

Sources of 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 electrical power generation. This study is an attempt to clarify and categorize the reasons for the exergy destruction taking place in combustion processes. The entropy production is separated into three subprocesses: (1) combined diffusion/fuel oxidation, (2) "internal thermal energy exchange" (heat transfer), and (3) the product constituent mixing process. Four plausible process paths are proposed and analyzed. The analyses are performed for two fuels: hydrogen and methane. The results disclose that the majority (about 3/4) of the exergy destruction occurs during the internal thermal energy exchange. The fuel oxidation, by itself, is relatively efficient, having an exergetic efficiency of typically 94% to 97%.

Key Words: Combustion, exergy, second-law analysis, power generation, irreversibility, thermodynamics

NOTATION

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
\dot{E}	Convective energy rate, kJ/s
F	Body force, N
\dot{g}	Volumetric rate of entropy production, kJ/K.m ³ s
h	Specific enthalpy, kJ/kgmole
\dot{J}_i	Molar flux of component i , kgmole/m ² s
\dot{N}	Molar flow rate, kgmole/s
P	Pressure, kPa
P_o	Atmospheric pressure, kPa
\dot{Q}	Heat transfer rate, kJ/s
R	Universal gas constant, kJ/kgmole.K
R_j	Rate of reaction j , kgmole/s
s	Specific entropy, kJ/kgmole.K
\dot{S}_p	Entropy production rate, kJ/K.s
T	Temperature, K
T_o	Reference temperature, K
v	Velocity vector, m/s
V	Volume, m ³

$\dot{\Lambda}$	Exergy rate, kJ/s
$\dot{\Lambda}_d$	Exergy destruction rate, kJ/s
λ	Chemical affinity, kJ/kgmole
μ_i	Chemical potential of component i , (kJ/kgmole fuel)
σ	Spatial thermal conductivity vector, kJ/m.K.s
T	Stress tensor, N/m ²
X_i	Mole fraction of component i

Subscripts

i	Mass stream index
j, n	Species index
•	Dead state conditions

Superscripts

Rate (per unit time)

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 conventional ("uncontrolled") 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, proposed by Dunbar and Lior (1990), is an alternative to the extremely difficult 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 uncertainties, the accuracy of the result is not likely to exceed that of the simplified solution shown here. The "rigorous" analysis has indeed 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; Poulidakos and Johnson, 1989), and the case of premixed flames stabilized above a flat-flame burner (Arpaci and Selamet, 1988), and even that required the use of a number of simplifications and empirical correlations.

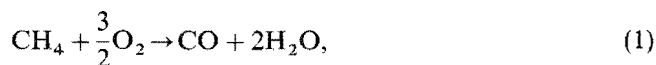
To conclude, while it is widely known by now that combustion creates a major exergy loss, it was not yet made clear how and where specifically this loss is incurred in this highly-complex process. Such quantitative understanding is sought in this study. Apart from its fundamental value, this understanding is a vital starting point for the search for practical means for the realization of more efficient combustion and power generation systems.

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 modeling 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, from balances on energy and chemical species, property relations, and the relevant temperature-dependent equilibrium constants. Two analyses are performed: one with hydrogen and one with methane as the fuel. The fuels are assumed to be pure, at the ambient conditions of 25°C, 1 atm. These conditions also define the dead (reference) state; for the hydrogen and methane fuels it is that of their combustion products: H₂O, and CO₂ and H₂O, respectively. 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%.

In the case of hydrogen combustion, the product gas stream is assumed to consist of unreacted diatomic hydrogen and oxygen, inert diatomic nitrogen, and water. This assumption is made even though there may in reality be additional species present at the calculated adiabatic flame temperatures, due to molecular dissociation, incomplete combustion, and other reactions. For example, at a temperature of 2500 K, there is a very small amount (less than 0.1%) of molecular dissociation of diatomic hydrogen, oxygen and nitrogen to the respective monatomic species, as well as similarly small amounts of dissociation of H₂O (cf. Vargaftik, 1975; Wark, 1977). The amount of OH⁻ and NO molecules formed is somewhat higher. While the inclusion of these additional reactions would make the results of the analysis slightly more precise, they would not have a significant effect on the objectives of this study, which is the understanding of the major sources of irreversibility in combustion, and would add much to the complexity of the analysis. Such minor side-reactions were therefore ignored in this study. Similarly, in the case of methane combustion, the reactions are described by



with inert nitrogen, carried in with the combustion air and removed with the combustion products, existing in both.

Second Law analysis

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

$$\sum_{\text{in}} \dot{\Lambda}_i = \sum_{\text{out}} \dot{\Lambda}_i + \dot{\Lambda}_d, \quad (3)$$

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

$$\dot{\Lambda}_i = \dot{N}_i a_{f_i} \quad (4)$$

where the total specific exergy of a given flow stream (e.g., stream i), as summed over all the species j , is

$$a_{f_i} = \sum_j X_{ij} a_{f_{ij}}, \quad (5)$$

where

$$a_{f_j} = h_j - T_o s_j - \mu_{oj} = h_j - T_o s_j - h_{oj} - T_o s_{oj}. \quad (6)$$

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

$$a_{f_{ij}} = a_{TM_{ij}} + a_{CH_{ij}}, \quad (7)$$

where the specific flow exergy, a_{f_j} , 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,

$$a_{TM_{ij}} = \int_{T_o}^T c_{p_{ij}} \left(1 - \frac{T_o}{T} \right) dT + RT_o \ln \frac{P}{P_o}, \quad (8)$$

$$a_{CH_{ij}} = h_{ij}(T_o) - T_o s_{ij}(T_o, P_o) + RT_o \ln X_{ij} - \mu_{o,ij}. \quad (9)$$

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

$$h_j = h_{j_o} + \int_{T_o}^T c_{p_j} dT, \quad (10)$$

and the entropies are expressed as

$$s_j = s_{j_o} + \int_{T_o}^T c_{p_j} \frac{dT}{T} - R \ln \frac{P_j}{P_o}. \quad (11)$$

The exergy destruction rate can also be expressed as

$$\dot{A}_d = T_o \dot{S}_p \quad (12)$$

and it was computed in this study in two ways: by using Eq. (4) and then by using Eq. (12), to double-check the correctness of the results.

The entropy for Eq. (12) was calculated from the balance

$$\dot{S}_p = \sum_i (\dot{N}_i s_i)_{out} - \sum_i (\dot{N}_i s_i)_{in} \quad (13)$$

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 Veys (1989).

Boundary conditions

The boundary conditions for the global, steady 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 Figure 1. Based on the equilibrium reaction equations, the extent of reaction basically becomes 1.00 (implying complete oxidation of fuel) above 50% excess air. The equilibrium, adiabatic,

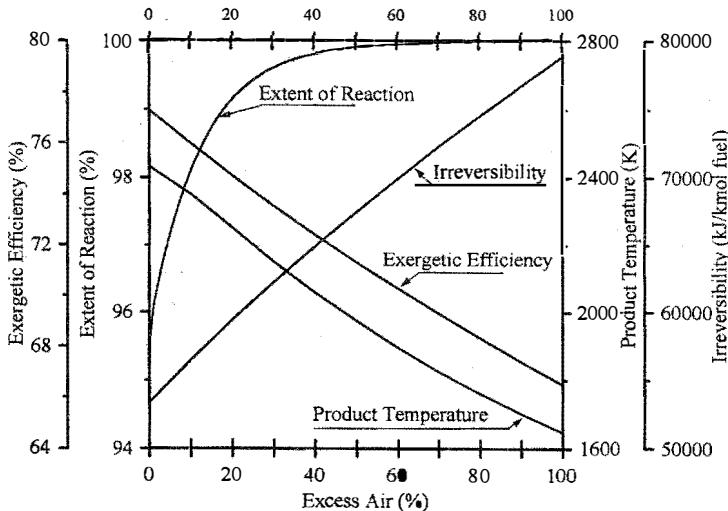


FIGURE 1 Exergetic Efficiency, Extent of Reaction, Product Temperature and Irreversibility, vs. Excess Air for Global Analysis of Hydrogen Combustion.

product gas temperature ranges from 1646 K to 2433 K, decreasing with an increase in the amount of excess air. The amount of entropy production during the combustion increases with excess air, ranging from 53, 667 to 78, 833 kJ/(kgmole H_2). Finally, the concomitant thermodynamic cost of this entropy production is determined by evaluating the exergy destruction (combustion irreversibility) displayed in Figure 1 via the exergy efficiency, as a function of the amount of excess air. The exergy efficiency is defined as the ratio of exergy outputs to exergy inputs. The exergetic efficiency of hydrogen combustion ranges from 66% to 77%, decreasing with increasing amount of excess air. The irreversibility is calculated by Equation (12). 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 (Eqs. 1 and 2) are contained in Figure 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.

The equilibrium, adiabatic, product gas temperature ranges from 1480 K to 2249 K, decreasing with an increase in the amount of excess air. The amount of entropy production increases with increasing amount of excess air, ranging from $(2.456)10^5$ to $(3.611)10^5$ kJ/(kgmole CH_4). The exergetic efficiency of methane combustion ranges from 60% to 72%, 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

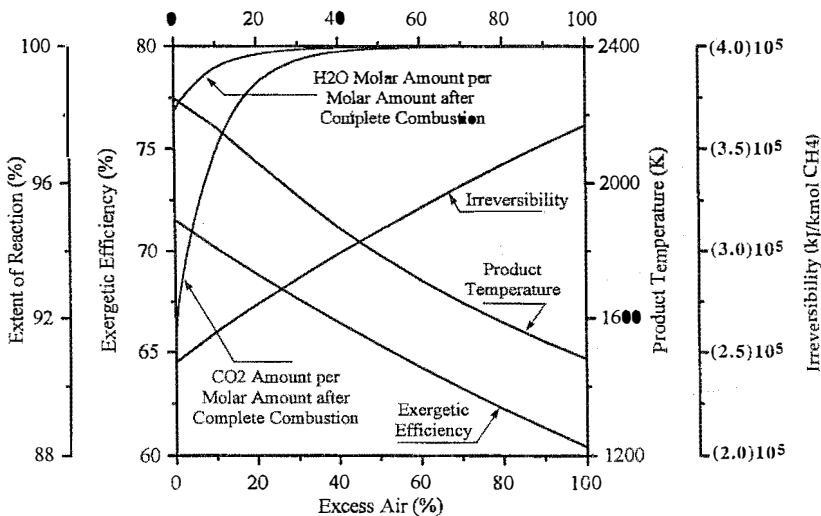


FIGURE 2 Exergetic Efficiency, Extent of Reaction, Product Temperature and Irreversibility vs. Excess Air for Global Analysis of Methane Combustion.

irreversibility has significant detrimental impact in all combustion-based energy conversion systems in the energy industry, such as residential and commercial space heating furnaces, industrial furnaces for materials processing, combustion chambers within power plant boilers, external combustion engines, and internal combustion engines (in which the irreversibilities are even higher). 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: reactant mixing, 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 (discussion of the breakdown of the exergy equation into its components can be found in Dunbár *et al.*, 1992). Integrating the equation over the volume of the system results in a relation for the global rate of entropy production:

$$\begin{aligned} \dot{S}_p &= \int_V \dot{g} dV \\ &= \int_V \frac{1}{T} \left\{ -(\sigma \cdot \nabla T) - (T \cdot \nabla V) - \sum_i [j_i \cdot \nabla (\mu_i - \mu_n)] + \sum_j \lambda_j R_j + \sum_i (j_i \cdot F_i) \right\} dV. \quad (14) \end{aligned}$$

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 the action of chemical potential gradients and body forces, respectively, on diffusion mass fluxes, and the fourth term is due to chemical reactions. The volume integrals in Equation (18) 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 fluid friction and body-force energy are negligible and that thus four physicochemical subprocesses are the primary contributors to the global rate of entropy production: (i) reactant diffusion, (ii) reaction (fuel oxidation), (iii) internal thermal energy exchange (i.e., heat transfer between gas constituents within the reactor), and (iv) 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 Global 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 molecules, which have an intrinsic affinity for each other, are "drawn" together in a diffusion process which consumes useful power, used to separate them from the reactant 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, and (3) "internal-thermomechanical energy" — associated with particle motions and intermolecular forces between system constituents (Hirschfelder *et al.*, 1954). Having stabilized (reacted), these interactions between the participating species have thus added to the system entropy, destroying potential useful power.

At the instant following the exothermic reaction, the product molecules leave the reaction site with a kinetic and photon energy which is much higher than the statistical average energy of the neighboring particles which have not reacted yet. Momentum (and associated kinetic energy) and radiative transfers therefore take place, bringing the reaction product temperature down to an equilibrium value consistent with that of the surrounding medium. This process, which is here called an "internal thermal energy exchange", also consumes useful power, increasing the entropy of the system. Finally, in a process which occurs simultaneously with the internal-thermal energy exchange, but, consistent with the approach in this study, 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 diffusion process where the oxygen and fuel molecules are drawn together),
- (2) a chemical reaction (oxidation of the fuel),
- (3) an internal-thermal energy exchange, where the product molecule "shares" its kinetic energy with its neighbors, and
- (4) 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 determination of subprocess irreversibilities, and to be physico-chemically plausible.

Path 1

In this process path the breakdown of combustion irreversibility 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 combined with fuel oxidation, (b) internal thermal energy exchange, and (c) product mixing.

Figure 3 displays schematically the technique of analysis. For example, in chamber 1, the oxygen (only the incremental stoichiometric amount which will react in this

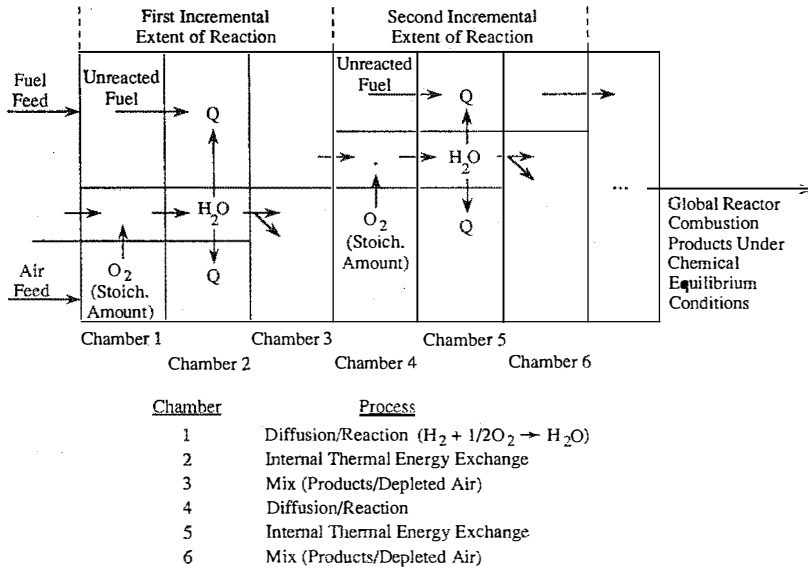


FIGURE 3 Hypothetical Combustion Chamber for Process Path 1.

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 characterized 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 temperatures 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 products from the reaction in chamber 1 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, with consequent gradual increase in temperature, until the gas constituents reach the fuel ignition temperature [assumed here to be 582°C for hydrogen and 690°C for methane, typical values for atmospheric pressure combustion of these fuels, taken from Babcock and Wilcox, 1978], whereupon the fuel oxidation is assumed to be instantaneous (i.e., all the remaining fuel is oxidized immediately at the fuel ignition temperature). This repetition till ignition, and not till the equilibrium temperature, which is higher, is more realistic,

since heat transfer following oxidation tends to diminish the temperature as compared with that predicted by equilibrium. 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 chosen for the process described in Figure 3. These results are displayed in Figures 4 and 5 for the cases of 0% and 50% excess air amount.

At a number of increments of about 30 the results approach a value which does not change with the increase of the number of increments. This convergence occurs because the changes in the conditions of the reactants diminish in each cell-increment as the number of increments increases, for given overall process beginning and end states. For example, when 500 increments are chosen, the increase in temperature in each increment is only about 1 to 2 K (in the computed case of 100% excess air).

The exergy destruction due to oxidation decreases with increasing number of increments because larger percentages 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 Figure 7. The significant result is that the largest subprocess exergetic

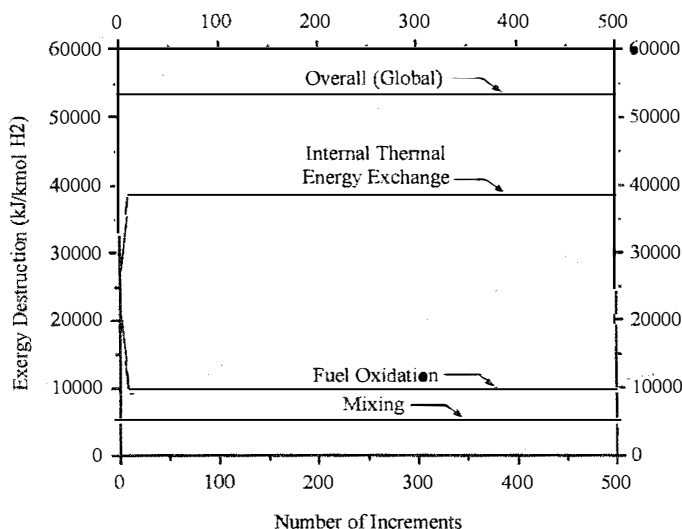


FIGURE 4 Exergy Destruction vs. Number of Process Increments for 0% Excess Air. Fuel: H₂.

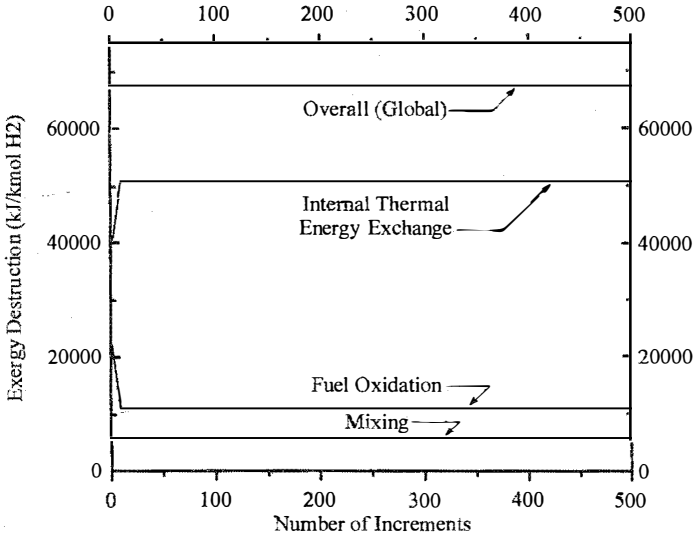


FIGURE 5 Exergy Destruction vs. Number of Process Increments for 50% Excess Air. Fuel: H₂.

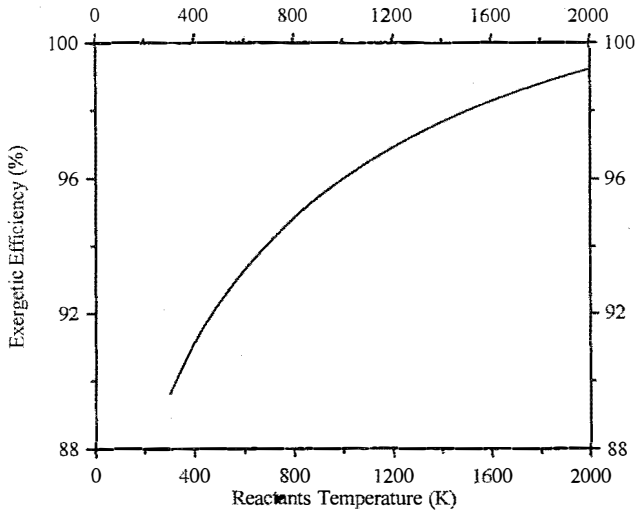


FIGURE 6 Exergetic Efficiency of Hydrogen Oxidation vs. Reactants Temperature.

consumption 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 constitutes about 15% to 18% of the total exergy loss, and gas constituent mixing (in chambers

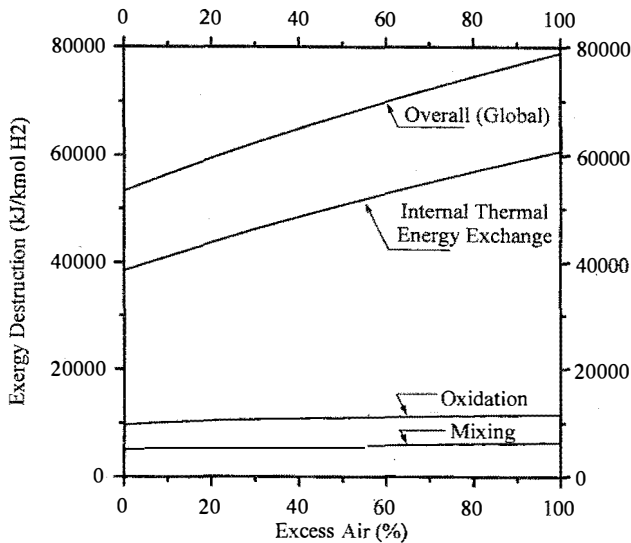


FIGURE 7 Hydrogen Combustion Subprocess Exergy Destruction vs. Excess Air, Path 1.

3, 6, etc., in Fig. 5) has an exergetic efficiency of 96.5% to 97.4%, constituting the remaining 8% to 10% of the total exergy loss.

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 Figure 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; each

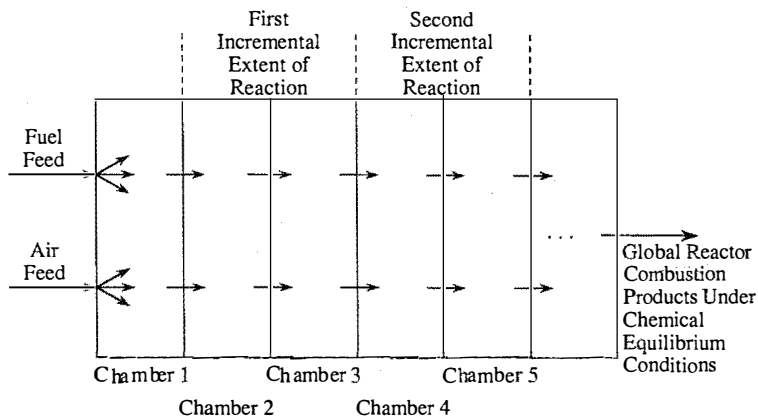


FIGURE 8 Hypothetical Combustion Chamber for Process Path 2.

stage consists of a two-step subprocess: (a) fuel oxidation, and (b) internal thermal energy exchange. These subprocesses are repeated until the required exit equilibrium product gas state is attained. Compared with Path 1, Path 2 allows, amongst other things, the determination of the exergy loss due to mixing of reactants. 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 equilibrium conditions.

As in the Path 1 study, an analysis was first performed to determine the sensitivity of the results to the chosen number of increments. The results of this analysis were similar to those shown in Figures 4 and 5 describing results of the Path 1 analysis. Two hundred increments were chosen for the Path 2 analysis, amply adequate to ensure results independent of increment number.

Qualitatively similar to the results of the Path 1 analysis, the largest exergy destruction, 66% to 73% of the total, takes place during the internal thermal energy exchange (chambers 3, 5, etc., Fig. 8). The fuel oxidation (chambers 2, 4, etc., Fig. 8) is responsible for 18% to 25% of the exergy destruction. The mixing process consumes about 8% to 10% of the total exergy destruction. The corresponding subprocess exergetic efficiencies, which reflect these results, are displayed in Figure 9.

Path 3

In this process path, described in Figure 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.

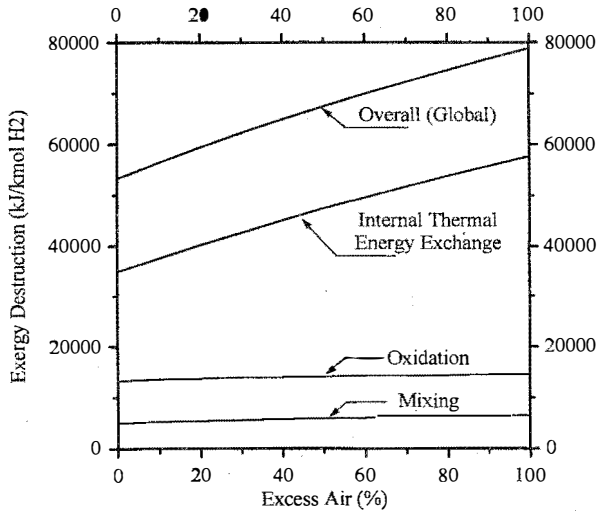


FIGURE 9 Hydrogen Combustion Subprocess Exergy Destruction vs. Excess Air, Path 2.

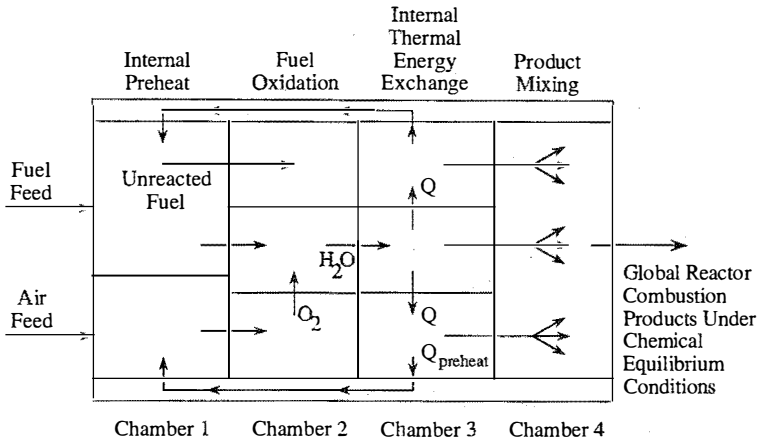


FIGURE 10 Hypothetical Combustion Chamber for Process Path 3.

As the air and fuel enter the reactor, these reactants are internally preheated (by radiation from the hot combustion products contained in chamber 3, for example). Upon reaching the ignition temperature, the fuel is oxidized instantaneously. The instant following this exothermic reaction, the product molecules transfer energy to the neighboring non-reacting constituents (such as excess oxygen, and N₂) in the internal thermal energy exchange subprocess. Finally, the oxidation products and the non-

reacting 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 reaction, 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, shown in Figure 11, 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.

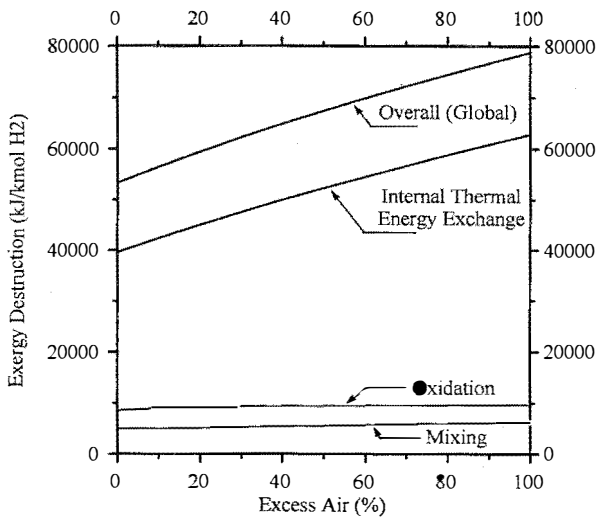


FIGURE 11. Hydrogen Combustion Subprocess Exergy Destruction, vs. Excess Air, Path 3.

Path 4

In this process path, described in Figure 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

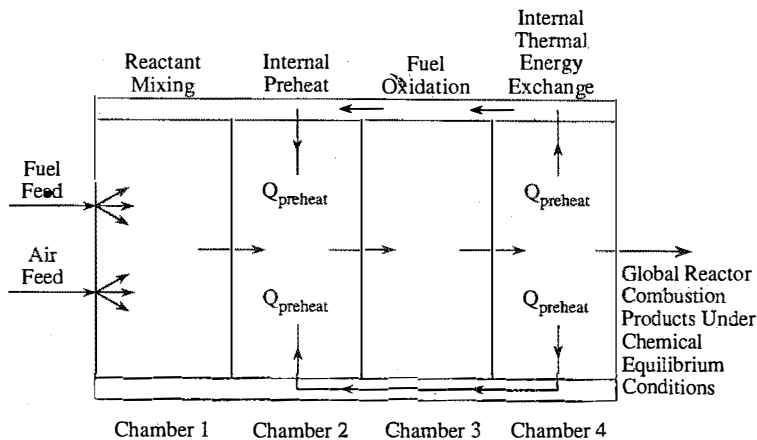


FIGURE 12 Hypothetical Combustion Chamber for Process Path 4.

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, shown in Figure 13, 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.

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, shown in Figure 14, 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 about 3% of the combustion exergy destruction.

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.

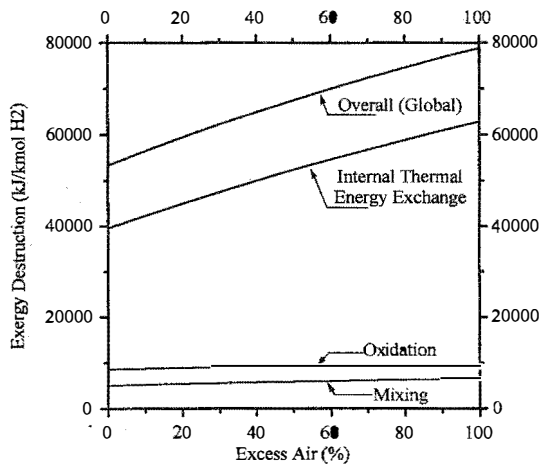


FIGURE 13 Hydrogen Combustion Subprocess Exergy Destruction, vs. Excess Air, Path 4.

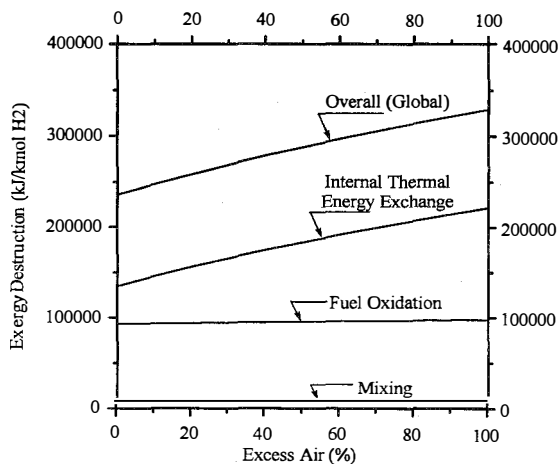


FIGURE 14 Methane Combustion Subprocess Exergy Destruction, vs. Excess Air, Path 4.

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 Figure 15, as a function of excess air.

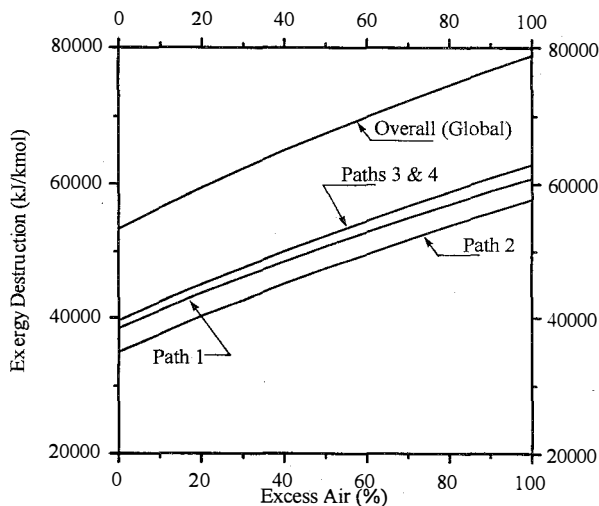


FIGURE 15 Exergy Destruction due to Internal Thermal Energy Exchange (for Hydrogen Combustion) vs. Excess Air.

The effect of pre-mixing

In the analysis of Paths 1 and 3 it was assumed that full mixing occurs after reaction, while in Paths 2 and 4 pre-mixing was assumed. As shown in Figure 15, no perceptible differences in exergy destruction due to the mixing subprocess were found between these modes of mixing.

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 via radiation and possibly conduction in the combustor walls.

To explain the effect of internal preheat and using Figure 15, 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. In path 1 it is assumed that 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 exchanged and internal preheating are responsible for approximately 74%–80% of the total combustion irreversibility. Consequently, 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 (Fig. 15) reveals that this internal preheating raises the internal heat transfer exergy destruction by approximately 7%–8% of the total combustion irreversibility.

CONCLUSIONS AND RECOMMENDATIONS

The understanding of the sources of combustion irreversibility and its underlying reasons was improved by employing a simplified method which does not require the solution of the spatial Navier-Stokes, energy and reaction kinetics equations. This method is approximate, since the overall exergy destruction is decomposed into hypothetical subprocess contributions, and the process is computed along several prescribed process paths. Nevertheless, useful and consistent results are obtained from the analysis: independent of the process path selected here, the major contribution to the destruction of useful energy occurring in typical gaseous hydrogen or hydrocarbon fuel combustion is likely due to the internal thermal energy exchange (heat transfer) between the particles within the system.

To reduce entropy production during combustion, this conclusion and the inevitability of this internal thermal energy exchange, point 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.

Recognizing this problem, Keenan (1941) discussed the concept of "reversible combustion", theoretically attained by preheating the reactants to the equilibrium temperature and partial pressures without allowing reaction; at these conditions the tendency toward chemical equilibrium has vanished. Subsequent gradual and reversible alteration of the temperature and pressure of the mixture, following the path of most stable states, he posited, would lead to increasingly greater combination of the reactants, resulting altogether in reversible combustion. This concept was expanded further by Obert (1948, 1973) and Beretta *et al.* (1992), all, however, acknowledging the practical difficulties associated with this conceptual procedure, such as the need to prevent reaction during the initial elevation to the reaction equilibrium conditions, the high temperatures at that state, and the need to have a reversible chemical combination process subsequently. Richter and Knoche (1983) proposed a conceptual approach to attain such reversible combustion by using a metal oxide as an intermediate material which would combine reversibly with the fuel, and then be restored to its original condition by a reversible reaction with air. Another way, employing fuel cells, is being explored by the authors (cf. Dunbar, 1983; Dunbar *et al.*, 1991). 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. All 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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REFERENCES

- Arai, N., Hasatani, M., Ninomiya, Y., Churchill, S. W. and Lior, N. (1986). A comprehensive kinetic model of char NO formation during the combustion of a single particle of coal char. *Proc. Combustion Institute 21st Symp. (International) on Combustion*, The Combustion Institute, Pittsburgh, PA. pp. 1207-1216.
- Arpaci, V. and Selamet, A. (1988). Entropy production in flames. *Combust. Flame*, **73**, 251-259.
- Babcock and Wilcox (1978). *Steam, its Generation and Use*. The Babcock and Wilcox Co., New York.
- Bejan, A. (1979). A study of entropy generation in fundamental convective heat transfer. *ASME J. Heat Transfer*, **101**, 718-725.
- Beretta, G. P., Lezzi, A. M., Niro, A. and Silvestri, M. (1992). On the concept of a reversible flame. *Flowers '92 Florence World Energy Research Symp.*, pp. 165-177.
- Buckmaster, J. D. and Ludford, G. S. S. (1982). *Theory of Laminar Flames*. Cambridge University Press, Cambridge.
- Dunbar, W. R. (1983). Computer Simulation of a High-Temperature Solid-Electrolyte Fuel Cell, M. S. Thesis, Marquette University, Milwaukee.
- Dunbar, W. R. and Lior, N. (1990). A Breakdown of the Exergy Losses in Combustion, *Proc. World Energy conf.*, Florence, Italy, Pergamon Press, Oxford. pp. 347-358.
- Dunbar, W. R., Lior, N. and Gaggioli, R. A. (1991). Combining fuel cells with fuel-fired power plants for improved exergy efficiency, *Energy*, **16**, 1259.
- Dunbar, W. R., Lior, N. and Gaggioli, R. A. (1992). The component equations of energy and exergy, *ASME J. Energy Resources Technology*, **114**, 75.
- Gaggioli, R. A. (1961). The concept of available energy. *Chem. Engrng Sci.*, **16**, 87.

- Gaggioli, R. A. (1962). The concepts of thermodynamic friction, thermal available energy, chemical available energy, and thermal energy. *Chem. Engng Sci.*, **17**, 523.
- Gaggioli, R. A., Yoon, J. J., Patulski, S. A., Latus, A. J. and Obert, E. F. (1975). Pinpointing the real inefficiencies in power plants and energy systems. In Gaggioli, R. A. (Ed.). *Proc. Amer. Power Conf.* Washington, D. C. pp. 671-679.
- Gurvich, L. V. and Veyts, I. V. (1989). *Thermodynamic Properties of Individual Substances*. Hemisphere Publishing Corp., New York.
- Hedman, B. A., Brown, H. L. and Hamel, B. B. (1990). Second Law Analysis of Industrial Processes. *Energy*, **5**, 931.
- Hirschfelder, J. O., Curtiss, C. F. and Bird, R. B. (1954). *Molecular Theory of Gases and Liquids*. Wiley, New York.
- Keenan, J. H. (1941). *Thermodynamics*, Wiley, N. Y., p. 269.
- Obert, E. F. (1948). *Thermodynamics*, McGraw-Hill, New York, p. 459.
- Obert, E. F. (1973). *Internal Combustion Engines and Air Pollution*, Harper and Row, New York, p. 84.
- Poulikakos, D. and Johnson, J. M. (1989). Second Law Analysis of Combined Heat and Mass Transfer Phenomena in External Flow. *Energy*, **14**, 67-73.
- Reynolds, W. C. and Perkins, H. C. (1977). *Engineering Thermodynamics*. McGraw-Hill, New York.
- Richter, H. J. and Knoche, K. F. (1983). Reversibility of combustion processes. In Gaggioli, R. A. (Ed.). *Efficiency and Costing, Second Law Analysis of Processes*, ACS Symp. Ser. 235, Washington, DC. pp. 71-75.
- Rodriguez, S. J. (1980). Calculation of available energy quantities. In Gaggioli, R. A. (Ed.). *Thermodynamics: Second Law Analysis*, Ch. 3, ACS Symp. Ser. 235, Washington, D. C.
- San, J. Y., Worek, W. M. and Lavan, Z. (1987). Entropy generation in combined heat and mass transfer. *Int. J. Heat Mass Transfer*, **30**, 1359-1368.
- Sonntag, R. E. and Van Wylen, G. J. (1982). *Introduction to Thermodynamics, Classical and Statistical*. Wiley, New York.
- Vargaftik, N. B. (1975). *Tables on the thermophysical properties of liquids and gases in normal and dissociated states*. 2nd Ed. Hemisphere, Washington, DC.
- Wark, K. (1977). *Thermodynamics*. McGraw-Hill, New York.