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The Exergy Fields in Processes

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Abstract
This paper is a very brief review of the method for analyzing the space and time dependent exergy and irreversibility fields in processes. It presents the basic equations, the method for their use, and three examples from the work of the author and his former graduate students: flow desiccation, combustion of oil droplets, and combustion of pulverized coal. Conclusions from this Second Law analysis are used to attempt process improvement suggestions.

Disciplines
Engineering | Mechanical Engineering

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The Exergy Fields in Processes

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Abstract. This paper is a very brief review of the method for analyzing the space and time dependent exergy and irreversibility fields in processes. It presents the basic equations, the method for their use, and three examples from the work of the author and his former graduate students:[1] flow desiccation, combustion of oil droplets, and combustion of pulverized coal. Conclusions from this Second Law analysis are used to attempt process improvement suggestions.

A PERSONAL INTRODUCTION

My interest in the examination of entropy production and exergy destruction in reaction processes, such as in combustion and in nuclear reactions started during my M.Sc. studies in which Arthur Shavit—who just a year earlier finished his Ph.D. studies at MIT under the guidance of George Hatsopoulos and Joseph Keenan—used their excellent and just published book "Principles of general thermodynamics", as the course text, in the course I took in graduate thermodynamics. After joining the faculty of the University of Pennsylvania I established personal contact with both Joe Keenan and George Hatsopoulos, and still remember very gratefully and fondly that Joe Keenan indulged this beginning Assistant Professor by agreeing to give a guest lecture in the graduate thermodynamics course I was teaching, and to discuss with me ranking problems in the field.

EXERGY AS AN EVALUATION CRITERION

Historically, Second Law analysis in its different forms, always focusing on entropy generation and irreversibility, was at first almost entirely oriented to power generation from heat, starting with the fundamental definitions by Gouy [1] and Stodola [2] and, based on Gibbs' work [3], expanded strongly by Keenan's "availability" concept ([4, 5]). Bošnjakovic [6] was one of the early leaders in applying the analysis to chemical processes in his "fight against irreversibility", followed by many others including Rant, who also coined the word exergy [7], Denbigh [8], Leites et al. [9], Brodyanski, Fratzscher, Szargut, Le Goff, Ishida, Rivero, Kjelstrup, and their co-workers.

It is increasingly recognized, and included by now in practically all textbooks on thermodynamics and energy systems design (cf. [10, 11, 12]) that exergy (or Second

[1] William R. Dunbar, Hassan S. Al-Sharqawi, Wladimir Sarmiento-Darkin, and Fanfan Xiong.

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Law) analysis must be added to the conventional energy accounting analysis during the conception, analysis, development, and design of such systems. Most of this analysis is nowadays conducted on the system level development, by evaluating the exergy values and changes of component input and output streams and energy interactions. While this can indeed identify the exergy destruction in a system component, it does not deliver the detailed information about the specific process phenomena, often space and time dependent, which causes the exergy changes in it. The phenomena may include heat transfer, mass transfer, fluid mechanics, chemical and/or nuclear reactions, and the presence of fields such as gravitational, electric and magnetic. This type of detailed analysis, which we shall call "intrinsic", due in the second phase of system development, is invaluable in accelerating the evolution of the innovative systems needed to meet the difficult demands of the coming century, and is the focus of this paper.

Although the objectives of exergy or entropy analysis appear to be obvious, it is very noteworthy to recall that the most important and useful ones are: (1) identification of the specific phenomena/processes that have large exergy losses or irreversibilities, (2) understanding why these losses occur, (3) evaluating how they change with any changes in the process parameters and configuration, and (4) as a consequence of all these, suggestions on how the process could be improved. A surprisingly large fraction of the publications in this field deal only with (1) above, and are therefore of little use, at best.

We start by presenting the basic field equations needed for the intrinsic exergy analysis, briefly survey the state of the art, and present specific examples from our work on convective desiccation and on combustion of oil droplets and of pulverized coal.

THE EXERGY/ENTROPY PRODUCTION FIELD EQUATIONS

The general transient rigorous physico-chemical partial differential equations for computing the intrinsic irreversibilities and exergy destruction in general, needed for this level of analysis, were developed and presented by Dunbar, Lior, and Gaggioli [13], based on earlier work by Hirschfelder et. al [14], Obert [15], and Gaggioli [16], [17]. This change of exergy in time and space was shown to have 30 components, each describing another aspect of the process. The breakdown into such detailed components allows a most careful and detailed examination of the source of irreversibility and exergy destruction.

The information needed for rigorous intrinsic exergy analysis

Evaluation of the magnitudes of these exergy components requires knowledge of the field parameters: velocities (and shear), pressure, temperature (and hence heat flux and the reversible entropy flux), the species concentration (and hence also the species mass flux, and the chemical potential), of the state equations for the materials used, to determine the thermophysical properties, and of the chemical reactions involved (to determine the chemical affinities, and reaction and species production rates) allows the computation of the exergy, exergy destruction, entropy, and entropy generation fields. All of these field parameters are obtained from the solution of the full field and state equations, consisting of the Navier-Stokes, energy, species conservation, entropy generation, and thermodynamic properties equations, combined in a combustion process with the reaction kinetics equations, all tightly coupled.

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An example of exergy analysis in combined flow, heat and mass transfer: convective desiccation

An exergy analysis of the water vapor adsorption process in a desiccant-air stream system, for laminar humid air flow over a desiccant flat bed, as well as in a desiccant-lined channel, and for turbulent humid air flow in such a channel, for different turbulence intensities was conducted [18], and a brief summary is given below.[2]

The physical system considered (Fig. 1) is a flat silica-gel-packed desiccant bed of length L with a uniform air stream passing over it in parallel.

The exergy was calculated using the velocity, temperature and concentration field results in the humid air flow and the desiccant, described in detail in [19]. It was found that the total exergy in the desiccant bed is about 25-fold lower than that in the humid air stream, and the overall average exergy in the combined desiccant-air stream system is dominated by the average chemical exergy in the air stream, so the values are nearly equal to those of the air stream. Typical results are shown in Fig. 2, as a function of the distance along the flow and of the time from the contact with the leading edge of the

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[2] Nomenclature:

b	thickness of silica gel bed, m
C	water vapor concentration, (kg water)/(kg mixture)
C_b	water concentration in desiccant bed, (kg water)/(kg bed+water mixture)
d_i	droplet initial diameter, m
D	droplet diameter, m
E	Exergy, kJ
E_d	exergy destruction in a control mass, kW
E_{in}	exergy flow into a control mass, kW
k_g	thermal conductivity of gas, kW/m
R	coal combustor radius
Re_L	Reynolds number $= u_\infty L/\nu_f$
R_∞	domain radius, m
s	specific entropy, kJ/kg K
$\dot{S}_c$	entropy production rate due to coupling of heat and mass transfer, kW/K
$\dot{S}_{ch}$	entropy production rate due to chemical reaction, kW/K
$\dot{S}_h$	entropy production rate due to heat transfer, kW/K
$\dot{S}_m$	entropy production rate due to mass transfer, kW/K
S	entropy, kJ/K
t	time, s
T	temperature, K
u	x component of velocity, m/s
W	water content in the desiccant, kg/kg
x	flow direction coordinate, m
y	coordinate perpendicular to x, m
Y_{O2}	mass fraction of oxygen
Z	the axial (flow) coordinate of the RCSC
$\dot{\omega}$	reaction rate, kg/m^{3}s
σ	desiccant bed porosity
subscripts	
o	pertaining to the dead state
4	free stream conditions

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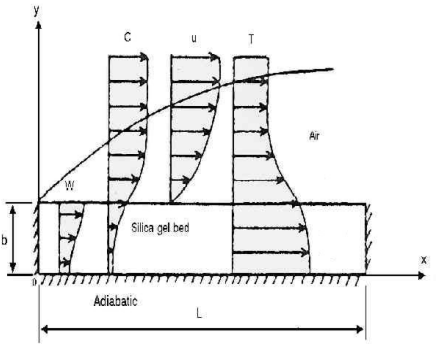

FIGURE 1. The physical model configuration for the flat desiccant bed of length L and thickness b.

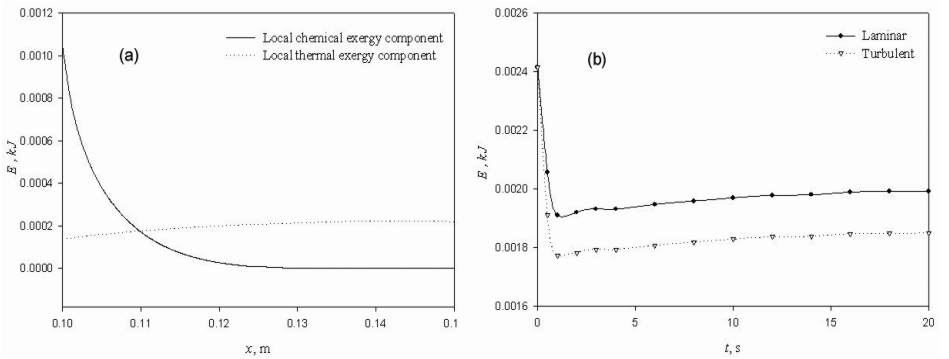

FIGURE 2. (a) Exergy components distribution along the bed in humid air stream. (b) Time dependence of overall average exergy in desiccant-airstream system for laminar and turbulent flows in channel.

bed, respectively. Most of the water absorption takes place in the first cm or so, where the corresponding release of heat of adsorption composes most of the exergy, and the chemical exergy component dominates downstream, where the adsorption diminished significantly. One of the exergy analysis results shown above indicates that the release of heat during the adsorption process expends exergy without any benefit. As a matter of fact, the resulting heating of the air stream being dehumidified is most often detrimental to the ultimate use of this air, such as in air-conditioning applications.

Conclusions and possible constructive uses of the exergy analysis of flow desiccation are:

- In laminar flow, a total of ~20% of the humid air exergy is expended in its drying, but 90% of this is a change in chemical exergy, needed anyway; the temperature rise is <2°C.
- In the desiccant, practically all of the exergy reduction is due to the release of absorption heat, and raising the solid temperature; desiccants with small heat of adsorption are thus desirable.

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- For the same inlet velocity, a desiccant-lined channel is more effective for dehumidification than a flat bed, and proportionally ~20% more exergy is expended.
- Turbulent flow improves dehumidification and proportionally increases exergy expenditure 27% for TI=1% and to 30% for TI=10%.
- Desiccant dehumidification analyzed here is generally an exergy efficient process, only <7% is destroyed due to unused heating.
- Residence times beyond 1.5 s, and beds longer than 1 cm are detrimental.
- Since most of the absorption/desorption takes place near the desiccant entrance and rapidly decreases, optimal design may result from beds which are thicker at the entrance and are gradually thinned with x.
- Synergistically with improved mass transfer coefficients, higher heat transfer coefficients improve efficiency for desiccants that have higher water uptake at lower temperatures.

EXERGY ANALYSIS IN COMBUSTION

Motivation

Past studies have shown that the combustion process typically destroys about one third of the exergy of the fuel. The significance is even clearer when one notes (cf. [20]) that of the many processes occurring in the typical electricity-producing power plant, combustion of the fuel is the single largest contributor of exergy losses in power production. It is thus of great interest to determine the magnitudes and causes of irreversibility in this process (cf. [21, 22]. Dunbar and Lior [23, 24], have probably been the first to evaluate the primary causes for irreversibility, using a somewhat heuristic finite increment exergy analysis method for a simple hydrogen or methane combustor.

An example: exergy analysis of oil droplet combustion [25, 26]

The droplet combustion process was described as follows: the droplet is introduced in a hot atmosphere, and hence its temperature starts to rise and consequently some of it begins to vaporize at its surface. The initial vaporization rate is slower because the droplet is cold, and it increases as the droplet heats up. Fuel vapor diffuses through the hot gas until the criterion for the combustion reaction is met. At this point the reaction starts and the fuel is oxidized to form carbon dioxide and water. The combustion heat released raises the temperature of the gas and of the droplet. Figure 3 illustrates the model. As the droplet continues vaporizing, its radius decreases, thus originating a moving interface between the liquid droplet surface and the outer, gaseous, domain. The process will continue until all the fuel is consumed.

A single spherical droplet of heptane was considered, and a model was developed and solved for the transient mass, temperature, and velocity fields in the gas and droplet (with the temperature and concentration dependence of the properties taken into account), which are then used for the Second Law analysis of the problem. A primary objective of this analysis is to calculate the exergy efficiency ε defined by $\varepsilon = 1 - \frac{E_d}{E_{in}}$ where E_d is the exergy destruction in the defined control mass, and E_{in} is the exergy inflow into it. To use this equation, it is necessary to compute the exergy destruction rate $\dot{E}_d = T_o\dot{S}$, where the total entropy change rate $\dot{S}$ was broken down into its components due to mass

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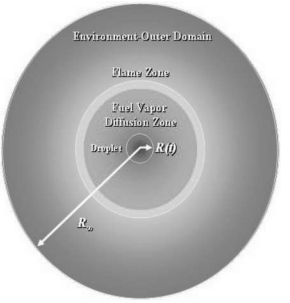

FIGURE 3. A simplified sketch of the burning droplet of regressing diameter $R(t)$.

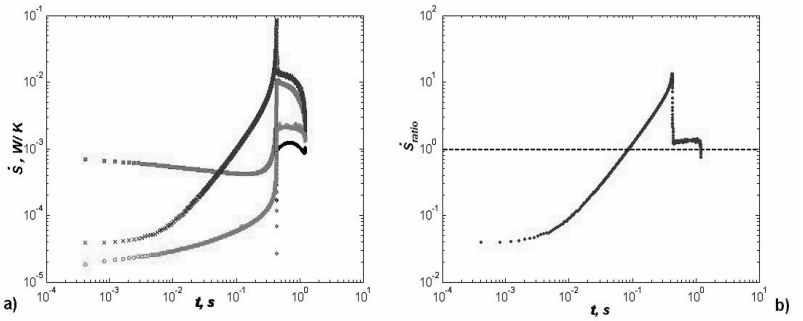

FIGURE 4. Computed history of: (a) $\dot{S}_{ch}$ ($\times$, blue), $\dot{S}_m$ ($\circ$, green), $\dot{S}_h$ ($\square$, red), and $\dot{S}_c$ ($\diamond$, black); and (b) $\dot{S}_{ratio}$ for an n-heptane droplet of $d_i = 0.1$ mm, $T_{li} = 293$ K burning in air at $T_{gi} = 1073$ K.

transfer ($\dot{S}_m$), heat transfer ($\dot{S}_h$), coupling between heat and mass transfer ($\dot{S}_c$), and the chemical reaction ($\dot{S}_{ch}$).

To compare the magnitudes of the chemical reaction entropy generation relative to the other entropy generation terms we also defined and calculated the ratio $\dot{S}_{ratio} = \frac{\dot{S}_{ch}}{\dot{S}_m + \dot{S}_h + \dot{S}_c}$. Figure 4a shows the contributions of each of the entropy terms, and Fig. 4b shows $\dot{S}_{ratio}$, as a function of time. As the droplet evaporation proceeds, the total entropy generation increases due to the increase in the concentration gradients and the increasing rate of the chemical reaction in the gas phase caused by the higher fuel concentration that has been diffused from the droplet, as shown in Fig. 4a. Only $\dot{S}_h$ decreases during the pre-combustion stage of the process [Fig. 4a] due to the diminution of the heat gradient in this period resulting from the progressive rise of the droplet temperature while the gas phase temperature does not vary significantly. Once combustion is attained (at t=0.432 s), the chemical reaction entropy component becomes the main contributor to the total entropy generation. The significance of the dominant role of the chemical component is better seen in Fig. 4b. It shows variation of $\dot{S}_{ratio}$ with respect to time. Figure 5 shows the computed chemical entropy generation during the droplet life. As shown in Fig. 4, the chemical entropy generation dominates the irreversibility production once combustion is attained and therefore Fig. 5 gives a good indication of the evolution of the local irreversibility generation during the combustion process. The rapid increase that the

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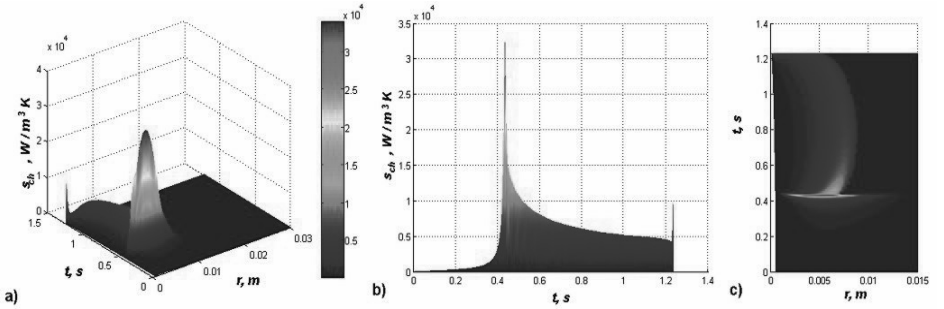

FIGURE 5. The computed (a) $\dot{S}_{ch}$ as a function of position and time, (b) $\dot{S}_{ch}$ evolution in time, and (c) contour plot for $\dot{S}_{ch}$; for an n-heptane droplet of $d_i = 0.1$ mm, $T_{li} = 293$ K burning in air at $T_{gi} = 1073$ K.

chemical entropy generation ($\dot{S}_{ch}$) exhibits when and where the combustion is triggered is clearly seen, and explained in more detail below. The peak value of the chemical entropy generation follows the flame evolution.

The chemical entropy generation term is a function of the gas temperature (T_g) and the reaction rate ($\dot{\omega}$). The maximum of is obtained at t=0.4356 s, which is about 3.4 ms after the criterion to achieve ignition ($T_g > 2000$ K) is met. The maximum of $\dot{S}_{ch}$ occurred at the same time that the maximum of $\dot{\omega}$ is reached, but about 5.4 ms before the maximum T_g is reached. This indicates that the maximum of $\dot{S}_{ch}$ is more influenced by the reaction rate than by the gas temperature profile. The second most important contributor to irreversibility generation is $\dot{S}_h$ that depends on $T_g - 1$, k_g, and $(\nabla T_g)^2$, and further analysis of these terms has shown that $k_g \nabla T_g$ has the dominant influence, interestingly in important part because of the variation of k_g with temperature.

An examination of several possibilities to reduce the irreversibility was made. First, to reduce the temperature gradients during the process, the initial environment temperature was increased by 100 K, from 1073 K to 1173 K, resulting in an increase of 3.7% in ε.

Another way was to examine the effect of slowing down the reaction, done in the analysis by reducing the pre-exponential factor in the kinetics expression to 1/3 of that in the base case value. It was found that the duration of the high entropy production during the combustion reaction is then shorter, while the magnitude of the entropy production rate remains basically the same, but, importantly, the droplet life is much longer for this case, t=1.6605 s, as compared to the other cases evaluated (t=1.233 s for the base-case and t=0.9315 s for $T_{gi} = 1173K$). Consequently the cumulative effect of $\dot{E}_d$ is bigger, counteracting in this way the lower instantaneous entropy values, and thus resulting in a lower ε value.

Since the total magnitude of $\dot{S}_P$ is similar for the evaluated cases for their pre- and post-combustion periods, and taking into consideration that E_{in} will always be the same at the end of the droplet life (because the fuel volume is the same), it is concluded that the duration of the droplet combustion is a key factor in the value of ε, and its reduction may increase ε. To reduce the duration of the droplet combustion, the reaction rate was accelerated by increasing the oxygen mole fraction in the air from 0.23 to 0.70, and this case was called "fast combustion". Table 1 summarizes the main results for these three attempts to increase ε.

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TABLE 1. Summary of results obtained in the attempts to increase the combustion exergy efficiency.

Attempt name	Conditions T_{gi} K	Y_{O2} in air	A	Ignition delay time s	Exergy destruction E_d J	Second law efficiency ε %
Base case	1073	0.23	A	0.432	5.140	68.4
High temperature	1173	0.23	A	0.092	4.749	70.9
Reduced $\dot{\omega}$	1073	0.23	$A/3$	1.195	5.165	68.2
Fast combustion	1073	0.70	A	0.084	4.409	73.2

An example: exergy analysis in a pulverized coal combustion process

In the course of research of a novel low NO_x pulverized coal combustor concept where the flame is stabilized by radiation and conduction from and through the combustor walls, respectively (the Radiatively/Conductively-Stabilized Pulverized Coal Combustor (RCSC), Kim and Lior [27, 28]), a rigorous intrinsic exergy analysis was also performed, and details can be found in [29]. The solution gives the 3-dimensional distribution of gas, particle and wall temperature, and radiation intensity, gas and particle velocity, and species concentrations. As stated earlier, this allows the determination of the spatial distribution of all of the components of exergy.

The computed temperature field in the combustor, for the gas and the coal particles (separately) is shown in Fig. 6. The primary flame region is the meniscus-shaped area about 1/3 down from the top. Among other things, one can observe the gradual heating of the gas and the coal particles, by convection and radiation from the combustor walls, the narrowness of the flame zone (which is an objective of this combustor) and the radial temperature drop due to wall heat losses. Since the thermal exergy is one of the major exergy components, the temperature field is an important indicator of the magnitude of this exergy component.

The thermomechanical, chemical, and total exergy distribution fields are shown in Figs. 8, 9, and 10, respectively (in these figures the direction perpendicular to the axial flow direction of the combustor, Z/R is the radial one, r/R; the numbers 1 along these axis represent $r/R = 0$ and $Z/R = 0$). Some of the conclusions from observing these distributions are: (i) the thermal exergy follows rather closely the temperature field, (ii) the chemical exergy starts decreasing when the volatiles start burning, and then decreases precipitously when the char starts burning, and (iii) the total exergy rises to a peak at the upstream face of the flame front where the temperature is high due to thermal feedback yet the chemical exergy hasn't been completely used up yet.

For the conditions of this study, about 30% of the original fuel exergy is destroyed in the combustion. Over 90% of exergy destruction takes place in the thin flame zone, and less than 10% destroyed downstream of the flame zone, the latter due to the temperature drop and heat loss due to the radiative and convective transport to the surrounding wall and exit. So far, only the effects of inlet air temperature, in the range of 573-973 K, were investigated; increasing it tended to slightly decrease the exergy efficiency, in part because of the increased heat losses.

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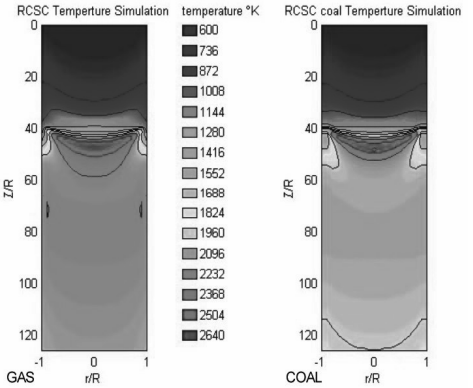

FIGURE 6. The computed temperature distribution for the gas and the coal particles (separately) in the Radiatively/Conductively-Stabilized Pulverized Coal Combustor (RCSC). The flow is downward. Coal feed rate = 0.2 g/s, equilibrium air/fuel ratio = 1.10, inlet air/fuel temperature = 573 K.

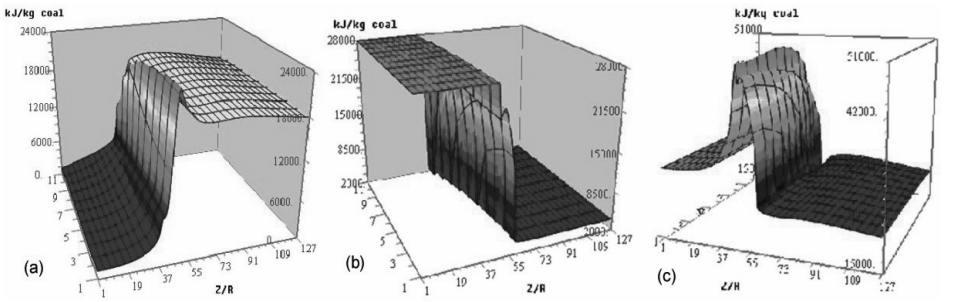

FIGURE 7. (a) Thermomechanical exergy distribution, (b) chemical exergy distribution, (c) total exergy distribution in the RCSC. Same conditions as in Fig. 6.

While one may draw many conclusions from this analysis about possible ways to improve the exergetic efficiency in this combustor, a couple are already evident. One is the effectiveness of thermal feedback: the thermal exergy is raised by this feedback upstream of the flame front to about 1/3 of its maximal value. Another is the possibility of the existence of an optimal combustor exit location for the mixture, where the exergy is higher than the one shown here and yet the reactions were completed to satisfactory extent.

ACKNOWLEDGMENTS

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