CHEMICAL ENGINEERING TRANSACTIONS

VOL. 57, 2017

A publication of
AIDIC
The Italian Association
of Chemical Engineering
Online at www.aidic.it/cet

Guest Editors: Sauro Pierucci, Jiří Jaromír Klemeš, Laura Piazza, Serafim Bakalis

ISBN 978-88-95608- 48-8; **ISSN** 2283-9216

Investigation by Thermodynamic Properties of Methane Combustion Mechanisms under Harmonic Oscillations in Perfectly Stirred Reactor

Luigi Acampora[a], Francesco S. Marra[b]

[a]Dipartimento di Ingegneria, Università degli Studi del Sannio – Piazza Roma 21, 80200, Benevento, Italy
[b]Istituto di Ricerche sulla Combustione, CNR – Via Diocleziano 328, 80124, Napoli, Italy
marra@irc.cnr.it

An analysis about the ability of selected global mechanisms in reproducing the correct dynamic behavior of a combustion reaction is conducted by investigating the behavior of the total entropy production rate in different ideal reactor configurations. The spontaneous ignition of a methane/air mixture at constant pressure in a batch reactor and the dynamic behavior of methane combustion in a PSR are investigated to elucidate the role of the rate of entropy produced by the chemical reactions. Four different chemical mechanisms for the methane-air combustion are compared, from one step to six steps global mechanisms and the detailed GRI mechanism assumed as reference mechanism. Results indicate that the analysis of entropy production in ideal reactors can be very useful to assess the ability of different chemical mechanisms in reproducing the dynamic behavior of unsteady combustion phenomena and combustion instabilities.

1. Introduction

The adoption of global or reduced mechanisms remains an obliged choice in several Computational Fluid Dynamics (CFD) simulations of combustion phenomena, especially in industrial applications. A large body of literature reports on global reaction mechanisms (e.g. Hjärtstam et al., 2012) or on approaches to obtain reduced or skeletal mechanisms from those detailed (Turányi and Tomlin, 2014).

Recent works by the authors show that global mechanisms fail to reproduce the dynamic behavior of even simple configurations, like the Perfectly Stirred Reactor (PSR) model, thus raising doubts about the possibility to conduct a correct analysis of transient or dynamic phenomena adopting such mechanisms (Acampora et al., 2016). Furthermore, they observed that skeletal mechanisms with a relatively large number of species, and therefore of reactions, are required to correctly reproduce the behavior of systems in dynamic conditions as well as some important characteristics of the combustion phenomena like ignition and extinction (Acampora et al., 2016). Finally, they pointed out that the ability of correctly reproducing the adiabatic flame temperature and the S-curve in the equivalence ratio - residence time plane was important for a proper choice of the global mechanism suitable for studying combustion oscillations (Marra et al., 2015).

In the present work, new insights are given by focusing on the analysis of few thermodynamics properties. Particularly, the entropy production analysis (EPA), recently adopted for skeletal mechanism generation by Kooshkbaghi et al (2014), is used as a post-processing tool to study the spontaneous ignition of a methane/air mixture at constant pressure in a batch reactor and the dynamic behavior of methane combustion in a PSR (subjected to harmonic oscillations of residence time) with both detailed and selected global mechanisms. The possibility to correlate the ability of selected global mechanisms in reproducing the correct dynamic behavior with the ability to reproduce the total entropy production rate (EPR) given by the detailed, reference, mechanism, is investigated. This analysis try to find out if the total EPR can play an important role in the selection of a global mechanism suitable for the simulation of unsteady conditions as those arising in combustion instabilities.

2. Entropy evaluation

The second principle of thermodynamics postulates the existence of a function of state, called entropy (S), which has the following characteristics (Prigogine, 1968): it is an extensive property; its change dS can be split into two parts: a contribution due to interactions with the exterior d_eS and a contribution due to changes inside the system d_iS. The entropy increase dS_i is never negative. It is zero when the system undergoes reversible changes only, but it is positive if the system is subject to irreversible processes as well. Considering the entropy as a function of internal energy U (neglecting any other contribution to the total energy), volume V and number n of moles of each species (Kuo, 2005), $S = S(U, V, n_1, n_2, \dots, n_{N_s})$:

$$dS = \left(\frac{\partial S}{\partial U}\right)_{V,n_j} dU + \left(\frac{\partial S}{\partial V}\right)_{U,n_j} dV + \sum_{k=1}^{N_s} \left(\frac{\partial S}{\partial n_k}\right)_{U,V,n_{j\neq k}} dn_k \tag{1}$$

The partial derivatives in the differential form Eq(1) can be expressed by using the definitions of absolute temperature T, pressure P and chemical potentials μ_k (Gyftopoulos and Beretta, 2005):

$$T = \left(\frac{\partial U}{\partial S}\right)_{V,n_j}, \quad P = -\left(\frac{\partial U}{\partial V}\right)_{S,n_j} = T\left(\frac{\partial S}{\partial V}\right)_{U,n_j}, \quad \mu_k = \left(\frac{\partial U}{\partial n_k}\right)_{S,V,n_{j\neq k}} = -T\left(\frac{\partial S}{\partial n_k}\right)_{U,V,n_{j\neq k}} \tag{2}$$

Therefore, the change in the entropy can be written in the form:

$$dS = \frac{1}{T} dU + \frac{P}{T} dV - \frac{1}{T}\sum_{k=1}^{N_s} \mu_k \, dn_k \tag{3}$$

If chemical reactions occur in the system, the change in the mole number dn_k of the k-th species may be due both to the external mass exchange with the surrounding d_en_k and to the internal change due to chemical reaction d_in_k (Kuo, 2005). Then, for a homogeneous, closed as well as open, system, two contribution arise:

$$d_eS = \frac{1}{T} dU + \frac{P}{T} dV - \frac{1}{T}\sum_{k=1}^{N_s} \mu_k \, d_en_k \tag{4}$$

$$d_iS = -\frac{1}{T}\sum_{k=1}^{N_s} \mu_k \, d_in_k \tag{5}$$

where d_iS represents the entropy change due to chemical reactions. The rate of change of the moles of the k-th species due to chemical reactions can be given in terms of production rates (Kuo, 2005):

$$\frac{d_in_k}{dt} = V\sum_{n=1}^{N_r} \left(\nu_{kn}^P - \nu_{kn}^R\right)\left(q_n^f - q_n^r\right) \tag{6}$$

where ν_{kn}^P and ν_{kn}^R are the stoichiometric coefficients on the products and reactants sides of the n-th reaction and the q_n^f and q_n^r are the corresponding forward and reverse rate of progress, respectively. Substituting equation Eq(6) in equation Eq(5), we obtain the rate of change of entropy due to chemical reactions:

$$\frac{d_iS}{dt} = -\frac{V}{T}\sum_{k=1}^{N_S}\sum_{n=1}^{N_r} \mu_k \left(\nu_{kn}^P - \nu_{kn}^R\right)\left(q_n^f - q_n^r\right) = \frac{V}{T}\sum_{n=1}^{N_r} a_n \left(q_n^f - q_n^r\right) \tag{7}$$

being:

$$a_n = -\sum_{k=1}^{N_S} \mu_k \left(\nu_{kn}^P - \nu_{kn}^R\right) \tag{8}$$

the chemical affinity (or De Donder's affinity) of the n-th reaction (Kuo, 2005). In this form, the change of entropy can be computed for any given, both irreversible or reversible, reaction. For a species in a mixture of ideal gases the chemical potentials can be expressed as (Gyftopoulos and Beretta, 2005):

$$\mu_k(T,P) = g_k(T,P^0) + RT\ln\left(X_k \frac{P}{P^0}\right) \tag{9}$$

where P^0 is the standard state pressure (usually 1 atm) and $g_k(T,P^0)$ is the standard state specific Gibbs free energy that is evaluated from standard state enthalpies and entropies:

$$g_k(T,P^0) = \frac{g_k^0}{RT} = \frac{h_k^0}{RT} - \frac{s_k^0}{R} \tag{10}$$

Standard state enthalpy and entropy can be computed from thermodynamic data by adopting the NASA polynomials (McBride et al., 1993).

3. Models description

3.1 Reactors governing equations

The ordinary differential equations governing the adiabatic, constant pressure batch reactor can be written as (Schwer et al., 2002):

$$\frac{dY_i}{dt} = \frac{W_i r_i}{\rho} \ , \ i = 1, \dots, N_S \ ; \qquad \frac{dT}{dt} = -\sum_{i=1}^{N_S} \frac{W_i r_i h_i}{\rho c_P} \tag{12}$$

Here t, ρ, T, N_S, c_P refer to time, gas density, temperature, number of species, and mixture constant pressure specific heat, respectively. Y_i, W_i, r_i, and h_i, are the mass fraction, molecular weight, net species production rate and specific enthalpy of the i-th species. The governing ordinary differential equations of the adiabatic, constant pressure PSR can be given as (Glarborg et al., 1986):

$$\frac{dY_i}{dt} = \frac{Y_{i,f} - Y_i}{\tau} + \frac{W_i r_i}{\rho} \ , \ i = 1, \dots, N_S \ ; \qquad \frac{dT}{dt} = \sum_{i=1}^{N_S} \frac{Y_{i,f}(h_{i,f} - h_i)}{\tau c_P} - \sum_{i=1}^{N_S} \frac{W_i r_i h_i}{\rho c_P} \tag{13}$$

where the subscript f indicates the feeding (inlet) conditions and $\tau = \rho V / \dot{m}_f$ is the nominal residence time related to the reactor volume (V) and the mass flow rate ($\dot{m}_f$). A sinusoidal perturbation of the residence time in the form $\tau_p = \tau[1 + \varepsilon \sin(2\pi f t)]$ is considered to study its effect on the methane combustion in a PSR.

3.2 Chemical mechanisms

Four different chemical mechanisms are used in this work to model the methane-air combustion (air composition approximated as O2 21%, N2 79% by volume).

Table 1: Reactions and Arrhenius parameters for WD mechanism (units in cm, s, cal, and mol)

Tag	Reactions	A	β	E_a	Reaction Orders
WD	CH4 + 1.5 O2 => CO2 + 2 H2O	2.118726×10^{11}	0	35000	$[CH4]^{0.2}$ $[O2]^{1.3}$

The Westbrook and Dryer (WD) global one step mechanism (Westbrook and Dryer, 1981) was developed to correctly predict the variation of flame speed with equivalence ratio. The reaction and Arrhenius parameters are shown in table 1 (A, β, and E_a refer respectively to pre-exponential factor, temperature exponent, and Activation Energy). The set 3 reported in the Westbrook and Dryer work was chosen to avoid negative reaction orders.

Table 2: Reactions and Arrhenius parameters for CM2 mechanism (units in cm, s, cal, and mol)

Tag	Reactions	A	β	E_a	Reaction Orders
CM2 *(1)*	CH4 + 1.5 O2 => CO + 2 H2O	2×10^{15}	0	35000	$[CH4]^{0.9}$ $[O2]^{1.1}$
CM2 *(2)*	CO + 0.5 O2 => CO2	2×10^{9}	0	12000	[CO] $[O2]^{0.5}$
CM2 *(2r)*	CO2 => CO + 0.5 O2	8.1104×10^{10}	0	77194	[CO2]

The global two-step mechanism by Bibrzycki et al. (2010), indicated as CM2, is a reaction mechanism developed to reproduce GRI flame speeds for various equivalence ratios. The authors show that good agreement between the GRI and the CM2 are obtained for fresh mixture with $T = 300$, pressure P=0.1 MPa and equivalence ratios between 0.6 and 1.0. The reactions and Arrhenius parameters are reported in table 2.

Table 3: Reactions and Arrhenius parameters for JL mechanism (units in cm, s, cal, and mol)

Tag	Reactions	A	β	E_a	Reaction Orders
JL *(1)*	CH4 + 0.5 O2 => CO + 2 H2	7.6864×10^{12}	0	30000	$[CH4]^{0.5}$ $[O2]^{1.3}$
JL *(2)*	CH4 + H2O => CO + 3 H2	3.84×10^{12}	0	30000	[CH4] [H2O]
JL *(3)*	CO + H2O => CO2 + H2	2.01×10^{12}	0	20000	[CO] [H2O]
JL *(3r)*	CO2 + H2 => CO + H2O	4.16057×10^{17}	-1.06114	30511.1798	[CO2] [H2]
JL (4)	H2 + 0.5 O2 => H2O	2.8492×10^{19}	-1	40000	$[H2]^{0.3}$ $[O2]^{1.55}$
JL (4r)	H2O => H2 + 0.5 O2	1.38099×10^{19}	-0.861783	97734.1716	$[H2]^{-0.7}$ $[O2]^{1.05}$ [H2O]
JL (5)	O2 <=> 2 O	1.5×10^{9}	0	113000	[O2]
JL (6)	H2O <=> H + OH	2.3×10^{22}	-3	120000	[H2O]

The 6 steps mechanism JL is a modified version of the well-known Jones and Lindstedt (1988) mechanism with inclusion of dissociation reactions (Frassoldati et al., 2009) for the combustion of methane in mixtures with air in premixed and diffusion flames. The JL was developed to take into account oxy-fuel combustion conditions. It is obtained by refitting kinetic parameters of the original four steps Jones and Lindstedt mechanism and introducing two dissociation reactions. Their kinetic parameters are shown in table 3.

The Gas Research Institute mechanism (GRI), also known as GRIMech (Smith et al., 2000), is probably the most widely known chemical kinetics mechanism used for modelling methane and natural gas combustion in air. The current version (version 3.0) consists of 325 chemical reactions and 53 species.

4. Entropy production analysis

In this section, the results of EPA on ignition in batch and PSR reactors and regime combustion in unsteady PSR subject to sinusoidal perturbation of residence time are reported to illustrate how this thermodynamic property can help in investigating the combustion behavior.

4.1 Batch reactor results

Ignition delay time (IDT) is a fundamental property of a combustible mixture related to the entire set of its thermodynamic properties. However, an exact and commonly accepted definition does not exist, being its evaluation based on a criterion selected upon the actual application and the available data like temperature, radicals or species time profiles (Warnatz et al., 2006).

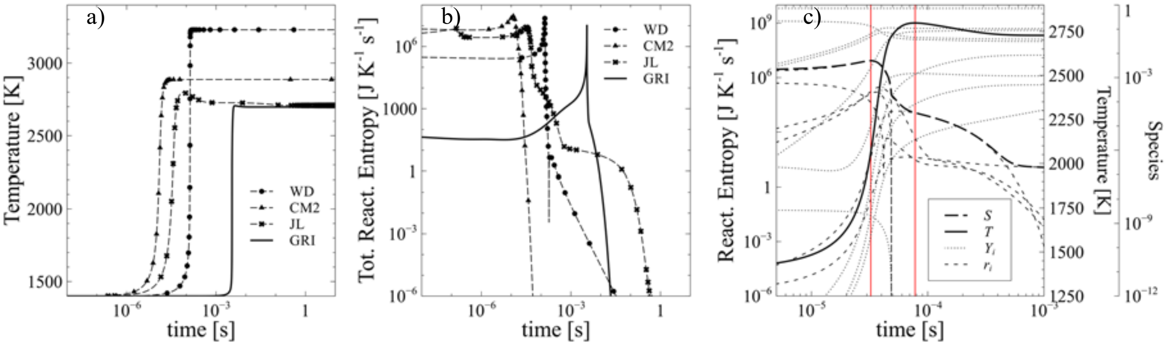

Figure 1: Temperature (a) and ERP (b) in a batch reactor and temperature, species mass fractions and reactions ERP for JL mechanism (c). Case $\varphi = 1$, $P = 1$ atm, $T_0 = 1400$ K.

In Figure 1, time profiles of temperature and total EPRs due to chemical reactions are compared for the different mechanisms analyzed. All the global mechanisms anticipate the ignition time with respect to the GRI. This is correlated with the lower value of the total EPR computed at the beginning of the process: while the temperature keeps very low at the beginning, the total EPR increases immediately and remains high up to the ignition time. Obviously, after ignition EPR drops to zero. To relate the maximum EPR with the temperature, Figure 1c shows, in the case of the JL mechanism, both the state variables (temperature and specie mass fractions) and EPRs. Two vertical lines mark the time of maximum EPR and maximum temperature. These are two separate times. The first one is very close to the time of the temperature inflection point: a correlation with the IDT can be suggested. A closer inspection of Figure 1c allows verifying that very few reactions significantly affect the total EPR at each stage of the ignition process in the case of the multistep JL mechanism. Actually, the EPRs of three different reactions almost overlap alternately the total EPR, dividing the ignition process into three stages: an early ignition stage, from the start of the process to $t = 4.86 \cdot 10^{-5}$ s, an intermediate stage up to $t = 4.77 \cdot 10^{-4}$ s and subsequently the final stage. This observation is at the base of the recently proposed method for the reduction of chemical mechanisms proposed by Kooshkbaghi et al, 2014.

4.2 Perfectly Stirred Reactor results

Simulations of the ignition process in a PSR initially filled with hot air at the temperature of 1400 K have been performed using the same chemical mechanisms. If the residence time τ is long enough, the combustible mixture of methane and air at stoichiometric composition fed at a temperature of 600 K, is able to ignite. Two different values of τ have been considered, $\tau = 0.001$ s, at which ignition is not predicted with the GRI, and $\tau = 0.1$ s, at which ignition is predicted with the same mechanism (see Figure 2). Results with $\tau = 0.001$ s with the other mechanisms are summarized in Figure 2a. This case clearly illustrates the benefits to conduct the entropy analysis of this ignition process.

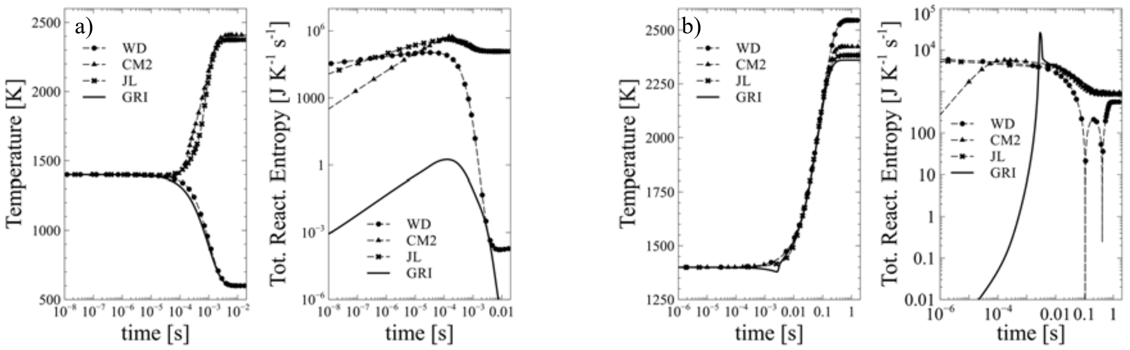

Figure 2: Temperature and EPR in a PSR. a) $\tau = 0.001$ *s, b)* $\tau = 0.1$ *s.* $\varphi = 1$*,* $P = 1$ *atm,* $T_0 = 1400$ *K,* $T_{in} = 600$ *K.*

At very early stages, when no information about the imminent ignition can be derived by the observation of the temperature, the total EPR appears to be a good precursor of the ignition. Nevertheless, the ability to reproduce the exact absolute value does not seem correlated to the ability in reproducing correctly the ignition phenomenon; e.g. in Figure 2a, the larger entropy production rate is obtained at the very early stages with the WD mechanism, which correctly does not predict ignition. Figure 2b ($\tau = 0.1$ s), shows that the mixture ignites with all mechanisms because of the most favorable conditions for ignition, but the dynamics of the early stage of the ignition process is not correctly reproduced by any of the global mechanisms. The CM2 and the JL mechanisms correctly approximates the final stage of the process.

4.3 Forced Perfectly Stirred Reactor results

Using as initial conditions the converged stable states obtained by time evolution in the preceding section, the effect of a periodic residence time is deepened. Figure 1 showed that the the JL mechanism exhibits the most complex behavior of entropy production during ignition. This can explain the largest phase shift that the temperature signal computed with the JL mechanism shows with respect to any other mechanism when the system is subject to a periodic forcing (see Figure 3). This shift appears almost independent from the frequency of the signal while increases increasing the residence time.

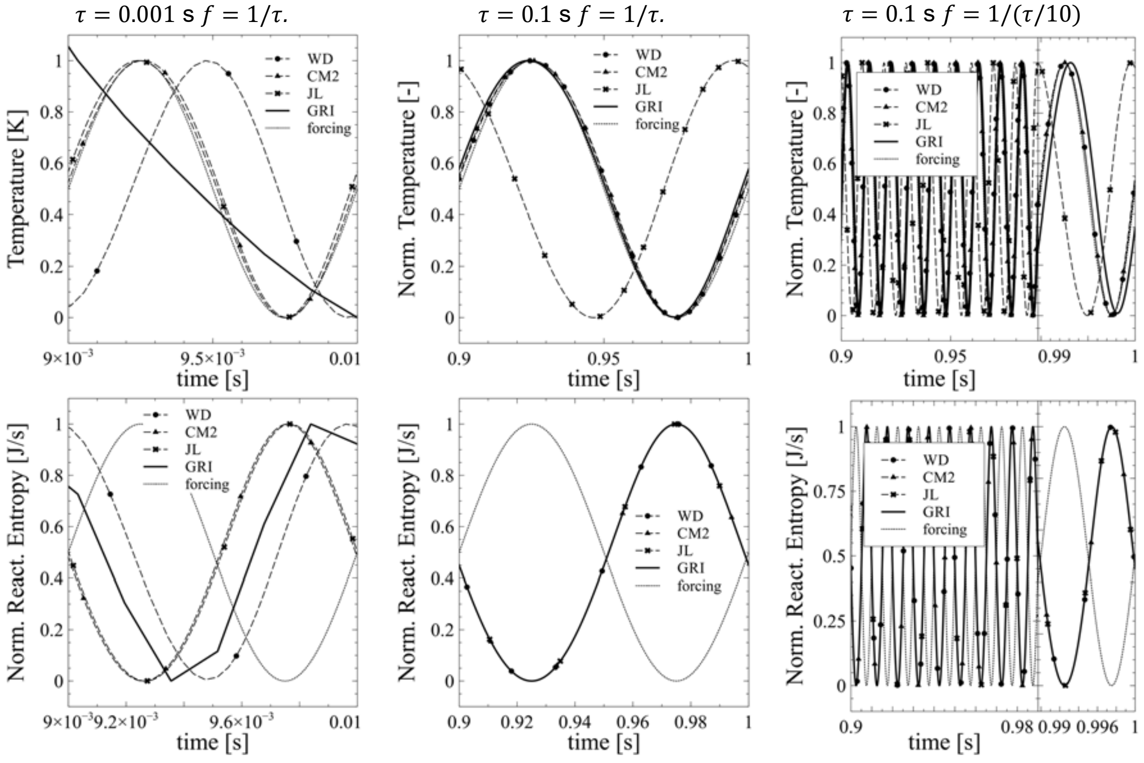
$\tau = 0.001$ s $f = 1/\tau.$ $\tau = 0.1$ s $f = 1/\tau.$ $\tau = 0.1$ s $f = 1/(\tau/10)$

Figure 3: Normalized temperature (top) and EPR (bottom) in a periodically forced PSR during a single residence time. Case $\tau = 0.1$ *s,* $\varphi = 1$*,* $P = 1$ *atm,* $T_0 = 1400$ *K,* $T_{in} = 600$ *K. Forcing of* τ *with* $\varepsilon = 0.1$*.*

The entropy signals at $\tau = 0.1$ s appear completely superposed for all mechanisms, independently from the frequency of forcing. This is explained by considering that for longer residence time the state of the systems, even if perturbed, is always in an equilibrium state: at each instant, the entropy produced by the reaction balance the entropy change between the reactants and products, resulting the feeding signal (the forcing signal) and the entropy signal in perfect opposition phase (decreasing the residence time, increases the feeding rate and so the total entropy produced).

Different is the case of $\tau = 0.001$ s, close to an approaching ignition state for forced not ignited solutions and to an approaching extinction state for forced ignited solutions (first column of Figure 3). In this case, the systems are not able to immediately equilibrate their state and thus they exhibit different EPR phase shifts. The ability of the system to follow this perturbation appears to depend upon the ratio of period of forcing and the IDT.

5. Conclusions

A study has been conducted, using different ideal reactors, to elucidate the role of the EPR by the chemical reactions, adopting four different chemical mechanisms for the methane-air combustion. Results indicate that the analysis of EPR in a batch reactor can be very useful to assess the ability of different chemical mechanisms in reproducing the dynamic behavior of ignition phenomena. EPR could also be useful in detecting early stage ignition conditions, giving a possible guidance in the analysis of full dimensional configurations. This property could be exploited also in the development of reliable computational procedure for the numerical integration of the very stiff equations arising in combustion modeling. Finally, it has been shown, analyzing the behavior of EPR in periodically forced PSRs, that indications about the stability of a given state could be derived by analyzing the phase shift of the EPR signal.

Reference

Acampora L., Marra F. S., Martelli E., 2016, Comparison of Different CH 4 -Air Combustion Mechanisms in a Perfectly Stirred Reactor with Oscillating Residence Times Close to Extinction, Combustion Science and Technology, 188, 707-718.

Frassoldati A., Cuoci A., Faravelli T., Ranzi E., Candusso C., Tolazzi D., 2009, Simplified kinetic schemes for oxy-fuel combustion, In 1st International conference on sustainable fossil fuels for future energy, 6-10.

Gyftopoulos E. P., Beretta G. P., 2005, Thermodynamics: Foundations and Applications. Dover Civil and Mechanical Engineering, Dover Publications, Mineola, New York, United States.

Glarborg P., Miller J. A., Kee R. J., 1986, Kinetic modeling and sensitivity analysis of nitrogen oxide formation in well-stirred reactors, Combustion and Flame, 65, 177-202.

Hjärtstam S., Normann F., Andersson K., Johnsson F. 2012, Oxy-Fuel Combustion Modeling: Performance of Global Reaction Mechanisms, Industrial & Engineering Chemistry Research, 51, 10327–10337.

Jones W. P., Lindstedt R. P.,1988, Global reaction schemes for hydrocarbon combustion, Combustion and Flame, 73, 233-249.

Kooshkbaghi M., Frouzakis C. E., Boulouchos K., Karlin I. V., 2014, Entropy production analysis for mechanism reduction, Combustion and Flame, 161, 1507–1515.

Kuo K. K., 2005, Principles of combustion. John Wiley & Sons, Hoboken, New Jersey, United States.

Marra F. S., Acampora L., Martelli E., 2015, Non-linear response to periodic forcing of methane-air global and detailed kinetics in continuous stirred tank reactors close to extinction conditions, International Journal of Spray and Combustion Dynamics, 7, 175–208.

McBride B. J., Gordon S., Reno M. A., 1993, Coefficients for calculating thermodynamic and transport properties of individual species, NASA Technical Report, NASA-TM-4513. NASA Lewis Research Center, Cleveland, Ohio, United States.

Prigogine I., 1968, Introduction to thermodynamics of irreversible processes. Interscience Publishers, New York, United States.

Smith G. P., Golden D. M., Frenklach M., Eiteener B., Goldenberg M., Bowman C. T., Hanson R. K., Gardiner W. C., Lissianski V. V., Qin, Z. W., 2000, GRI-Mech 3.0.

Schwer D. A., Tolsma J. E., Green W. H. Jr., Barton P. I., 2002, On upgrading the numerics in combustion chemistry codes, Combustion and Flame, 128, 270-291.

Turányi T., Tomlin A. S., 2014, Analysis of kinetic reaction mechanisms. Springer, Berlin, Germany.

Warnatz J., Maas U., Dibble, R. W., 2006, Combustion: physical and chemical fundamentals, modeling and simulation, experiments, pollutant formation. Springer, Berlin, Germany.