UNDERSTANDING COMBUSTION IRREVERSIBILITY

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ABSTRACT

Approximately 1/3 of the useful energy of the fuel is
destroyed during the combustion process used in electri-
cal power generation. This work is an attempt to clarify
and categorize the reasons for the exergy destruction
taking place during uncontrolled fuel oxidation. The
entropy production is separated into three subprocesses:
(1) a combined diffusion/fuel oxidation, (2) an "internal
thermal energy exchange" (heat transfer), and (3) the
product constituent mixing process. Four plausible
process paths are proposed and analyzed. Hydrogen and
methane are considered as the fuels. The results disclose
that the majority (about 3/4) of the exergy destruction
occurs during the internal thermal energy exchange. The
fuel oxidation, itself, is relatively efficient, having
an exergetic efficiency of typically 94% to 97%.

NOMENCLATURE

a_{CH} specific chemical exergy, kJ/kgmole
a_f specific flow exergy, kJ/kgmole
a_{TM} specific thermal mechanical exergy, kJ/kgmole
c_p molar specific heat, kJ/kgmole-°K
E convective energy rate, kJ/s
h specific enthalpy, kJ/kgmole
N molar flow rate, kgmole/s
N_a sum of total number of moles of mixture at reactor
exit
N_p molar production rate, kgmole/s
P pressure, kPa
P_0 atmospheric pressure, kPa
Q heat transfer rate, kJ/s
R universal gas constant, kJ/kgmole-°K
R_f fuel consumption rate, kgmole/s
s specific entropy, kJ/kgmole-°K
S_p entropy production, kJ/°K
T temperature, °K
T_0 reference temperature, °K
A exergy rate, kJ/s
A_d exergy destruction rate, kJ/s

λ chemical affinity, kJ/kgmole
μ electrochemical potential, kJ/kgmole
ν stoichiometric coefficient, kgmole/(kgmole fuel)

χ mole fraction

subscripts
i mass stream index
j species index

superscripts
`   rate (per unit time)
^   per kgmole

INTRODUCTION

Past studies have revealed the combustion process, of the
many processes occurring in the typical electricity-
producing power plant, as the single largest contributor
of exergy losses (cf. Gaggioli et al., 1975). With
present technology, fuel oxidation by uncontrolled
(conventional) combustion at atmospheric pressure
consumes about 1/3 of the fuel's utilizable energy. The
objective of this work is to investigate the sources of
this irreversibility and its underlying reasons.

Specifically, the approach taken in this study is to (i)
describe and quantify the overall (global) entropy
production taking place during combustion, and (ii)
separate and quantify the amount of entropy production
associated with the subprocesses of combustion, namely
constituent mixing, oxidation, and internal thermal
energy exchange, along four conceivable representative
paths of the global combustion process. This computation
along prescribed process paths is an alternative to the
practically intractable rigorous solution of the full
field and state equations (Navier-Stokes, energy, entropy
generation, and thermodynamic properties, cf. Gaggioli
1961, 1962) combined in a combustion process with mass
transfer and reaction kinetics equations, all tightly
coupled. Rigorous analysis of combustion can be performed
(cf. Buckmaster and Ludford, 1982, Arai et al., 1986) but
due to the many simplifications that are introduced to
ease the mathematical problem, and the many uncertain-
ties, especially in the reaction kinetics, the results
are not accurate anyway.

A particular difficulty in applying such formal analysis
to the determination of entropy production (exergy

destruction) is the fact that irreversible thermodynamic processes are path-dependent. Without exact knowledge of the sequence of processes and reactions in the combustion process, the solution of the full field, state, and kinetic equations will provide results which are much harder to obtain and probably no more accurate than those obtained from the below-described analysis along prescribed paths. It is noteworthy that the "rigorous" analysis has so far only been applied to the simplest heat/mass transfer problems, such as flow in two- dimensional channels without any chemical reactions (Bejan, 1979, San et al., 1987), and even that required the use of a number of simplifications and empirical correlations.

GLOBAL ANALYSIS

General Description
We consider steady combustion in a well-insulated combustion chamber. The term "global" refers here to consideration of the combustor as a single "black-box" control volume, with conditions known or determined only at the control-volume inlet and outlet. The global combined First and Second Law analysis is performed here first, and the equilibrium state of the combustor products, the extent of reaction (defined as the molar amount of fuel reacted per mole of fuel input), and the effects of excess air are determined. Two analyses are performed: one with hydrogen and one with methane as the fuels. They are assumed to be pure, at the ambient conditions of 25°C, 1 atm. The oxidant is atmospheric air with an assumed composition of 21% oxygen and 79% nitrogen. The amount of excess air is varied, ranging from 0%-100%. Dissociation of hydrogen and oxygen is deemed negligible (Wark, 1977) at the adiabatic flame temperatures of these reactions.

Mathematical Modeling
Due to the adiabatic boundary restriction and the fact that no work is produced during conventional combustion, the exergy balance is

$$\sum_{in} \Lambda_i = \sum_{out} \Lambda_i + \Lambda_d, \tag{1}$$

i.e., the useful energy associated with the entering matter is equal to the available energy of the exiting matter plus the irreversible destruction of exergy associated with the combustion. Here, the total flow exergy of stream i is

$$\Lambda_i = \dot{N}_i \hat{a}_{f_i} \tag{2}$$

where the total specific exergy of a given flow stream (e.g., stream i) is

$$\hat{a}_{f_i} = \sum_j \chi_{ij} \hat{a}_{f_{ij}} \tag{3}$$

The specific flow exergies are evaluated by employing calculational procedures found in the literature (cf. Rodriguez, 1980), by first separating them into their thermomechanical and chemical components

$$\hat{a}_{f_{ij}} = \hat{a}_{TM_{ij}} + \hat{a}_{CH_{ij}}, \tag{4}$$

where the specific flow exergy, a_f, is composed of two exergy contributions: (1) the specific thermomechanical exergy, a_{TM}, and (2) the specific chemical exergy, a_{CH}. Assuming ideal gas behavior for all components,

$$\hat{a}_{TM_{ij}} = \int_{T_o}^{T} \hat{c}_{p_{ij}} [1 - (T_o/T)] dT + \hat{R}T_o \ln(P/P_o), \tag{5}$$

$$\hat{a}_{CH_{ij}} = \hat{h}_{ij}(T_o) - T_o \hat{s}_{ij}(T_o, P_o) + \hat{R}T_o \ln \chi_{ij} - \mu_{ij}^o. \tag{6}$$

Here for all chemical species j in gas stream i the enthalpies are thus expressed as

$$\hat{h}_j = \hat{h}_{j_o} + \int_{T_o}^{T} \hat{c}_{p_j} dT, \tag{7}$$

and the entropies are expressed as

$$\hat{s}_j = \hat{s}_{j_o} + \int_{T_o}^{T} \hat{c}_{p_j} (dT/T) - \hat{R} \ln(P_j/P_o). \tag{8}$$

The exergy destruction rate can also be expressed as and it was computed in this study in two ways: by using

$$\Lambda_d = T_o \dot{S}_p. \tag{9}$$

Eq. (1) and then by using Eq. (9), to double-check the correctness of the results.

The entropy for Eq. (9) was calculated from the balance

$$\dot{S}_p = \sum_i (\dot{N}_i \hat{s}_i)_{prod} - \sum_i (\dot{N}_i \hat{s}_i)_{reac}. \tag{10}$$

From conservation of chemical species

$$\sum_{out} \dot{N}_i = \sum_{in} \dot{N}_i + N_{p_i}, \tag{11}$$

where the equation of reaction equilibrium is

$$\sum_{prod} v_i \mu_i - \sum_{reac} v_i \mu_i = 0, \tag{12}$$

which can be reduced to an expression for the equilibrium constant, K_p

$$K_p = \frac{\prod_{prod} N_i^{v_i'}}{\prod_{reac} N_i^{v_i'}} \left(\frac{P}{N_a} \right)^{\Delta v}. \tag{13}$$

With no heat or work transfer across the combustor boundaries, the energy conservation equation is

$$\sum_i (\dot{N}_i \hat{h}_i)_{prod} = \sum_i (\dot{N}_i \hat{h}_i)_{reac}. \tag{14}$$

Enthalpies of formation, absolute entropies, chemical exergies, and ideal gas heat capacity coefficients were obtained from Reynolds and Perkins (1977), Rodriguez (1980), Sonntag and Van Wylen (1982), and Gurvich and Veyts (1989).

Boundary Conditions
The boundary conditions for the global reactor are: (1) the fuel and air entrance temperatures are at the assumed reference, ambient temperature of 25°C, (2) incoming fuel and air compositions, (3) the product gas stream exits the reactor under chemical equilibrium conditions, (4) all gas streams are at atmospheric pressure, and (5) the combustion chamber (reactor) walls are adiabatic.

Results of the Global Analysis
Results of the global analysis of hydrogen combustion are contained in Fig. 1. Based on the equilibrium reaction equations (12) and (13), the extent of reaction basically becomes 1.00 (implying complete oxidation of fuel) above 50% excess air. The equilibrium, adiabatic, product gas temperature ranges from 1646°K to 2433°K, decreasing with an increase in the amount of excess air. The exergy efficiency is defined, as are all efficiencies in this
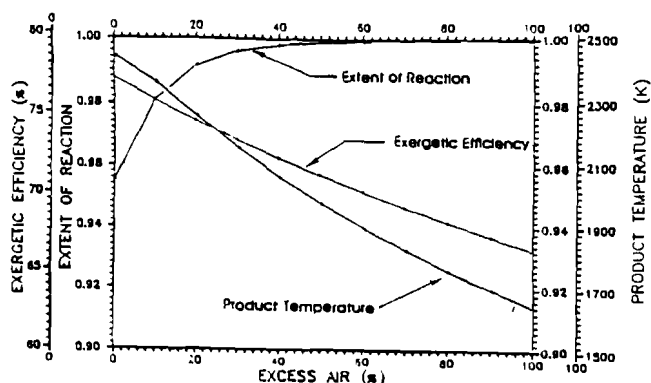
Fig. 1 Exergetic efficiency, extent of reaction and product temperature, vs. excess air, for global analysis of hydrogen combustion.

work, as the ratio of exergy outputs to exergy inputs. The exergetic efficiency of hydrogen combustion ranges from 66.5% to 77.3%, decreasing with increasing amount of excess air. In conclusion, such conventional combustion destroys approximately 23% to 34% of the useful energy of hydrogen fuel for the investigated range of excess air.

Results of the global analysis of methane combustion are contained in Fig. 2. For the range of excess air amount studied, the extent of reaction for water formation ranges from 0.981 to 1.00, basically becoming 1.00 (implying complete formation of water) above 40% excess air. The extent of reaction for carbon dioxide formation ranges from 0.909 to 1.00, basically becoming 1.00 above 50% excess air.
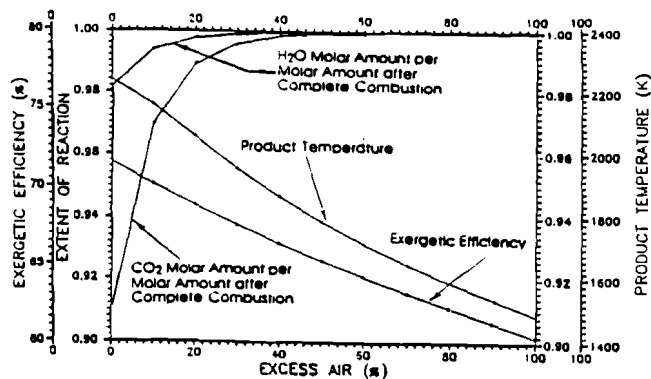

Fig. 2 Exergetic efficiency, extent of reaction and product temperature, vs. excess air, for global analysis of methane combustion.

The equilibrium, adiabatic, product gas temperature ranges from 1480°K to 2249°K, decreasing with an increase in the amount of excess air. The exergetic efficiency of methane combustion ranges from 60.4% to 71.6%, decreasing with increasing amount of excess air. In other words, conventional combustion destroys approximately 28% to 40% of the useful energy of methane fuel for the investigated range of excess air.

The significant degradation of the potential to produce useful work, during combustion, computed above to be 23% to 40% with hydrogen and methane as fuels, was also observed for other types of hydrocarbon fuel combustion (cf. Hedman et al. 1980). This irreversibility has significant detrimental impact in all combustion-based

energy conversion systems in our energy industry, such as residential and commercial space heating furnaces, industrial furnaces for materials processing, internal and external combustion engines, and combustion chambers within power plant boilers. It is thus important to improve our understanding of the phenomena contributing to entropy generation in combustion, and we approach it in the following by a breakdown and quantification of the subprocesses taking place during combustion.

The initial condition before fuel combustion (state 1) includes a fuel stream and an air stream, both at ambient temperature and pressure. The final condition, that after fuel combustion (state 2), is characterized by (i) the presence of a number of new chemical species (e.g., water, carbon dioxide), (ii) a higher temperature, and (iii) all constituents being mixed. The processes which cause these physical changes, fuel oxidation, heat transfer, and product mixing produce the aforementioned amounts of irreversible entropy production. The immediate objective is to conceptually separate and quantify the amounts of entropy production associated with these various physicochemical subprocesses of combustion.

BREAKDOWN OF ENTROPY PRODUCTION IN COMBUSTION

Hirschfelder, Curtiss and Bird (1954) present an expression for the local rate of entropy production. Integrating their equation over the volume of the system results in a relation for the global rate of entropy production:

$$\dot{S}_p = \int g dV$$

$$= \int (1/T) \{ -(\sigma \cdot \nabla T) - (\tau : \nabla v) \qquad (15)$$

$$-\sum_i [J_i \cdot \nabla (\mu_i - \mu_n)] + \sum_j \lambda_j R_j + \sum_i (J_i \cdot g_i) \} dV.$$

The first term on the right-hand-side is the contribution to entropy production due to heat transfer, the second term is that due to momentum transfer (fluid friction), the third and fifth terms are those due to diffusion, and the fourth term is due to chemical reactions. The volume integrals in equation (15) are process-dependent and hence, path-dependent in the thermodynamic sense. To evaluate these volume integrals, the approach taken here is to assume hypothetical sequences of subprocesses, wherein these volume integrals may then be evaluated by surface integrals.

In this study, it is assumed that three physicochemical subprocesses are the primary contributors to the global rate of entropy production: (i) reactant diffusion and fuel oxidation, (ii) internal thermal energy exchange (i. e., heat transfer between gas constituents within the reactor), and (iii) product mixing. Because the magnitudes of the various contributions to entropy production are path-dependent, four conceivable process-paths are studied and the results thereof are compared. Two of these paths assume incremental stages of fuel oxidation; two assume instantaneous fuel oxidation. The equations used are those described in the Mathematical Analysis section above.

The combustion process is envisioned here to proceed in the following manner. As the air and fuel enter the reactor, the oxygen and fuel molecule "sense" each other's presence. They have an intrinsic affinity for each other -- yearning to react due to the greater chemical stability of the oxidation product(s) in comparison to that of the reactants. Thus, the oxygen and fuel molecules are "drawn" together in a diffusion

process which consumes useful power, used to "pull" them from the mixed gas stream.

Having approached the fuel, and with the possibility of a number of series/parallel steps, the oxygen reacts with the fuel, forming product molecules. During this process, there is a concomitant energy conversion: net changes of energy in the forms of (1) "internal-chemical energy" -- energy associated with intramolecular forces, (2) radiation energy (in the case of chemical reactions, most likely, x-ray radiation) and (3) "internal-thermo-mechanical energy" -- associated with particle motions and intermolecular forces between system constituents (Hirschfelder et al., 1954). Having stabilized (react-ed), the participants have added to the system entropy, destroying useful power.

At the instant following the exothermic reaction, the product molecules leave the reaction site with a kinetic energy which is much higher than the statistical average kinetic energy of the neighboring particles. Momentum (and associated kinetic energy) transfers therefore take place, bringing the reaction product temperature down to an equilibrium value consistent with that of the sur-rounding medium. This process, which is here called an "internal thermal energy exchange", also consumes useful power by increasing the entropy of the system. Finally, in a process which occurs simultaneously with the internal-thermal energy exchange, but separated here for the sake of insight, the product molecules mix with the remaining global system constituents, further reducing the system exergy. Hence, the above description provides a categorization (breakdown) of subprocesses that occur within the global combustion process. To summarize, the processes are theoretically separated as follows:

(1) a combined diffusion process (where the oxygen and fuel molecules are drawn together) and a chemical reaction (oxidation of the fuel),

(2) an internal-thermal energy exchange, where the product molecule "shares" its kinetic energy with its neighbors, and

(3) a mixing process whereby system constituents mix uniformly.

The contributions to exergy destruction are calculated below for four process paths. The paths were chosen to represent somewhat limiting conditions in the determina-tion of subprocess irreversibilities, and to be physico-chemically plausible.

Path 1

In this process path the breakdown of combustion irre-versibility is investigated by assuming that (i) fuel oxidation occurs in stages of reaction (i.e., not instantaneously), and (ii) fuel combustion takes place in the subprocess order of (a) reactant diffusion and fuel oxidation, (b) internal thermal energy exchange, and (c) product mixing. Thus, with this scheme, the global combustion process is envisioned to proceed as follows.

Fig. 3 displays schematically the technique of analysis. For example, in chamber 1, the oxygen (only the incremen-tal stoichiometric amount which will react in this chamber) enters a compartment where it reacts with the incremental amount of fuel consumed. Upon reaction, the products exit into chamber 2 at the temperature charac-terized by a completed reaction in an adiabatic chamber. Flowing in a separate compartment, isolated from the reaction momentarily, is the amount of unreacted fuel and the oxygen-depleted air/product streams.

In chamber 2, heat transfer (but no mass transfer) is allowed to take place between the gas particles in the separated compartments of this chamber. All gas tempera-tures exiting chamber 2 are the same (i.e., thermal equilibrium is assumed). Thus, the additional boundary conditions for chamber 2 are: (1) heat transfer (but no mixing) allowed between the compartments within the reactor (but no heat transfer to ambient surroundings), and (2) thermal equilibrium between all constituents at the exit of chamber 2.

Finally, the reaction products and the unreacted air components mix in chamber 3. The boundary conditions for chamber 3 are: (1) uniform mixture of all reaction products and oxygen-depleted air stream at exit, and (2) adiabatic boundaries.
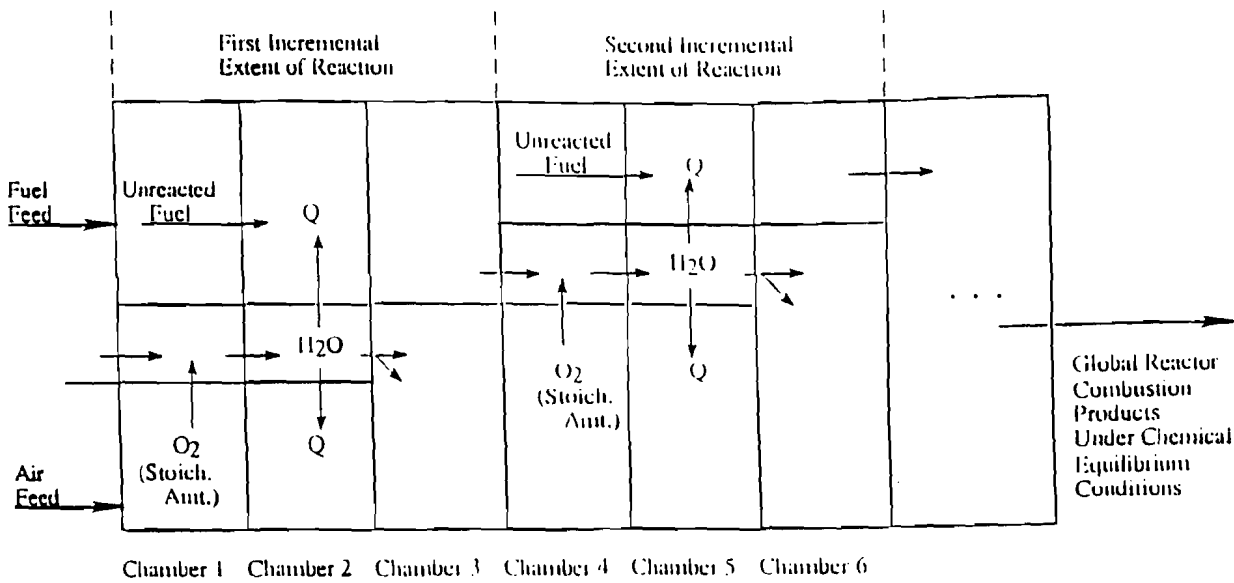
Following the first incremental extent of reaction, the gas components flow into chamber 4, repeating these steps of combustion for the second (and subsequent) incremental extent(s) of reaction. This procedure is repeated until the gas constituents reach the fuel ignition temperature, whereupon the fuel oxidation is assumed to be instanta-neous (i.e., all the remaining fuel is oxidized immedi-ately at the fuel ignition temperature). The assumed fuel ignition temperatures are 582°C for hydrogen and 690°C for methane (Babcock and Wilcox, 1978). The final products of combustion then exit the reactor under the required global system equilibrium conditions.

Effects of increment size. An analysis was first performed to determine the sensitivity of the results to the number of increments in the process described in Fig. 3. These results are displayed in Figures 4 and 5 for the cases of 0% and 50% excess air amount.

As shown, at a number of increments of about 100 the results approach a value which does not change with the increase of the number of increments. This is because the reactants' conditions have smaller changes, for given overall process beginning and end states, as the number of increments becomes larger. For example, the increase in temperature in each increment, for an excess air value of 100% and at 500 increments is only about 1 to 2 K.

The exergy destruction due to oxidation decreases with increasing number of increments because larger percentag-es of the fuel oxidation are evaluated under more efficient conditions; i.e., at higher temperatures and therefore closer to equilibrium (hence more reversible see Fig. 6). Five hundred increments were chosen for the following combustion irreversibility breakdown analysis, thus assuring the determination of increment-size-independent exergy destruction values for the assumed sequence of subprocesses in this path.

Breakdown of Overall Exergy Consumption. The relevant results of the breakdown of exergy losses in hydrogen combustion are given in Fig. 7. The significant result is that the largest subprocess exergetic consump-tion takes place during the internal thermal energy exchange (chambers 2, 5, etc. in Fig. 3). The exergetic efficiency of this subprocess is 73% to 83%, decreasing with increasing amounts of excess air, i.e. approximately 72-77% of the overall exergy loss of the combustion process is associated with it. The reaction (oxidation, in chambers 1, 4, etc., in Fig. 3) has a 94% to 95% exergetic efficiency and destroys about 15% to 18% of the total exergy loss, and gas constituent mixing (in chambers 3, 6, etc., in Fig. 3) has an exergetic effi-ciency of 96.5% to 97.4%, destroying the remaining 8% to 10% of the total exergy loss.

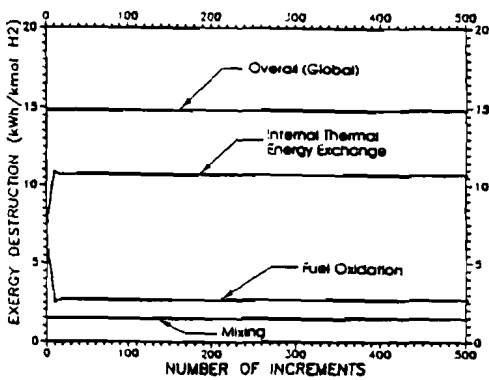| Chamber	Process
1	Diffusion/Reaction ($H_2 + 1/2 O_2 \rightarrow H_2O$)
2	Internal Thermal Energy Exchange
3	Mix (Products/Depleted Air)
4	Diffusion/Reaction
5	Internal Thermal Energy Exchange
6	Mix (Products/Depleted Air)

Fig. 3 Hypothetical combustion chamber for Process Path 1.

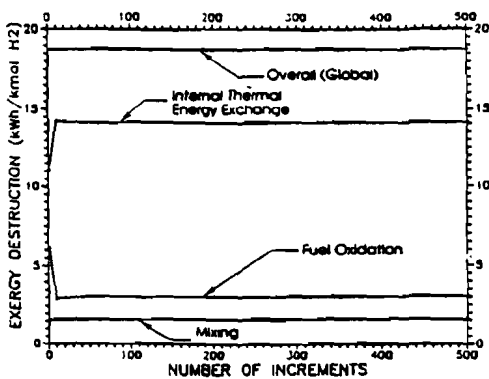Fig. 4 Exergy destruction vs. number of process increments, for 0% excess air.

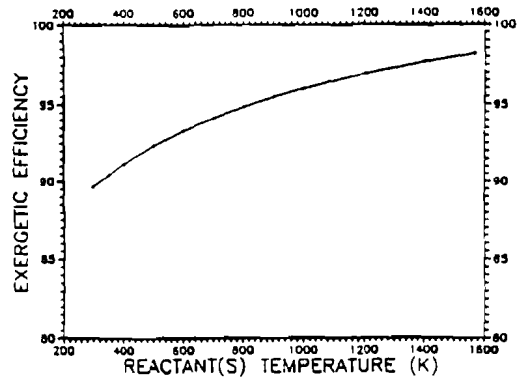Fig. 5 Exergy destruction vs. number of process increments, for 50% excess air.

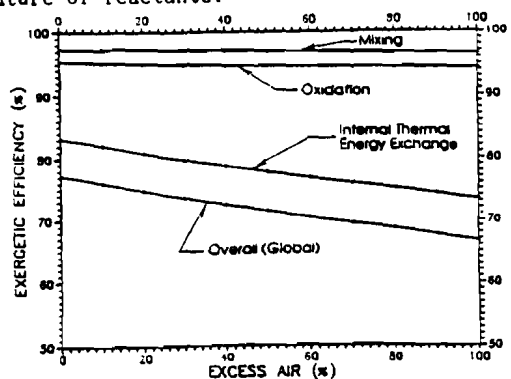Fig. 6 Exergetic efficiency of hydrogen oxidation vs. temperature of reactants.

Fig. 7 Exergetic efficiency of the hydrogen combustion process, Path 1, vs. excess air.

The overall (global) exergetic efficiency ranges from 66.5% to 77.3%, decreasing with increasing amounts of excess air.

Path 2

In this process path, described in Fig. 8, we study the breakdown of combustion irreversibility assuming that (i) all the fuel and air mixed in the first step, before reaction, (ii) fuel oxidation occurs progressively in a number of discrete stages of reaction, and (iii) fuel combustion takes place in a repeating series of two-step subprocesses: (a) fuel oxidation, and (b) internal thermal energy exchange. These subprocesses are repeated until the required exit equilibrium product gas state is attained. The boundary conditions for chamber 1 in which mixing takes place (Fig. 8) are: (1) the incoming matter rate, composition, and temperature for both the fuel and air, (2) adiabatic boundaries, (3) no chemical reactions, and (4) the gas constituents exit as a uniform mixture. The boundary conditions for the fuel oxidation chambers (2, 4, etc., Fig. 8) are: (1) adiabatic boundaries, (2) the gas constituents exit as a uniform mixture, (3) the oxidation product gas constituents (their quantity computed from the increment in extent of reaction) exit under complete adiabatic reaction conditions, and (4) the gas constituents not involved in the oxidation exit with the same temperature as that when entering the chamber.

Finally, following the fuel oxidation, the internal thermal energy exchange subprocess occurs (in chambers 3, 5, etc., Fig. 8). The boundary conditions for these chambers are: (1) adiabatic boundaries, (2) uniform mixture of gas constituents, (3) thermal equilibrium prevails between all system gas constituents at the exit.

Following the first incremental extent of reaction, the gas components flow into the downstream chambers, repeating these steps of combustion for the subsequent incremental extent(s) of reaction. This procedure is repeated until the gas constituents reach the fuel ignition temperature, whereupon the fuel oxidation is assumed to be instantaneous (i.e., all the remaining fuel is oxidized immediately at the fuel ignition temperature). The final products of combustion then exit the reactor under the required global system equilibr conditions.

As in the Path 1 study, an analysis was first perforr to determine the sensitivity of the results to the cho number of increments. The results of this analysis w similar to those shown in Figs. 4 and 6 describ. results of the Path 1 analysis. Two hundred increme were chosen for the Path 2 analysis, amply adequate ensure results independent of increment number.

Qualitatively similar to the results of the Path analysis, the largest exergy destruction, 66% to 73% the total, takes place during the internal thermal ener exchange (chambers 3, 5, etc., Fig. 8). The fu oxidation (chambers 2, 4, etc., Fig. 8) is responsib for 18% to 25% of the exergy destruction. The mixi process consumes about 8% to 10% of the total exer destruction. The corresponding subprocess exerget efficiencies, which reflect these results, are display in Fig. 9.
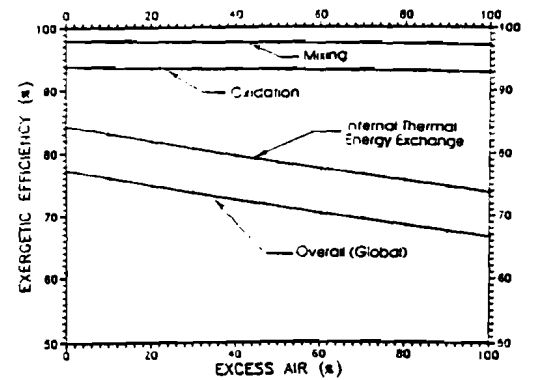

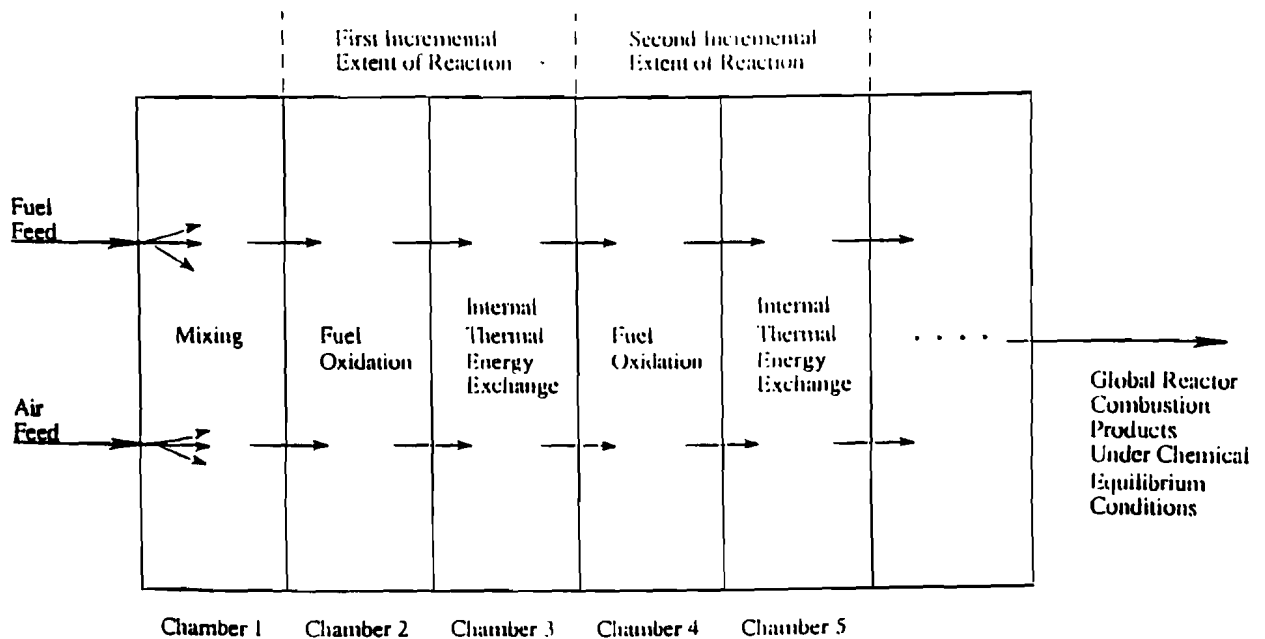Fig. 9 Exergetic efficiency of the hydrogen combusti process, Path 2, vs. excess air.

Fig. 8 Hypothetical combustion chamber for Process Path 2.

Path 3

In this process path, described in Fig. 10, we study the breakdown of combustion irreversibility assuming that (i) the fuel and air are internally preheated to the ignition temperature, (ii) the fuel is oxidized instantaneously at the ignition temperature, and (iii) fuel combustion takes place in the subprocess order of (a) internal reactant preheating, (b) reactant diffusion/fuel oxidation, (c) internal thermal energy exchange, and (d) product mixing. Thus, with this scheme, the global combustion process is envisioned to proceed as follows.

As the air and fuel enter the reactor, these reactants are internally preheated (via, e.g., back radiation from the downstream combustion products). Upon reaching the ignition temperature, the fuel is oxidized instantaneously. The instant following this exothermic reaction, the product molecules transfer energy to the neighboring constituents in the internal thermal energy exchange subprocess. Finally, the oxidation products and inert gas constituents mix uniformly. The boundary conditions for chamber 1 are: (1) the incoming matter rate, composition, and temperature for both the fuel and air, (2) no chemical reactions, and (3) both the fuel and air exit the chamber at the ignition temperature.

In chamber 2, the fuel and oxygen react instantaneously. The boundary conditions for this chamber are: (1) product gas exits at a temperature characterized by a completed reaction in an adiabatic chamber, (2) the amount of unreacted fuel and the oxygen-depleted air exit at the same temperature as when entering chamber 2, and (3) adiabatic boundaries.

In chamber 3, internal heat transfer (but no mixing) is allowed to take place (i) between the gas particles in the separated compartments of this chamber, and (ii) between the gas in this chamber and the lower temperature fuel and air in chamber 1. Thermal equilibrium prevails between all constituents at the chamber 3 exit.

Finally, in chamber 4, all the constituents mix uniformly. Thus, the two additional boundary conditions for this chamber are: (1) adiabatic boundaries, and (2) uniform composition and temperature at the chamber exit, the exiting gas leaving under the required global chemical equilibrium conditions.

Qualitatively similar to the results of the studies performed using Paths 1 and 2, the internal thermal energy exchange subprocess is again responsible for the majority of the combustion irreversibility. According to the results of this study, this subprocess, which includes the effects of internal preheating, destroys approximately 74% to 80% of the total exergy destroyed in the process. The fuel oxidation destroys about 12% to 16% of the total exergy destroyed, and the mixing process is responsible for approximately 8% to 10% of the combustion exergy destruction. The exergetic efficiencies, reflecting also these results, are displayed in Fig. 11.
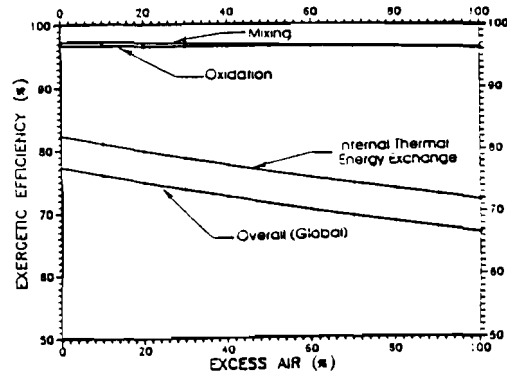

Fig. 11 Exergetic efficiency of the hydrogen combustion process, Path 3, vs. excess air.
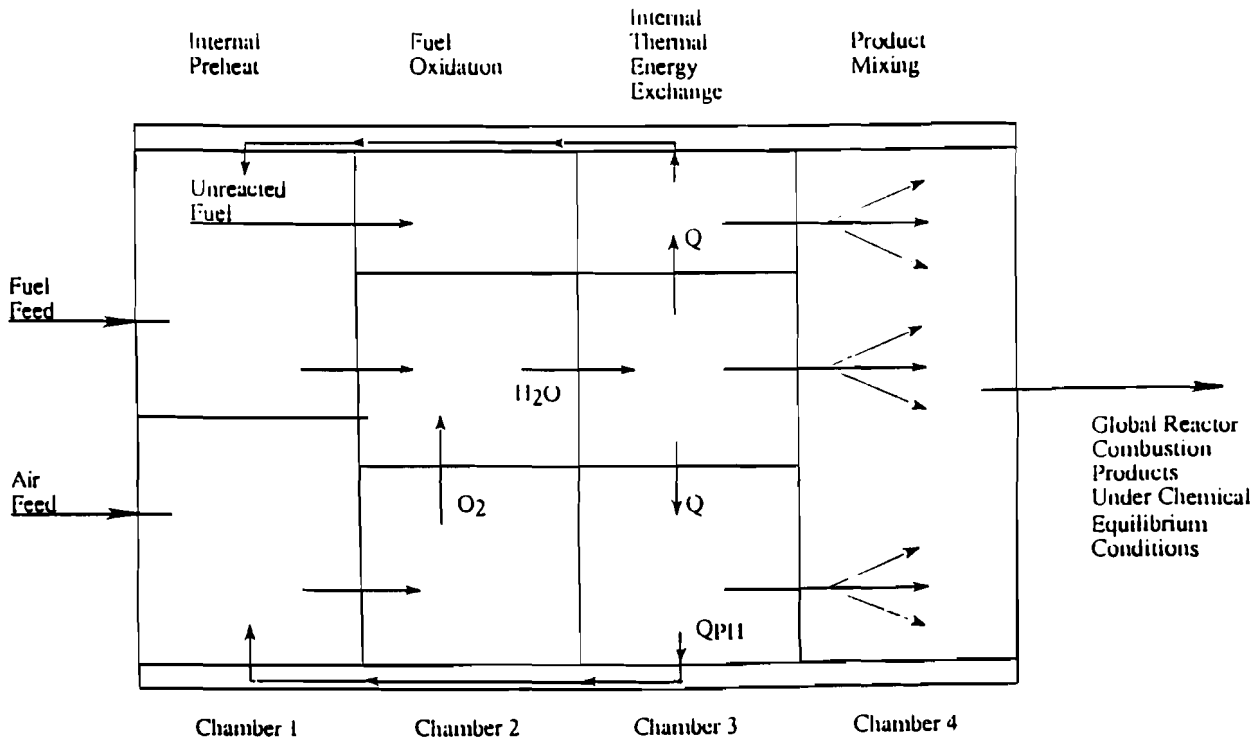

Fig. 10 Hypothetical combustion chamber for Process Path 3.

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Path 4

In this process path, described in Fig. 12, we study the breakdown of combustion irreversibility assuming that (i) the fuel and air are internally preheated to the ignition temperature. (ii) the fuel is oxidized instantaneously at the ignition temperature, and (iii) fuel combustion takes place in the subprocess order of (a) reactant mixing, (b) internal reactant preheating, (c) fuel oxidation, and (d) internal thermal energy exchange. The global combustion process is thus envisioned to proceed as follows.

As the air and fuel enter the reactor, the reactants mix uniformly. Although internal preheating is occurring at the same time, the internal preheat process is analyzed separately in order to quantify the irreversibility associated with these two subprocesses. Thus, after the mixing, the reactants are internally preheated to the ignition temperature. Following the mixing and internal preheating processes, the fuel is oxidized instantaneously at the ignition temperature. Finally, the internal thermal energy exchange subprocess occurs, wherein the products then exit the reactor under thermal and chemical equilibrium conditions.

As shown, in chamber 1, all the reactant gas constituents mix uniformly. The boundary conditions for this chamber are: (1) the incoming matter rate, composition, and temperature for both the fuel and air, (2) no chemical reactions, (3) the gas exits with a uniform composition at ambient temperature and pressure, and (4) adiabatic boundaries.

In chamber 2, the fuel and air are internally preheated to the ignition temperature. The source of heat is the hot product gas in chamber 4, downstream of the fuel oxidation chamber. The additional boundary conditions for this chamber are: (1) no chemical reactions, and (2) both the fuel and air exit the chamber at the ignition temperature.

In chamber 3, the fuel and oxygen react instantaneously. The boundary conditions for this chamber are: (1) the oxidation product gas molecule exit at a temperature characterized by a completed reaction in an adiabatic chamber, (2) the unreacted fuel and air, and the inert gases exit at the same temperature as when entering chamber 3, and (3) adiabatic boundaries.

Finally, in chamber 4, internal heat transfer occurs (i) between the gas constituents in this chamber, and (ii) between the gas in this chamber and the lower temperature fuel and air in chamber 2. The product gas exits chamber 4 under thermal and chemical equilibrium conditions.

Again qualitatively similar to the results of the studies performed using Paths 1, 2 and 3, the internal thermal energy exchange subprocess is responsible for the majority of the combustion irreversibility. According to the results of this study, this subprocess, which includes the effects of internal preheating, destroys approximately 74% to 80% of the total exergy destroyed in the process. The fuel oxidation destroys about 12% to 16% of the total exergy destroyed, and the mixing process is responsible for approximately 8% to 9% of the combustion exergy destruction. The exergetic efficiencies, reflecting also these results, are displayed in Fig. 13.

To observe the effect of fuel type on combustion subprocess irreversibility, the Path 4 combustion process was reevaluated using methane as fuel. Qualitatively, the results are similar to those obtained from the hydrogen combustion breakdown analysis. The internal thermal energy exchange subprocess is responsible for the majority of the combustion irreversibility. This subprocess, which includes the effects of internal preheating, destroys approximately 57% to 67% of the total exergy destroyed in the process. The fuel oxidation destroys about 30% to 40% of the total exergy destroyed, and the mixing process is responsible for
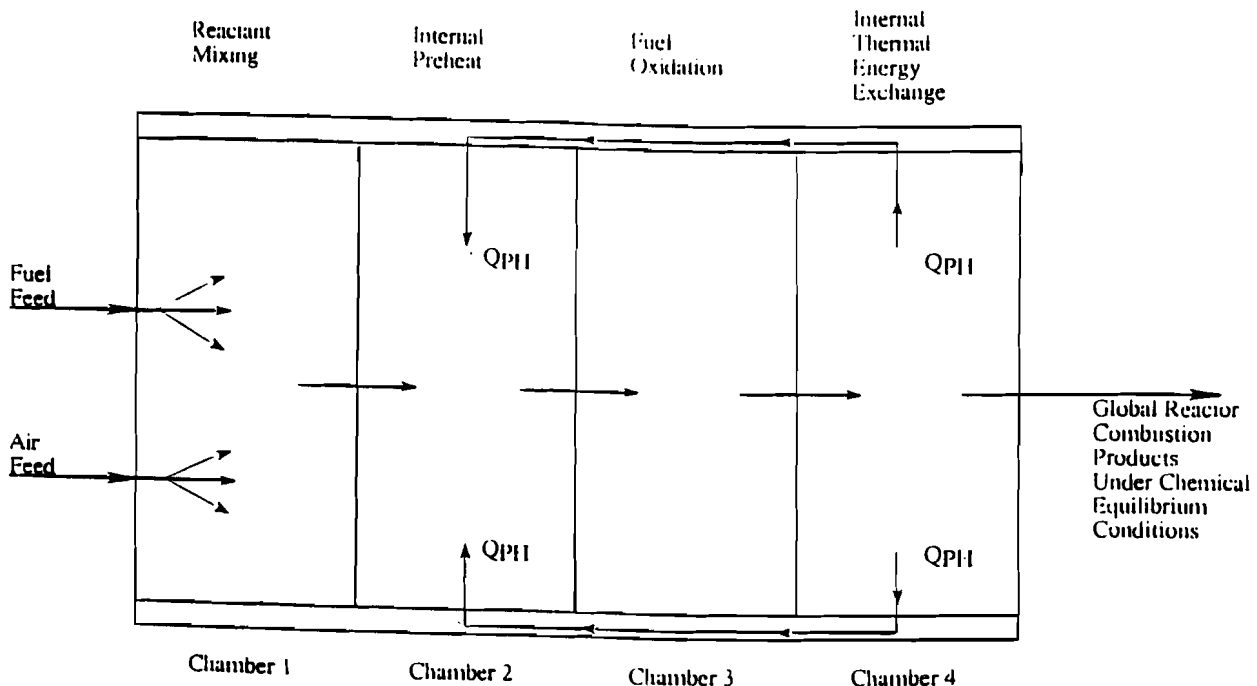

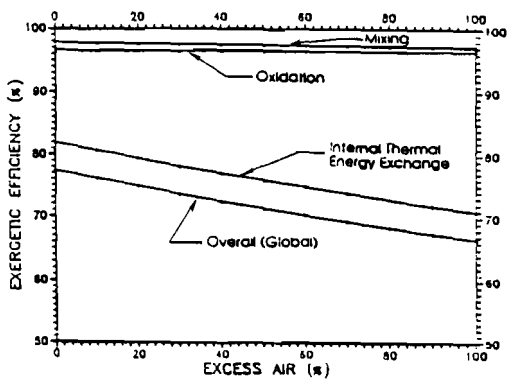Fig. 12 Hypothetical combustion chamber for Process Path 4.

Fig. 13 Exergetic efficiency of the hydrogen combustion process. Path 4, vs. excess air.

about 3% of the combustion exergy destruction. The exergetic efficiencies, reflecting also these results, are displayed in Fig. 14.
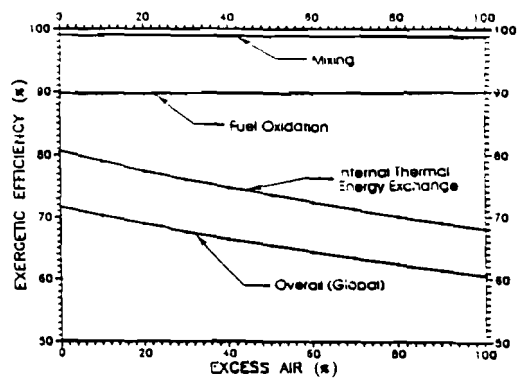

Fig. 14 Exergetic efficiency of the methane combustion process. Path 4, vs. excess air.

The main difference between the hydrogen and methane combustion exergy destruction breakdown results is that the methane oxidation subprocess destroys a fraction of the overall exergy loss which is about 2.5-fold larger than that destroyed in hydrogen combustion, and the destruction of exergy in the internal energy exchange and mixing are smaller.

ADDITIONAL DISCUSSION

Comparison of the Results from the Four Process Paths Analyzed

The results of the four different hypothetical process paths have revealed that the internal thermal energy exchange subprocess is responsible for more than 2/3 of the global exergy destruction. This is shown in Fig. 15, as a function of excess air.

The Effect of Pre-mixing

Paths 1 and 3 assume that full mixing occurs after reaction, while Paths 2 and 4 assume pre-mixing. No perceptible differences were found between these modes of mixing in the exergetic efficiency of the mixing subprocess.

The Effect of Internal Preheat

As discussed earlier, internal preheating is the process wherein fuel and air are preheated within the combustion

chamber prior to reaction by heat transfer from hot upstream products of reaction and the colder entering fuel and air (reactants), via radiation and possibly conduction in the combustor walls.
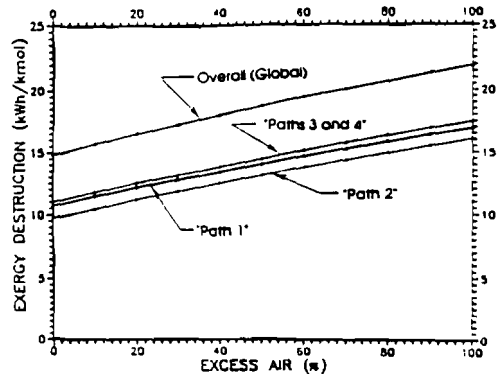

Fig. 15 Exergy destruction due to internal thermal energy exchange in hydrogen combustion, vs. excess air.

To explain the effect of internal preheat let us consider first the results from Path 1 and Path 3, which differ primarily by the fact that Path 3 has internal preheat while Path 1 does not. Path 1 assumes the fuel is oxidized in increments until the ignition temperature is attained, whereupon the remaining fuel is oxidized. With this scheme, approximately 10-25% of the fuel is oxidized prior to reaching the fuel ignition temperature. In this path, 72%-77% of the total combustion exergy destruction occurs due to the internal thermal energy exchange subprocess.

Path 3, on the other hand, assumes the identical sequence of subprocesses, except that, prior to any oxidation, the reactants are heated to the ignition temperature, at which the fuel is then oxidized instantaneously. The results of this scheme disclose that the internal thermal energy exchange and internal preheating are responsible for approximately 74%-80% of the total combustion irreversibility. Thus, according to these results, internal preheating to the ignition temperature prior to reaction causes the internal heat transfer irreversibility to increase by about 2%-3% of the total combustion irreversibility. A similar comparison between the results of Paths 2 and 4" reveals that this internal preheating raises the internal heat transfer exergy destruction by approximately 7%-8% of the total combustion irreversibility. These effects are also displayed in Fig. 15.

CONCLUSIONS AND RECOMMENDATIONS

The understanding of the sources of combustion irreversibility and its underlying reasons was improved by decomposing the overall exergy destruction into hypothetical subprocess contributions. The results obtained from the analysis indicate that the major contribution to the destruction of useful energy occurring in typical gaseous hydrocarbon fuel combustion is due to the internal thermal energy exchange (heat transfer) between particles within the system.

Since these kinetic energy (or momentum) transfers are inevitable, to reduce entropy production during combustion the above conclusion points to the need to seek means for reducing the amount of conversion of the reactants' "chemical energy" to the form of "thermal

energy" which causes this undesirable internal thermal energy exchange.

One such way, employing fuel cells, is already being explored by the authors (cf. Dunbar 1983, Dunbar et al. 1990). Described briefly, fuel oxidation performed in fuel cells produces useful work (electricity) during the process, thus generating less internal thermal energy and entropy between the process end-states, and resulting in a significantly more efficient process. An alternative technique, using metal oxides, was proposed by Richter and Knoche (1983). These are good examples of how exergy analysis leading to fundamental understanding of process irreversibilities can point to the development of more efficient practical processes.

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