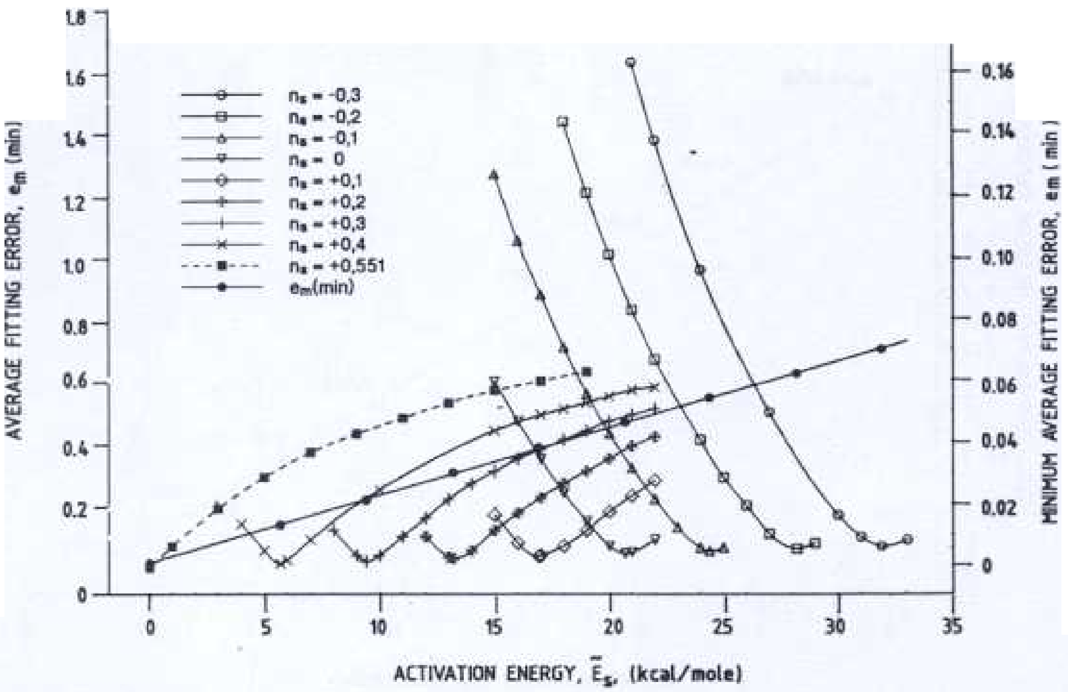

Figure 1. Average fitting error (left axis) and minimum average fitting error (right axis) *vs* surface activation energy $\tilde{E}_s$ for the indicated values of n_s. Nonmetallised composite solid propellant AP2 with 1984 data set.

$$Error = \frac{1}{N}\sum_{j=1}^{N}\frac{\left|\bar{r}_{b,\,Arr}(\bar{p}_j, n_s, \tilde{E}_s) - \bar{r}_{b,\,Vieille}(\bar{p}_j)\right|}{\bar{r}_{b,\,Vieille}(\bar{p}_j)} \tag{11}$$

N being the total number of experimental observations. In general, for a given n_s, this function would manifest a well-defined minimum for a specific value of $\tilde{E}_s$, as shown in Fig. 1. The computation was then systematically repeated for a wide range of n_s values; notice in particular the monotonic trend for $n_s = n$ (= 0.551 in the 1984 data set). A surprising overall result was eventually found: The couple of parameters n_s, $\tilde{E}_s$ providing the minimum average fitting error is quite closely a straight line[35] when plotted *vs* Arrhenius activation energy

$$n_s = 2.66 \cdot 10^{-5}(-\tilde{E}_s) + 0.551$$

where $\tilde{E}_s$ is measured in cal/mole. Figure 2 shows the linear dependence of n_s on $\tilde{E}_s$ and, parametrically overlapped, the minimum average fitting error increasing from near-zero for $\tilde{E}_s = 0$ to larger values for increasing $\tilde{E}_s$. Moreover, the minimum average fitting error also revealed a linear dependence on $\tilde{E}_s$, as shown in Fig. 1.

4.2 Theoretical Analysis

D. Lunghi[39] analytically proved the existence of the above linear relationship [Eqn (12)] and was able to point out the relevant parameters buried in it by writing

$$n_s = n - n_{T_s}\frac{\tilde{E}_s}{\Re T_{s,ref}} \tag{13}$$

where $T_{s,ref}$ is the steady surface temperature at $\bar{p} = p_{ref} = 68$ atm. The relationship of Eqn (13) and numerical evaluations of Eqn (12), are simply approximate expressions of the exact surface pyrolysis Jacobian.

5. LINEAR FREQUENCY RESPONSE FUNCTIONS

A well-established approach to assess intrinsic stability of a combustion configuration resorts to the frequency response function for the linear

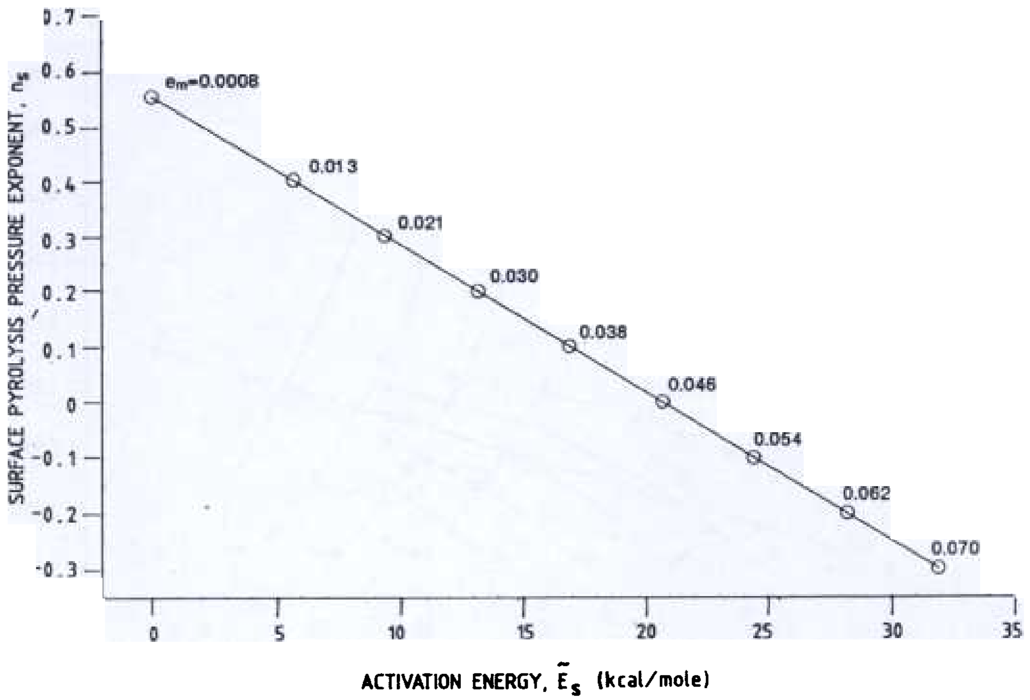

Figure 2. Plot of n_s vs $\tilde{E}_s$ based on experimental burning rate and surface temperature data. Nonmetallised composite solid propellant AP2 with 1984 data set.

approximation of the problem. Fluctuations of burning rate, subsequent to an externally-controlled sinusoidal fluctuation of pressure with angular frequency, ω, are sought for. Thus, for example, burning rate pressure-driven frequency response is a complex function defined as

$$R_p(\omega)=\frac{m'/\overline{m}}{p'/\overline{p}} \tag{14}$$

The basic mathematical assumption of linear theories is that all time-dependent variables (...) can be expressed as the sum of a steady-state value and a small disturbance of the type $(...)' \cdot e^{i\omega t}$, whose amplitude has to be determined but is always much smaller than the steady-state counterpart. The reason to mention this classical approach here is that it offers evidences in favour of finite surface pyrolysis Jacobian (for Arrhenius pyrolysis when Vieille ballistic law is enforced).

5.1 Pressure-Driven Burning Rate Frequency Response

An analytical exercise, made by Delu[36] revealed an inconsistency of sharp flames. The classical static limit for pressure-driven burning R_p ($\omega \rightarrow 0$) = n , discussed by Culick[10] would not hold in general. Only by allowing $n_s \neq 0$, this limit would be verified in general. This problem was revisited by Culick[37] and a linear relationship

$$n_s=n+(\beta_g-2n)\,\frac{\tilde{E}_s}{\Re\overline{T}_s}\,\frac{Q_g-c_g(\overline{T}_f-\overline{T}_s)}{c_g\overline{T}_s} \tag{15}$$

involving also gas-phase properties was obtained[15] Thus, finite n_s may be required by gas-phase considerations independently on other needs.

5.2 Pressure-Driven Surface Temperature Frequency Response

The static limit of several frequency response functions was evaluated by Baraledi[38]. In particular, for pressure-driven burning, surface temperature fluctuations are given by

$$R_{p,T_s}(\omega) \equiv \frac{T'_s / \bar{T}_s}{p' / \bar{p}} = \frac{R_p(\omega) - n_s}{\dfrac{\tilde{E}_s}{\Re \bar{\bar{T}}_s}} \tag{16}$$

whose static limit is

$$\lim_{\omega \to 0} R_{p,T_s}(\omega) = \lim_{\omega \to 0} \frac{T'_s / \bar{T}_s}{p' / \bar{p}} = \frac{n - n_s}{\dfrac{\tilde{E}_s}{\Re \bar{\bar{T}}_s}} \tag{17}$$

implying

$$n_s = n - n_{T_s} \frac{\tilde{E}_s}{\Re \bar{\bar{T}}_s} \tag{18}$$

This relationship, involving only surface properties corresponds to the pyrolysis Jacobian recently re-discussed[18,19] in the ZN framework. Thus, for a given operating pressure, a precise dependence of n_s from several interplaying parameters exists. Yet the relationship of Eqn (18), while better defining the former findings by Oleari[35] and Lunghi[39] reported in Section 4, is only a local expression of the full Arrhenius pyrolysis Jacobian.

6. SURFACE PYROLYSIS JACOBIAN

In the original ZN formulation of pressure-driven burning[4,5], four nondimensional steady-state parameters were introduced to describe the dependence of ballistic properties on pressure

$$\nu \equiv \left[\frac{\partial \ln \bar{m}}{\partial \ln \bar{p}}\right]_{T_1 = const} \quad \text{and}$$

$$\mu \equiv \frac{1}{(\bar{T}_s - T_1)} \left[\frac{\partial \bar{T}_s}{\partial \ln \bar{p}}\right]_{T_1 = const} \tag{19}$$

and ambient temperature

$$k \equiv (\bar{T}_s - T_1) \left[\frac{\partial \ln \bar{m}}{\partial T_1}\right]_{\bar{p} = const} \quad \text{and}$$

$$r \equiv \left[\frac{\partial \bar{T}_s}{\partial T_l}\right]_{\bar{p} = const} \tag{20}$$

where $\bar{m}_s = \rho_c \bar{r}_b = \bar{m}$ is the steady surface mass burning rate. A possible correlation among the four sensitivity parameters is revealed by the Jacobian defined as

$$\delta \equiv \frac{\partial(\ln \bar{m}, \bar{T}_s)}{\partial(\ln \bar{p}, T_l)} = \nu r - \mu k \tag{21}$$

When δ = 0, one of the four parameters can be evaluated from the remaining three. A finite value of the Jacobian, although suspected for different compositions, cannot be experimentally shown in a convincing way due to inherent difficulties in measuring surface temperatures even under steady conditions[40].

For pressure-driven burning, the following conversion table was used from the FM definitions when Arrhenius pyrolysis and Vieille ballistic law are enforced:

$$\nu = n$$

$$\mu = n_{T_s} \frac{\bar{T}_s}{\bar{T}_s - T_1}$$

$$k = \sigma_p \cdot (\bar{T}_s - T_1) = 1 / B$$

$$r = \frac{[\partial \ln \bar{m} / \partial T_l]_{\bar{p} = const}}{[\partial \ln \bar{m} / \partial \bar{T}_s]_{\bar{p} = const}} = \frac{\sigma_p}{\dfrac{\tilde{E}_s}{\Re \bar{\bar{T}}_s} \dfrac{1}{\bar{\bar{T}}_s}}$$

$$= \frac{\bar{\ }}{AB}$$

implying

$$\frac{k}{r} = (\bar{T}_s - T_1)\frac{[\partial \ln \bar{m} / \partial T_1]_{\bar{p}=const}}{[\partial \bar{T}_s / \partial T_1]_{\bar{p}=const}}$$

$$= (\bar{T}_s - T_1)\left[\frac{\partial \ln \bar{m}}{\partial \bar{T}_s}\right]_{\bar{p}=const}$$

$$\frac{\tilde{E}_s}{\Re \bar{T}_s}\frac{\bar{T}_s - T_1}{\bar{T}_s} \qquad (26)$$

Thus,

$$\frac{\delta}{r} \equiv \frac{1}{r}\frac{\partial(\ln \bar{m}, \bar{T}_s)}{\partial(\ln \bar{p}, T_1)} = \nu - \mu\frac{k}{r} = n_s \text{ (ZN)} \qquad (27)$$

$$n_s = n - n_{T_s}\frac{\tilde{E}_s}{\Re \bar{T}_s} \text{ (Arrhenius)} \qquad (28)$$

are respectively the ZN and Arrhenius FM counterparts of the same quantity, associated with the local surface pyrolysis Jacobian, already met in the previous Eqns (12) and (13) [approximate expressions proposed by Oleari[35] and Lunghi[39]] and Eqn (18).

7. PYROLYSIS AT CONSTANT PRESSURE

Two different mathematical functions of the same independent variables are said locally equivalent to a zero-order if the same output value is provided by the two functions for the same input values. Likewise, the two functions are said locally equivalent to the n^{th} order if, in addition, the same n^{th} derivatives are found for the same input values. By applying this general concept to the steady burning rate functions as described by the ballistic and pyrolysis laws, the surface pyrolysis Jacobian reveals a simple and intuitive mathematical interpretation. Indeed, for any arbitrary but well-identified working pressure $\bar{p}_x$ inside the tested pressure interval p_{low}–p_{hig}, one obtains the following constraints:

(a) For a zero-order contact, the two steady-state burning rates are exactly coincident

$$[\bar{r}_b(\bar{p}_x)]_{ballistic} = [\bar{r}_b(\bar{p}_x)]_{pyrolysis} \equiv \bar{r}_b(\bar{p}_x) \qquad (29)$$

(b) For a first-order contact, the two first derivatives also must exactly coincide

$$\left[\frac{d\bar{r}_b(\bar{p}_x)}{d\bar{p}}\right]_{ballistic} = \left[\frac{\partial \bar{r}_b(\bar{p}_x)}{\partial \bar{p}} + \frac{\partial \bar{r}_b(\bar{p}_x)}{\partial \bar{T}_s}\frac{d\bar{T}_s}{d\bar{p}}\right]_{pyrolysis} \qquad (30)$$

yielding Eqns (8) and (9) for the steady surface temperature dependence on pressure

$$\left[\frac{d\bar{r}_b(\bar{p}_x)}{d\bar{p}}\right]_{ballistic} = \left[\frac{\partial \bar{r}_b(\bar{p}_x)}{\partial \bar{p}} + n_{T_s}\frac{\bar{T}_s}{\bar{p}_x}\frac{\partial \bar{r}_b(\bar{p}_x)}{\partial \bar{T}_s}\right]_{pyrolysis} \qquad (31)$$

(c) For a second-order contact, the two second derivatives also must exactly coincide

$$\left[\frac{d^2\bar{r}_b(\bar{p}_x)}{d\bar{p}^2}\right]_{ballistic} = \left[\frac{\partial^2 \bar{r}_b(\bar{p}_x)}{\partial \bar{p}^2} + \frac{\partial^2 \bar{r}_b(\bar{p}_x)}{\partial \bar{T}_s^2}\left(\frac{d\bar{T}_s}{d\bar{p}}\right)^2 + \frac{\partial \bar{r}_b(\bar{p}_x)}{\partial \bar{T}_s}\frac{d^2\bar{T}_s}{d\bar{p}^2}\right]_{pyrolysis} \qquad (32)$$

Following are the details of some case studies.

7.1 Arrhenius Pyrolysis Plus Vieille Ballistics

(a) Zero-order contact implies

$$\tilde{A}_s(\bar{p}_x) = \frac{a_p \bar{p}_x^n}{\bar{p}_x^{n_s}\exp\left(-\frac{\tilde{E}_s}{\Re \bar{T}_s(\bar{p}_x)}\right)} \qquad (33)$$

(b) First-order contact implies

$$n_s = n - n_{T_s}\frac{\;}{\Re \bar{T}_s} \qquad (34)$$

Thus, from a geometrical viewpoint, the surface pyrolysis Jacobian simply means a common tangent for the steady burning rate as evaluated by the pyrolysis and ballistic laws.

(c) Second-order contact implies

$$\left[\frac{n_s-n}{\bar{p}_x}+\frac{\tilde{E}_s}{\Re\bar{T}_s}\frac{1}{\bar{T}_s}\frac{d\bar{T}_s}{d\bar{p}}\right]^2_{\bar{p}=\bar{p}x}+\frac{\tilde{E}_s}{\Re\bar{T}_s}\frac{1}{\bar{T}_s}$$
$$\left.\frac{d^2\bar{T}_s}{}-\frac{2}{}\left(\frac{d\bar{T}_s}{d\bar{p}}\right)^2+\frac{1}{\bar{p}_x}\frac{d\bar{T}_s}{d\bar{p}}\right]_{\bar{p}=\bar{p}x}=0 \tag{35}$$

yielding, in general

$$\frac{\tilde{E}_s}{\Re\bar{T}_s}\frac{1}{\bar{T}_s}$$
$$\left[\frac{d^2\bar{T}_s}{d\bar{p}^2}-\frac{2}{\bar{T}_s}\left(\frac{d\bar{T}_s}{d\bar{p}}\right)^2+\frac{-}{\bar{p}_x}\frac{d\bar{T}_s}{d\bar{p}}\right]_{\bar{p}=\bar{p}_x}=0 \tag{36}$$

If Eqn (9) is assumed for the steady surface temperature dependence on pressure, then

$$\frac{\tilde{E}_s}{}\left[\frac{n_{T_s}}{}\right]^2=0 \tag{37}$$

from which one obtains the trivial solution

$$\tilde{A}_s(\bar{p}_x)=a_p \tag{38}$$

$$n_s(\bar{p}_x)=n \tag{39}$$

$$\tilde{E}_s=0 \tag{40}$$

7.2 KTSS Pyrolysis Plus Vieille Ballistics

(a) Zero-order contact implies

$$\tilde{B}_s(\bar{p}_x)=\frac{a_p\bar{p}_x^n}{\bar{p}_x^{n_s}[\bar{T}_s(\bar{p}_x)-T_1]^{w_s}} \tag{41}$$

(b) First-order contact implies for the common tangent condition

$$n_s=n-n_{T_s}w_s\frac{\bar{T}_s}{\bar{T}_s-T_1} \tag{42}$$

(c) Second-order contact implies, in general

$$w_s\frac{\bar{T}_s}{\bar{T}_s-T_1}\frac{1}{\bar{T}_s}$$
$$\left[\frac{d^2\bar{T}_s}{d\bar{p}^2}-\frac{1}{\bar{T}_s-T_1}\left(\frac{d\bar{T}_s}{d\bar{p}}\right)^2+\frac{1}{\bar{p}_x}\frac{d\bar{T}_s}{d\bar{p}}\right]_{\bar{p}=\bar{p}_x}=0$$

yielding, if Eqn (9) is assumed for the steady surface temperature dependence on pressure

$$w_s\frac{\bar{T}_s}{\bar{T}_s-T_1}\left[\frac{n_{T_s}}{\bar{p}_x}\right]^2\left(1\quad\frac{\bar{T}_s}{}\right.$$

from which one obtains the trivial solution

$$\tilde{B}_s(\bar{p}_x)=a_p$$

$$n_s(\bar{p}_x)=n$$

$$w_s=0$$

In summary, the trivial solution for ballistics is

Arrhenius	KTSS
$\tilde{A}_s(\bar{p}_x)=a_p$	
$n_s(\bar{p}_x)=n$	
$E_s=0$	

7.3 Arrhenius Pyrolysis Plus Zeldovich Ballistics

(a) Zero-order contact implies

$$\tilde{A}_s(\bar{p}_x)=\frac{\frac{m_p}{\rho_c}\exp\left(-\frac{\tilde{E}_{Ze}}{\Re\bar{T}_s(\bar{p}_x)}\right)}{\bar{p}_x^{n_s}\exp\left(-\frac{\tilde{E}_s}{\Re\bar{T}_s(\bar{p}_x)}\right)} \tag{48}$$

(b) First-order contact implies

$$n_s=-n_{T_s}\frac{\tilde{E}_s-\tilde{E}_{Ze}}{\Re\bar{T}_s} \tag{49}$$

(c) Second-order contact implies, in general

$$\frac{\tilde{E}_s - \tilde{E}_{Ze}}{\Re \bar{T}_s} \cdot \frac{1}{\bar{T}_s} \left[\frac{d^2 \bar{T}_s}{d\bar{p}^2} - \frac{2}{\bar{T}_s} \left(\frac{d\bar{T}_s}{d\bar{p}} \right)^2 + \frac{1}{\bar{p}_x} \frac{d\bar{T}_s}{d\bar{p}} \right]_{\bar{p}=\bar{p}_x} = 0 \tag{50}$$

yielding, if Eqn (9) is assumed for the steady surface temperature dependence on pressure,

$$\frac{\tilde{E}_s - \tilde{E}_{Ze}}{\Re \bar{T}_s} \left[\frac{1}{\bar{p}_x} \right]^2 = 0 \tag{51}$$

If $\tilde{E}_{Ze} = \tilde{E}_s$ is selected, then one recovers the natural solution

$$\tilde{A}_s(\bar{p}_x) = m_p / \rho_c \tag{52}$$

$$n_s = 0 \tag{53}$$

$$\tilde{E}_s = \tilde{E}_{Ze} \tag{54}$$

Notice that in all cases the trivial solution can be replaced, for finite $\bar{p}_x$, by the special constraint $n_{T_s} = 0$ implying in turn $\bar{T}_s = const$, i.e, the steady surface temperature is pressure-independent (as assumed in the original Zeldovich[1] papers.

8. ARRHENIUS PYROLYSIS OVER FINITE PRESSURE INTERVAL

It is wished to determine the best functions $\tilde{A}_s(\bar{p})$ and $n_s(\bar{p})$ for a finite operating pressure interval p_{low}–p_{hig}. For any arbitrary but well identified working point, $\bar{p}_x$, one can approximate the measured steady burning rate by the phenomenological Arrhenius pyrolysis law of Eqn (3) rather than selected empiric ballistic law [Eqn (8)] In doing so, the total quadratic error is

$$f(\langle n_s \rangle, \langle \tilde{A}_s \rangle) = \int_{p_{low}}^{p_{hig}} \left\{ \ln \bar{r}_b(\psi) - \ln < \tilde{A}_s > - \langle n_s \rangle \ln \psi + \frac{\tilde{E}_s}{\Re \bar{T}_s(\psi)}) \right\}^2 d\psi \tag{55}$$

where the integrand function is just the difference between the two ideal burning rate expectations. The following specific question is asked: what are those special values of $\langle n_s \rangle$ and $\langle \tilde{A}_s \rangle$ allowing the best approximation of the steady burning rate ballistic law for Arrhenius pyrolysis while keeping $\tilde{E}_s$ constant and finite positive ? This matter, already discussed by DeLuca[16], *et al.* is only summarised here.

8.1 Arrhenius Pyrolysis Plus Vieille Ballistics

When Arrhenius pyrolysis and Vieille ballistic law [Eqn (5)] are enforced, the condition of constrained minimum, in general, is determined by

$$\ln \langle \tilde{A}_s \rangle = \ln a_p + E_5 \cdot \tilde{E}_s \tag{56}$$

$$\langle n_s \rangle = n - n_{T_s} \frac{\tilde{E}_s}{\Re \langle \bar{T}_s \rangle} \tag{57}$$

where E_5 is a computed quantity, while $< \bar{p} >$ and $< \bar{T}_s >$ are average values of pressure and surface temperature[16].

8.2 Arrhenius Pyrolysis Plus Zeldovich Ballistics

When Arrhenius pyrolysis and Zeldovich ballistic law [Eqn (6)] are enforced, the condition of constrained minimum, in general, is determined by

$$\ln \langle \tilde{A}_s \rangle = \ln (m_p / \rho_c) + E_5 \cdot (\tilde{E}_s - \tilde{E}_{Ze}) \tag{58}$$

$$\langle n_s \rangle = -n_{T_s} \frac{\tilde{E}_s - \tilde{E}_{Ze}}{\Re \langle \bar{T}_s \rangle} \tag{59}$$

where the slope of $\ln < \tilde{A}_s >$ *vs* $\tilde{E}_s$ is again given by E_5, while the intercept for $\tilde{E}_s = 0$ is $\ln(m_p/\rho_c) - E_5 \cdot \tilde{E}_{Ze}$ instead of the previous In a_p. If $\tilde{E}_{Ze} = \tilde{E}_s$ is selected, then one simply obtains

$$\ln \langle \tilde{A}_s \rangle = \ln (m_p / \rho_c) \tag{60}$$

$$\langle n_s \rangle = 0 \tag{61}$$

From these findings, several interesting results follow immediately:

(a) For $p_{hig} \to p_{low}$, i.e., when the test pressure interval p_{low}–p_{hig} shrinks to a working point, $\bar{p}_x$, Vieille ballistics yields

$$\ln\left\langle \tilde{A}_s \right\rangle \to \ln \tilde{A}_s = \ln(a_p \bar{p}^n \quad \left(\ln\bar{p}^{n_s} \quad \frac{\tilde{E}_s}{\Re \bar{\bar{T}}_s} \right) \tag{62}$$

$$\langle n_s \rangle \to n_s = n - n_{T_s} \frac{\tilde{E}_s}{\Re \bar{\bar{T}}_s}$$

while Zeldovich ballistics yields

$$\ln\left\langle \tilde{A}_s \right\rangle \to \ln \tilde{A}_s = (m_p / \rho_c) - \frac{\tilde{E}_s - \tilde{E}_{Ze}}{\Re \bar{\bar{T}}_s}$$

$$\langle n_s \rangle \to n_s = -n_{T_s} \frac{\tilde{E}_s - \tilde{E}_{Ze}}{\Re \bar{\bar{T}}_s}$$

recovering in both cases the previous results from Section 7. Thus, the best couple ln $\tilde{A}_s$ and n_s is exactly deduced for averaged and local operating conditions as well (only pressure in this instance) and for both ballistic laws.

(b) All of the above results are obtained by considering the ideal ballistic Eqns (8) and (9) and pyrolysis Eqns (3) or (4) laws only. In particular, the minimum total error is zero: For Vieille ballistics when $\tilde{E}_s = 0$, for Zeldovich ballistics when $\tilde{E}_s - \tilde{E}_{Ze} = 0$. The total minimum error evaluated by using directly the experimental data points will, in general, be found near to, but not exactly at, $\tilde{E}_s = 0$ (Vieille) or $\tilde{E}_s - \tilde{E}_{Ze} = 0$ (Zeldovich).

(c) The various expressions previously found for Arrhenius pyrolysis combined with Vieille ballistics are local representations of the full expression obtained in Eqn (57). For example, the earlier findings by Oleari[35] and Lunghi[39], reported in Section 4, are just special cases of Eqn (57); in particular, Eqn (13) was obtained by taking the $\tilde{A}_s$ value at the reference surface temperature, while the error computation shows indeed a linear dependence on $\tilde{E}_s$ in the original plots (Figs 1 and 2).

(d) Under steady conditions, a linear relationship exists between ln $\tilde{A}_s$ and $\tilde{E}_s$ as a simple mathematical property of the governing set of equations, being the burning rate assigned. The slope of this relationship depends very weakly on the pressure range.

(e) Under steady conditions, another linear relationship exists between n_s and $\tilde{E}_s$, again as a simple mathematical property of the governing set of equations. The last two findings shed new light on the kinetic compensation effect discussed by Brill[25,26], which now includes ln $\tilde{A}_s$ as well as n_s and appears to be valid for any material obeying the fundamental steady burning rate laws (Vieille or Zeldovich ballistic laws and Arrhenius pyrolysis law).

9. COMPARISON OF QSHOD SURFACE PYROLYSIS

For surface driven burning, the relevant ballistic properties can conveniently be collected under two nondimensional parameters, a and b[15]. These are broadly defined in terms of burning surface and gas-phase properties, respectively as

$$a \equiv \left[(T_s - T_1) \frac{\partial \ln m_s}{\partial T_s} \right]_{T_s = \bar{T}_s} \tag{66}$$

$$b \equiv \left[\left(\frac{\partial \tilde{q}_{g,s}}{\partial m_s} + Q_s \right) \frac{\partial \ln m_s}{\partial T_s} \right]_{T_s = \bar{T}_s} \quad \frac{c_g - c_c}{c_c} \tag{67}$$

where $m_s = \rho_c r_b = m$ is any monotonic pyrolysis law describing mass production at the burning surface. In general $a > 0$, while $-\infty < b < +\infty$; both parameters implicitly depend on the radiant flux intensity as well in case of radiation-driven burning in the limit of surface absorption.

Also, all QSHOD frequency response functions, whether FM or ZN, can be cast in the standard 'two parameter' form[10]. From a formal viewpoint, a universal law for pressure-driven frequency response functions can be established. Only parameter B (essentially related to the flame description) takes different values for different configurations, while parameter A (related to surface pyrolysis) is not affected (see summarising table below).

- Parameter A, related to surface pyrolysis, is defined in general[11] as

$$A \equiv \left[(T_s - T_1)\frac{\partial \ln m_s}{\partial T_s}\right]_{T_s=\bar{T}_s}$$

$$a = \frac{\tilde{E}_s}{\Re \bar{T}_s}\,\frac{\bar{T}_s - T_1}{\bar{T}_s} = w_s \tag{68}$$

- Parameter B, essentially related to the flame description, takes different values for different flame structures[15].

In their classical analysis of premixed flames, Denison and Baum[6] introduced three parameters (A_{DB}, α_{DB}, and q_{DB}) and formulated the instability condition for a steady-state burning propellant as $q_{DB} > 1$ and $q_{DB}^2 - q_{DB} - 2A_{DB} > 0$, exactly matchig the ZN stability conditions[5]. A full discussion is reported by Williams[29]. Similar results were later found by KTSS[7] for diffusion flames and BM[12] for a generic QSHOD flame, again using three parameters (w_s, B_{KTSS}, A_{KTSS} and A_{BM}, B_{BM}, R_{BM}.)

In the linear regime, a complete formal equivalence between FM and ZN QSHOD frameworks exists, including the unbounded response limit of pressure-driven frequency responses[15] as

$$A = A_{DB} = w_s = A_{BM} = \frac{\tilde{E}_s}{\quad}\,\frac{\bar{T}_s - T_1}{\bar{T}_s} = a = \frac{k}{r}$$

$$B = \dot{\alpha}_{DB} = B_{KTSS} = \frac{B_{BM} - n_s}{n - n_s} = \frac{1}{\sigma_p(\bar{T}_s - T_1)}$$

$$= \frac{+A-K}{\quad} = \frac{1+a-b}{a} = \frac{1}{k}$$

$$K = q_{DB} = A_{KTSS} = R_{BM} = 1 + \frac{\tilde{E}}{\Re \bar{T}_s}$$

$$\frac{\sigma_p(\bar{T}_s - T_1) - 1}{\sigma_p \bar{T}_s} = 1 + A - AB = b = 1 + \frac{k}{r} - \frac{1}{r}$$

where, in general, all parameters are pressure-dependent. The positions in Eqns (69)-(71) make all the reported relationships (for stability boundary and oscillation frequency) equivalent and interchangeable, and thus independent of the specific flame model or approach (ZN *vs* FM). Notice that actually only two parameters are needed, as first recognised in the ZN approach[3].

10. RESULTS & DISCUSSIONS

This section is mainly focussed on Arrhenius pyrolysis and Vieille ballistic law, in view of the great practical relevance of these otherwise simply phenomenological expressions. Appropriate remarks can be repeated for the other combinations of pyrolysis and ballistic laws tested in this paper.

The idea of finite n_s was discussed, in several instances, in the literature[8-10,12-14], but no conclusive answer was ever given to this elusive question. Theoretical investigations introduced finite n_s without however suggesting recommended values, experimental investigations were unfocused. However, the careful and systematic experimental work by Brown and Muzzy[12] stands out. Standard T-burner results were collected from a large variety of composite AP-based solid propellants[12]. Statistical analysis of the collected data indicated that negative n_s would often be required to fit the implemented theoretical model, which in turn is a particular case of the general FM QSHOD solution[15] . Their results appear now of great interest, also in view of the stated skepticism by the authors about the negative n_s values found in their own investigation. Notwithstanding this, 9 out of the 23 tested propellants revealed statistically significant $n_s \neq 0$ and 2 of them featured $n_s < 0$. Against their own belief, their findings show that: (i) $n_s < 0$ is favoured by decreasing pressure[12]; (ii) n_s would increase with increasing catalyst per cent (from 0.13 % to 0.50 % copper chromate[12]); (iii) $n_s < 0$ is favoured by a lower oxidizer per cent[12] (78 % *vs* 84 %). It was also noticed that relatively large values of n_s up to 3.6 were found for a moderate pressure of 200 psi (about 13.6 atm). While finding (i) is in agreement with Eqn (57), findings (ii) and (iii) have no direct confirmation. However, since surface temperature usually increases with burning rate, it is expected that findings (ii) and (iii) also would qualitatively agree with Eqn (57). Although not explained on physical basis and notwithstanding the interfering effects of heterogeneity, these experimental results prove the existence of finite n_s (both above and below zero) beyond any reasonable doubt, in the framework of a careful data reduction scheme.

In this paper, a different viewpoint is taken: the simplest surface pyrolysis expression is assumed [Eqn (3) or Eqn (4)] and the buried features are derived based on direct experimental information and simple mathematical properties. No specific pyrolysis model is pre-emptively assumed; furthermore, no attempt is made to validate any specific pyrolysis model. In general, the surface activation energy can be evaluated from Eqn (57) as

$$\widetilde{E}_s = \frac{n - n_s(\bar{p})}{n_{T_s}} \Re \overline{T}_s(\bar{p})$$

$$\text{or} \quad \widetilde{E}_s = \frac{n - \langle n_s \rangle}{n_{T_s}} \Re \langle \overline{T}_s \rangle \tag{72}$$

showing that Arrhenius phenomenological law essentially measures the surface temperature dependence on pressure. Particular cases follow immediately. For example, the traditional $n_s = 0$ implies a well specific value of the surface activation energy at each operating pressure

$$\widetilde{E}_s = \frac{n}{n_{T_s}} \Re \overline{T}_s(\bar{p})$$

$$\text{or} \quad \overline{E}_s = \frac{n}{n_{T_s}} \Re \langle \overline{T}_s \rangle \tag{73}$$

and thus a conflicting situation – or a redundant information – if n, n_{T_s}, and $\widetilde{E}_s$ are evaluated independently (as usually done). This limitation of the traditional Arrhenius pyrolysis law is formally overcome by including the proper value of n_s. The special but interesting case $n = 0$ (plateau burning) implies

$$\widetilde{E}_s = \frac{n_s(\bar{p})}{n_{T_s}} \Re \overline{T}_s(\bar{p})$$

$$\text{or} \quad \widetilde{E}_s = -\frac{\langle n_s \rangle}{n_{T_s}} \Re \langle \overline{T}_s \rangle$$

requiring $n_s < 0$ to be physically plausible, while $n < 0$ (mesa burning) necessarily implies $n_s < 0$. Likewise, the particular value $n_{T_s} = 0$ (constant surface temperature) implies

$$\langle n_s \rangle = n_s = n = const.$$

In addition, more complex situations may arise by which other physical factors can affect the pyrolysis law; different physical meaning and values of the parameters appearing in Eqn (57) would then be implied. Similar remarks, but not necessarily the same, were already made by Brewster,[18-19] *et al.* in the ZN framework; differences are due to the zero-order condensed-phase decomposition there implemented in lieu of the conventional Arrhenius pyrolysis discussed in this paper.

The energetic materials considered in this paper are listed in Table 1. The related steady ballistic properties (burning rate and surface temperature) are listed in Table 2. The original data points, shown in Fig. 3 (steady burning rate) and

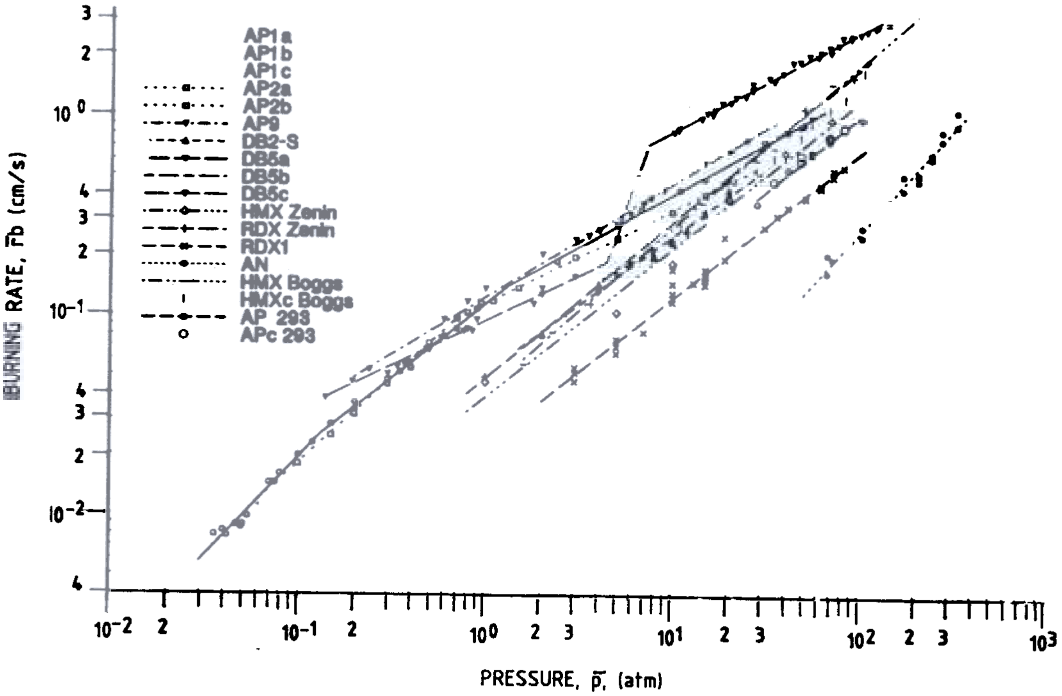

Figure 3. Plot of experimental steady burning rate *vs* pressure for the indicated solid propellants compositions

Fig. 4 (steady surface temperature), were obtained in this Laboratory (AP1, AP2, AP9, DB2-S, DB5, RDX1) or collected from the literature (AP and HMX[41], N and NB [28], HMX and RDX[42,43]. The data from this Laboratory were, in general, obtained by using the strand burners and microthermocouple setups[44]. Based on this experimental knowledge, a summarising list of the relevant values showing the standard Arrhenius pyrolysis parameters and the computed values of ln $<\tilde{A}_s>$ and $\langle n_s \rangle$ discussed in Section 8, is given in Table 3.

Typical trends for a variety of solid propellants are illustrated in Figs 3-6. A systematic revision is being performed of the experimental work conducted in this Laboratory and elsewhere. Marginal differences wrt previous experimental data sets published by this research group may be found due to the extensive data revision being performed. At any rate, the behaviour of the tested double-base and AP-based propellants, respectively below, say 2 atm and 0.1 atm is only indicative. The recommended procedure involves two main steps. First, the steady burning rate is measured over the wanted pressure range and is obtained (if needed, different values over different pressure intervals are enforced) as shown in Fig. 3. Then, the steady surface temperature is measured over the wanted pressure range and n_{T_s} is obtained (if needed, different values over different pressure intervals are enforced) as shown in Fig. 4. Finally, the steady plot of ln $\bar{r}_b$ *vs* $1/\bar{T}_s$ is obtained for both $n_s = 0$ and n_s = finite [16]. It was also observed that only minute differences, over the explored pressure interval, appear when implementing $n_s = 0$ or n_s finite from Eqn (28) or $\langle n_s \rangle$ finite from Eqn (57). This fact explains why the explicit pressure dependence has thus far been so elusive. Similar trends were observed by Brewster[18,19], *et al.* comparing the zero-order condensed-phase decomposition with the conventional Arrhenius pyrolysis for a noncatalysed double-base propellant.

Both ln $<\tilde{A}_s>$ and $\langle n_s \rangle$ are expected to linearly depend on $\tilde{E}_s$, due to a mathematical property of Arrhenius pyrolysis combined with Vieille ballistic law [see Eqn (56) and (57)], respectively. This was illustrated[16] for several solid propellants. Further, as shown in Fig 5, it is reassuring that the expected linear dependence of $<\tilde{A}_s>$ on $\tilde{E}_s$, closely reproduces the detailed kinetic compensation

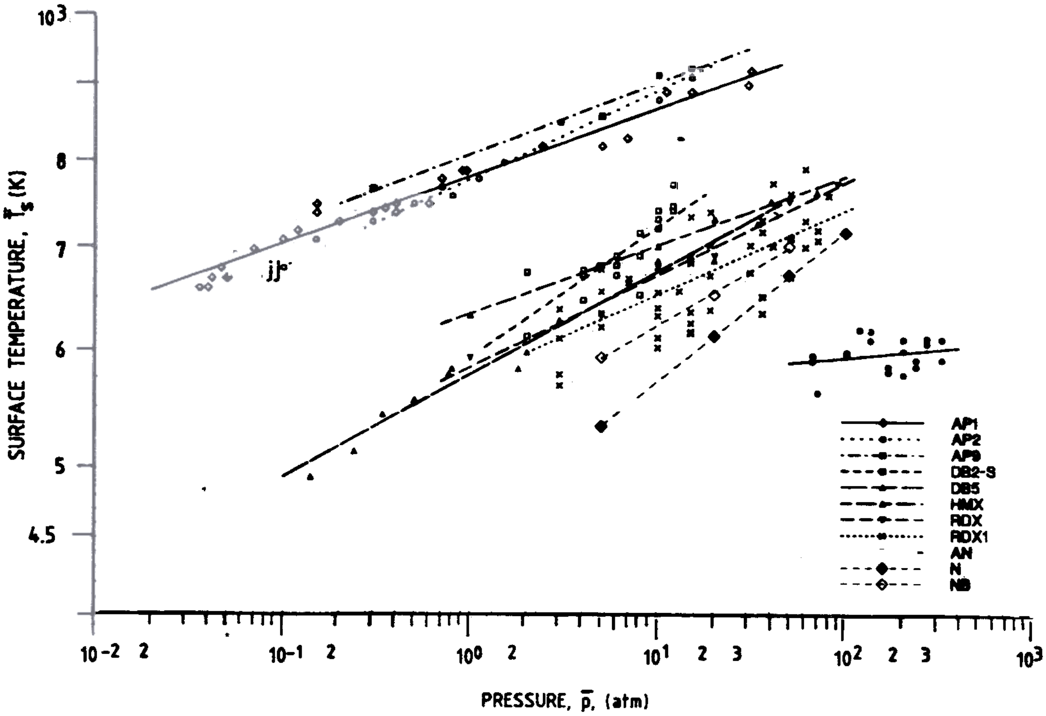

Figure 4. Plot of experimental steady surface temperature *vs* pressure for the indicated solid propellants compositions

plots recently published for HMX and RDX monopropellants[25].

The complex dependence of n_s on pressure, illustrated in Fig. 6, reveals a smooth decrease of n_s with decreasing pressure contrasted by sharp breaks of n. Sharp transitions are sometimes observed in the experimental trends. For example, AP-based composite propellants feature a well defined increase of n when the steady operating pressure falls below, say 1 atm (cf. Fig. 3), likely due to controlling mechanism switching from a mainly diffusive to a mainly premixed flame. Within the experimental accuracy, such an abrupt change is commonly observed for steady burning rate but is

Table 2. Ballistic properties of tested propellants

Propellant	Burning rate			Surface temperature		
	$R_{b,\,ref}$ (cm/s)	n		$T_{s,ref}$ (K)	n_{T_s}	
AP1a	1.132	0.526	for 1.30 < p < 31.00 atm			
AP1b	2.735	0.749	for 0.13 < p < 1.30 atm	947.0	0.045	for 0.036 < p < 31 atm
AP1c	13.429	1.003	for 0.036 < p < 0.13 atm			
AP2a	0.854	0.473	for 0.70 < p < 15.00 atm	999.8	0.059	for 0.075 < p < 15 atm
AP2b	5.243	0.869	for 0.075 < p < 0.7 atm			
AP6	0.837	0.460	for 1.00 < p < 30.00 atm	1000.0		0.053
AP9	1.415	0.575	for 0.30 < p < 25.00 atm	987.4	0.047	for 0.3 < p < 15 atm
DB2-S	0.962	0.687	for 2.00 < p < 20.00 atm	856.4	0.087	for 2.0 < p < 12 atm
DB5a	2.281	0.504	for 7.30 < p < 125.8 atm			
DB5b	335.400	2.745	for 4.46 < p < 7.30 atm	771.8	0.069	for 0.14 < p < 38 atm
DB5c	0.653	0.455	for 0.14 < p < 4.46 atm			
N	0.808	0.657	for 5.00 < p < 100.00 atm	692.3	0.100	for 5.000 < p < 100 atm
NB	1.434	0.711	for 5.00 < p < 50.00 atm	717.4	0.074	for 5.000 < p < 50 atm
HMX	0.933	0.750	for 1.00 < p < 70.00 atm	768.3	0.0454	for 1.000 < p < 70 atm
RDX	1.355	0.787	for 1.00 < p < 90.00 atm	756.9	0.0614	for 1.000 < p < 90 atm
RDX1	0.522	0.740	for 1.00 < p < 81.00 atm	730.8	0.0608	for 1.000 < p < 81 atm

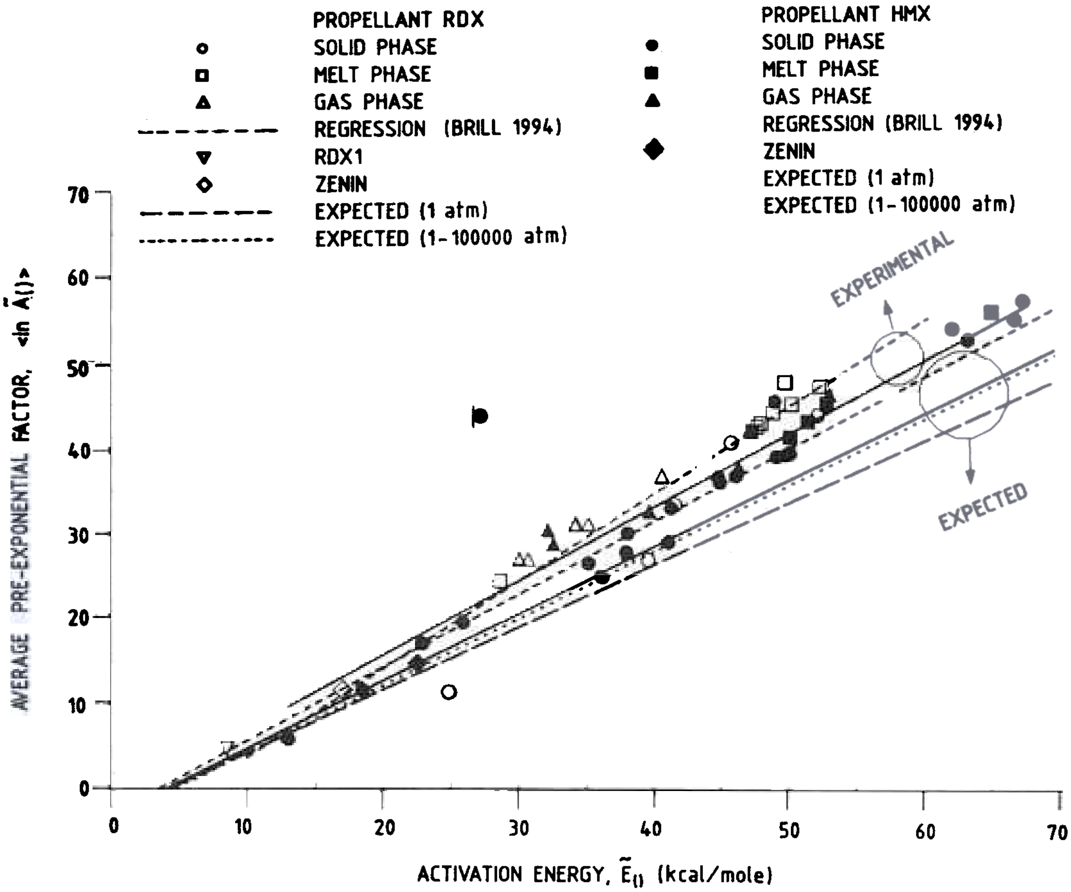

Figure 5. Linear dependence of ln $<\tilde{A}_{()}>$ on activation energy $\tilde{E}_{()}$ for HMX and RDX monopropellants compared to the corresponding kinetic compensation plots under a variety of operating conditions at 1 atm. The expected pressure effect is indicated by contrasting the lines respectively obtained at 1 atm and over 1-100,000 atm interval.

Table 3. Arrhenius pyrolysis properties of some tested propellants

Propellant	$<T_s>$ (K)		Arrhenius ($n_s \neq 0$)			Arrhenius ($n_s = 0$) Computed			Arrhenius ($n_s = 0$) Experimental		
		Tested pressure range	$\tilde{E}_s$	$\ln <\tilde{A}_s>$	$<n_s>$	$\tilde{E}_s$	$\ln <\tilde{A}_s>$	$<n_s>$	$\tilde{E}_s$	$\ln <\tilde{A}_s>$	$<n_s>$
DB2-S	687.2	for 2.00 $< p <$ 12 atm	10500	5.893	0.0178	10779	6.128	0	7017	3.395	0
DB 5a	704.6	for 7.30 $< p <$ 38 atm	10500	7.705	-0.0137	10223	7.944	0	6811	4.966	0
N	637.2	for 5.00 $< p <$ 100 atm	10500	8.149	-0.1726	8315	8.445	0	7992	5.591	0
NB	652.1	for 5.00 $< p <$ 50 atm	10500	7.233	0.1111	12445	7.500	0	12339	8.984	0
HMX	717.8	for 1.00 $< p <$ 70 atm	23000	14.909	0.0176	23552	5.267	0	22529	14.667	0
RDX	698.6	for 1.00 $< p <$ 90 atm	20000	14.0007	-0.0980	17785	6.157	0	17032	11.601	0

$\tilde{E}_s$ ($n_s \neq 0$) obtained from literature (references 28 and 42)

$\tilde{E}_s$ ($n_s = 0$) computed, obtained from $\tilde{E}_s = \dfrac{n}{n_{T_s}} \Re\langle \overline{T}_s \rangle$ [see Eqn (73)]

$\tilde{E}_s$ ($n_s = 0$) experimental, obtained from regression of ballistic data (see Table 2)

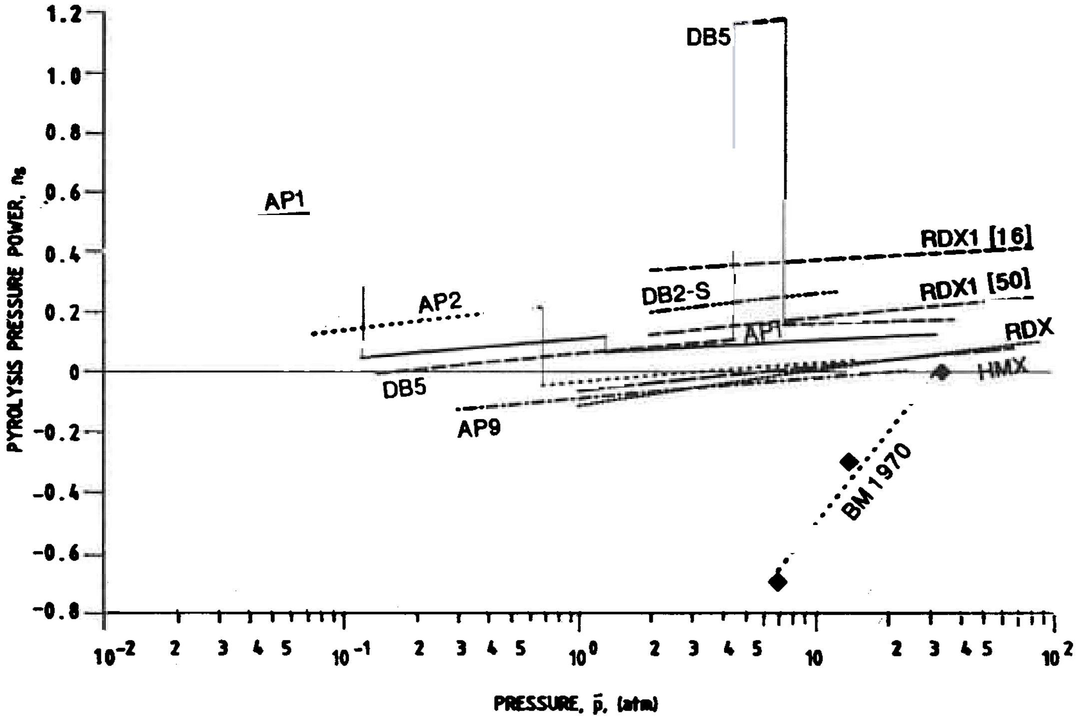

Figure 6. Plot of n_s *vs* pressure for a variety of solid propellants compared to BM results

not obvious for steady surface temperature (cf. Fig. 4). At any rate, the overall surface activation energy will also feature a well defined increase. This effect is observed for both unmetallised and metallised AP-based composite propellants. Another example of sharp transition is observed when crossing the super-rate region of catalysed double-base propellants (cf. Fig. 3): in this case the value of n, while very large over the super-rate region, is roughly kept across it.

11. CONCLUSIONS & FUTURE WORK

A revision of experimental and theoretical work performed long ago in this Laboratory again brought to light some old conclusions[39,39] showing that in general, finite n_s is required for consistency of Arrhenius pyrolysis with the classical Vieille ballistic law. This is more a mathematical than a physical requirement. The pyrolysis Jacobian, well known in the ZN approach and recently re-emphasised by Brewster[18-21], *et al.* has a well defined counterpart in the FM approach. The limitations of the classical Arrhenius pyrolysis law, in particular, have been underlined. The obtained results are supported by a variety of arguments.

A simple but general method is available to verify the consistency of any pyrolysis law for energetic materials. For Arrhenius and KTSS zero-order pyrolysis laws, the inclusion of explicit pressure dependence is necessary but not sufficient condition, to make them acceptable with Vieille ballistic law, whereas for Zeldovich ballistic law $n_s = 0$. In general, for Arrhenius or KTSS pyrolysis laws it is confirmed that $n_s = 0$ is just a special condition of the more general Eqn (63) and that n_s may be negative for large enough surface activation energy and/or low enough surface temperature and $n \leq 0$ (plateau or mesa burning), while the averaged $< n_s >$ is less prone to do so. The wide body of results already available on energetic material burning, including fundamental results, is still valid and may even feature a better agreement with experimental results if the pressure dependence of surface pyrolysis is enforced. Bridges with the past are not destroyed.

Combined experimental results of steady burning rate and surface temperature were reported for about a dozen of different solid propellants. The minimum error between the steady burning ballistic Eqn (8) and Arrhenius pyrolysis laws is found near

$\widetilde{E}_s = 0$ (Vieille ballistics) or $\widetilde{E}_s - \widetilde{E}_{Ze} = 0$ (Zeldovich ballistics). Relevant values of In $<\widetilde{A}_s>$ and $\langle n_s \rangle$ were computed; the linear dependences of $\ln < \widetilde{A}_s >$ and $\langle n_s \rangle$ on $\widetilde{E}_s$ were found to be a general mathematical property of Arrhenius law. The effects of surface pyrolysis explicitly pressure dependent, although modest on steady-state burning, are potentially far-reaching for unsteady regime and/or unstable burning. The finite n_s contributes a term to the pressure-driven frequency response function sometimes neglected in the competent literature. The intrinsic stability boundaries are not directly affected by finite n_s, but the position of the operating point on the intrinsic stability map is sensibly affected by the value of n_s[17].

This analysis has so far evidenced the need of a mathematically consistent formulation of the basic laws. More fundamental work as to the structure of surface layer and possible interactions with external radiation is in progress.

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