PARAMETRIC EXAMINATION OF THE DESTRUCTION OF AVAILABILITY DUE TO COMBUSTION FOR A RANGE OF CONDITIONS AND FUELS

A Thesis

by

PRAVEEN SHIVSHANKAR CHAVANNAVAR

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

August 2005

Major Subject: Mechanical Engineering

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Approved by:

Chair of Committee,	Jerald A Caton
Committee Members,	Kalyan Annamalai
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ABSTRACT

Parametric Examination of the Destruction of Availability Due to Combustion for a Range of Conditions and Fuels. (August 2005)

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A comprehensive second law analysis of combustion for a range of conditions and fuels was completed. Constant pressure, constant volume and constant temperature combustion processes were examined. The parameters studied were reactant temperature, reactant pressure, equivalence ratio and the fuels themselves. In addition, the contribution and relative significance of the various components (thermo-mechanical, reactive and diffusion) to the mixture availability was examined. Also, the effect of reactant mixture dissociation was incorporated into the combustion analysis.

It was found that for similar initial conditions, constant pressure combustion and constant volume combustion exhibited similar trends. For constant temperature combustion, the trend is significantly different from the constant pressure and constant volume combustion, with almost the entire reactant availability being destroyed due to combustion at lower temperatures.

Amongst the parameters examined, reactant mixture temperature had the most significant effect on the fraction of availability destroyed during combustion. The percentage availability destroyed reduced from 25 to 30% at 300 K to about 5% at 6000 K for constant pressure and constant volume combustion processes.

The effect of the reactant mixture pressure on the fraction of availability destroyed was more modest. The values for the percentage availability destroyed for pressures ranging from 50 kPa to 5000 kPa were found to lie within a range of 5%.

The effect of equivalence ratio on the fraction of reactant mixture availability destroyed was also documented. In general, it was found that the destruction of availability decreased with increasing equivalence ratios. This value, however, accounts for the availability due to fuel like species in the product mixture. Therefore, for practical applications, combustion of the stoichiometric mixture would be preferred over the rich equivalence ratios.

It was found that the fraction of reactant availability destroyed increased with increasing complexity of the fuel’s molecular structure.

In addition, it was shown that the diffusion availability terms is small and may be neglected, while the reactive availability and thermo-mechanical availability are more significant.

ACKNOWLEDGEMENTS

I would like to thank my committee chair, Dr. Jerald Caton, for his time and effort. He was instrumental in my finishing this work. His help and guidance in the development of the program and the subsequent analysis of the results were responsible for the successful completion of this work. Without his probing questions, I would have struggled to identify the bugs in the code, let alone eliminate them.

I would also like to thank my committee members, Dr. Kalyan Annamalai and Dr. Yassin Hassan, whose cooperation and support allowed me to finish this work within the various constraints of time and resources. In addition, I would like to thank Dr. William Marlow for kindly agreeing to substitute for Dr. Yassin Hassan during the thesis defense.

Further, I would like to thank the Oak Ridge National Labs for funding the project, thus allowing me to explore the combustion process and related phenomena. The support was greatly appreciated. The contents of this thesis, however, do not necessarily reflect the opinions or views of the sponsors.

In closing, I would like to express my gratitude to everyone who helped and supported me in my current endeavor.

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NOMENCLATURE

$(F:A)_{Actual}$	Actual fuel air ratio
$(F:A)_{Stoichiometric}$	Stoichiometric fuel air ratio
a	Number of moles of fuel
a_1	Coefficient 1 for least square polynomial fit for determining thermodynamic properties
a_2	Coefficient 2 for least square polynomial fit for determining thermodynamic properties
a_3	Coefficient 3 for least square polynomial fit for determining thermodynamic properties
a_4	Coefficient 4 for least square polynomial fit for determining thermodynamic properties
a_5	Coefficient 5 for least square polynomial fit for determining thermodynamic properties
a_6	Coefficient 6 for least square polynomial fit for determining thermodynamic properties
a_7	Coefficient 7 for least square polynomial fit for determining thermodynamic properties
A_{Abs}	Absolute availability
$A_{Abs,f}$	Absolute flow availability
A_{Ch}	Chemical availability
A_{Dest}	Availability destroyed
$A_{Dest,TM}$	Thermo-mechanical availability destroyed
A_{Diff}	Diffusion availability
A_{Final}	Final total availability of mixture (after combustion)
$A_{Initial}$	Initial total availability of mixture (before combustion)
A_P	Product mixture availability
$A_{P, TM}$	Product mixture thermo-mechanical availability
A_R	Reactant mixture availability
$A_{R, TM}$	Reactant mixture thermo-mechanical availability
$A_{Reactive}$	Reactive availability of mixture
A_T	Availability due to heat transfer
A_{TM}	Thermo-mechanical availability of system
A_{Total}	Total availability of system

$A_{Total,f}$	Total flow availability of system
A_W	Availability due to work performed
b	Number of moles of air
b_1	Coefficient 8 for least square polynomial fit for determining thermodynamic properties
b_2	Coefficient 9 for least square polynomial fit for determining thermodynamic properties
C_P	Constant pressure specific heat
f_{O2}	Mole fraction of oxygen in atmosphere
g	Gibbs energy
ΔG	Change in Gibbs energy associated with a reaction
h_k	Enthalpy of species k
H	Enthalpy of system
MW_{Air}	Molecular weight of air
MW_{Fuel}	Molecular weight of fuel
n	Number of moles
P	Pressure
$\dot{Q}$	Heat transfer across system boundary
$\bar{R}$	Universal gas constant
r_{DAC}	Percentage availability destroyed
s_k	Entropy of species k
S	Entropy of system
T	Temperature
u_k	Internal energy of species k
U	Internal energy of system
V	Volume
x	Number of atoms of carbon per fuel molecule
y	Number of atoms of hydrogen per fuel molecule
y_k	Mole fraction of species k
y_{Total}	Total number of moles in mixture
z	Number of atoms of oxygen per fuel molecule

Greek symbols

ϕ	Equivalence ratio

μ	Chemical potential

Superscripts

0	Restricted dead state conditions

Subscripts

0	Reference (atmospheric) conditions
k	species index

I. INTRODUCTION

Modern societies have an almost insatiable need for energy. Despite significant efforts to find alternate sources of energy, combustion of fossil fuels is the leading provider for energy in most societies, with the exception of a few. The main reasons for this dependence on fossil fuels are high power density, cost effectiveness and easy availability. Conversion of the chemical energy stored in these fuels requires an intermediate combustion process to release the latent energy of the fuels, except in some cases such as the fuel cells. The importance of the combustion processes is thus readily evident.

Internal combustion engines are the most common prime movers. They are readily employed for a wide range of applications and can be powered on various fuels depending on the local availability. Their many advantages and relative lack of competition has made internal combustion engines one of the preferred devices for converting the chemical energy of fuels into mechanical energy.

The current work attempts to understand the destruction of availability in combustion processes with specific application to internal combustion engines. However, the analysis is not restricted to internal combustion engines and is applicable to all combustion processes.

Availability

Availability is a measure of the energy available for useful work in a system. This property is also referred to as exergy. Availability is a better measure of the work that may be extracted from a system rather than properties such as the internal energy or enthalpy of the system. No device or process can extract a quantity of work greater than the availability of the system without violating the second law of thermodynamics. Thus, the availability of a system also helps to define the upper limit on the efficiency of the device/process.

Following usual conventions [1-3], the absolute availability, A_{Abs} of a system is defined as

$$A_{Abs} = U - T_0 S + P_0 V \tag{1.1}$$

where U, S and V are the internal energy, entropy and volume of the system respectively, while T_0 and P_0 are the reference temperature and pressure. The work that may be extracted from a system is also limited by the reference conditions. The work that may be extracted from the system is then given by the (thermo-mechanical) availability, A_{TM}, of the system, which is defined as

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This thesis follows the style and format of Energy.

$$A_{TM} = (U - U^0) - T_0(S - S^0) + P_0(V - V^0) \quad (1.2)$$

where U^0, S^0 and V^0 are the internal energy, entropy and volume of the restricted dead state respectively.

The restricted dead state is achieved by allowing the system to come to thermo-mechanical equilibrium with the environment, typically the atmosphere. The restricted dead state has the same pressure and temperature as the environment, however, the composition of the restricted dead state is the same as that of the original system and is not necessarily the same as that of the environment. The current work uses this definition of the restricted dead state, in conformance with the standard literature [1-3], with a temperature of 298.15 K and pressure 101.325 kPa for the restricted dead state and the reference conditions.

This difference in composition between the restricted dead state and the environment can be exploited to further obtain work from the system. This work, obtained by allowing the restricted dead state to come to chemical equilibrium with the environment, is referred to as the chemical availability, A_{Ch}, of the system.

$$A_{Ch} = \sum_{k=1}^{n} N_k \left(\mu_k^0 - \mu_{k,0} \right) \quad (1.3)$$

where N_k is the number of moles of the respective species (k) and $\mu_{k,0}$ and μ_k^0 are the chemical potentials of the respective species in the restricted dead state and the environment, respectively. The chemical potentials may further be expressed as:

$$\mu_k = g_k(T_0, P_0) + \bar{R}T_0 \ln\left(\frac{p_k}{p_0}\right) \quad (1.4)$$

where g_k is the Gibbs energy of the k^{th} species in the mixture, $\bar{R}$ is the Universal gas constant and p_k is the partial pressure of the k^{th} species in the mixture. If the restricted dead state and the environment, both had the same constituent species, differing only in their respective compositions, the Gibbs energy term would cancel out, leaving a simpler expression for the chemical availability of the system

$$A_{Diff} = \bar{R}T_0 \sum_{k=1}^{n} N_k \ln\left(\frac{p_k^0}{p_{k,0}}\right) \quad (1.5)$$

The difference in concentrations of the various species in the system and the atmosphere may be exploited by first separating the various components in the mixture (using devices such as semi-permeable membranes) and then allowing them to expand or compress to the atmospheric partial pressures, as the case may be. Work may be gained or lost during this process and this creates an additional potential for work. Since this term may be attributed to the work obtained by allowing the species in the system to diffuse to the atmospheric concentrations, it would be appropriate to refer to this as the “diffusion availability”. It may be noted that diffusion availability of a system can be positive or negative, depending on the concentrations of the various species in the system.

The diffusion availability of a system is largely ignored since its contribution is often small relative to the thermo-mechanical availability A_{TM} of the system. Also, it is not easy to extract the diffusion availability component of the availability since it would require the use of semi-permeable membranes to extract the various species in the mixture before allowing them to diffuse to atmospheric concentrations.

It is also evident from the expression for the diffusion availability of a system that it depends on the composition of the environment. The assumed composition of the atmosphere therefore, makes a difference on the diffusion availability of the system. The current work uses a standard wet atmospheric composition (See Appendix II) unless otherwise stated.

The availability of a system, A_{Total}, incorporating the various components would then be

$$A_{Total} = (U - U_0) - T_0(S - S_0) + P_0(V - V_0) + \sum_{k=1}^{n} N_k \left(\mu_k^0 - \mu_{k,0}\right) \tag{1.6}$$

The above expression for availability is valid for closed systems. For open systems, the flow availability, $A_{Total,f}$ needs to be considered. This is defined as

$$A_{Total,f} = (H - H^0) - T_0(S - S^0) + \sum_{k=1}^{n} N_k \left(\mu_k^0 - \mu_{k,0}\right) \tag{1.7}$$

where H and H^0 are enthalpies of the system and the restricted dead state respectively.

In general, then, the availability of a system, A_{Total}, may be expressed as a sum of the thermo-mechanical availability and chemical availability.

$$A_{Total} = A_{TM} + A_{Ch} \tag{1.8}$$

The chemical availability term may further be split into constituents, the reactive availability and diffusive availability as:

$$A_{Total} = A_{TM} + A_{\text{Reactive}} + A_{Diff} \tag{1.9}$$

Objective

The objective of this work was to gain a better understanding of the fundamentals of combustion processes by studying the availability destruction during various combustion processes –

- Constant pressure (Isobaric)
- Constant volume (Isochoric)

- Constant temperature (Isothermal)

A parametric study of the combustion process was conducted for a range of fuels. The various properties of the system such as the enthalpy, internal energy and entropy were determined and used to calculate the availability of the system. The diffusion availability component was included in the analyses conducted, to quantify the contribution of this component to the overall availability of the system.

The analyses conducted considered equilibrium products of combustion and also examined the effect of dissociation of the reactant mixture on the availability analysis.

In addition, a compilation of the National Aeronautics and Space Administration (NASA), Lewis polynomial coefficients as described by Zehe et al [4] was completed for some commonly encountered fuels. These coefficients are used in least square polynomial fits for obtaining the various thermodynamic properties. This has been discussed in more detail in a subsequent section of this work.

II. LITERATURE REVIEW

Review of previous work

Second law analyses are particularly valuable tools in the design and analysis of thermal systems since they help in identifying sources of irreversibility in the system. The second law has been applied to analysis of internal combustion engines, turbines and power plants. As stated previously, the current work aims to understand availability losses during combustion regimes from the viewpoint of implementing these strategies for more efficient combustion in engines.

Significant work has been done with regard to applying the second law to engine simulations in the past. Past work has been done on both, spark ignition and compression ignition engines. A discussion of these analyses applying the second law to study internal combustion engines was conducted by Caton [5]. The review conducted by Caton [5] provides an overview of availability analysis of engines. The past work completed on engines will not be reviewed in detail for this study. Most of the work conducted does not include the diffusive availability term from the chemical availability component and are restricted to a engine combustion processes.

One of the first works to include a rigorous treatment of the chemical availability component in availability analysis of the engines was conducted by Van Gerpen and Shapiro [6]. Van Gerpen and Shapiro outline the need for including the chemical availability component for availability analysis. They also conclude that the chemical availability contribution is significant and needs to be incorporated into the calculations to obtain an accurate estimate of the irreversibility of the processes. The work by Van Gerpen and Shapiro [6] showed that the chemical availability increases in significance with increasing temperature and pressure and for richer equivalence ratios. This is mainly due to the increased concentrations of species such as carbon monoxide and hydrogen which are not present in the atmosphere and have a significant chemical energy associated with them.

Dunbar and Lior [7] focus primarily on determining the processes contributing to the destruction of availability during constant pressure combustion in their study. They divided the overall combustion process into a number of hypothetical sub-processes and determined the contribution of these to the destruction of availability. While this approach is not a rigorous model of the combustion process, it provides a reasonable estimate of the relative contribution of the various sub-processes to the destruction of availability in the combustion process.

The work conducted by Dunbar and Lior [7] was restricted to constant pressure combustion for an adiabatic combustion chamber. The focus of the analysis was for electric power generation, but would be applicable for all constant pressure combustion systems. Two fuels, hydrogen (H_2) and methane (CH_4) were considered in the study. The overall combustion process was divided into mixing, fuel oxidation and internal thermal energy transfer, and the irreversibility due to these processes was estimated. The study also noted that the destruction of availability was greatest at lower reactant temperatures and decreased as the reactant temperature was increased. The study also considered various hypothetical combustion chamber designs to study the effect of the combustion chamber on the combustion irreversibility.

Dunbar and Lior [7] concluded that the majority of the irreversibility in a typical combustion system is due to the internal thermal energy exchange. They also conclude that it would be possible to achieve reversible combustion by preheating and compressing/expanding the reactants to the equilibrium temperatures and pressures before allowing them to react. Such reversible combustion would not be feasible, mainly due to the material constraints, since current material technology is not sufficiently advanced to allow for such high temperatures to be achieved.

The problem of achieving reversible combustion is discussed in greater detail by Richter and Knoche [8]. The concept of using metal oxides to achieve the overall combustion through a series of intermediary reactions was evaluated. The work also compared the availability losses for constant pressure, constant volume and constant temperature combustion. This is useful in identifying which combustion regime is more efficient, at least in theory. Richter and Knoche [8] concluded that the exergy losses were greatest for a constant pressure adiabatic combustion and least for constant temperature isothermal combustion (for an initial reactant mixture condition of 300 K and 1 bar).

A detailed analysis of constant volume combustion was conducted by Caton [9]. The analysis considered the constant volume, adiabatic combustion of iso-octane (C_8H_{18}). The effect of frozen and equilibrium products of combustion was analyzed. In addition, the effect of various parameters such as temperature, pressure and equivalence ratio on the mixture availability was documented. The percentage availability destroyed, r_{DAC}, (defined as $r_{DAC} = \frac{A_{DAC}}{A_R} x100$, where A_{DAC} is the availability destroyed and A_R is the reactant availability) was determined for constant volume combustion for a range of reactant temperatures, pressures and equivalence ratios.

Caton [9] found that the effect of initial pressure on the destruction of availability was modest compared to the effect of the initial reactant mixture temperature. He also noted that the percentage destruction of reactant availability was significantly reduced at higher reactant mixture temperatures. Caton [9] noted that the percentage of availability destroyed typically ranged from 5% to 25%, which is also in agreement with the values obtained from various engine analyses [5]. The value of 5% was obtained at higher reactant temperatures, in excess of 3000 K.

Lutz et al. [10] compared the thermodynamic efficiency of fuel cells and Carnot cycles and showed that both are limited by the second law of thermodynamics, and that the theoretical maximum efficiency of the Carnot cycle and the fuel cells are equivalent. Lutz et al. [10] also evaluated the Carnot efficiency at the combustion temperature, T_C, which is the temperature at which reversible combustion occurs. The work focuses mainly on the use of hydrogen with some discussion of methanol and methane.

Daw et al. [11] examine a conceptual isobaric combustion process with reduced combustion irreversibility. Their work primarily focused on the effect of preheating the reactants on reducing the irreversibility losses during the combustion processes. Daw et al. [11] also examined the influence of excess air (equivalence ratio) in the reactant mixture on the irreversibility during combustion. Daw et al. [11] conclude that by allowing the oxidation to occur more progressively and at elevated temperatures, the irreversibility due to the combustion process can be reduced, though not completely eliminated. A completely reversible combustion process can never be achieved since there is always some irreversibility associated with the mixing of the fuel and air streams.

Summary

Second law analysis of system provides important information about the systems/processes which is not obtainable from the first law analysis of a system. Second law analyses have been conducted on engines and power generation systems to identify and eliminate sources of irreversibility.

Combustion of fuels is a significant contributor to the irreversibility in these systems. It has been noted by many authors [7-11] that it would be possible, at least theoretically, to design combustion devices with significantly higher efficiencies. The major hindrance in the development of such devices is the lack of suitable materials to withstand the high temperatures encountered.

Past availability analysis work has been focused on a particular device or process. No attempt has been made to compare the different combustion processes to identify more efficient combustion strategies.

Also, some of the previous work does not include the chemical availability component in the analysis. Under some conditions, this term is indeed small and may be neglected, but as shown by Van Gerpen and Shapiro [6], this is not always the case and that the chemical availability term needs to be included for a more complete and accurate understanding of the availability changes during the combustion processes.

Motivations

From the literature review, it is evident that a comprehensive second law examination of combustion processes is lacking. Such a study would provide a more fundamental understanding of combustion processes and help in identifying strategies to reduce the destruction of availability during combustion processes.

Some work has been done towards applying the second law to combustion by Dunbar and Lior [7] (constant pressure combustion) and Daw et al. [11] (constant pressure combustion) and Caton [9] (constant volume). These studies however, were restricted to a particular combustion process and did not rigorously quantify the contribution of the various availability terms.

The current study hopes to apply the second law to the various combustion processes, while relaxing most of the approximations and simplifications made in the past. It is hoped that a comprehensive examination of the various parameters will provide a more fundamental and complete understanding of the combustion processes.

The current work also aims to incorporate various fuels into the study to allow for comparison of the combustion of different fuels. This would allow the various fuels to be compared to each other on the basis of their relative second law efficiencies.

It is hoped that the results of this work would finally lead to the design of more efficient combustion devices.

Layout

The following sections outline the process of modeling the various combustion processes, the output obtained from these models and the discussions and comparisons thereof.

Section III, General Analysis and Development of Code, deals with the derivations, general analysis and the procedure followed during the development of the combustion models for constant pressure, constant volume and constant temperature conditions. It also lists the assumptions and approximations invoked during the current study. This section also includes a brief discussion of the NASA Lewis polynomial coefficients [4] used for determination of the various thermodynamic properties.

Section IV, Results and Discussion, presents the results from the current work. The results are presented in three sub-sections – constant pressure, constant volume and constant temperature. For each of these combustion conditions, the effect of various parameters, namely, reactant temperature, reactant pressure, equivalence ratio and fuels is examined.

Section IV also contains the comparison and discussion of the current work with those from the past. The results from the current work are related to past work and the differences analyzed. Some level of validation is also achieved in this section by comparing the results from the current work with the relevant values present in the literature from past work. In addition, an attempt is made to demonstrate the practical applications of the results from the current study in achieving more efficient combustion.

Section V, Summary and Conclusion, provides a brief summary and conclusion of the results obtained.

III. GENERAL ANALYSIS AND DEVELOPMENT OF CODE

For determination of the availability of the system, the various thermodynamic properties of the reactant and product mixtures are required. This section discusses the process of developing the code for obtaining the availabilities and consequently, the fraction of reactant mixture availability destroyed during the various combustion modes.

General information

The various thermodynamic properties were determined from the NASA Lewis polynomial coefficients [4] developed as least square fits to data at the NASA Glenn Research Center. The latest “7+2” coefficient data was used for determination of the properties. These coefficients were also compiled for some of the common fuels (See Appendix II). The values of the coefficients for the various species may be substituted into the appropriate equations to obtain the required thermodynamic property. The compiled coefficients were also used to generate the thermodynamic properties for the fuels and compared with the properties obtained by using the coefficients listed by Heywood [12]. It was noted that there was some deviation between the properties obtained by using the two sets at higher temperatures. This is discussed in more detail in a subsequent section.

The relevant equations for determining the thermodynamic properties are as follows –

Heat Capacity

$$\frac{\mathrm{C_p^o}}{\bar{\mathrm{R}}} = a_1 T^{-2} + a_2 T^{-1} + a_3 + a_4 T + a_5 T^2 + a_6 T^3 + a_7 T^4 \tag{3.1}$$

Enthalpy

$$\frac{\mathrm{H_o(T)}}{\bar{\mathrm{R}}\mathrm{T}} = -a_1 T^{-2} + a_2 T^{-1} \ln T + a_3 + a_4 \frac{T}{2} + a_5 \frac{T^2}{3} + a_6 \frac{T^3}{4} + a_7 \frac{T^4}{5} + \frac{b_1}{T} \tag{3.2}$$

Entropy

$$\frac{\mathrm{S_o(T)}}{\bar{\mathrm{R}}} = -a_1 \frac{T^{-2}}{2} - a_2 T^{-1} + a_3 \ln T + a_4 T + a_5 \frac{T^2}{2} + a_6 \frac{T^3}{3} + a_7 \frac{T^4}{4} + b_2 \tag{3.3}$$

The use and implementation of these coefficients is discussed in greater detail by Zehe et al. [4]. The updated coefficients are also available online at the NASA website [13].

For determination of the equilibrium product composition, the program interfaced with the program developed by Gordon and McBride [14] for calculation of Complex Equilibrium compositions and Applications (CEA). The program generated the appropriate input file for the

CEA code and then read the appropriate values from the generated output file. The CEA code allows for various input conditions. The input conditions used in this study were –

- Specified temperature and pressure (tp)
- Specified internal energy and density (uv)
- Specified enthalpy and pressure (hp)

During the calculations, the program requires the values for the change in Gibbs energy due to oxidation of various species (ΔG^0). The program uses the values from its database, unless the user overrides these values. The values in the database are from Moran and Shapiro [1], with the values for the rarer species having been calculated manually.

Assumptions and approximations

The following assumptions and approximations were made during the course of this work –

1. Adiabatic combustion chamber conditions were assumed during constant pressure and constant volume analyses.
2. It was assumed that the products of combustion had enough time to attain the equilibrium composition.
3. Ideal gas behavior was assumed throughout the analyses.
4. The distribution of the various species and the distribution of pressure and temperature in the combustion chamber was assumed to be uniform.

The carbon formed during dissociation of fuel mixture was assumed to be in vapor phase. At increasingly higher temperatures (past 4300 K), carbon does indeed exist as a gas. At lower temperatures, this assumption reduces the accuracy of the values obtained, though not significantly.

Development of program

After collecting the relevant input information from the user through the graphical user interface, the program begins the calculations for the various mixture properties. The program is designed to handle fuels of the form $C_xH_yO_z$. The total number of moles in the reactant mixture at the assigned pressure and temperature is calculated using the ideal gas equation

$$PV = n\bar{R}T \tag{3.4}$$

where P is the system pressure, V the volume, T the temperature, n the number of moles and $\bar{R}$ the Universal Gas constant. The general reaction representing the combustion process would then be given by

$$a\left(C_xH_yO_z\right)+b\left(Air\right)\longrightarrow \text{Products} \tag{3.5}$$

where a and b are the number of moles of the fuel and the air, respectively. Setting the number of moles of fuel as unity (a=1) and assuming stoichiometric composition of the reactant mixture, the value of b may be determined as follows

$$b=\left(2ax+\frac{ay}{2}-az\right)x\left(\frac{1}{2f_{O_2}}\right) \tag{3.6}$$

where f_{O_2} is the mole fraction of oxygen in the atmosphere. The default mole fractions correspond to the standard air composition as described in Appendix I. However, the user may override these values to specify other non-standard values, if so desired.

The stoichiometric fuel air ratio was then calculated as

$$\left(F:A\right)_{Stoichiometric}=\left(\frac{a\bullet MW_{Fuel}}{b\bullet MW_{Air}}\right) \tag{3.7}$$

where MW_{Fuel} and MW_{Air} are the molecular weight of fuel and air respectively. The actual fuel air ratio, ϕ may then be calculated as

$$\left(F:A\right)_{Actual}=\left(F:A\right)_{Stoichiometric}x\phi \tag{3.8}$$

Once the actual fuel air ratio is determined, the total number of moles of fuel and air in the reactant mixture are easily determined. To determine the availability of the reactant mixture, the mixture enthalpy, internal energy and entropy are required. These are calculated as follows –

$$H=\sum_{k=1}^{n}n_kh_k \tag{3.9}$$

$$U=\sum_{k=1}^{n}n_ku_k \tag{3.10}$$

The entropy values need to be corrected to account for the partial pressures of the various species before being summed to obtain the mixture entropy. The appropriate expression for this is

$$S=\sum_{k=1}^{n}n_k\left[S_{0,k}(T)-\bar{R}\ln\left(\frac{p_k}{p_0}\right)\right] \tag{3.11}$$

where $S_{0,k}$ is entropy of species k at the reactant temperature, T. This expression may also be related to the mole fraction of the respective species as follows

$$S=\sum_{k=1}^{n} n_k\left[S_{0,k}(T)-\bar{R}\ln\left(\frac{y_k}{y_{Total}}\right)\right] \tag{3.12}$$

In some of the following cases, high reactant temperatures are considered. For these cases, dissociation of the reactants can occur. In case dissociation of the reactant mixture is considered, the number of species is increased to account for the dissociated species that may arise due to the dissociation of the fuel air mixture. The species (all gaseous) considered in the dissociation of the reactant mixture are –

- Hydrogen, H_2
- Hydrogen atom, H
- Hydroxyl radical, OH
- Water, H_2O
- Oxygen, O_2
- Oxygen atom, O
- Argon, Ar
- Nitrogen, N_2
- Nitrogen atom, N
- Carbon dioxide, CO_2
- Carbon monoxide, CO
- Methane, CH_4
- Acetylene, C_2H_2
- Carbon, C
- Carbon 2, C_2
- Carbon 3, C_3
- CH

It was noted that the fuel air mixtures decompose largely into these species, with the mole fractions of other species of the order of 10^{-4} or lesser. Once the thermodynamic properties of the system have been determined, the availability may be calculated as

$$A_{Abs}=U-T_0S+P_0V \qquad \text{for a closed system} \tag{3.13}$$

$$A_{Abs,f}=H-T_0S \qquad \text{for an open system} \tag{3.14}$$

To obtain the availability of the system, the availability of the restricted dead state needs to be determined. A similar procedure is employed to determine the thermodynamics properties, with the temperature and pressure equated to the ambient temperature and pressure.

$$A^0=U^0-T_0S^0+P_0V^0 \qquad \text{for a closed system} \tag{3.15}$$

$$A_f^0 = H^0 - T_0 S^0 \qquad \text{for an open system} \qquad (3.16)$$

The fuel in the reactant mixture also contains chemical energy which needs to be accounted for during the analysis. The chemical energy associated with a fuel (or fuel like) species is simply the change in Gibbs energy as the species reacts to form the standard species present in the atmosphere. This chemical energy of the species is the reactive availability of the system.

$$A_{\text{Reactive}} = \sum_{k=1}^{n} n_k \Delta G_k^0 \qquad (3.17)$$

where ΔG^0 is the change in Gibbs energy due to oxidation of the fuel (See Appendix III for a listing of the change in Gibbs energy values used). Note that A_{Reactive} is the reactive availability and does not include the diffusion availability as discussed in previous sections.

The diffusion availability component is determined by first converting all the constituent species of the system into species present in the atmosphere through chemical reactions. The conversion of these species into standard atmospheric species involves corresponding changes in Gibbs free energy due to these reactions and these terms also contribute to the overall reactive availability of the system. The diffusion availability, which is essentially the work potential as the various species come to equilibrium with their respective atmospheric concentrations, is then determined using the relation

$$A_{Diff} = \sum_{k=1}^{n} n_k \bar{R} T \ln\left(\frac{y_k}{y_{k,0}}\right) \qquad (3.18)$$

It may be noted that combining the equations for A_{Reactive} and A_{Diff} would give the change in chemical potentials of the species. The total availability, A_{Total}, of the system is then the sum of the various availability components discussed above.

$$A_{Total} = \left(A_{Abs} - A^0\right) + A_{\text{Reactive}} + A_{Diff} \qquad (3.19)$$

This relation may also be expressed in terms of the thermodynamic properties as

$$A_{Total} = \left(U - U^0\right) - T_0\left(S - S^0\right) + P_0\left(V - V^0\right) + \sum_{k=1}^{n} n_k \Delta G_k^0 + \sum_{k=1}^{n} n_k \bar{R} T \ln\left(\frac{y_k}{y_{k,0}}\right) \text{for a closed system} \qquad (3.20)$$

$$A_{Total,f} = \left(H - H^0\right) - T_0\left(S - S^0\right) + \sum_{k=1}^{n} n_k \Delta G_k^0 + \sum_{k=1}^{n} n_k \bar{R} T \ln\left(\frac{y_k}{y_{k,0}}\right) \qquad \text{for an open system} \qquad (3.21)$$

The next stage is to determine the product composition from the equilibrium code. This is done by choosing the appropriate constraints on the system. For a constant volume, closed system, the internal energy and density of the system are held fixed. For a constant pressure, open system, the enthalpy and pressure of the system are fixed. For constant temperature combustion, the temperature and the pressure or volume of the system are fixed. The product mixture composition, temperature and pressure are then obtained from the equilibrium code.

The current work allows either complete products of combustion or equilibrium products of combustion to be specified. Complete products of combustion consists of only the following species in the product mixture –

- Carbon dioxide, CO_2
- Water, H_2O
- Nitrogen, N_2
- Oxygen, O_2
- Argon, Ar

The equilibrium products of combustion consists of the following set of potential species in the product mixture –

- Carbon dioxide, CO_2
- Carbon monoxide, CO
- Water, H_2O
- Hydroxyl radicals, OH
- Hydrogen, H_2
- Hydrogen atom, H
- Oxygen, O_2
- Oxygen, O
- Nitrogen, N_2
- Nitrogen, N
- Nitrogen oxide, NO
- Nitrogen oxide, NO_2
- Argon, Ar

A similar procedure is then adopted to determine the product mixture availability, A_P. Once the reactant mixture availability and product mixture availability are known, an availability balance may be performed to determine the availability destroyed due to the combustion process.

$$A_{Dest} = A_{Initial} - A_{Final} + A_T + A_W \tag{3.22}$$

where A_{Dest} is the availability destroyed due to combustion, $A_{Initial}$ is the initial availability of the system and A_{Final} is the final availability of the system, A_T is the availability due to the heat transfer into or out of the system and A_W is the availability due to any work interaction.

Throughout the following analyses, no work is being done or extracted from the systems. The term, A_W, is therefore zero. For the constant pressure combustion and constant volume combustion analyses, adiabatic conditions are assumed and therefore, $A_T = 0$. For the constant temperature combustion, A_T is not zero and needs to be determined appropriately as outlined in the following section. $A_{Initial}$ and A_{Final} are to be determined appropriately using the relations outlined previously in this section.

It can also be shown that the availability destroyed during constant pressure and constant volume combustion is the same as $T_0\Delta S$. For constant temperature combustion, an additional term accounting for the heat transfer needs to be introduced. Therefore,

$$A_{Dest,TM} = A_{\mathrm{R,TM}} - A_{\mathrm{P,TM}} = T_0\Delta S \qquad \text{for constant pressure and constant volume combustion} \tag{3.23}$$

$$A_{Dest,TM} = A_{R,TM} - A_{P,TM} - A_T = T_0\Delta S - \dot{Q}\left(1-\frac{T_0}{T}\right) \text{for constant temperature combustion} \tag{3.24}$$

This equality is used as an internal consistency check in the program. It may also be noted that this destruction of availability does not include the chemical availability terms ($A_{Reactive}$ and A_{Diff}). The irreversibility due to change in these availability terms is in addition to the availability destroyed due to the thermo-mechanical changes ($A_{Dest,TM}$).

The percentage availability destroyed, r_{DAC}, is calculated as –

$$r_{DAC} = \left(\frac{A_R - A_P}{A_R}\right)x100 \tag{3.25}$$

The above expression is applicable to constant volume and constant pressure combustion regimes. For constant temperature combustion, the appropriate expression is

$$r_{DAC} = \left(\frac{A_R - A_P - A_T}{A_R}\right)x100 \tag{3.26}$$

where A_T is the availability due to the heat transfer out of the system. The term A_T may be determined based on the Carnot cycle efficiency as follows

$$A_T = (H_R - H_P)\,x\left(1-\frac{T_0}{T}\right) \qquad \text{for constant temperature, isobaric combustion} \tag{3.27}$$

$$A_T = (U_R - U_P)\,x\left(1-\frac{T_0}{T}\right) \qquad \text{for constant temperature, isochoric combustion} \tag{3.28}$$

The difference in reactant and product mixture enthalpies (H_R – H_P) is the heat transfer, $\dot{Q}$, across the system boundary to maintain constant system temperature during isobaric combustion. Similarly, the difference in reactant and product mixture internal energies (U_R – U_P) is the heat transfer, $\dot{Q}$, across the system boundary to maintain constant system temperature during isochoric combustion. The term $\left(1-\frac{T_0}{T}\right)$ is due to the Carnot cycle efficiency which limits the useful work that might be extracted from the heat transfer across the system boundary.

IV. RESULTS AND DISCUSSION

This section presents the results from the study on the various combustion processes. The results are presented for constant pressure combustion, constant volume combustion and constant temperature combustion in that order.

The fuels considered in this analysis are –

- Hydrogen, H_2
- Methane, CH_4
- Propane, C_3H_8
- Iso-octane, C_8H_{18}
- Acetylene, C_2H_2
- Benzene, C_6H_6
- Methanol, CH_3OH
- Ethanol, C_2H_5OH

The results presented are for equilibrium products of combustion, unless otherwise stated. For consistent comparison of the results, combustion of iso-octane at 500 kPa, equivalence ratio of 1.0 was set as the base case. This set of initial conditions was chosen for its relevance to combustion in internal combustion engines. The temperature and pressure typically obtained in internal combustion engines at the end of the compression stroke are of the order of 500 K and 500 kPa, respectively [9]. These values therefore, allow for an examination of the destruction of availability during the subsequent combustion process in the engine.

The parameters studied in the various combustion regimes were pressure, temperature, equivalence ratio and fuel. These parameters were varied over wide ranges to capture all trends. In some cases, the parameter values may be unrealistic. For example, reactant temperatures greater than about 1000 K are highly unlikely in practical systems. At high reactant temperatures, the species may dissociate. The effect of reactant dissociation is considered in a subsequent section.

Constant pressure combustion

Constant pressure combustion occurs in open systems. To obtain the product mixture composition, the enthalpy and pressure were held constant and the mixture was allowed to attain the corresponding equilibrium composition.

Parameter #1: Reactant temperature

The effect of reactant mixture temperature on the availability curves and the percentage availability destroyed was studied by varying the temperature from 300 K to 6000 K.

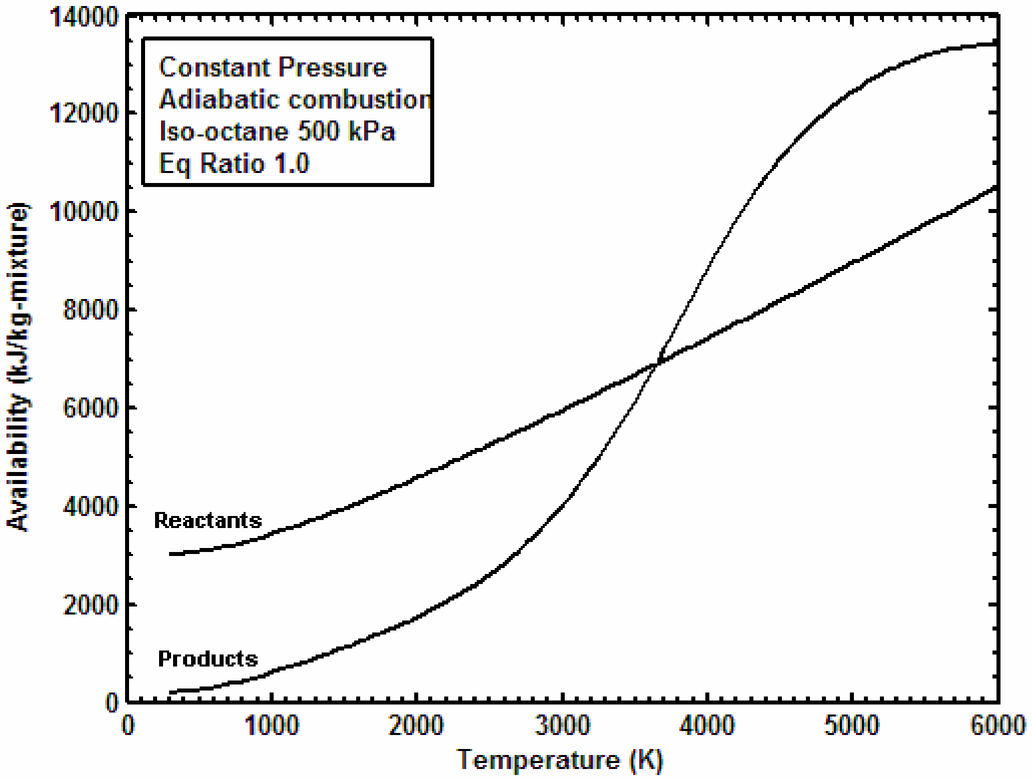


Fig. 1. Reactant and product mixture availabilities as a function of temperature for reactant pressure of 500 kPa and φ = 1.0, constant pressure combustion.

Fig. 1 shows the variation of the reactant and product mixture availabilities. The reactant mixture availability increases monotonically with temperature. The product mixture availability increases much more sharply past 2500 K, corresponding to the formation of the equilibrium products of combustion. The increased availability of the incomplete products of combustion such as carbon monoxide and hydrogen cause the sharp rise in product mixture availability.

Fig. 2 shows the percentage destruction of availability for the constant pressure (500 kPa) combustion of iso-octane over the temperature range of 300 K to 6000 K. The percentage availability destroyed decreases rapidly with increasing temperature from a value of about 29% at 300 K to about 4.5% at 6000 K. The plot shows that the irreversibility due to constant pressure combustion decreases with increase in reactant temperature, with smaller fractions of the original reactant mixture availability being destroyed at combustion corresponding to higher reactant temperatures.

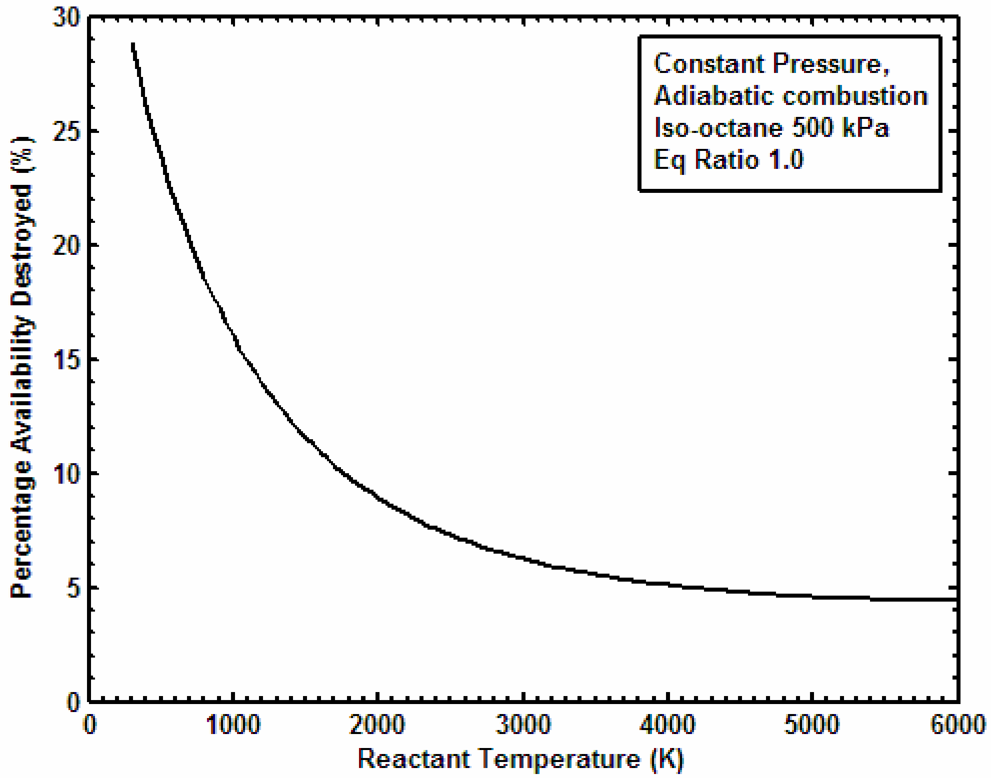


Fig. 2. Percentage availability destroyed as a function of reactant temperature for constant pressure combustion of iso-octane, reactant pressure of 500 kPa.

Parameter #2: Reactant pressure

The effect of the reactant mixture pressure on the availability curves and the percentage availability destroyed was studied. Fig. 3 shows the variation in reactant mixture availability for a range of pressures – 50 kPa, 100 kPa, 500 kPa, 1000 kPa and 5000 kPa. The reactant mixture availability was found to increase with increasing pressure. The effect of the increased pressure on the reactant mixture availability, however, was relatively modest.

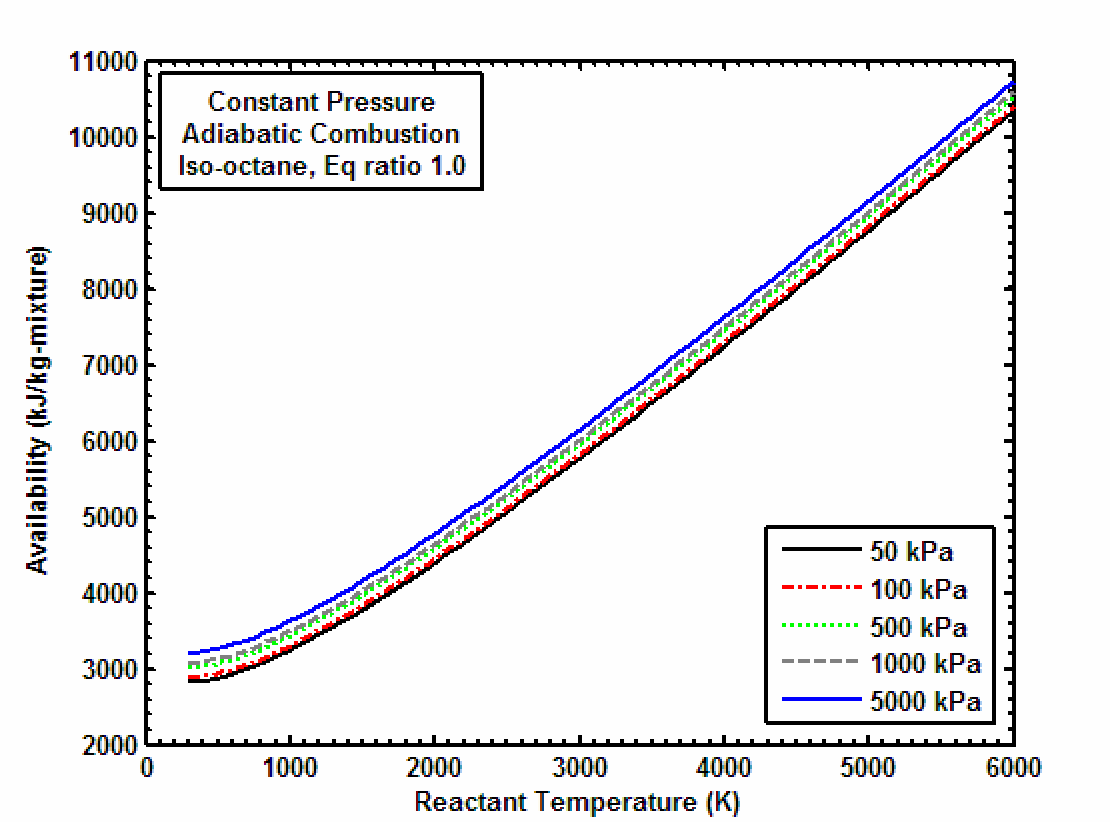


Fig. 3. Reactant mixture availability as a function of temperature for a range of pressures, constant pressure conditions.

Fig. 4 shows the variation of the product mixture availability for the same set of reactant mixture pressures. The trend of the product mixture availability is not the same as that for the reactant mixture availability. At lower product temperatures (lesser than 2500 K), the product mixture availability is higher for higher pressures. With increasing temperatures, however, higher pressures suppress the formation of the incomplete products of combustion, leading to lower product mixture availability. For very high product mixture temperatures (greater than 4000 K), the product mixture availability begins to decrease due to a rapid increase in the restricted dead state availability. This is due to the changed composition of the restricted dead state due to the decomposition of the nitrogen molecules present in the mixture into nitrogen atoms. Higher pressures suppress the dissociation of the nitrogen molecules and therefore, decrease in value at higher temperatures as compared to product mixtures at lower pressures.

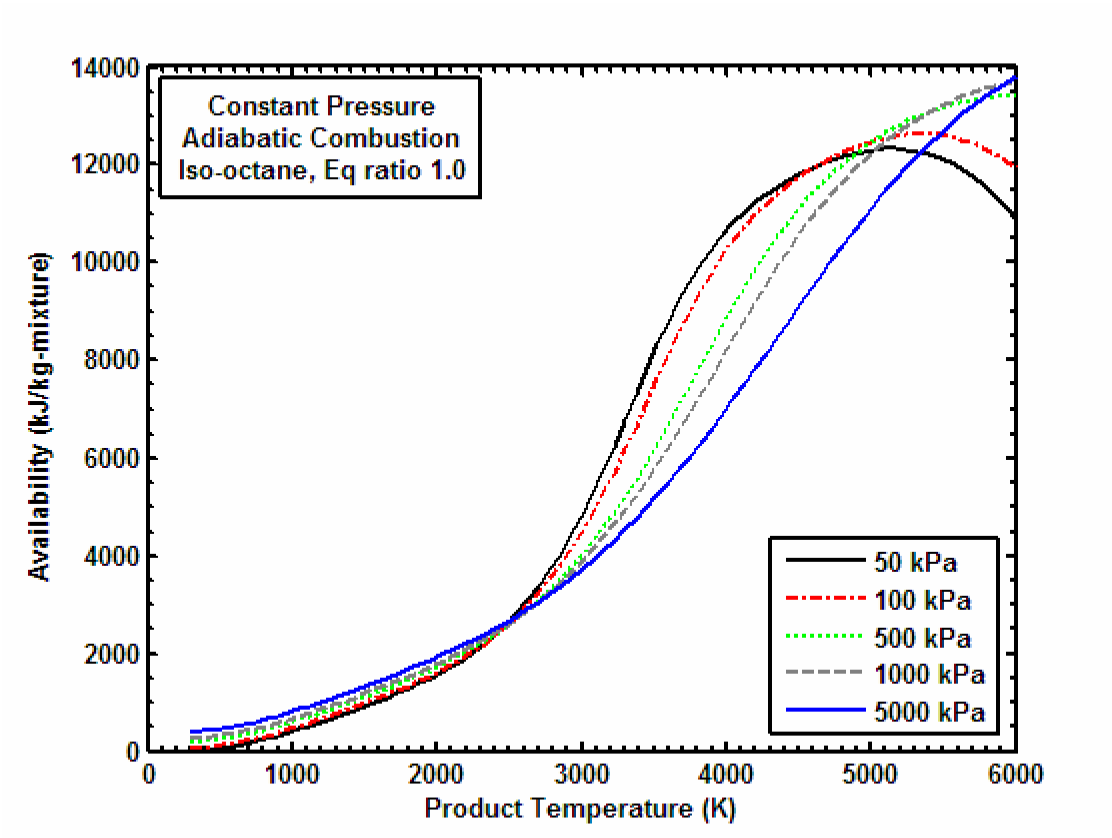


Fig. 4. Product mixture availability as a function of temperature for a range of pressures, constant pressure conditions.

Fig. 5 shows the percentage availability destroyed during constant pressure combustion for the same set of initial reactant pressures. The percentage availability destroyed values range from 26.5% to 31% at 300 K for the set of pressures considered and from 4% to 5% for the same set at 6000 K. The plot shows that a greater percentage of the availability is destroyed for lower reactant pressures, compared to higher reactant pressures. This trend persists over the entire temperature range and is due to the fact that higher pressures lead to higher product mixture temperatures, allowing for lesser destruction of availability due to the combustion process.

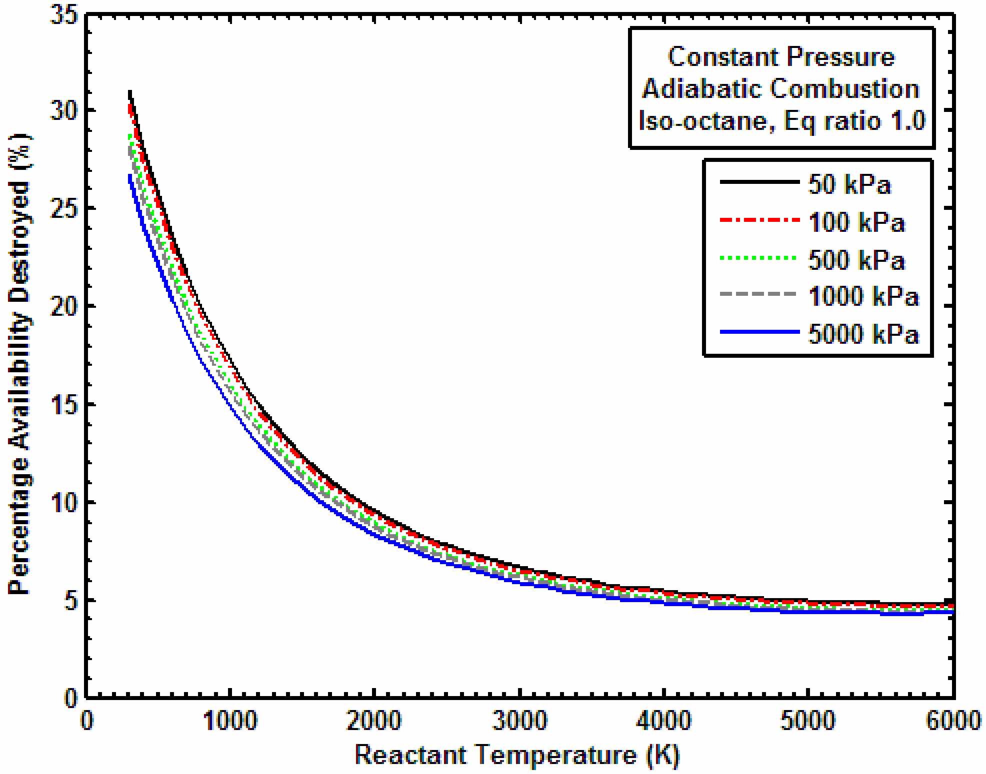


Fig. 5. Percentage availability destroyed as a function of reactant temperature for a range of pressures, constant pressure combustion.

Parameter #3: Equivalence ratio

For studying the effect of equivalence ratio, ϕ, on the destruction of availability, the constant pressure combustion of iso-octane at 500 kPa was considered. First, lean equivalence ratios ($\phi \leq 1$) will be examined and then rich equivalence ratios ($\phi \geq 1$). Fig. 6 shows the percentage availability destroyed curves for equivalence ratios ranging from 0.1 to 1.0. For a reactant temperature of 300 K, the percentage availability destroyed is higher for leaner equivalence ratios, with the percentage availability destroyed value being highest for the equivalence ratio of 0.1 and lowest for the equivalence ratio of 1.0. This is because combustion of the richer mixtures (but still lean) leads to formation of products at higher temperatures, thus reducing the destruction of availability. The percentage availability destroyed values drop more rapidly with increasing temperatures for the leaner equivalence ratios than for equivalence ratios closer to the stoichiometric ratio. At higher temperatures (greater than 2500 K), the values of the percentage availability destroyed converge to a value of about 4% for all equivalence ratios. The trend at the higher temperatures is actually the reverse of the trend at lower temperatures, but the values are closely spaced and may not be readily discernible due to the scale of the plot. This reversal of the trend is due to the fact that the reactive availability (chemical energy) of the reactant mixture with lean equivalence ratios is negligible compared to the thermo-mechanical availability of the mixture at higher temperatures. As a consequence, the percentage availability destroyed due to combustion is lesser for the leaner reactant mixtures.

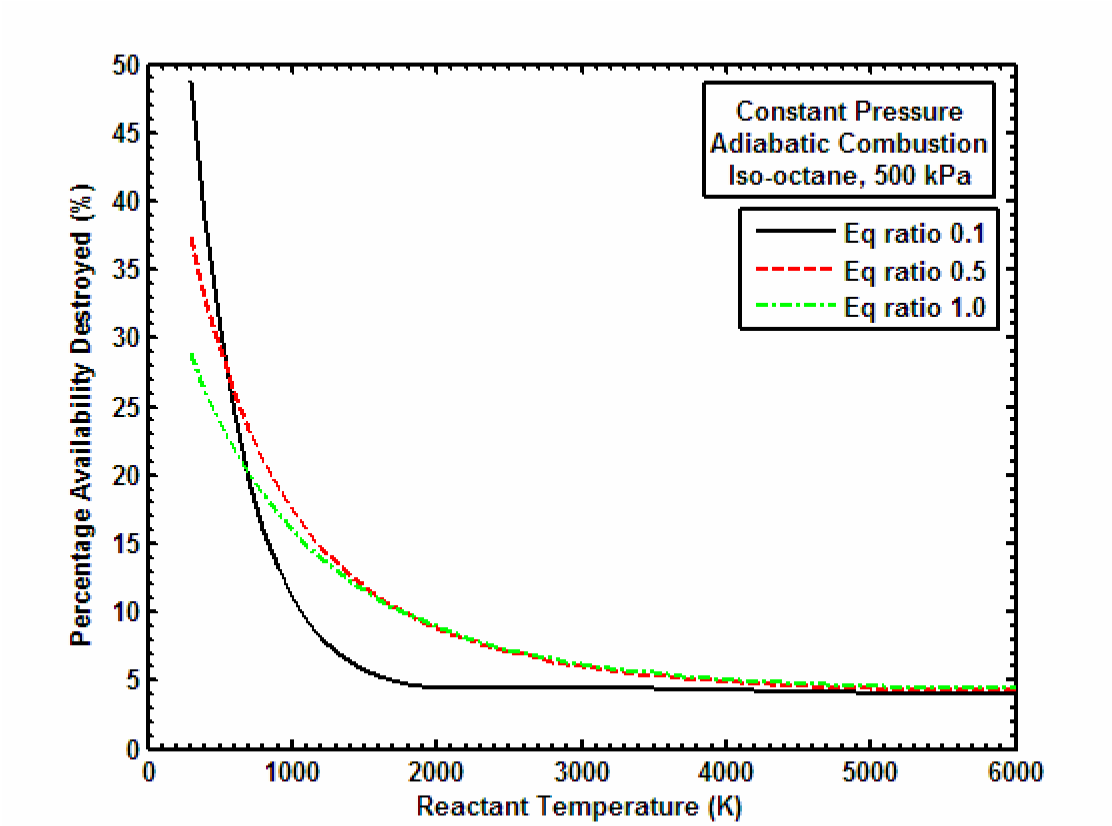


Fig. 6. Percentage availability destroyed for lean equivalence ratios, constant pressure combustion of iso-octane at 500 kPa.

Fig. 7 shows the percentage availability destroyed values for rich equivalence ratios, ranging from 1.0 to 2.0. Corresponding to reactant temperatures of 300 K, the percentage availability destroyed value is highest for the stoichiometric equivalence ratio and lowest for the equivalence ratio of 2.0. With increasing temperatures, the percentage availability destroyed values for the different equivalence ratios converge to a value of about 4%. The trend at higher temperatures, once again, is the reverse of that at lower temperatures. Note that the lower percentage availability destroyed for rich equivalence ratios ($\phi \geq 1$) does not necessarily imply that combustion of rich equivalence ratios is to be preferred. The values shown in the plot account for the reactive availability term of the species present in the product mixture. In practical applications, the utilization of this availability will require additional subsequent combustion processes. If this availability due to the incomplete products of combustion in the product mixture is not considered to be useful, then the fraction of availability destroyed is least for the stoichiometric mixture.

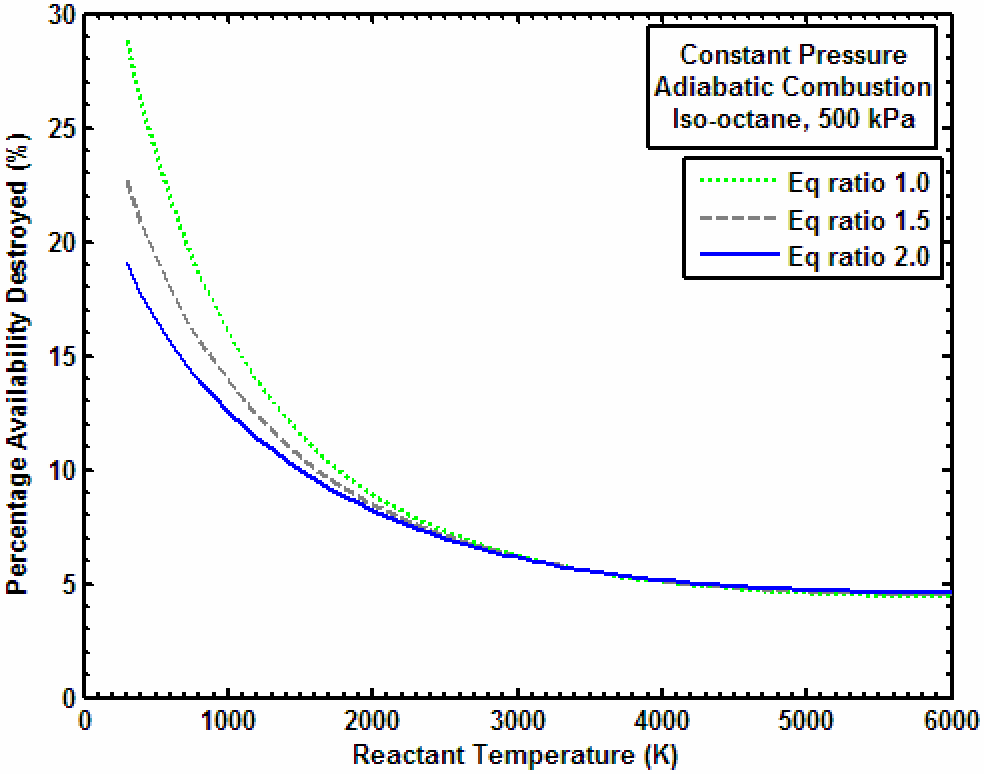


Fig. 7. Percentage availability destroyed for rich equivalence ratios, constant pressure combustion of iso-octane at 500 kPa.

Fig. 8 shows the effect of equivalence ratio on the final product mixture temperature. The plot shows the product mixture temperatures for a range of initial reactant mixture temperatures. The final product mixture temperatures were higher for richer equivalence ratios up to an equivalence ratio of 1.0. This is simply a consequence of the lesser chemical energy present in leaner reactant mixtures. The lesser chemical energy present translates into lower energy being liberated during the combustion process and consequently, a lower final product mixture temperature. It may also be noted that the product mixture temperatures obtained corresponding to higher reactant temperatures (past 3000 K) are lower than the reactant mixture temperatures. However, at such high temperatures, the dissociation of the reactants also has significant effect on the mixture properties and needs to be accounted for. This is discussed in greater detail in a subsequent section.

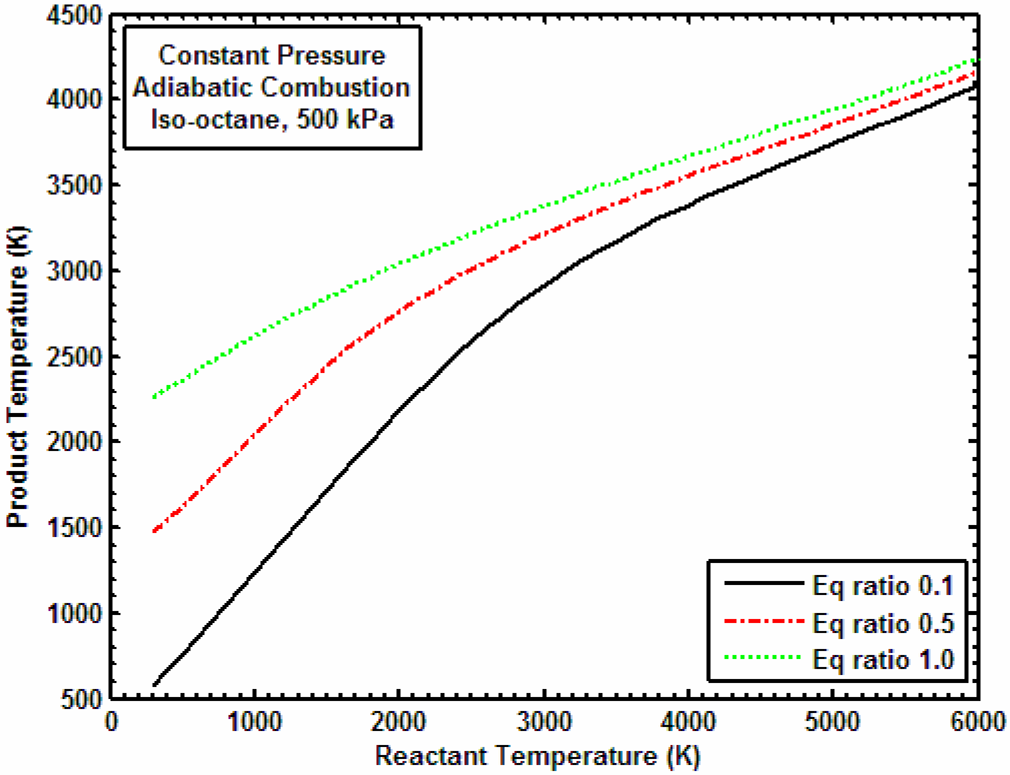


Fig. 8. Product mixture temperature for a range of lean equivalence ratios, constant pressure combustion of iso-octane at 500 kPa.

Similarly, Fig. 9 shows the effect of equivalence ratios on the product mixture temperature for rich equivalence ratios ($\phi \geq 1$). For reactant mixture temperature of 300 K, the highest product mixture temperature was achieved for a mixture with an equivalence ratio of 1.0, with the product mixture temperature dropping for richer reactant mixtures. This is because the richer reactant mixtures do not have sufficient air for oxidation of the fuel present, with the additional fuel thus acting largely as a dilutant. With increasing reactant temperatures, the trend changes, with higher product mixture temperatures achieved for richer reactant mixtures. At higher reactant temperatures (greater than 2500 K), higher product mixture temperatures are achieved for the richer reactant mixtures since the products formed are the incomplete products of combustion, requiring less than the stoichiometric amount of air for their formation.

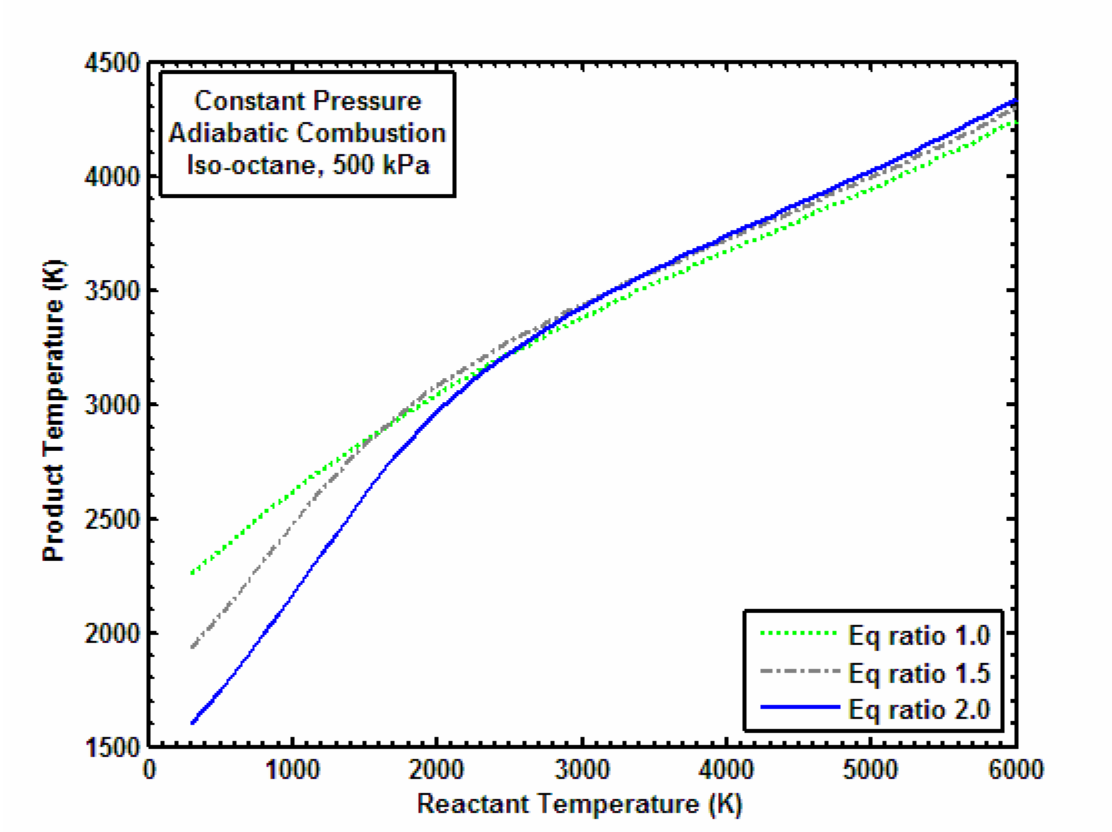


Fig. 9. Product mixture temperature for a range of rich equivalence ratios, constant pressure combustion of iso-octane at 500 kPa.

Fig. 10 shows the variation of the final product mixture temperature with reactant mixture equivalence ratio for the combustion of iso-octane at 500 kPa and a reactant mixture temperature of 300 K. It was noted that the final product mixture temperature initially increased with increasing equivalence ratios, before decreasing again with increasingly richer equivalence ratios, with the peak product mixture temperature corresponding to near stoichiometric reactant mixture.

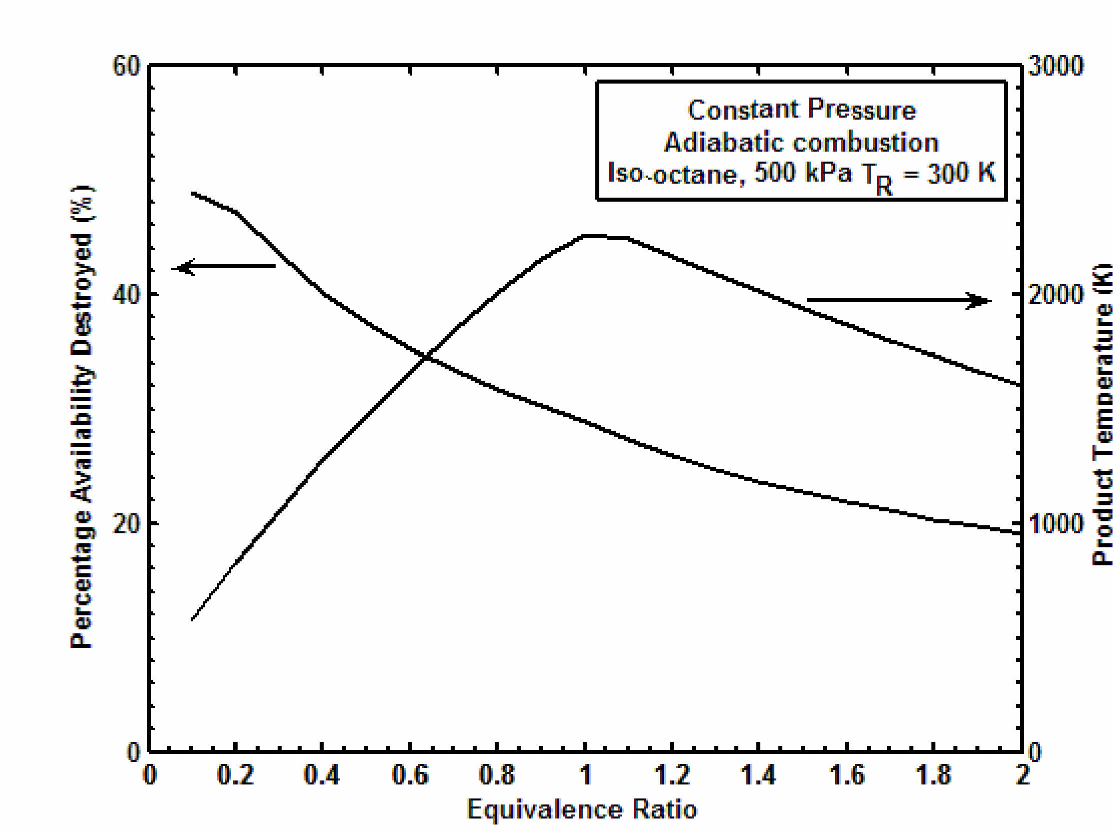


Fig. 10. Percentage availability destroyed and product mixture temperature as a function of equivalence ratio, for constant pressure combustion of iso-octane at 500 kPa and 300 K.

Also shown in Fig. 10 is the percentage availability destroyed values for the same combustion conditions. The percentage availability destroyed decreases monotonically with increasing equivalence ratios. This is because of the reduced irreversibility associated with the combustion of richer reactant mixtures. Once again, it may be noted that combustion of richer mixtures ($\phi > 1$) destroys lesser fraction of the reactant availability, but is not of practical use since the availability is present in the form of chemical energy associated with the incomplete products of combustion, which necessitates further combustion of the product mixture to liberate this energy.

Parameter #4: Fuels

In addition to the parameters discussed in the preceding sections, the fuel affects the fraction of availability that is destroyed during the combustion process. Fig. 11 shows the percentage availability destroyed during the constant pressure combustion of various fuels at 500 kPa and an initial reactant mixture temperature of 300 K.

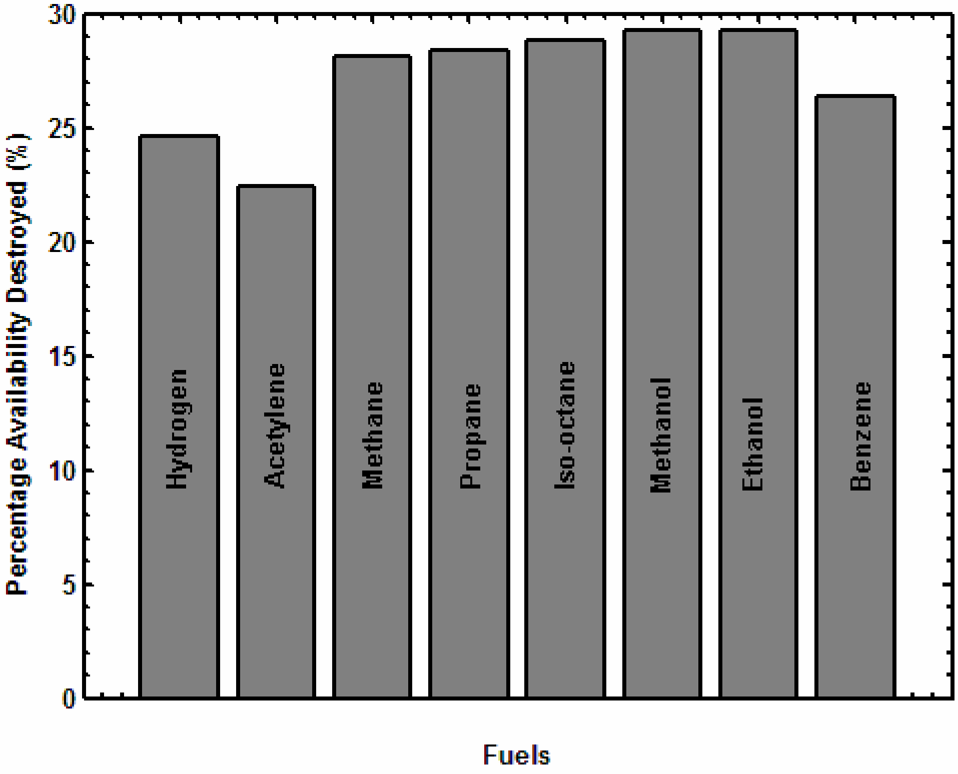


Fig. 11. Percentage availability destroyed during constant pressure combustion of different fuels at 500 kPa and an initial reactant temperature of 300 K.

The fraction of availability destroyed during combustion for the set of conditions outlined above was found to be in the range of 22% to 29%. In general, the destruction of availability was found to increase with increasing complexity of the fuel molecules. The values calculated for the percentage of availability destroyed during the combustion of the different fuels were determined from the availability balance, as outlined in Section III. Combustion of acetylene was found to destroy the least fraction of the reactant mixture availability (~22% as compared to ~25% for hydrogen). However, the availability balance accounts for the chemical (reactive and diffusion) availability of the mixtures. If only the destruction of the thermo-mechanical availability is evaluated, hydrogen is found to destroy a smaller fraction of availability as compared to acetylene (and other fuels).

Importance of chemical availability

One of the objectives of this study was to quantify the contribution and effect of the diffusion availability on the destruction of availability during the combustion of various fuels. To understand the contribution of the various terms to the total availability, the various components of the mixture availability were calculated and plotted separately. The total mixture availability was split into three components – the thermo-mechanical availability, reactive availability and the diffusion availability.

The thermo-mechanical availability of a system is due to its pressure and temperature. The reactive availability of a system is due to the work that may be obtained during the process of converting the various species in the system into species present in the atmosphere. The reactive availability of a mixture also includes the work that may be extracted by allowing the various species to subsequently come to equilibrium with the atmosphere. The reactive availability and the diffusion availability, together, comprise the chemical availability of a mixture. This section shows the magnitudes and relative importance of these availability terms for the reactant and product mixtures as a function of temperature.

Fig. 12 shows the contribution of the various components to the total reactant availability. For the reactant mixture, the chemical availability is the dominant component at lower temperatures. The thermo-mechanical component increases rapidly in significance with increasing temperatures, while the contribution of the chemical availability component remains fixed in magnitude. The diffusion availability component is also fixed in magnitude and is largely insignificant compared to the other availability terms.

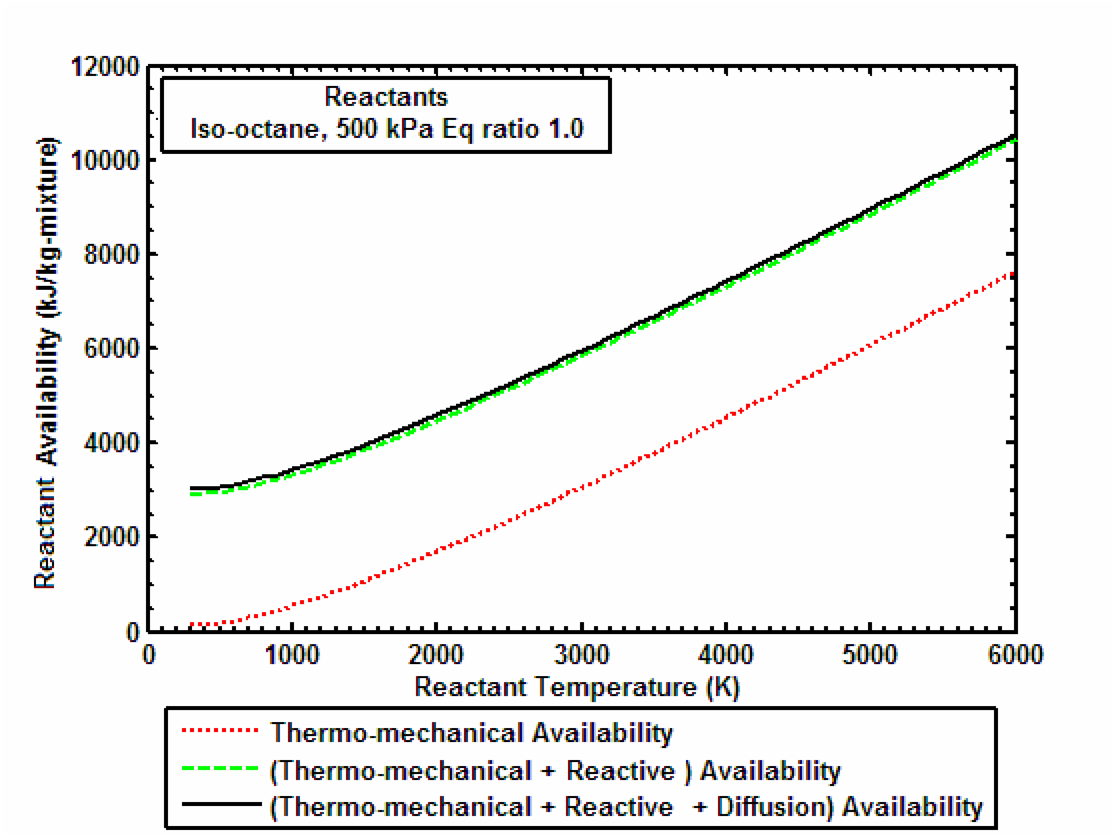


Fig. 12. Various components of the total reactant mixture availability for stoichiometric mixture of iso-octane at 500 kPa and φ=1.0.

Fig. 13 shows a similar plot of the various components of the total mixture availability for the product mixture corresponding to constant pressure combustion of iso-octane at 500 kPa as a function of temperature. Once again, the diffusion availability has a fixed magnitude and is generally insignificant in comparison with the other availability terms of the mixture. The thermo-mechanical component of the availability is small at low temperatures, increasing in magnitude with increasing temperatures. The decrease in the availability at temperatures greater than 500) K is due to the dissociation of the nitrogen molecules, as explained previously. The reactive availability is also small initially at low temperatures. This is because the products of combustion at the lower temperatures comprise almost entirely of the complete products of combustion – carbon dioxide and water. These species do not have any chemical energy available for useful work, by conversion to species present in the atmosphere. With increasing temperatures, the product mixture's chemical availability increases sharply after 2500 K. This corresponds to the occurrence of the incomplete products of combustion such as hydrogen, carbon monoxide etc. These species have chemical energy (reactive availability) associated with them, available for extraction by allowing them to react to form the standard atmospheric species. The contribution due to these species increases with temperature, and at higher temperatures, is more significant than the thermo-mechanical availability of the mixture.

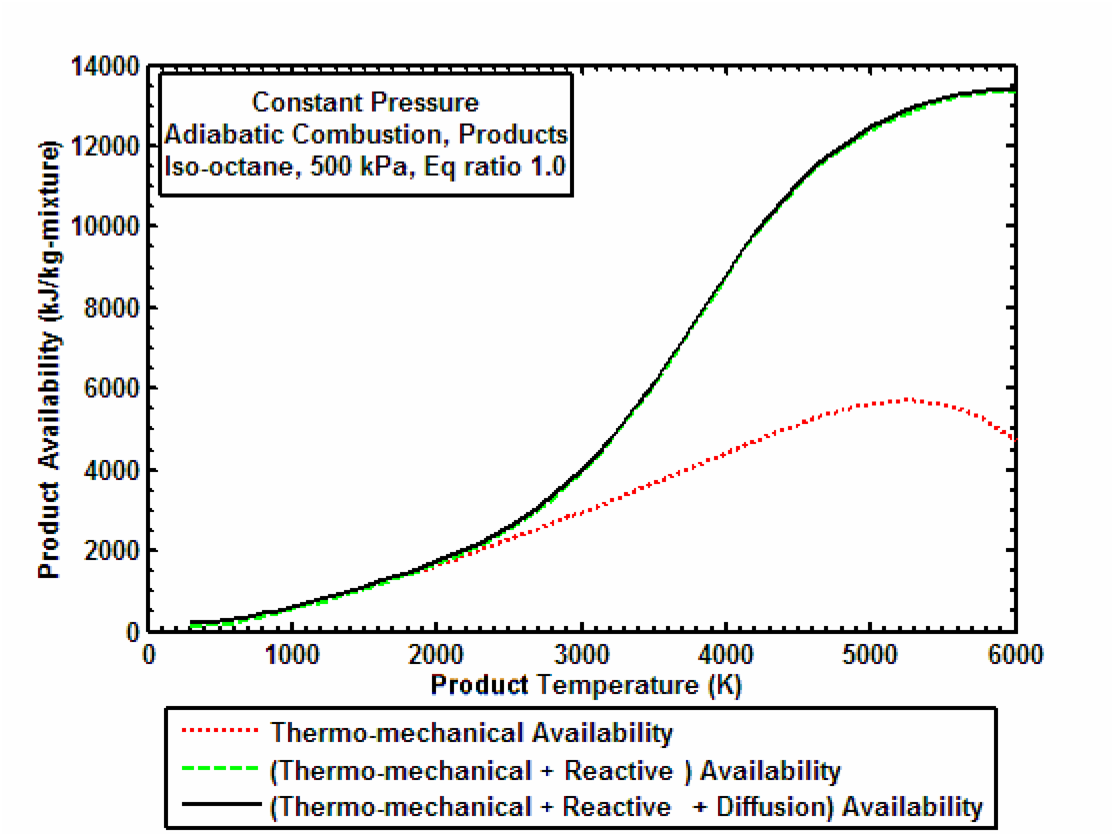


Fig. 13. Various components of the total product mixture availability, for stoichiometric mixture of iso-octane at 500 kPa, constant pressure combustion.

Effect of reactant dissociation

The results and discussions in the preceding sections have considered constant pressure combustion with equilibrium products of combustion. The reactants have been assumed to be stable at the elevated temperatures considered. However, this is strictly not true, since the fuels and even the components of air tend to dissociate at the higher temperatures in some of these discussions. The effect of dissociation was incorporated into this study by allowing the various reactant mixture components to dissociate independently, without reacting with each other.

Fig. 14 shows the availability of the reactant mixture with and without consideration of the reactant mixture dissociation. It is evident that dissociation of the reactants alters the availability of the mixture significantly at higher temperatures. The mixture enthalpy is also altered once this effect is accounted for, causing the corresponding change in product mixture properties. The increased reactant mixture availability is due to the fact that the dissociated reactant mixture species contain additional energy, absorbed during the process of breaking the various chemical bonds. This additional energy would need to be supplied to maintain the reactant mixture temperature.

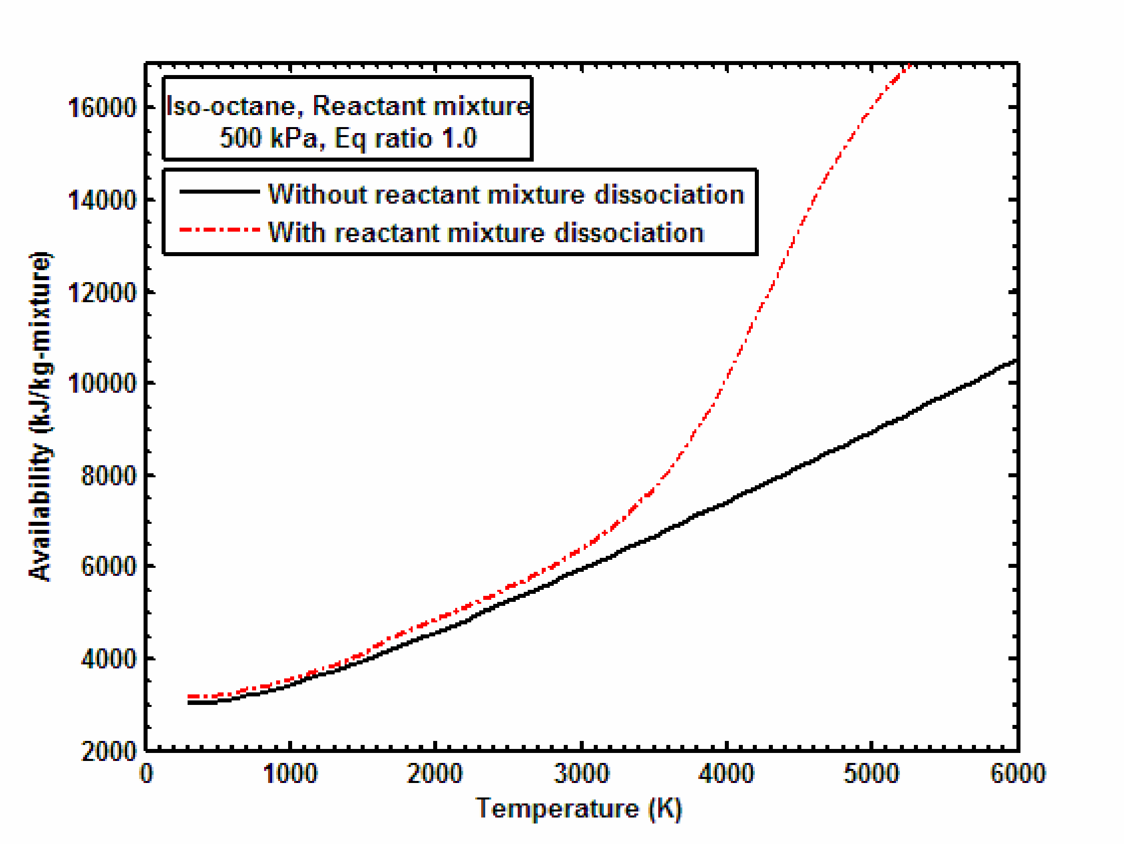


Fig. 14. Effect of reactant mixture dissociation on availability, constant pressure conditions.

Fig. 15 shows the percentage of reactant mixture availability destroyed for constant pressure combustion of iso-octane, after accounting for the reactant mixture dissociation. The initial difference in values at lower reactant temperatures (lesser than 1500 K) are due to the fact that iso-octane is an unstable compound and given infinite time, would dissociate into methane, carbon and hydrogen. At the lowest temperatures, the dissociation reaction would be slow and this effect would not be observed (limited by chemical kinetics). For a more stable fuel such as methane or hydrogen, the two curves would merge at the lower reactant temperatures.

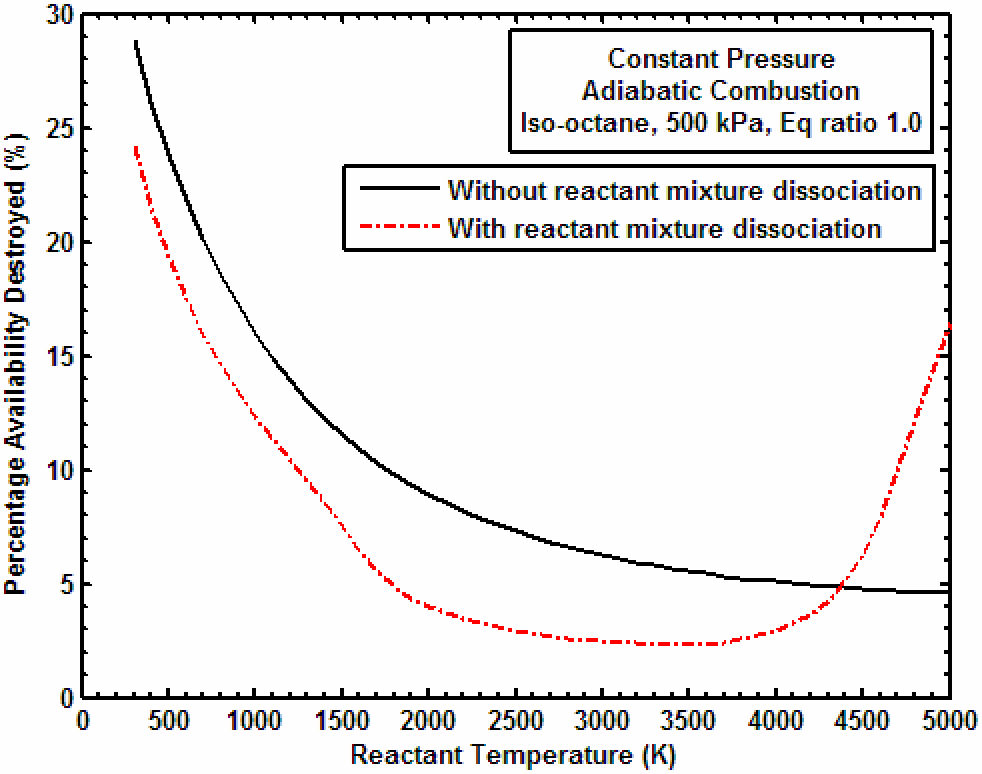


Fig. 15. Percentage availability destroyed during constant pressure combustion of iso-octane at 500 kPa, with and without reactant mixture dissociation.

The two curves (with and without reactant mixture dissociation) in Fig. 15 follow the same trend with increasing temperatures until a reactant temperature of about 1500 K. Beyond this temperature, the dissociation effects become significant and cause the curve with the dissociation effects considered to deviate from the other curve. At higher temperatures, the curve considering the dissociation of reactants rises higher than the other curve indicating increased availability destruction. This is because the dissociated reactant mixture has additional energy as compared to the non-dissociated reactant mixture, which has not been lost during the combustion process.

Fig. 16 shows the final product mixture temperature as a function of the reactant temperature mixture, with and without the reactant mixture dissociation effects being considered. It is once again evident that the two curves are in near agreement at lower temperatures. For high temperatures (greater than 3500 K), incorporating the dissociation effects leads to higher product temperatures at higher reactant mixture temperatures. This is because the dissociated reactant mixture possesses higher enthalpy than the non-dissociated reactant mixture. This causes the correspondingly higher product mixture temperatures.

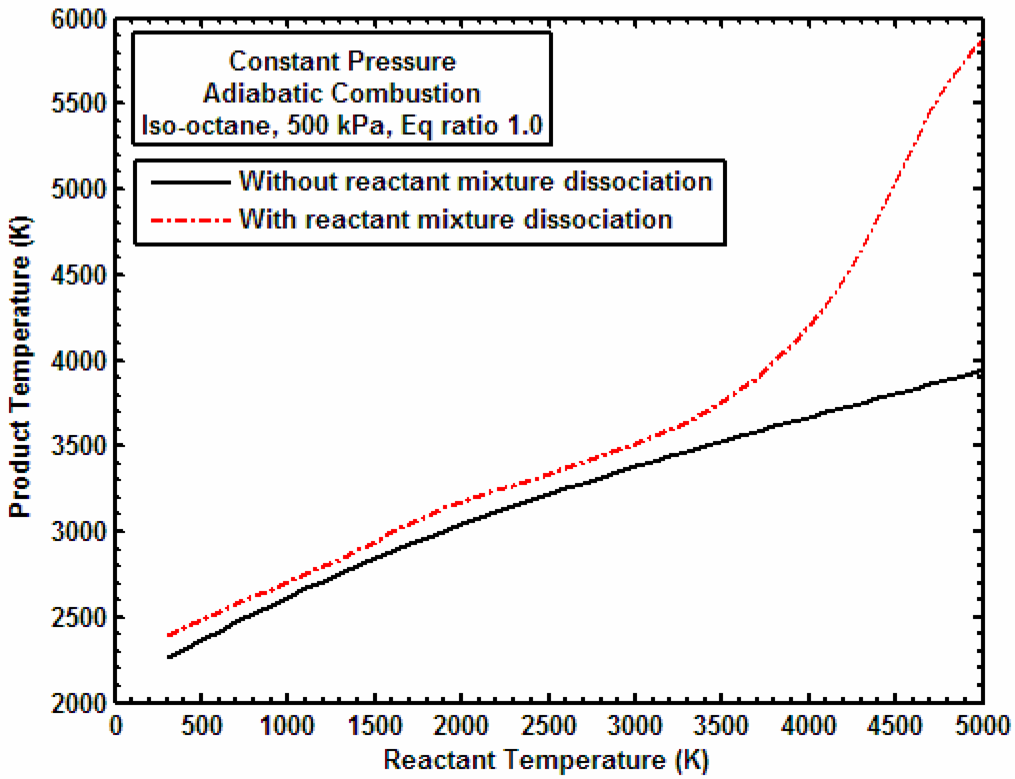


Fig. 16. Product mixture temperature as a function of reactant mixture temperature, with and without dissociation of reactants for constant pressure combustion of iso-octane at 500 kPa.

Constant volume combustion

Constant volume combustion occurs in closed systems. To obtain the product mixture composition, the internal energy and density of the reactant mixture were held constant while the mixture was allowed to attain the equilibrium composition. The final product mixture pressure is different than the initial reactant mixture pressure.

Parameter #1: Reactant temperature

The effect of reactant mixture temperature on the availability curves and the percentage availability destroyed was studied by varying the temperature from 300 K to 6000 K.

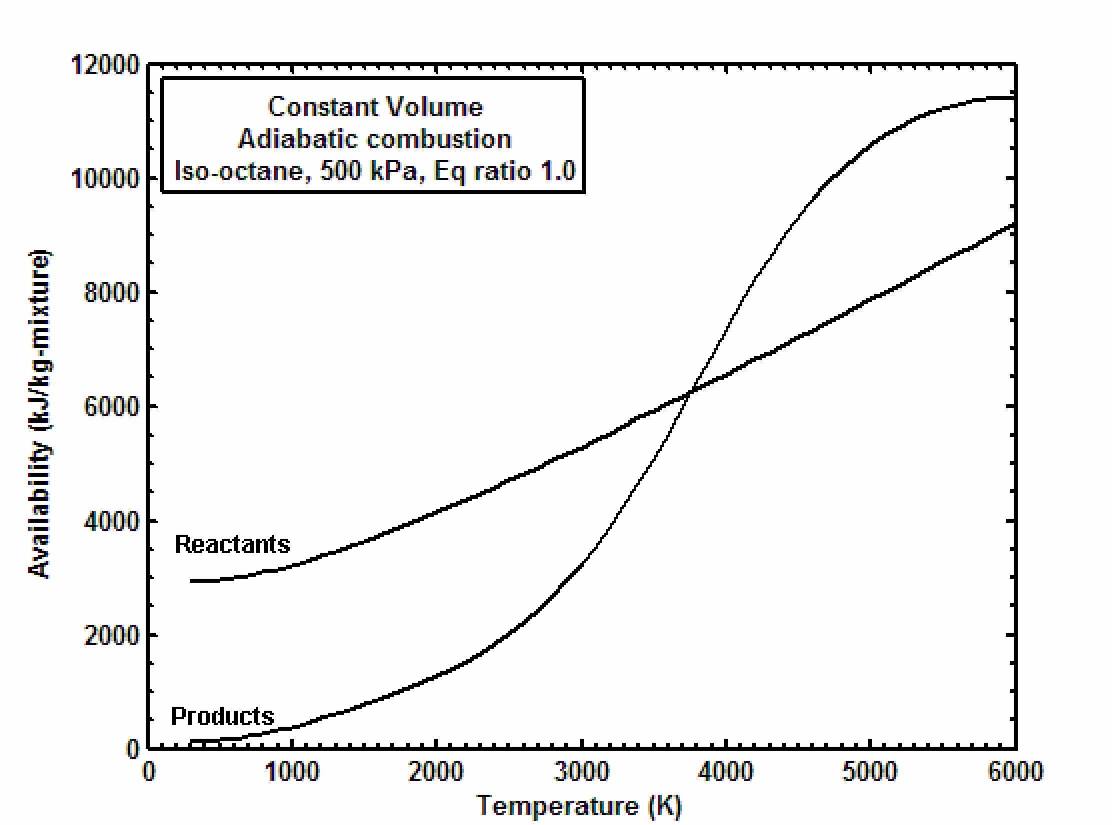


Fig. 17. Reactant and product mixture availabilities as a function of temperature for reactant pressure of 500 kPa and φ = 1.0, constant volume combustion.

Fig. 17 shows the variation of the reactant and product mixture availability as a function of the reactant mixture temperature. The reactant mixture availability increases monotonically with increasing temperature. The product mixture availability rises sharply after about 2500 K, due to the increased presence of the incomplete products of combustion. . Again, the product mixture availability decreases past 5000 K due to the dissociation of the nitrogen molecules, resulting in higher restricted dead state availability for the product mixture. The trends for both reactant mixture availability and product mixture availability are similar to those obtained for constant pressure combustion conditions.

Fig. 18 shows the percentage availability destroyed as a function of the initial reactant mixture temperature. The fraction of the reactant availability destroyed as a consequence of the combustion process decreases rapidly with increasing temperatures. The effect of increasing reactant mixture temperature on the percentage availability destroyed is moderated past 4000 K.

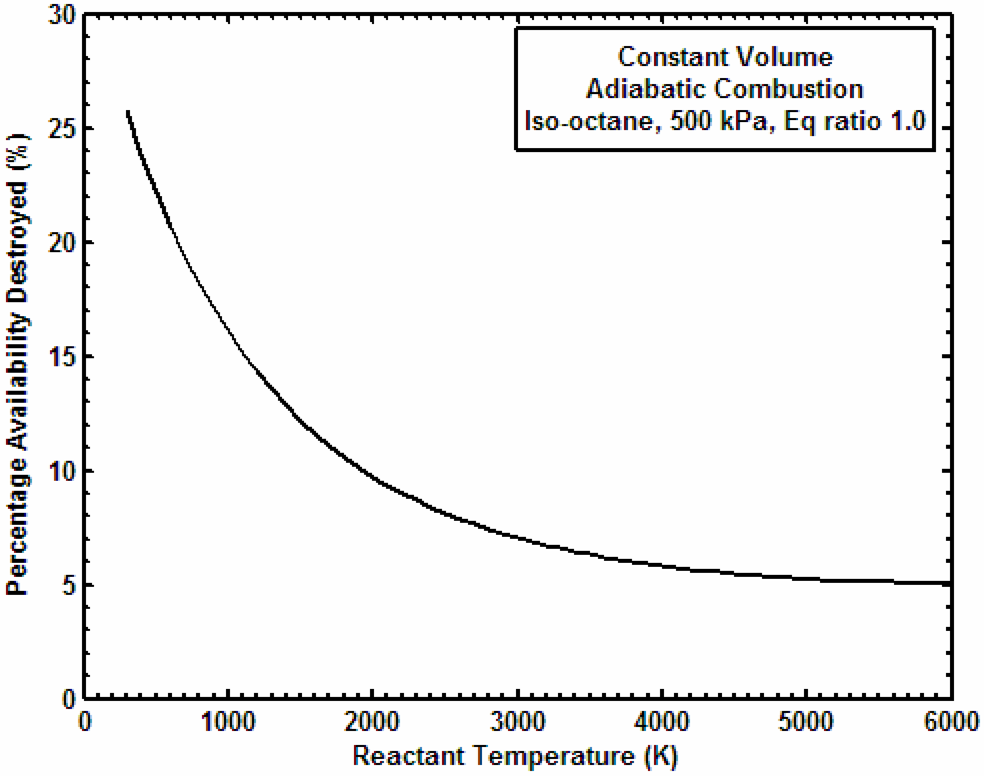


Fig. 18. Percentage availability destroyed as a function of reactant temperature, constant volume combustion of iso-octane, reactant pressure 500 kPa.

Parameter #2: Reactant pressure

The effect of the initial reactant mixture pressure on constant volume combustion was studied for a range of pressures. Fig. 19 shows the variation of the reactant mixture availability as a function of the reactant mixture temperature for pressures ranging from 50 kPa to 5000 kPa. The effect of increase in the pressure is modest compared to the effect of other parameters. The availability of the reactant mixtures with lower reactant pressures is higher at higher temperatures. This is because of the P_0V term in the availability expression. The reactant mixtures with lower pressures have a greater potential to do work due to compression of the system while coming to thermo-mechanical equilibrium with the environment. This is reflected in the divergence of the availability curves at higher temperatures.

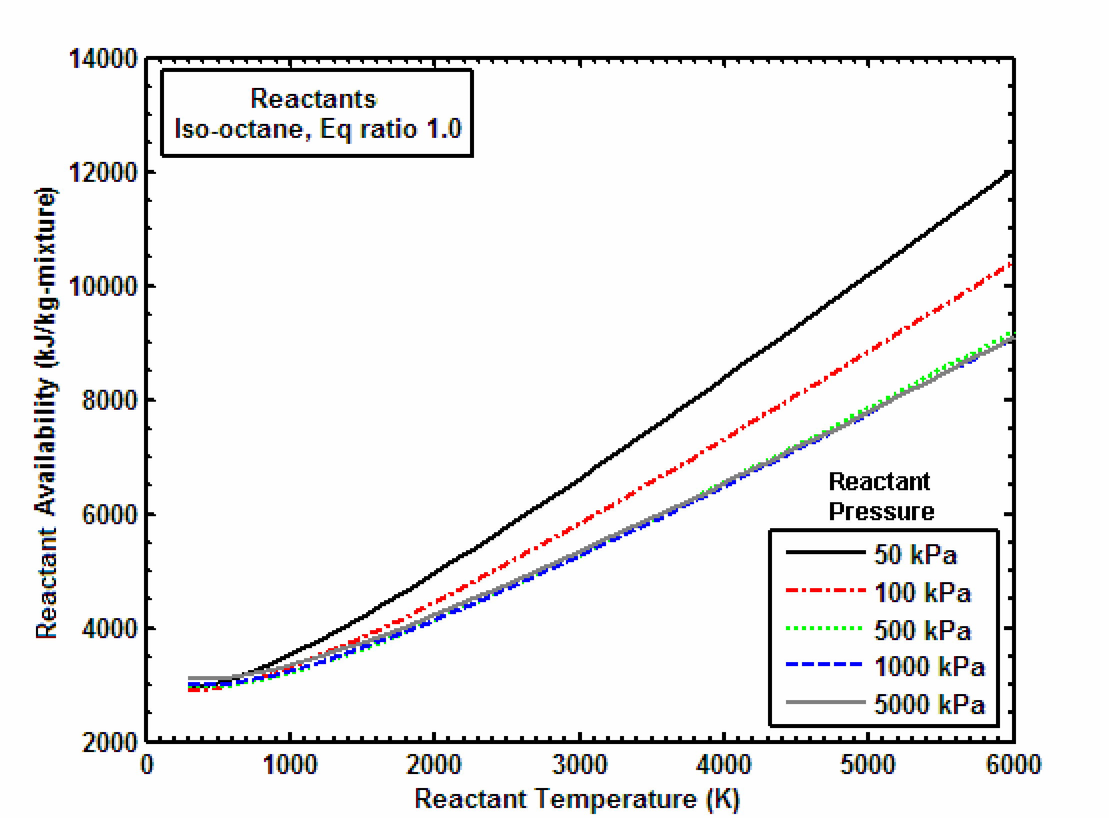


Fig. 19. Reactant mixture availability as a function of reactant temperature for a range of reactant pressures for constant volume conditions.

Fig. 20 shows the availability curves for the product mixture as a function of the temperature for the same set of initial reactant mixture pressures. At lower temperatures, the product mixtures corresponding to higher initial reactant pressures have greater availability than those corresponding to lower initial reactant pressures. With increase in temperature, the trend is reversed, with the mixtures corresponding to lower pressures possessing greater availability. This is once again due to the greater potential to do work while coming to thermo-mechanical equilibrium with the environment as explained for the reactant mixture case. For temperatures greater than 5000 K, the availability curves decrease due to the dissociation of the nitrogen in the mixture. As noted during constant pressure combustion, the availability curves start decreasing at lower temperatures for lower pressures since the higher pressure suppress the dissociation of the nitrogen molecules.

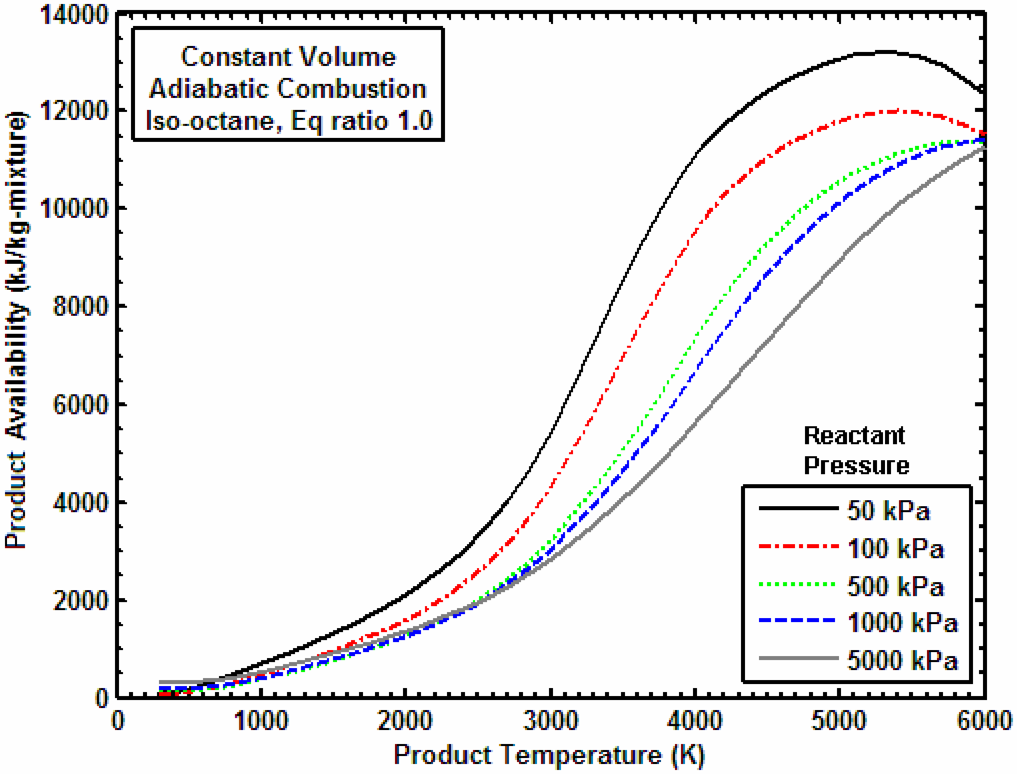


Fig. 20. Product mixture availability as a function of product temperature for a range of reactant pressures for constant volume conditions.

Fig. 21 shows the corresponding percentage of the reactant mixture availability destroyed as a consequence of constant volume combustion for various initial reactant mixture pressures. At lower temperatures, the percentage of reactant mixture availability destroyed is roughly the same for all pressures. With increasing temperatures, the trend is reversed, but the values are largely the same. Thus, the initial reactant mixture pressure has no significant effect on the percentage of the reactant mixture availability that is destroyed during constant volume combustion.

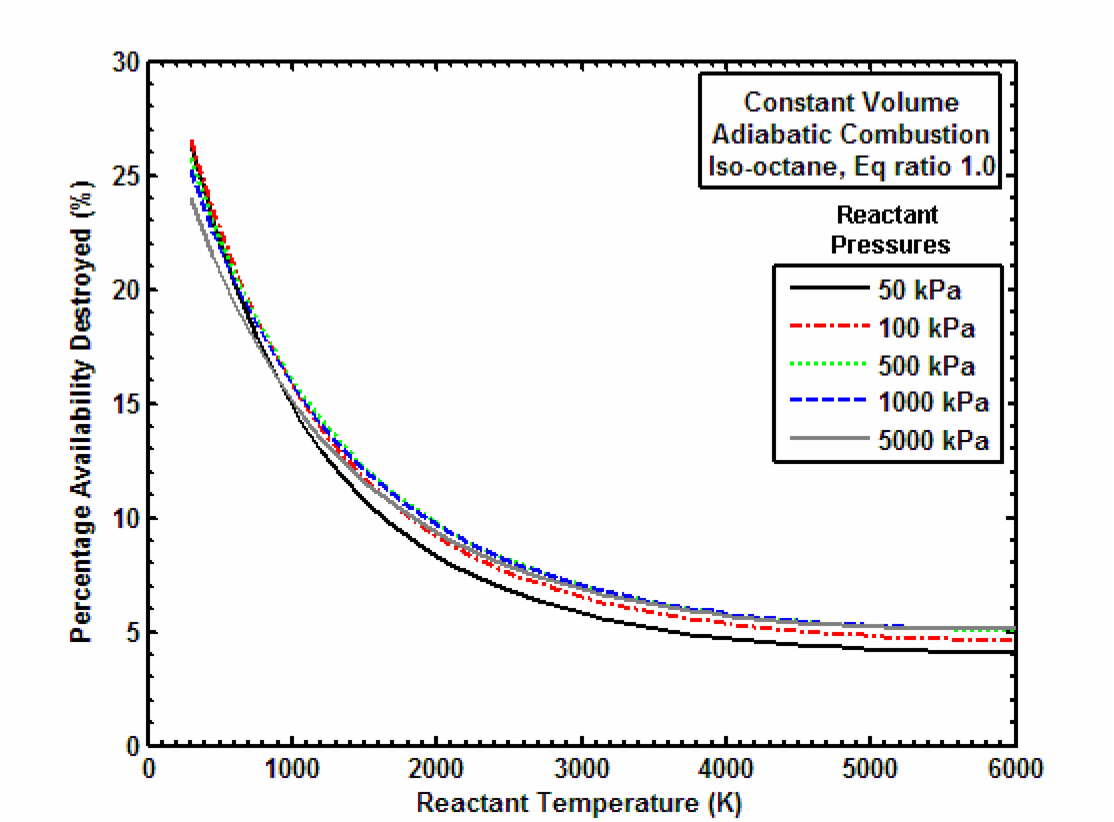


Fig. 21. Percentage availability destroyed as a function of reactant temperature for a range of reactant pressures for constant volume combustion.

Parameter #3: Equivalence ratio

For studying the effect of equivalence ratio, ϕ, on the destruction of availability, the constant volume combustion of iso-octane at reactant pressure of 500 kPa was considered. Fig. 22 shows the percentage of reactant mixture availability destroyed for the constant volume combustion of lean reactant mixtures, with equivalence ratios ranging from 0.1 to 1.0. Initially, corresponding to a reactant mixture temperature of 300 K, the greatest fraction of reactant availability is destroyed during the combustion of the reactant mixture with an equivalence ratio of 0.1, with the least destruction occurring during combustion of the stoichiometric mixture. At higher temperatures, this trend gets reversed, with the greatest fraction of availability being destroyed during combustion of the stoichiometric mixture and combustion of the reactant mixture with an equivalence ratio of 0.1 results in the least destruction of availability. The effect is least noticeable at higher temperatures, with the curves converging to a common value. Once again, the percentage availability decreases more rapidly for leaner equivalence ratios. This is similar to the trend observed during constant pressure combustion and the reason for this trend is that the chemical energy present in the leaner mixtures is negligible as compared to the thermo-mechanical availability at higher temperatures.

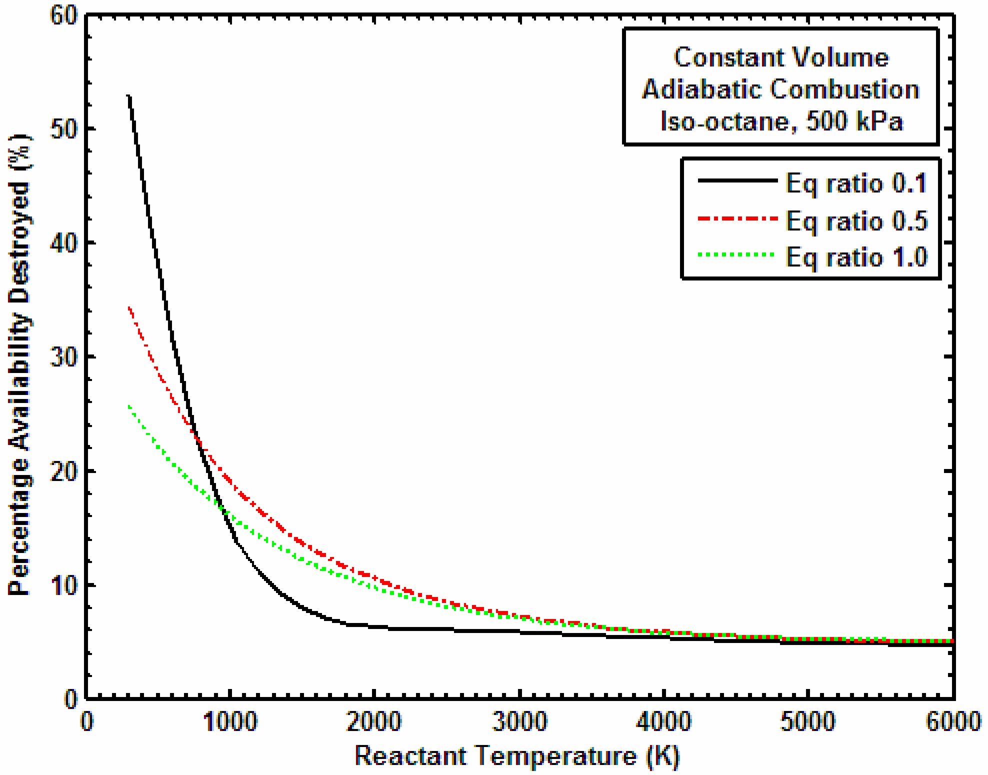


Fig. 22. Percentage availability destroyed for lean equivalence ratios, constant volume combustion of iso-octane, reactant mixture at 500 kPa.

Fig. 23 shows the results for the destruction of availability for rich reactant mixtures, with equivalence ratios ranging from 1.0 to 2.0. At lower reactant mixture temperatures, combustion of the stoichiometric mixture causes the least destruction of availability, while combustion of the reactant mixture of equivalence ratio of 2.0 leads to the greatest percentage loss of the reactant mixture availability. At higher temperatures, the curves once again converge to a common value. Again, combustion of mixtures with equivalence ratios greater than 1.0 is not necessarily to be the preferred. The lower percentage availability destroyed during the combustion of the richer equivalence ratios ($\phi \geq 1$) is due to the reactive availability of the incomplete products of combustion. Subsequent additional combustion processes would be needed to utilize this availability.

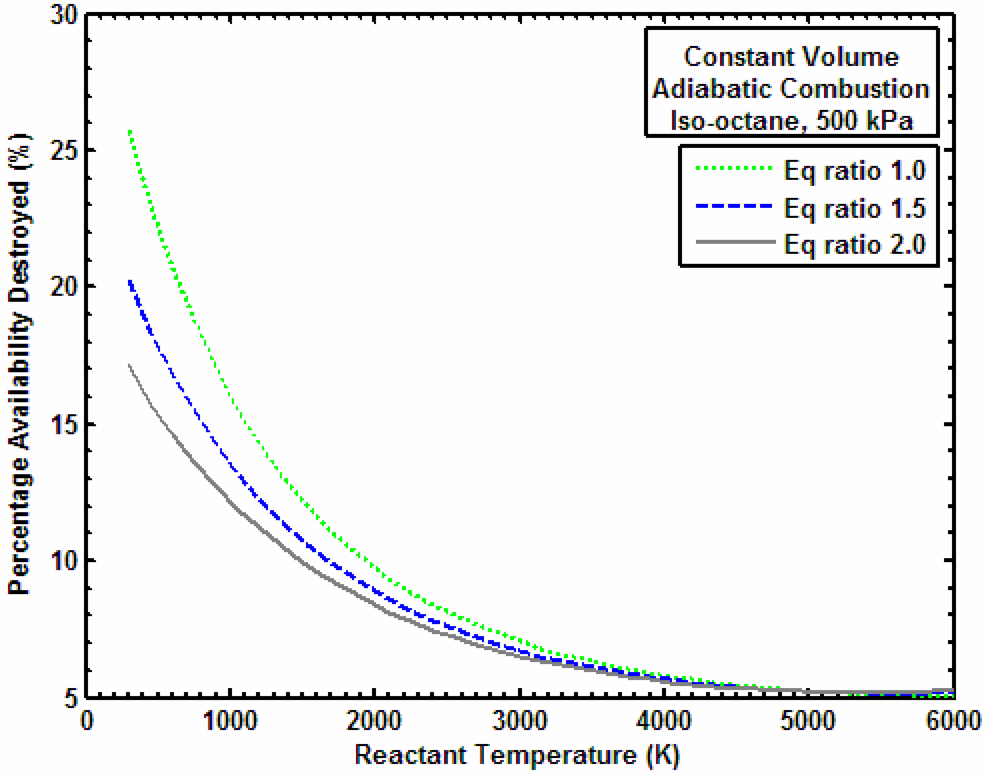


Fig. 23. Percentage availability destroyed for rich equivalence ratios, constant volume combustion of iso-octane, reactant mixture at 500 kPa.

Fig. 24 shows the effect of the equivalence ratio of the reactant mixture on the final product mixture for the constant volume combustion of iso-octane with reactant pressure of 500 kPa. Richer (but still lean) reactant mixtures result in higher product mixture temperatures and pressures after combustion. This is simply a consequence of the greater chemical energy available initially in the reactant mixtures as the equivalence ratio tends to 1.0. The liberation of this chemical energy during combustion leads to corresponding higher product mixture temperatures.

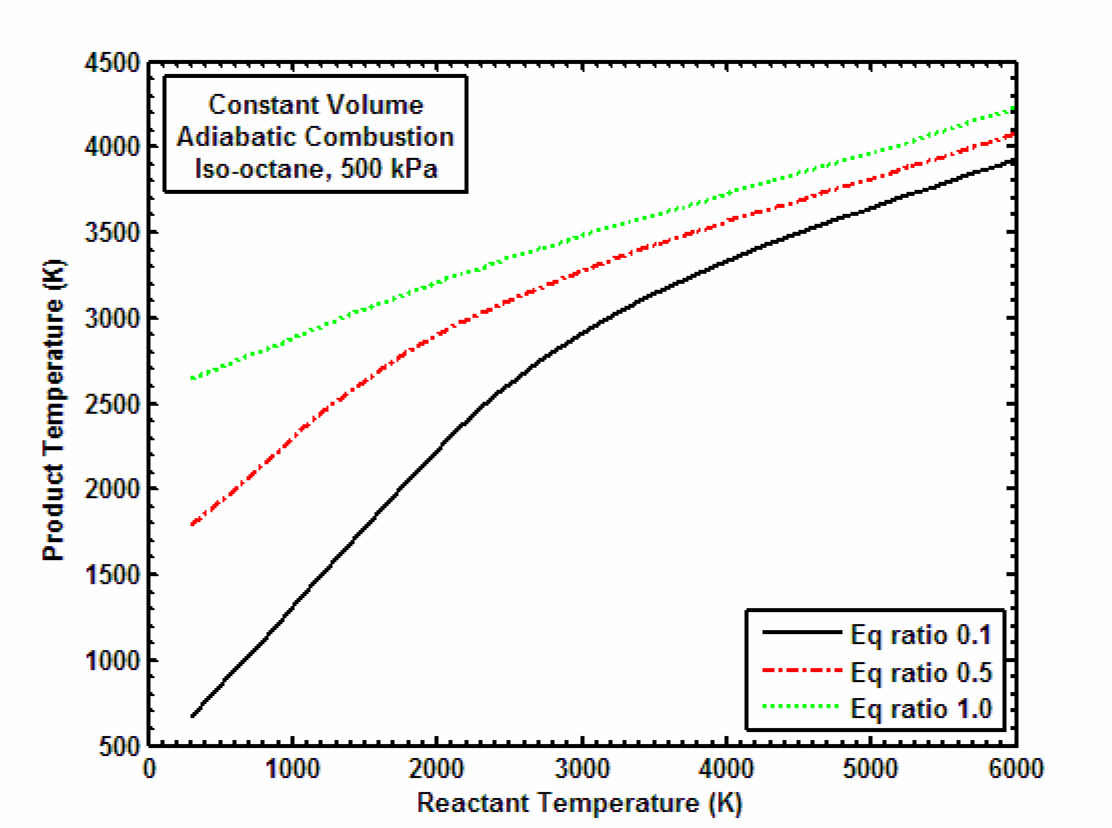


Fig. 24. Product mixture temperature for a range of lean equivalence ratios, constant volume combustion of iso-octane at 500 kPa.

Fig. 25 shows similar results for the product mixture temperatures for richer ($\phi \geq 1$) reactant mixtures. At lower reactant temperatures (reactant temperatures less than 1000 K), the reactant mixture corresponding to stoichiometric ratio results in the highest product mixture temperature. This is because of the complete combustion occurring for the stoichiometric mixture. However, for higher reactant mixture temperatures (reactant temperatures greater than 1000 K), this trend changes with the combustion of progressively richer equivalence ratios leading to higher product mixture temperatures. As discussed earlier during the constant pressure combustion, this occurs due to the formation of the incomplete products of combustion at higher temperatures, thus allowing the richer reactant mixtures to liberate more energy.

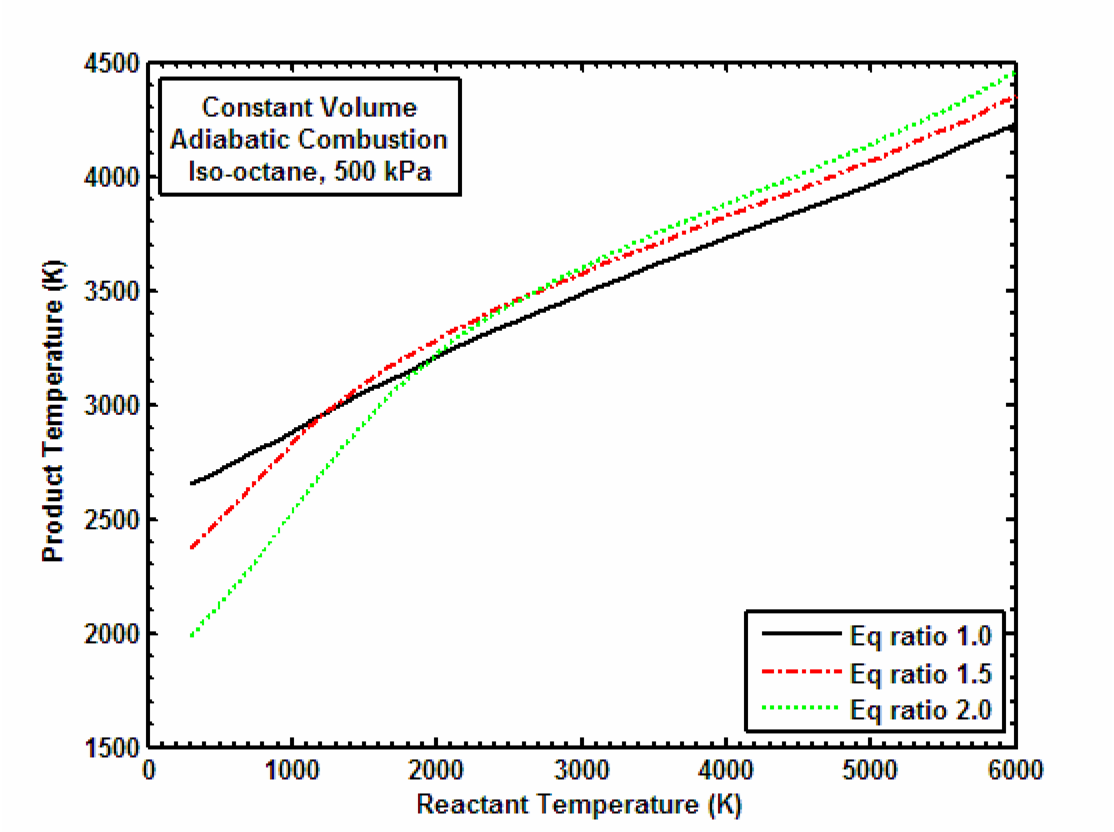


Fig. 25. Product mixture temperature for a range of rich equivalence ratios, constant volume combustion of iso-octane at 500 kPa.

Fig. 26 presents the effect of equivalence ratio on the product mixture temperature and the percentage of reactant mixture availability destroyed during constant volume combustion of iso-octane, for reactant mixture temperature of 300 K and pressure 500 kPa. The percentage of reactant mixture availability destroyed decreases monotonically with increasing equivalence ratios from 53% for an equivalence ratio of 0.1 to 17% for an equivalence ratio of 2.0. The values computed for the percentage availability destroyed account for the product mixture reactive availability. This requires additional combustion processes to allow the energy to be utilized. Thus increasingly rich reactant mixtures would not be the optimum equivalence ratio.

The product mixture temperature initially increases with increasing in the equivalence ratio, before decreasing again. The peak product mixture temperature was obtained corresponding to a reactant mixture equivalence ratio of about 1.1. This is a well documented trend, occurring due to the formation of incomplete products of combustion, allowing more energy liberation for an equivalence ratio of 1.1 rather than for the stoichiometric mixture.

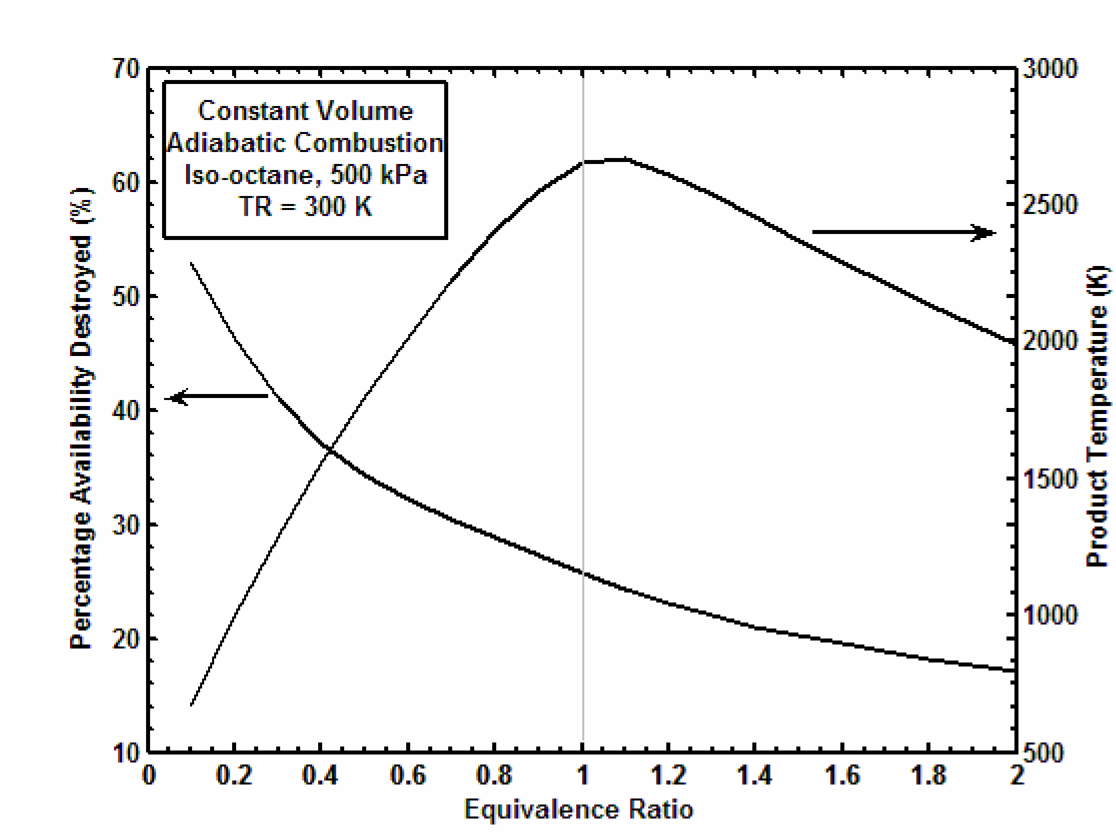


Fig. 26. Percentage availability destroyed and product mixture temperature as a function of equivalence ratio, for constant volume combustion of iso-octane, reactant pressure 500 kPa and temperature 300 K.

Parameter #4: Fuels

For comparison of the destruction of availability during combustion, the combustion of various fuels was considered for an initial reactant mixture temperature of 300 K, reactant pressure of 500 kPa and an equivalence ratio of 1.0.

The trend in destruction of availability during constant volume combustion of fuels is the same as during constant pressure combustion. Fig. 27 shows the destruction of availability as a consequence of the constant volume combustion of the various fuels.

The percentage destruction of availability due to combustion ranged between 19% and 26%, with increasing destruction of availability generally occurring for combustion of fuels with more complicated molecular structures. The values are computed using the availability balance and the destruction of availability is the least for acetylene. If only the thermo-mechanical availability destroyed is considered, combustion of hydrogen destroys the least fraction of availability. This is similar to the trend observed during constant pressure combustion of the various fuels.

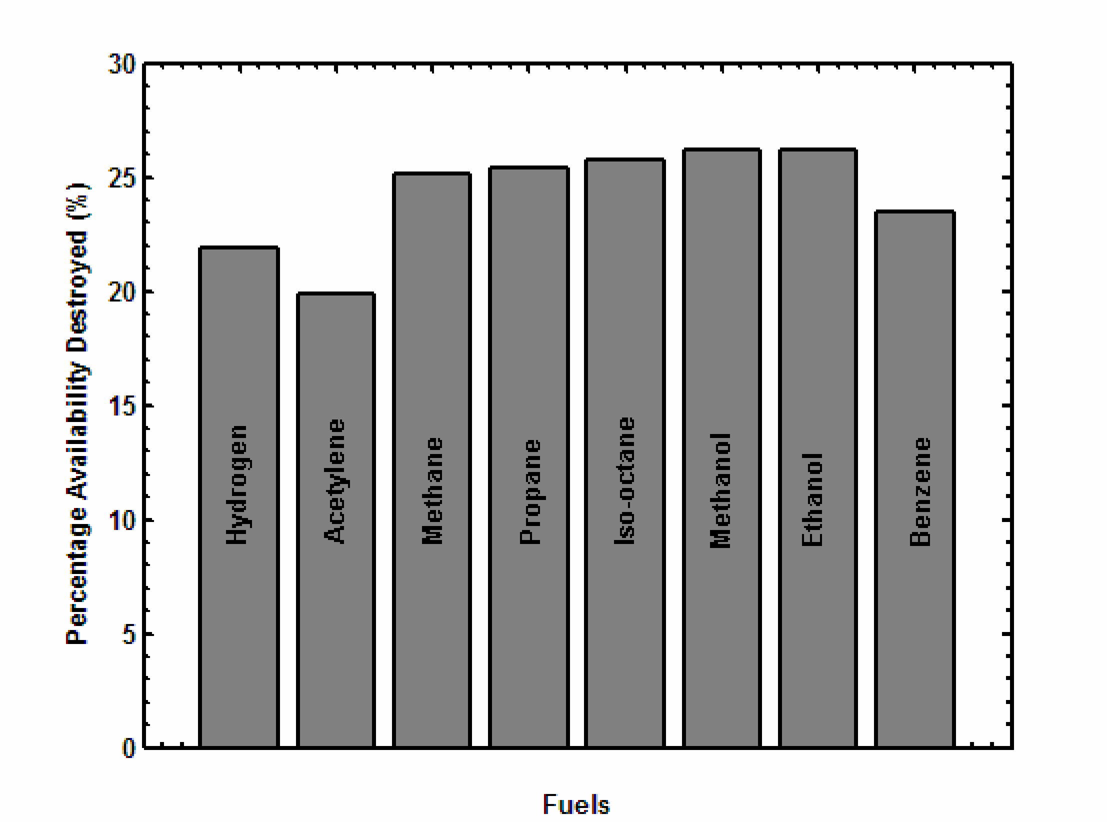


Fig. 27. Percentage availability destroyed during constant volume combustion of different fuels for reactant pressure of 500 kPa and initial reactant temperature of 300 K.

Importance of chemical availability

The contribution and significance of the chemical availability to the total mixture availability for constant volume combustion was analyzed similarly to the analysis for constant pressure combustion. The total mixture was split into three components – thermo-mechanical, reactive and diffusion availability. Once again, diffusion availability is actually a part of the chemical availability but has been determined and plotted separately for purposes of illustration and better understanding.

Fig. 28 shows the individual contributions of these terms to the total reactant mixture availability. As expected, at 300 K, the contribution of the thermo-mechanical term to the overall availability is negligible, increasing in magnitude and significance with increase in temperatures. The reactive availability term, due to the chemical energy of the fuel is constant in magnitude and is significant in its contribution to the total mixture availability. The diffusion availability is also fixed in magnitude, but is insignificant in its contribution to the total mixture availability.

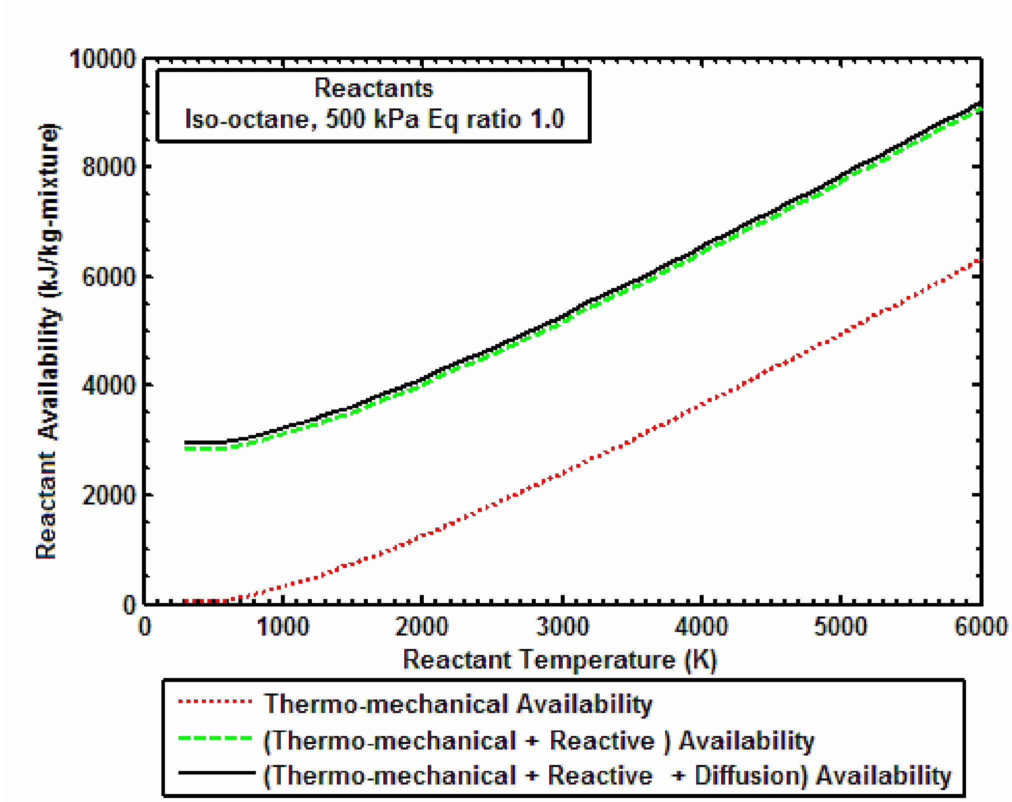


Fig. 28. Various components of the total reactant mixture availability for stoichiometric mixture of iso-octane for reactant pressure 500 kPa for constant volume conditions.

Fig. 29 shows the contribution of the various availability terms to the total product mixture availability. At 300 K, all three components are small in magnitude. The thermo-mechanical availability increases with increasing temperature and is dominant until about 2500 K. Beyond this temperature, the increased presence of the incomplete products of combustion contributes to the reactive availability term and this term subsequently increases sharply. The diffusion availability component is fixed in magnitude and is once again of insignificant proportions compared to the total mixture availability.

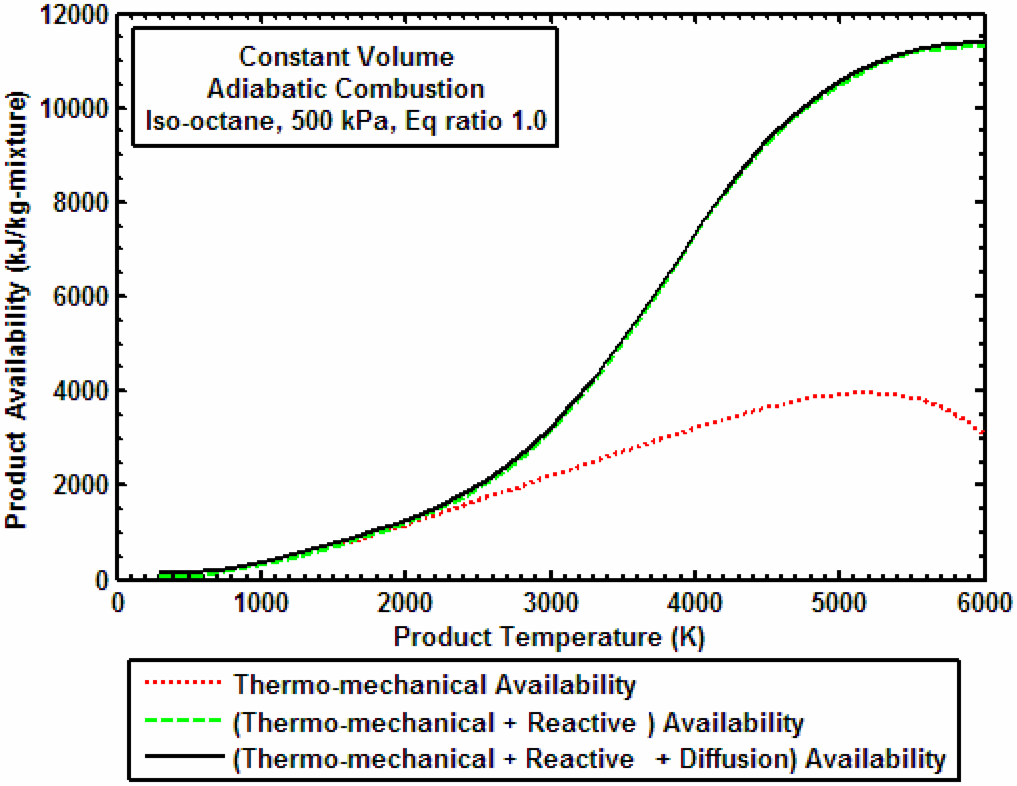


Fig. 29. Various components of the total product mixture availability, for stoichiometric mixture of iso-octane for reactant pressure of 500 kPa, constant volume combustion.

Effect of reactant dissociation

During the examination of the effect of the various parameters on the destruction of availability during combustion, the dissociation of the reactant mixture has been neglected. It has already been shown during analysis of the constant pressure combustion that dissociation of the reactant mixture has a significant effect on the mixture properties at higher temperatures. The product mixture properties also need to be corrected to account for the effect of the reactant mixture dissociation.

Fig. 30 shows the availability curves for the reactant mixture, with and without the effect of dissociation incorporated, for a reactant mixture containing iso-octane and air at 500 kPa. For temperatures beyond 3500 K, the dissociation effects start becoming significant and the variation between the two curves increases rapidly with increasing temperatures. This additional energy would need to be supplied to maintain the reactant mixture temperature.

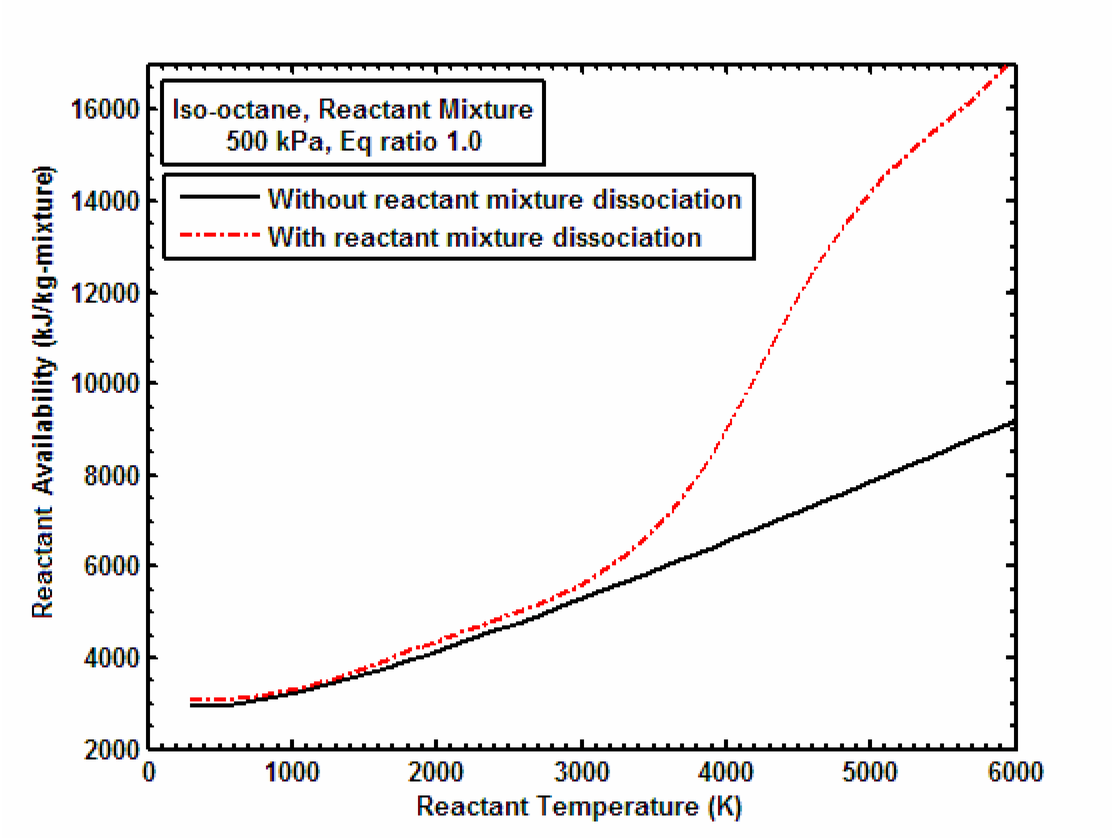


Fig. 30. Effect of reactant mixture dissociation on availability for constant volume conditions.

Fig. 31 shows the percentage of reactant mixture availability destroyed during constant volume combustion of iso-octane with an initial reactant mixture pressure of 500 kPa, after accounting for the dissociation of the reactant mixture. The two curves are almost parallel at lower temperatures (temperatures lesser than 3500 K), with the difference in values being due to the fact that iso-octane decomposes into methane, carbon and hydrogen over infinite time. At higher temperatures (temperatures greater than 3500 K), however, the curves show a marked difference, with the curve considering dissociation effects rising steeply. This trend is similar to that encountered during constant pressure combustion. The reason for the steep rise is because of the fact that the dissociated reactant mixture species possess greater energy, as compared to the non-dissociated species as a consequence of the energy absorbed by the species during the process of the chemical bonds being broken. The increased destruction of availability past 4000 K is due to the fact that the dissociated reactant mixture has increased availability, lost due to the combustion process.

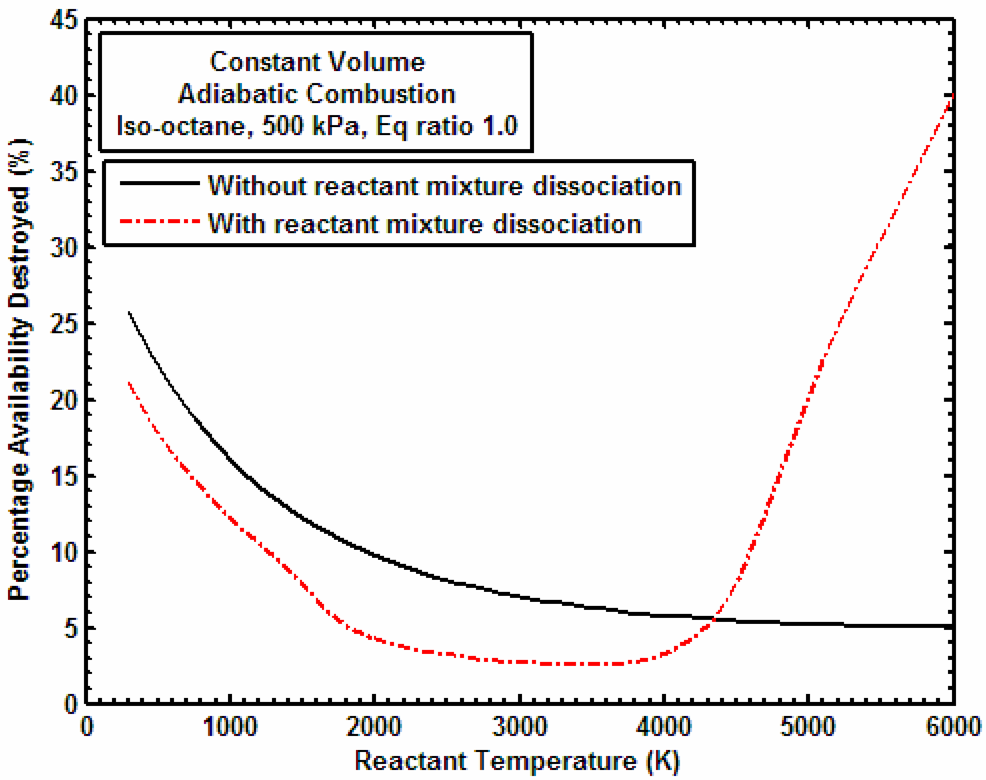


Fig. 31. Percentage availability destroyed during constant volume combustion of iso-octane, for reactant pressure of 500 kPa, with and without reactant mixture dissociation.

Fig. 32 shows the effect of reactant dissociation on the product mixture temperature values. Without accounting for the dissociation of the reactant mixture temperatures, the final product mixture temperature is underestimated significantly at higher reactant mixture temperatures. This is because the dissociated reactant mixture has greater internal energy as compared to the non-dissociated reactant mixture at the same temperature.

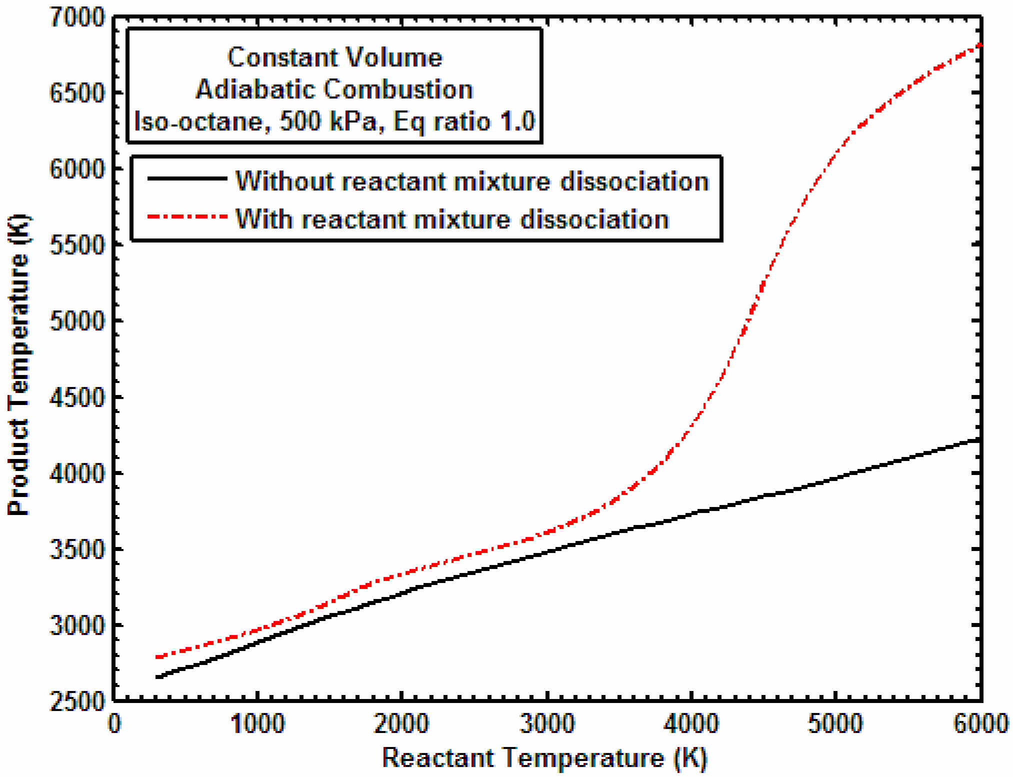


Fig. 32. Product mixture temperature as a function of reactant mixture temperature, with and without dissociation of reactants for constant volume combustion of iso-octane for reactant pressure of 500 kPa.

For constant volume combustion, dissociation of the reactant mixture also affects the final product mixture pressure. Fig. 33 shows the effect of the reactant mixture dissociation on the product mixture pressure. The increase in the product mixture pressure is proportional the increase in the product mixture temperature.

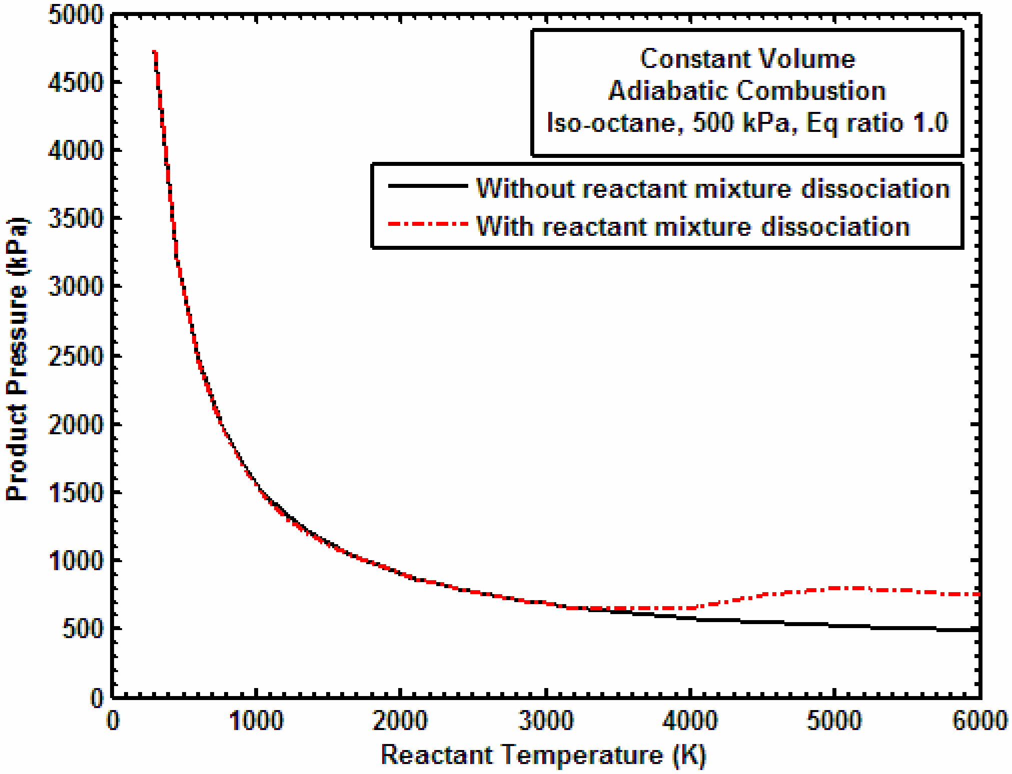


Fig. 33. Product mixture pressure as a function of reactant mixture temperature, with and without dissociation of reactants for constant volume combustion of iso-octane for reactant pressure of 500 kPa.

Constant temperature combustion

Constant temperature combustion was the third combustion process considered in this study. Constant temperature combustion refers to combustion of the reactant mixture at a fixed temperature. In addition to the mixture temperature, either the pressure or the volume of the system needs to be constant. Thus constant temperature combustion may either be isobaric or isochoric. Another difference between constant pressure and constant volume combustion and constant temperature combustion is the heat transfer across the system boundary for constant temperature combustion. This heat transfer has the potential to do work with the use of a suitable heat engine and therefore needs to be accounted for, as described in the preceding section. The results for these combustion modes are discussed in this section.

Parameter #1: Reactant temperature

Fig. 34 shows the availability curves for the reactant and product mixtures for constant temperature, isobaric conditions. These curves are identical to the availability curves obtained previously for the constant pressure combustion, and are repeated here for convenience.

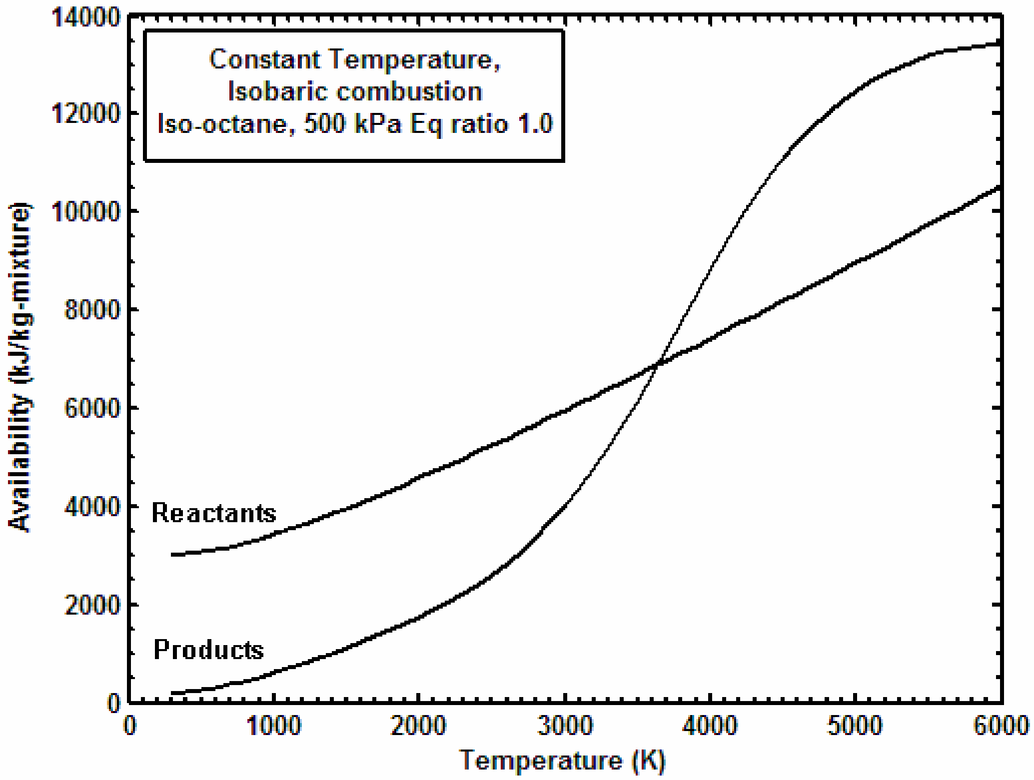


Fig. 34. Reactant and product mixture availabilities as a function of temperature for reactant pressure of 500 kPa and φ = 1.0, constant temperature, isobaric combustion.

Similarly, Fig. 35 shows the availability curves for the reactant and product mixtures for constant temperature, isochoric conditions. The curves are identical to the curves obtained for the mixture availabilities during constant volume combustion. The reactant mixture availability increases monotonically with increasing temperatures while the product mixture availability rises steeply after 2500 K due to the formation of the incomplete products of combustion.

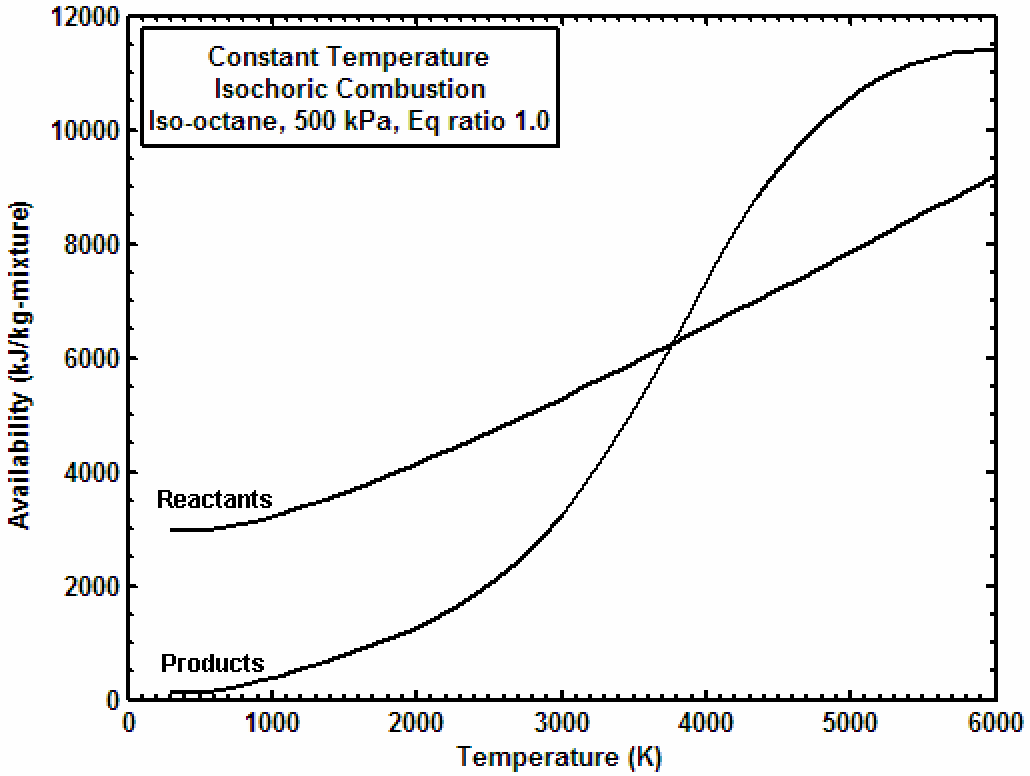


Fig. 35. Reactant and product mixture availabilities as a function of temperature for reactant pressure of 500 kPa and φ = 1.0, constant temperature, isochoric combustion.

Fig. 36 shows the percentage availability destroyed as a function of the mixture temperature for constant temperature, isobaric combustion. The fraction of availability destroyed as a result of the combustion process drops rapidly with increasing mixture temperatures. At a temperature of 300 K, almost all of the availability in the reactant mixture is destroyed due to constant temperature, isobaric combustion. In other words, the potential to do work from the combustion products is nearly completely destroyed as the temperature is kept low by the use of heat transfer. As the temperature increases, the percentage availability destroyed decreases up to a temperature of about 4000 K. The fraction of reactant availability destroyed increases for temperatures greater than about 4000 K. This is due to the fact that at these high temperatures, the reactant mixture availability increases more rapidly than the product mixture availability. This is because of the dissociation of the nitrogen molecules as discussed previously.

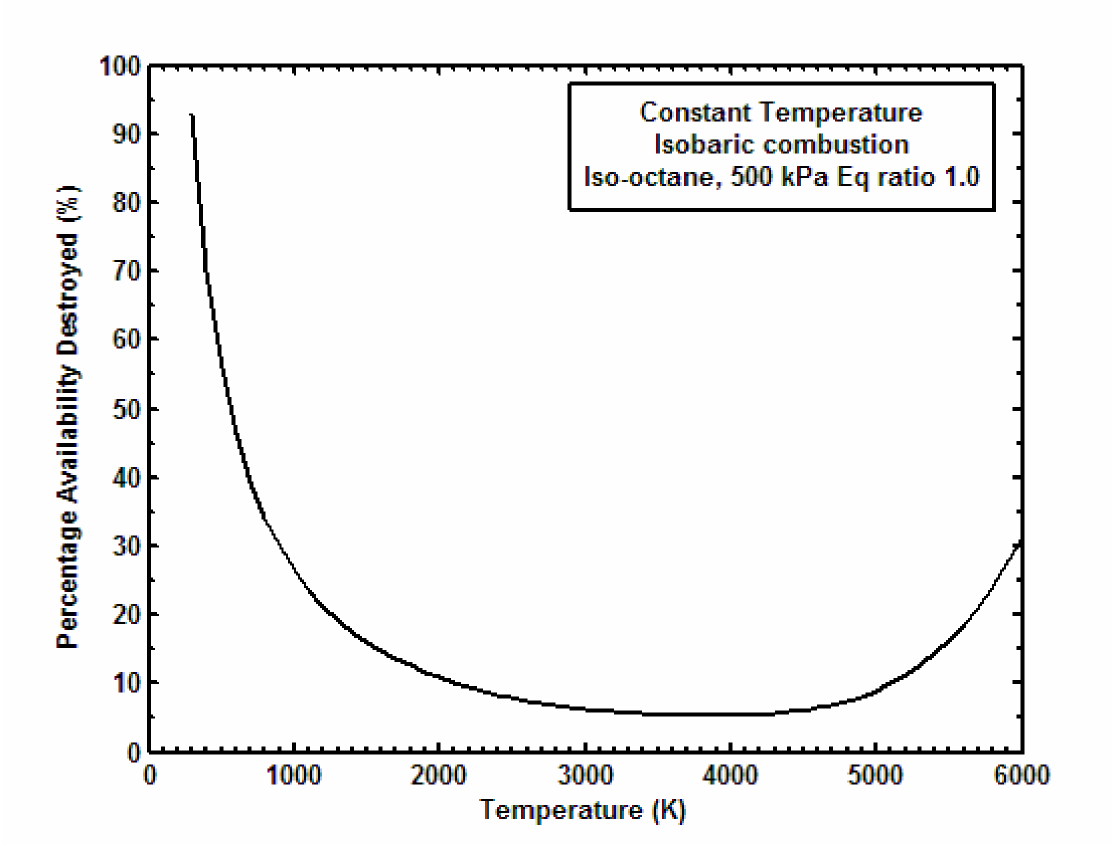


Fig. 36. Percentage availability destroyed as a function of reactant temperature for constant temperature, isobaric combustion of iso-octane, reactant pressure of 500 kPa.

Fig. 37 shows the percentage availability destroyed during the constant temperature, isochoric combustion of iso-octane. The trend is similar to that obtained in Fig. 36 for constant temperature, isobaric combustion of iso-octane. The fraction of availability destroyed is once again observed to decrease rapidly with increasing mixture temperature before rising again at higher mixture temperatures. The rise in the fraction of availability destroyed at high temperatures (greater than 4000 K) is because the reactant mixture availability increases more rapidly than the product mixture availability due to the dissociation of nitrogen molecules.

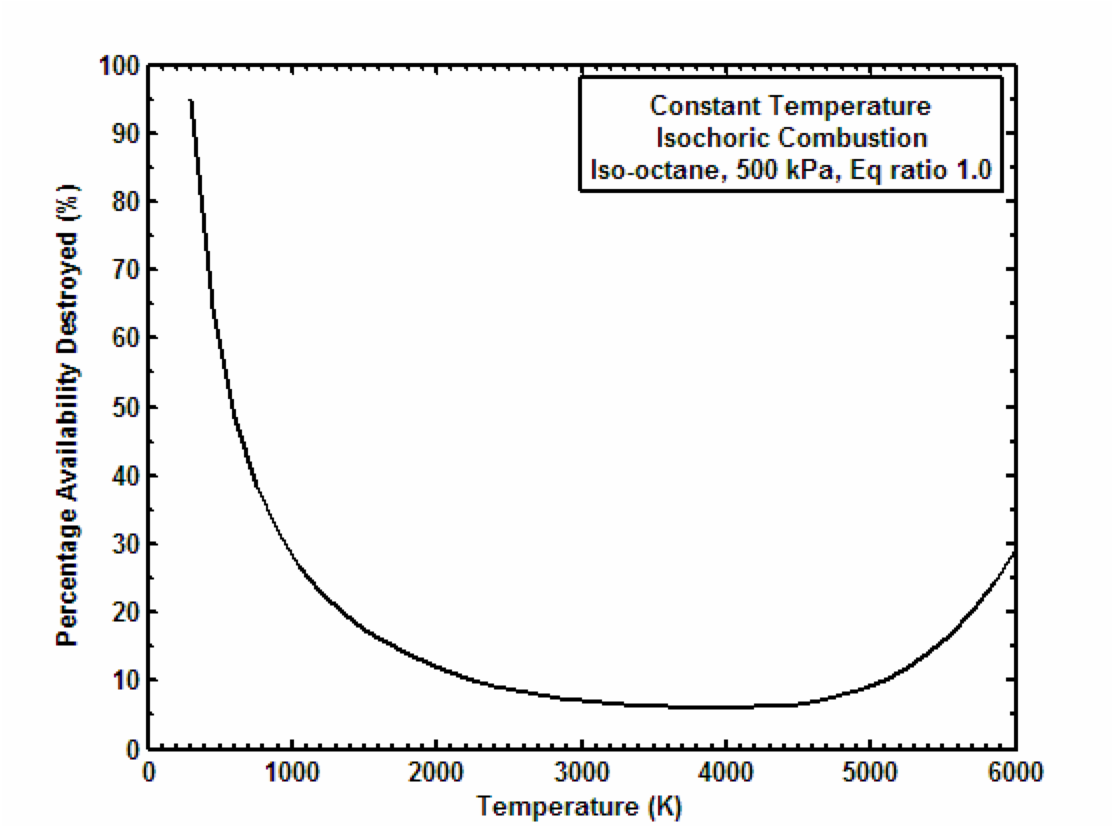


Fig. 37. Percentage availability destroyed as a function of reactant temperature for constant temperature, isochoric combustion of iso-octane, reactant pressure of 500 kPa.

Fig. 38 shows the enthalpy for the reactant and product mixtures for the range of temperatures. From the figure, it would appear that for temperatures greater than 3500 K, the combustion of iso-octane is an endothermic reaction. This is however, not the case, with the products appearing to have greater enthalpy than the reactants due to the fact that the dissociation of the reactant mixture species has been neglected. Once this is accounted for, the product mixture enthalpy is always lower than the reactant mixture enthalpy.

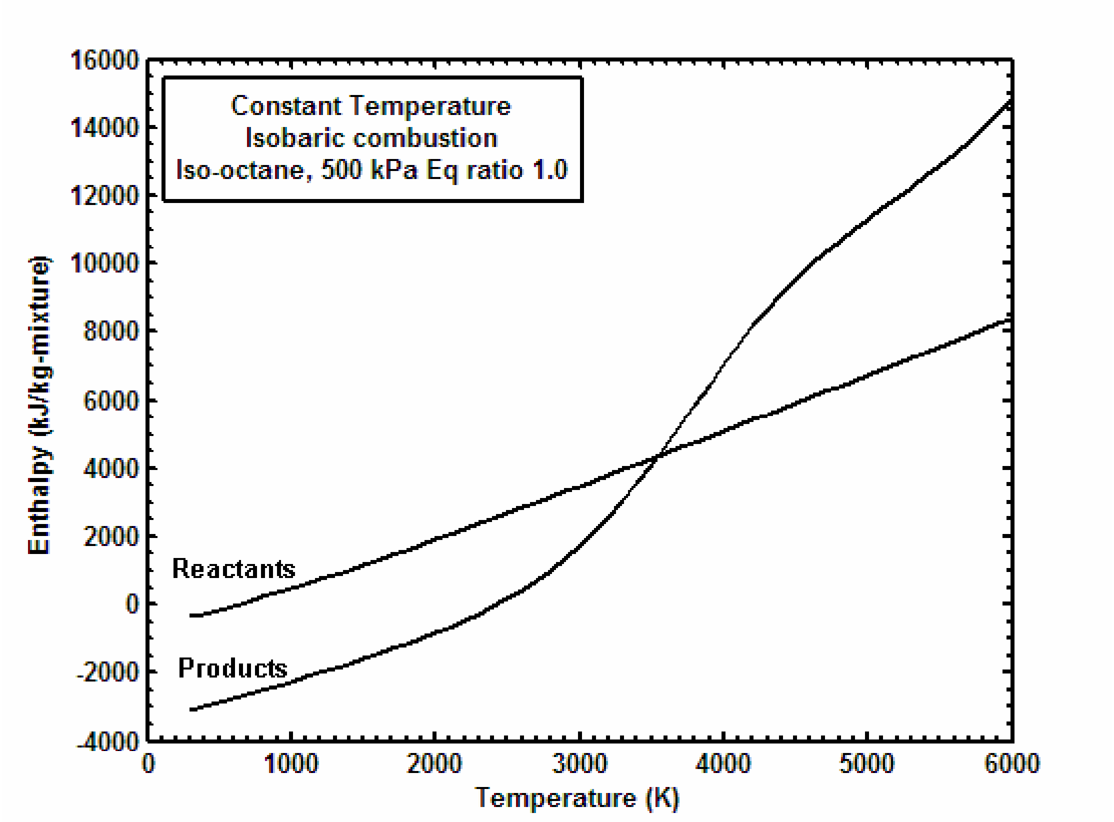


Fig. 38. Reactant and product mixture enthalpies as a function of temperature for reactant pressure of 500 kPa and φ = 1.0, constant temperature, isobaric combustion.

A similar explanation applies to the constant temperature, isochoric combustion of iso-octane. The internal energy curves for the reactant and product mixture are shown in Fig. 39. Again, at higher temperatures, the product mixture appears to possess greater internal energy than the reactant mixture, since these curves have not been corrected for dissociation effects.

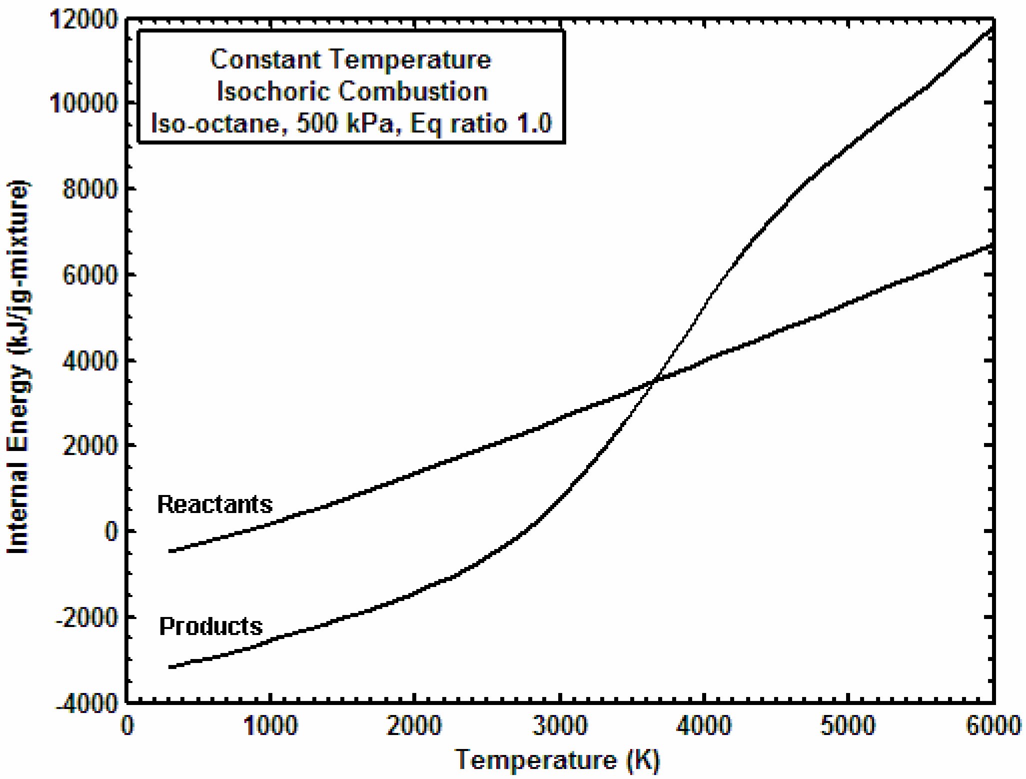


Fig. 39. Reactant and product mixture internal energies as a function of temperature for reactant pressure of 500 kPa and φ = 1.0, constant temperature, isochoric combustion.

Parameter #2: Reactant pressure

Fig. 40 shows the percentage of the reactant mixture availability destroyed during the constant temperature, isobaric combustion of iso-octane for a range of pressures. It is evident that the effect of the reactant mixture pressure on the fraction of reactant mixture availability destroyed is negligible. The curves diverge past 4000 K, but again, this is due to the dissociation of the reactant mixture being neglected. If the dissociation effects are considered, the reactant mixture rises sharply at higher temperatures, and the sharp rise in the percentage availability destroyed past 4000 K is moderated.

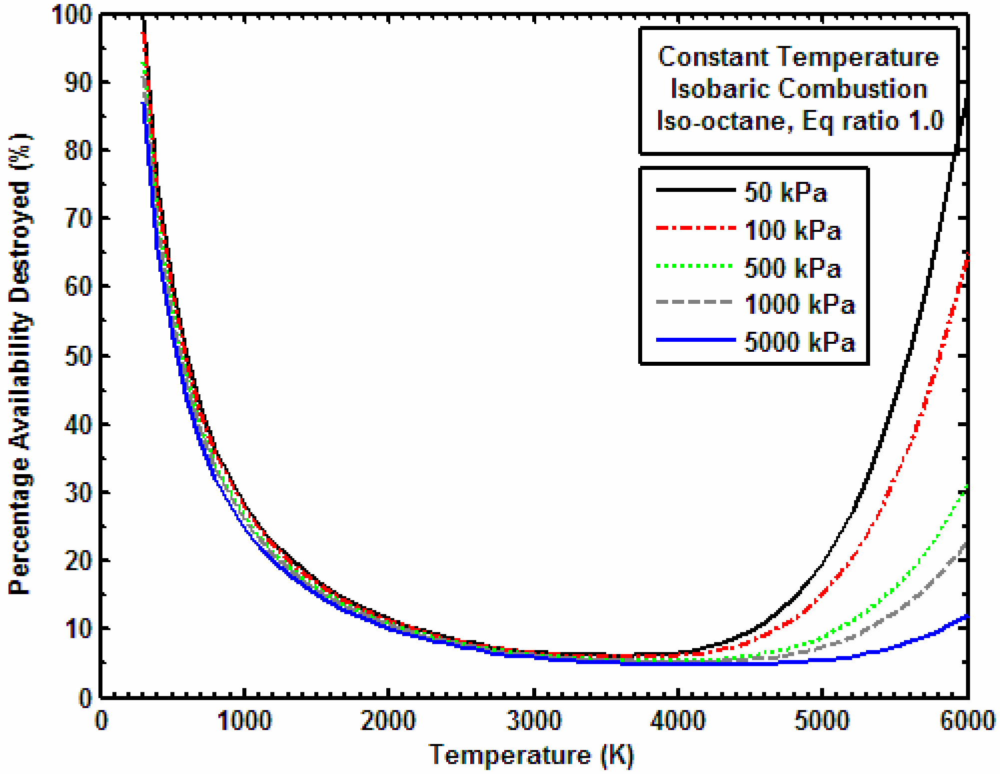


Fig. 40. Effect of pressure on percentage availability destroyed during constant temperature, isobaric combustion of iso-octane.

Fig. 41 shows the effect of the initial reactant mixture pressure on the percentage of reactant mixture availability destroyed during constant temperature, isochoric combustion of iso-octane. The effect of the reactant mixture pressure on the fraction of availability destroyed is once again largely insignificant until about 4000 K.

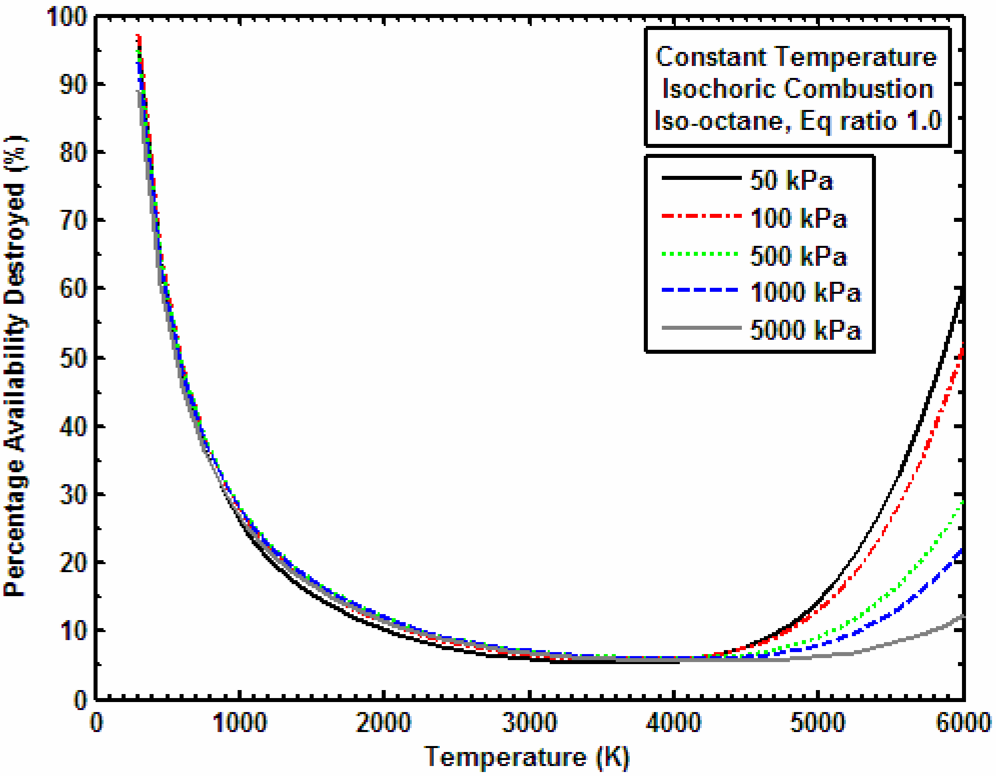


Fig. 41. Effect of pressure on percentage availability destroyed during constant temperature, isochoric combustion of iso-octane.

Parameter #3: Equivalence ratio

The constant temperature combustion process was analyzed for the effect of equivalence ratio on the percentage of reactant mixture availability destroyed. A range of lean reactant mixtures were considered with equivalence ratios ranging from 0.1 to 1.0 and rich equivalence ratios from 1.0 to 2.0.

Fig. 42 shows the percentage of reactant mixture availability destroyed for the lean equivalence ratios during constant temperature, isobaric combustion of iso-octane at 500 kPa as functions of temperature. Varying the equivalence ratio affects the fraction of availability destroyed. At lower temperatures (below 4000 K), the percentage availability destroyed is greater for richer equivalence ratios (but still less than 1.0). These values converge at about 4000 K, before diverging again. The trend, however, is reversed for temperatures beyond 4000 K. The rise in percentage availability destroyed due to combustion past 4000 K is due to the dissociation of the nitrogen molecules and therefore, the values are higher for leaner reactant mixtures.

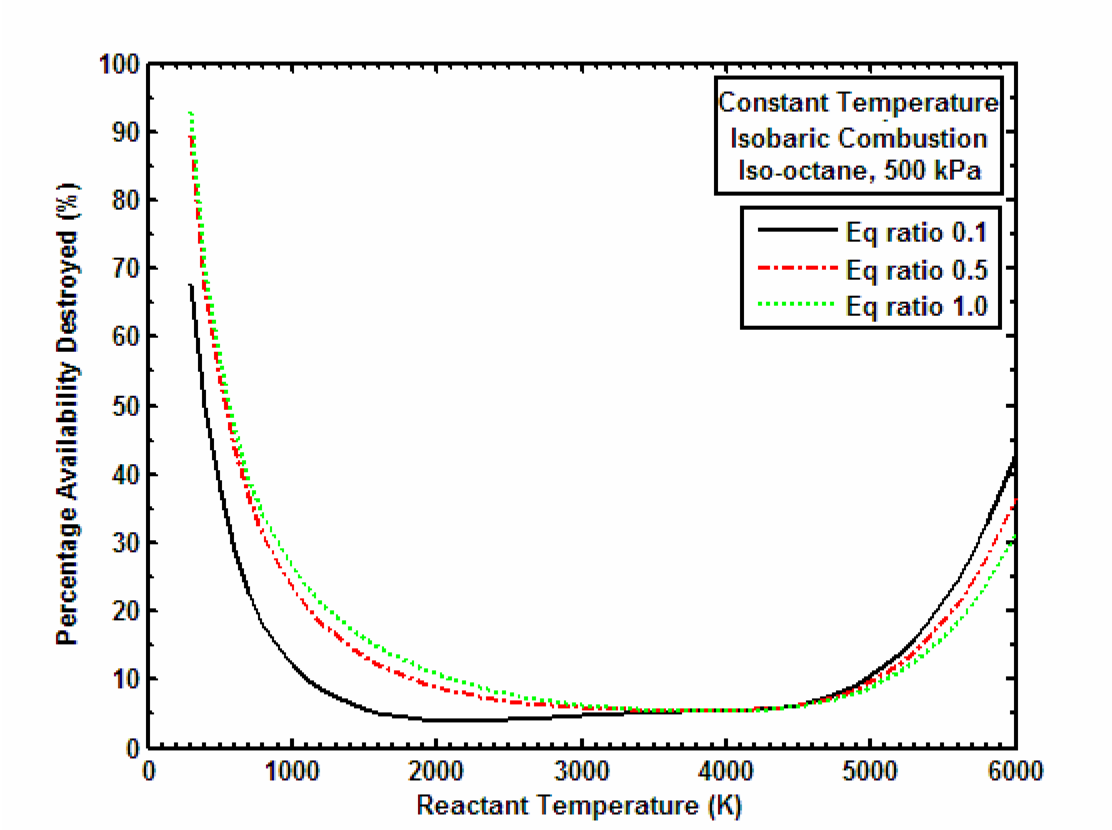


Fig. 42. Percentage availability destroyed for lean equivalence ratios, constant temperature, isobaric combustion of iso-octane, reactant mixture at 500 kPa.

Fig. 43 shows the fraction of availability destroyed during constant temperature, isobaric combustion for rich equivalence ratios. The fraction of availability destroyed at lower temperatures is highest for the stoichiometric mixture, and least for the equivalence ratio of 2.0. With increasing temperatures, the curves converge to a single value.

Again, it should be noted that the combustion of rich mixtures destroys smaller fractions of the reactant availability, but this includes the reactive availability of the product mixture which is not available for direct conversion into work and needs additional combustion to liberate the energy. The general trend is in keeping with the trend observed for the leaner equivalence ratios ($\phi \leq 1$), with similar explanations for the trends observed.

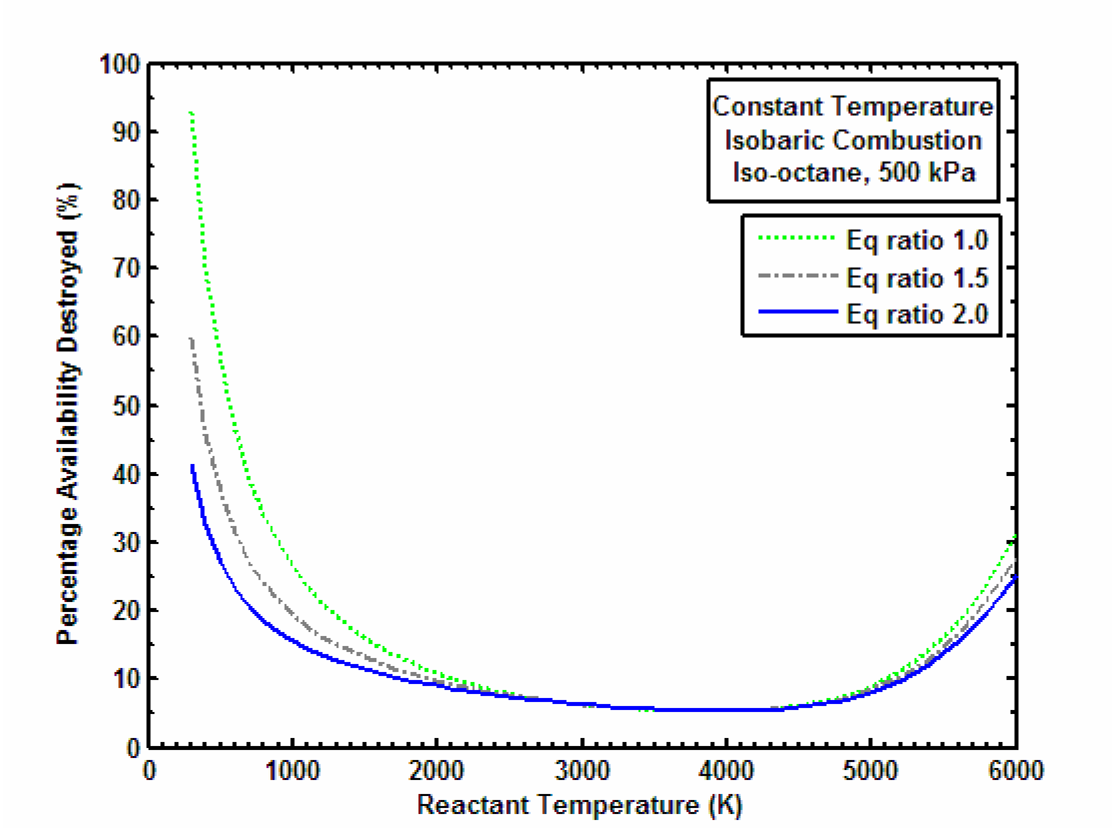


Fig. 43. Percentage availability destroyed for rich equivalence ratios, constant temperature, isobaric combustion of iso-octane, reactant mixture at 500 kPa.

Fig. 44 shows the effect of the reactant mixture equivalence ratio on the fraction of the availability destroyed during constant temperature, isochoric combustion for the lean range of equivalence ratios. The equivalence ratio of the reactant mixture does not significantly affect the percentage of the availability destroyed. The destruction of availability is greatest for the stoichiometric mixture and the least for the equivalence ratio of 0.1. The difference in the values of the percentage of reactant mixture availability destroyed increase with increasing temperatures, before converging once again. For temperatures below about 3500 K, the percentage of availability destroyed is greater for richer equivalence ratios (but still lean). With further increase in temperature, the trend is reversed, with greater fractions of the reactant availability destroyed due to combustion for leaner mixtures. The explanation for these trends is once again the same as those for constant temperature, isobaric combustion outlined previously.

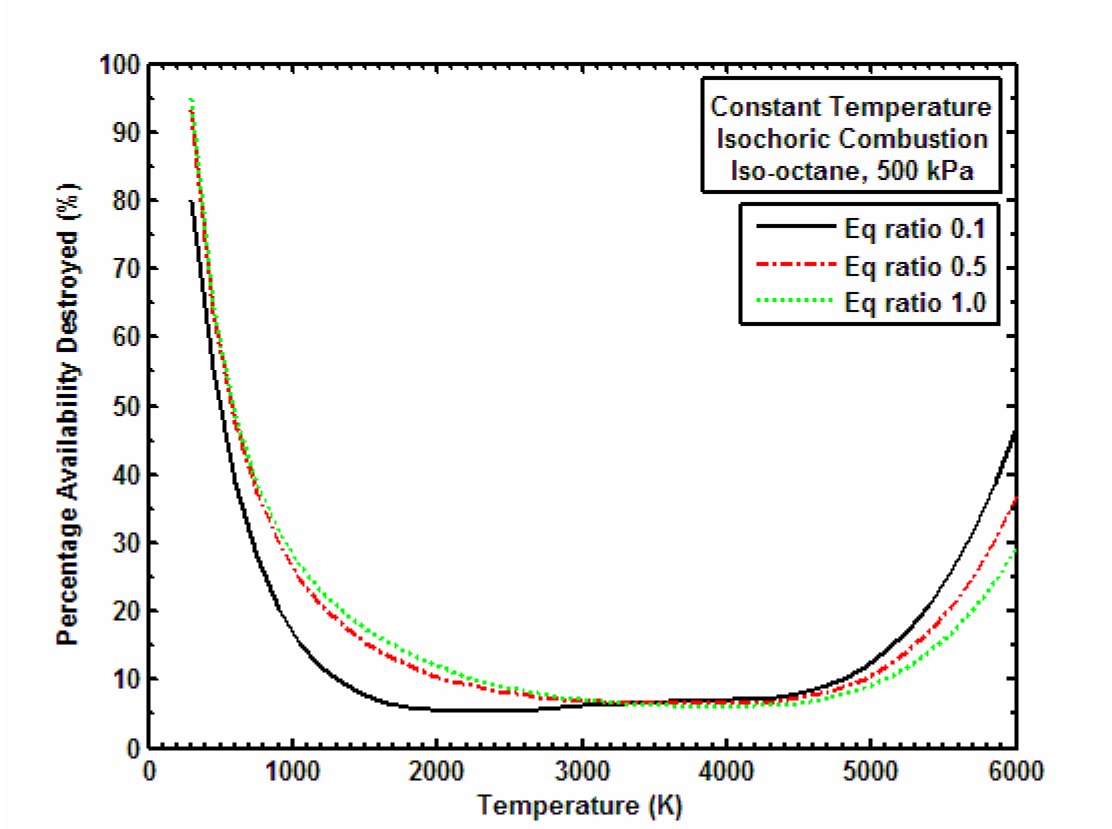


Fig. 44. Percentage availability destroyed for lean equivalence ratios, constant temperature, isochoric combustion of iso-octane, reactant mixture at 500 kPa.

The equivalence ratio has a more pronounced effect on the percentage of availability destroyed for richer equivalence ratios. Fig. 45 shows the variation of the percentage of the availability destroyed as a function of the equivalence ratio. The destruction of availability is greatest for the stoichiometric ratio and least for the richest equivalence ratio of 2.0. At higher temperatures, these values converge, before diverging once again past 5000 K. The trend in the percentage availability destroyed for the various equivalence ratios is reversed past 5000 K, once again due to the effect of the nitrogen dissociation leading to decreasing product mixture availability.

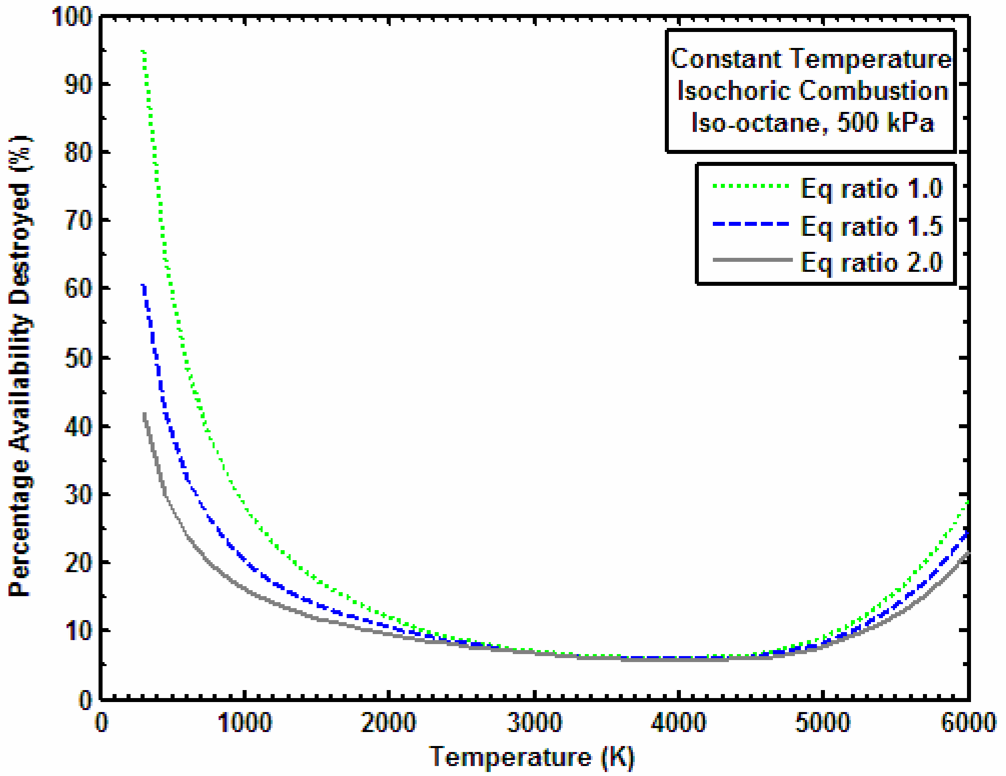


Fig. 45. Percentage availability destroyed for rich equivalence ratios, constant temperature, isochoric combustion of iso-octane, reactant mixture at 500 kPa.

Parameter #4: Fuels

To compare the effect of different fuels on the fraction of availability destroyed during the combustion process, the constant temperature combustion of the various fuels was considered for a reactant mixture pressure of 500 kPa at temperature of 1000 K. This temperature (1000 K) was chosen since it is more representative of the temperatures encountered in practical combustion systems. Fig. 46 shows the values for the percentage of the reactant mixture availability destroyed during the constant temperature, isobaric combustion of the fuels. Once again, the destruction of availability was greatest for the combustion of more complicated fuels.

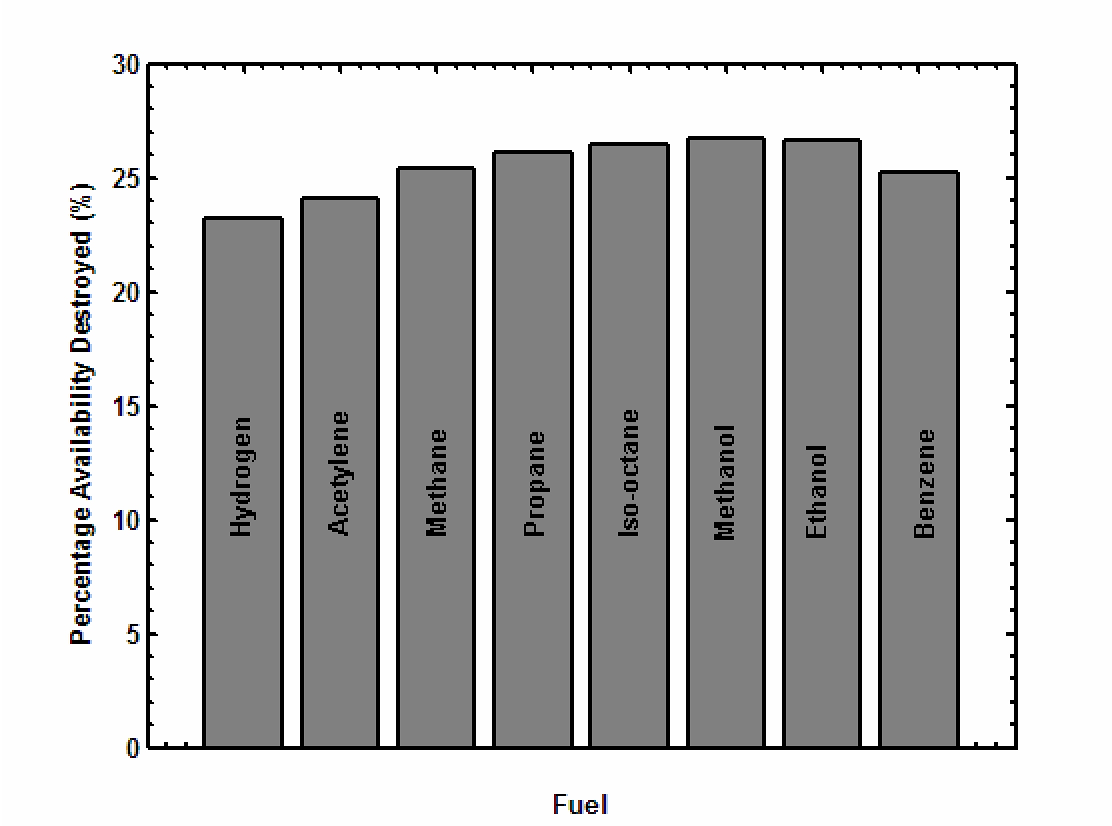


Fig. 46. Percentage availability destroyed during constant temperature, isobaric combustion of different fuels at 500 kPa and a temperature of 1000 K.

Fig. 47 shows the percentage destruction of availability during the combustion of the same set of fuels during constant temperature (1000 K), isochoric conditions. The trend in terms of the availability destroyed is similar to the constant temperature, isobaric combustion.

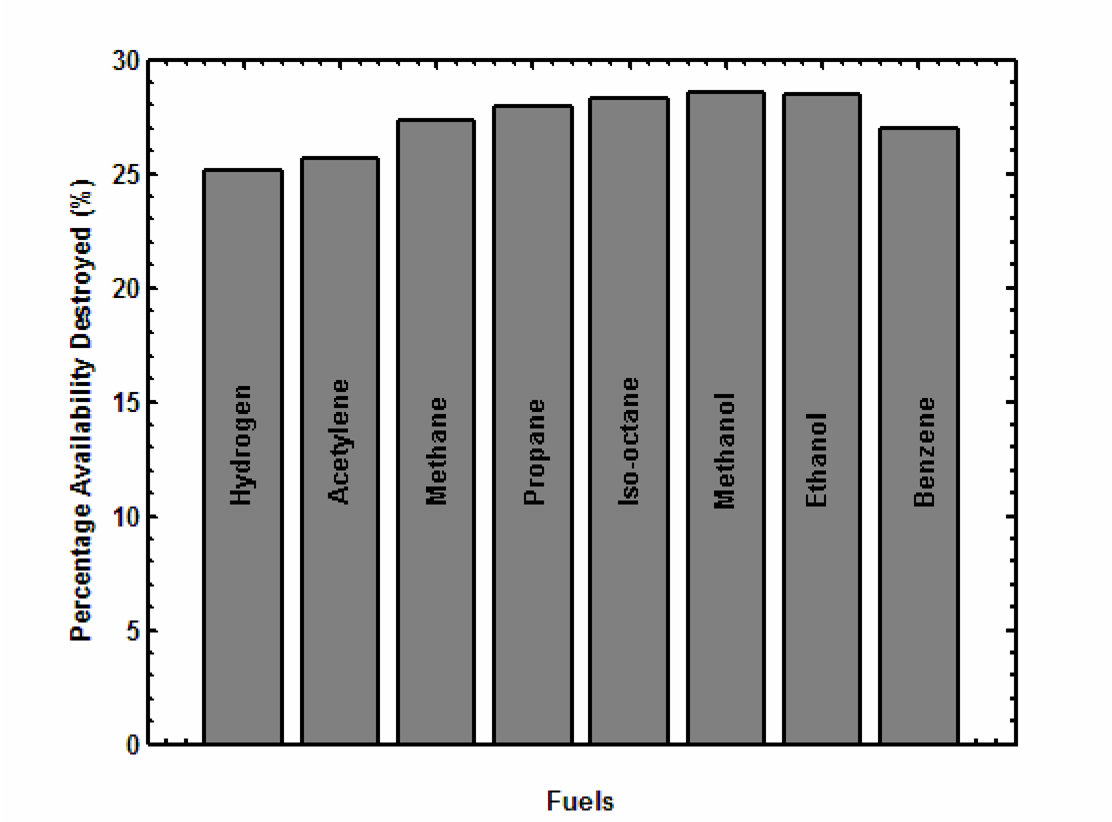


Fig. 47. Percentage availability destroyed during constant temperature, isochoric combustion of different fuels at 500 kPa and a temperature of 1000 K.

Importance of chemical availability

The various components of the reactant and product mixture availability were split into their components to analyze the contribution of each term to the total mixture availability. Once again, the available energy due to the diffusion of the species into the atmosphere was separated out of the chemical availability term.

Fig. 48 shows the total reactant mixture availability and the contribution of the various components to the total availability. The plot is the same as those obtained previously for the constant pressure and constant volume combustion since the reactant mixture is essentially the same for all these cases.

The thermo-mechanical availability varies with temperature, from a negligible contribution at low temperatures to a more significant contribution at higher temperatures. For a given equivalence ratio, the reactive availability is fixed in magnitude and is due to the chemical energy of the fuel component of the mixture. The diffusion availability is also fixed in magnitude and is insignificant in its contribution to the total availability.

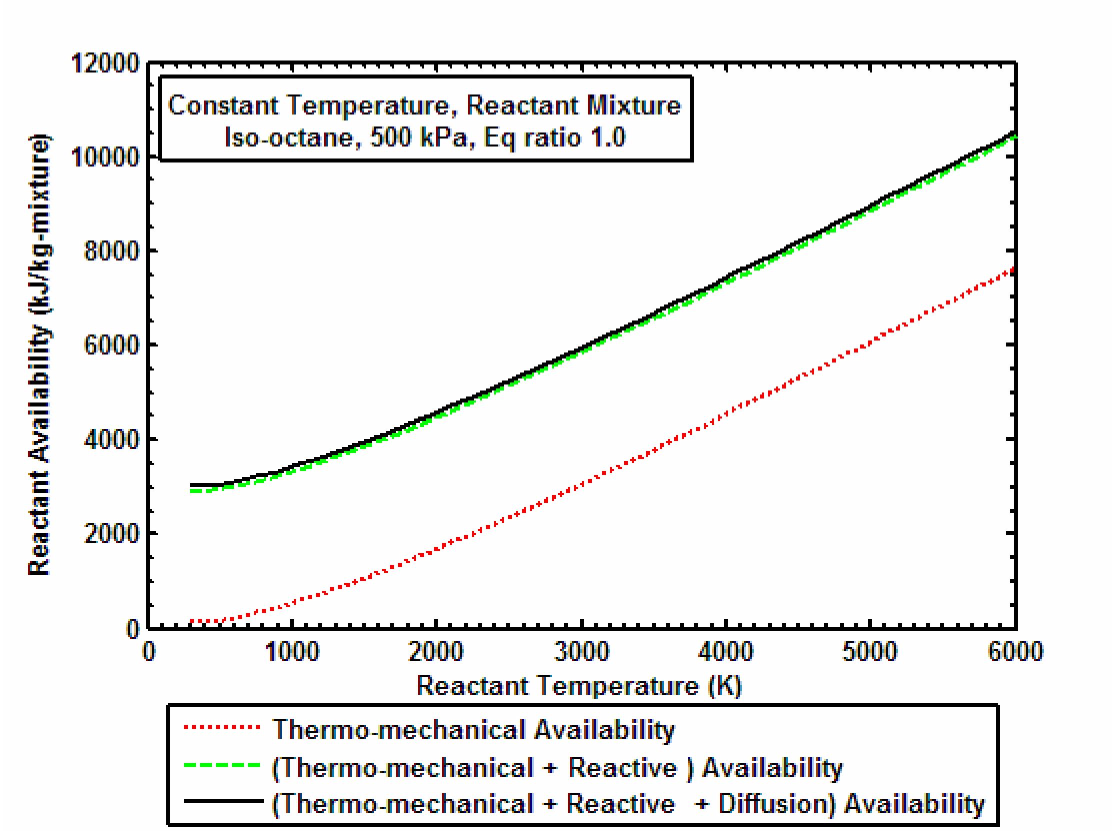


Fig. 48. Various components of the total reactant mixture availability for stoichiometric mixture of iso-octane at 500 kPa, constant temperature conditions.

Fig. 49 shows the variation of the various availability components for the product mixture after constant temperature, isobaric combustion. The trend is once again similar as obtained previously, with the thermo-mechanical availability increasing in magnitude and significance with increasing temperatures. The reactive availability is also negligible at low temperatures, but increases rapidly past 3000 K to become the dominant term at higher temperatures. The diffusion availability is fixed in magnitude with changing temperatures and is not a significant contributor to the total mixture availability.

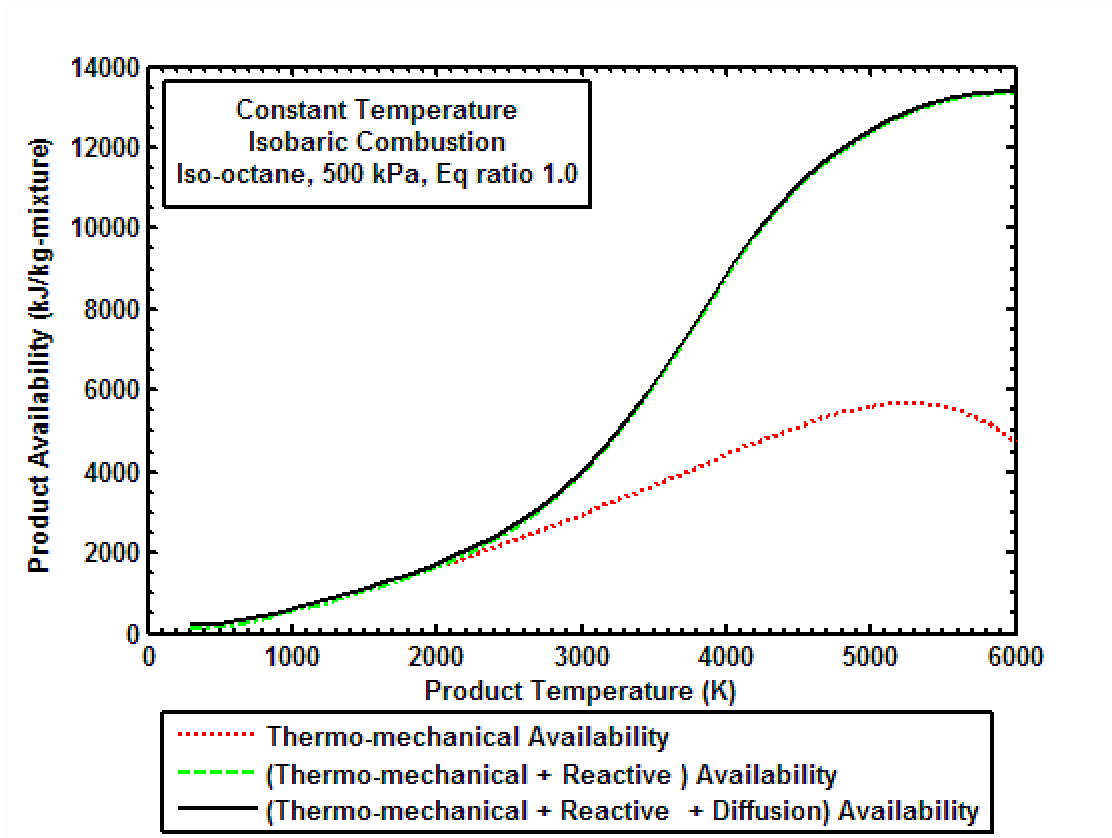


Fig. 49. Various components of the total product mixture availability for stoichiometric mixture of iso-octane at 500 kPa, constant temperature, isobaric conditions.

Fig. 50 shows the total availability and its components for the product mixture of constant temperature, isochoric combustion. The graph obtained is similar to the one in Fig. 49, with only the values of the availability varying. The thermo-mechanical availability term is therefore small at lower temperatures, increasing in both, magnitude and significance with temperature. The reactive availability is small initially, increasing in magnitude and significance at higher temperatures. At higher temperatures, the reactive availability is the most significant contribution to the total mixture availability. The diffusion availability term, as always, is fixed in magnitude and does not make a significant contribution to the total mixture availability.

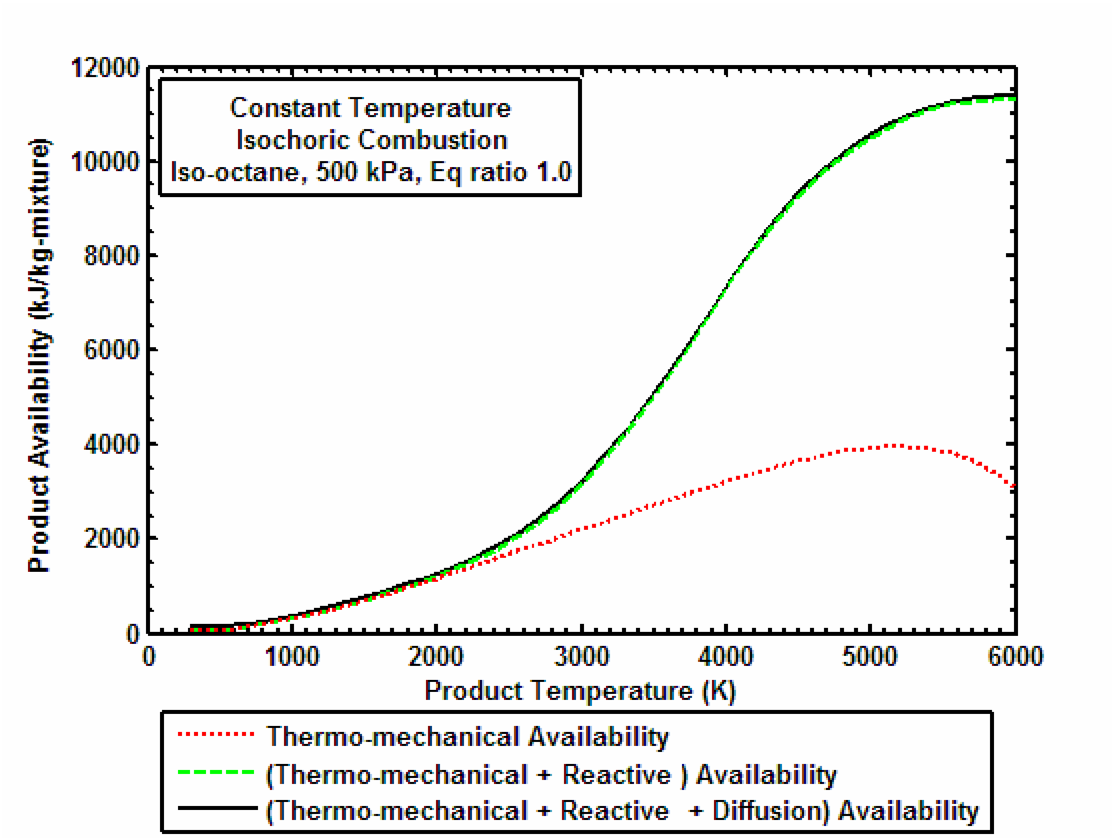


Fig. 50. Various components of the total product mixture availability for stoichiometric mixture of iso-octane at 500 kPa, constant temperature, isochoric conditions.

Effect of reactant dissociation

As discussed in preceding sections, the reactant mixture species dissociate at higher temperatures. This changes the mixture properties of the reactant mixture and consequently, the product mixture. This section outlines the effect of dissociation on the mixture properties for constant temperature combustion.

Fig. 51 shows the reactant availability, with and without the dissociation of the reactant mixture, as a function of the reactant temperature. For temperatures greater than about 3500 K, the effect of the reactant mixture dissociation is significant and causes a sharp rise in the mixture availability. This reflects the energy needed to break the chemical bonds, which leads to the increased availability of the mixture.

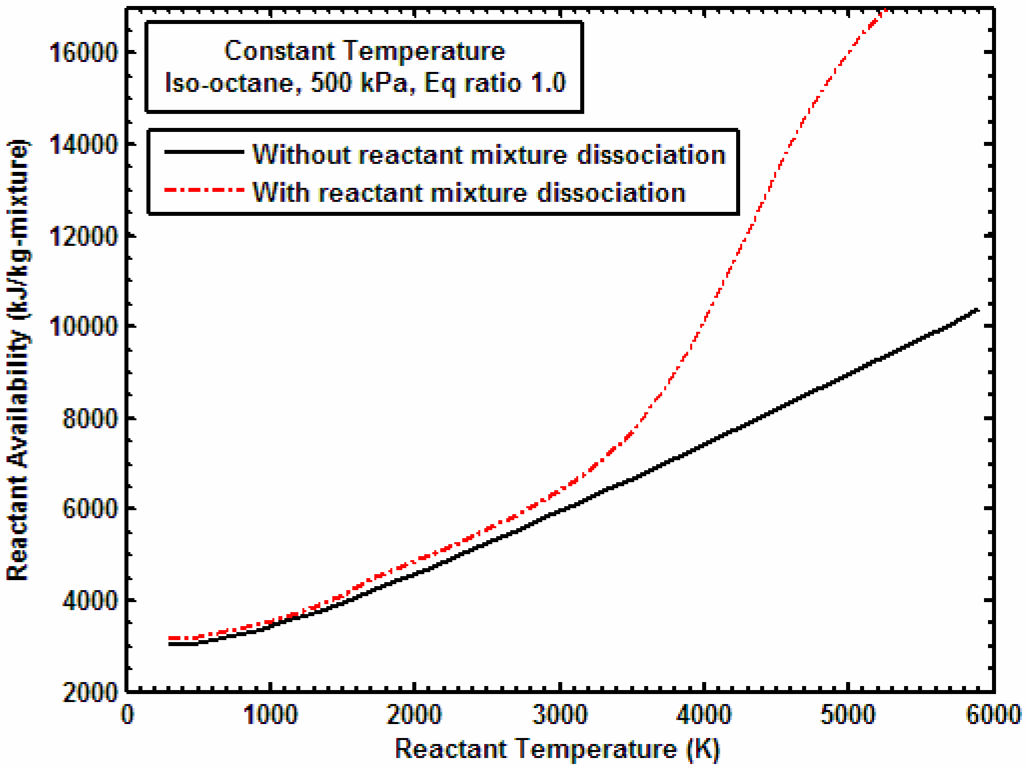


Fig. 51. Effect of reactant mixture dissociation on availability, constant temperature conditions.

Fig. 52 shows the effect of reactant mixture dissociation on the percentage of reactant availability destroyed during constant temperature, isobaric combustion of iso-octane at 500 kPa as a function of temperature. As expected, the effect of reactant mixture dissociation is negligible at low temperatures, becoming significant only at higher temperatures.

The significant difference between the two curves (showing percentage availability destroyed with and without reactant dissociation) is that incorporation of the dissociation effects causes the availability destroyed curve to shift lower at higher temperatures. For the constant volume and constant pressure combustion conditions, the effect was the reverse – causing the availability destroyed to rise sharply at high temperatures. This is because the reactant availability increases sharply once reactant mixture dissociation effects are considered, causing the percentage destruction of availability to be lesser than without the effects of reactant mixture dissociation.

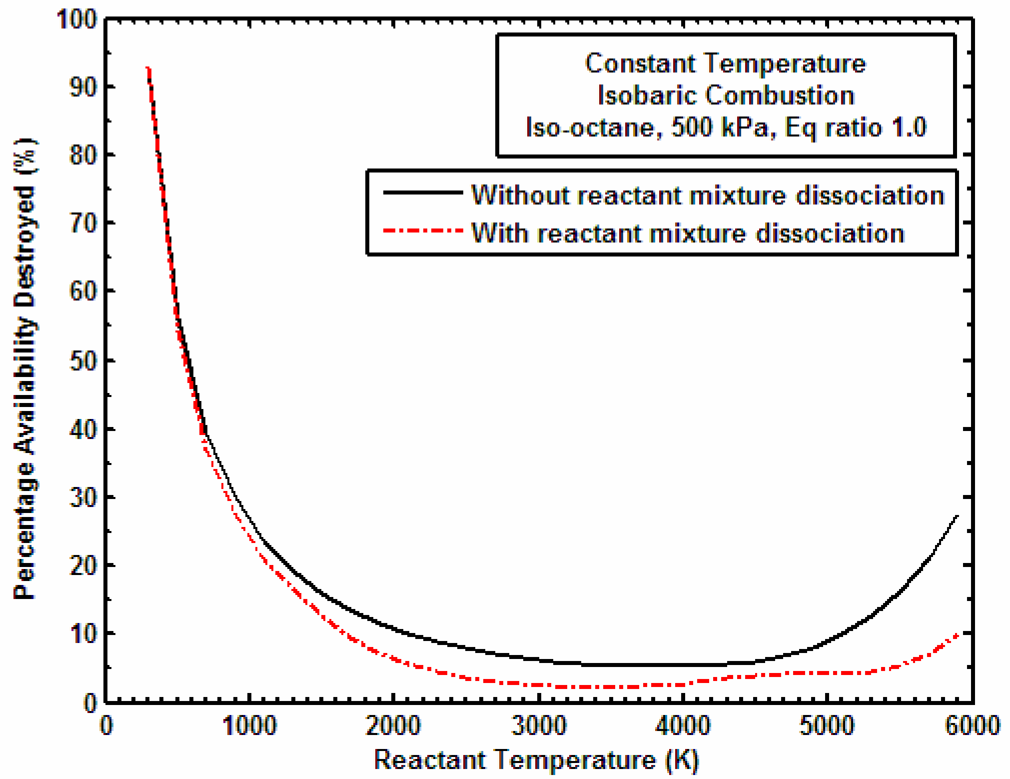


Fig. 52. Percentage availability destroyed during constant temperature, isobaric combustion of iso-octane, for reactant pressure of 500 kPa, with and without reactant mixture dissociation.

Fig. 53 shows the effect of reactant dissociation on the percentage of availability destroyed during constant temperature, isochoric combustion of iso-octane. The effect of dissociation is again similar to that for constant temperature, isobaric combustion of iso-octane. Dissociation causes the availability destroyed curve to be shifted to lower values at higher temperatures, indicating more efficient combustion.

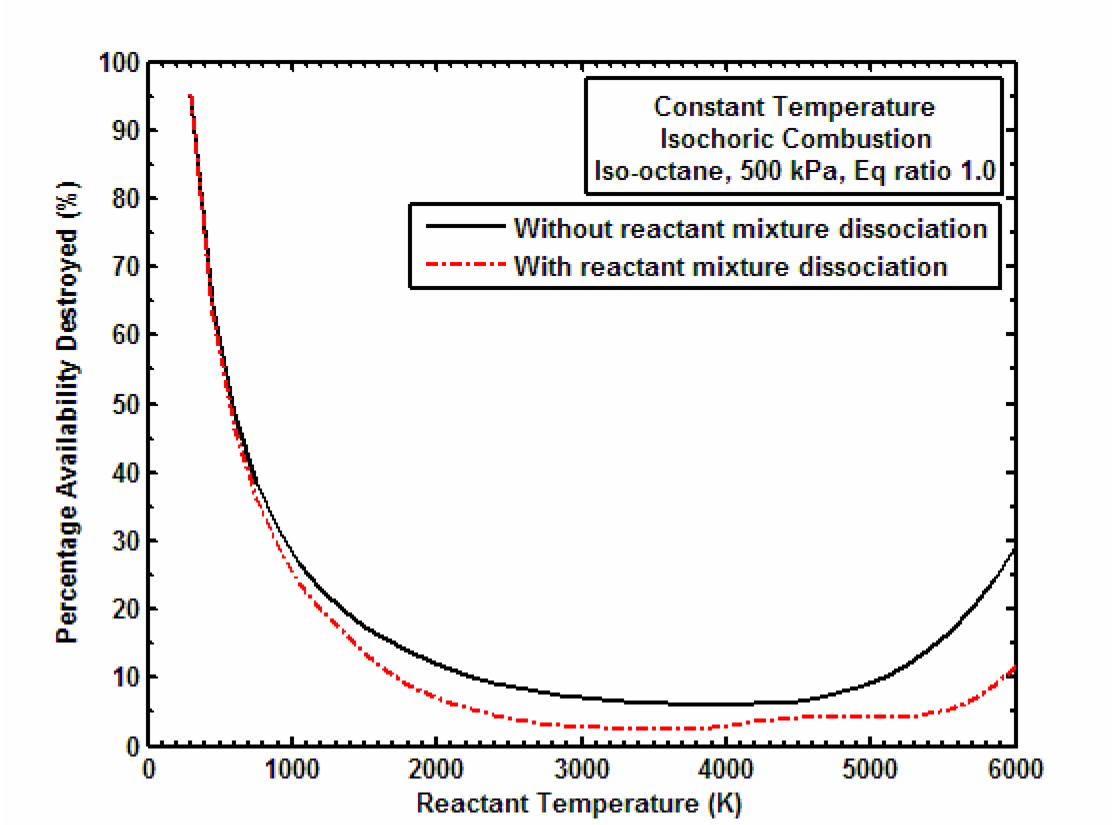


Fig. 53. Percentage availability destroyed during constant temperature, isochoric combustion of iso-octane, for reactant pressure of 500 kPa, with and without reactant mixture dissociation.

Discussion and comparison to Dunbar and Lior [7] analysis

As discussed in Section II, Dunbar and Lior [7] conducted an analysis of constant pressure combustion and attempted to quantify the various sources of irreversibility during the combustion process. They also discussed the exergetic efficiency of the oxidation of hydrogen as a function of the reactant temperature. Fig. 54 shows the values obtained from the current study for the exergetic efficiency (Exergetic efficiency = 100 – Percentage availability destroyed) for the oxidation of hydrogen at constant pressure.

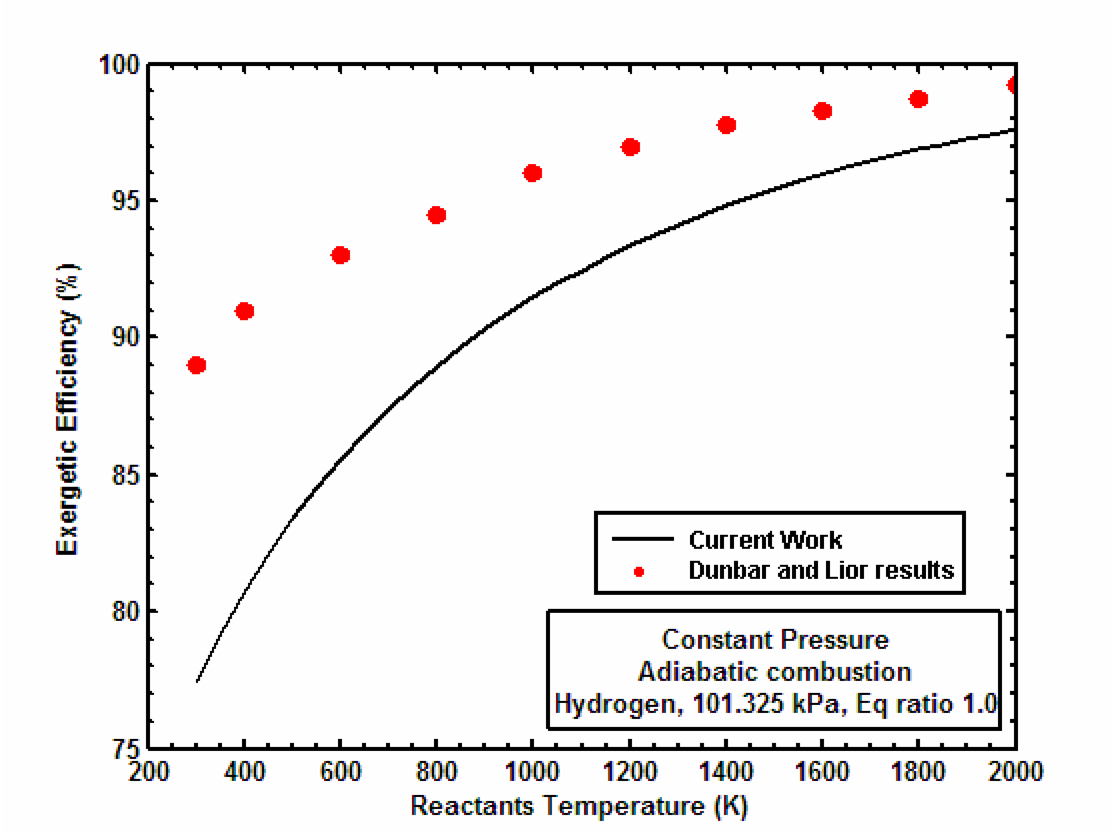


Fig. 54. Exergetic efficiency of constant pressure oxidation of hydrogen.

As expected, the exergetic efficiency of the oxidation process increases with increasing reactant temperature, before tending to an asymptote at higher reactant temperatures. While the trends agree, the values themselves differ in magnitude as seen in Fig. 54. This is because of the difference in the reactant mixture specifications. Dunbar and Lior [7] consider the fuel and air to enter as two different streams, entering the combustion chamber at reference pressure and temperature while the current study considers pre-mixed reactant mixtures. Also, the values from the Dunbar and Lior [7] analysis are for the exergetic efficiency of the oxidation process, while the results from the current study incorporate the contributions of other sources of irreversibility also. This is the cause for the difference in the values. It may also be noted that Dunbar and Lior [7] considered air to be a mixture of nitrogen and oxygen (N_2: 71%; O_2: 21%) and considered only complete products of combustion (The results presented from the current work account for these differences in air and product composition).

Discussion and comparison to Caton [9] analysis

Caton [9] completed a parametric study of constant volume combustion. He examined the effect of parameters such as the reactant temperature, pressure and equivalence ratio on the availability destroyed during the combustion process. An attempt is made here to compare and correlate the results from this work to those presented by Caton [9].

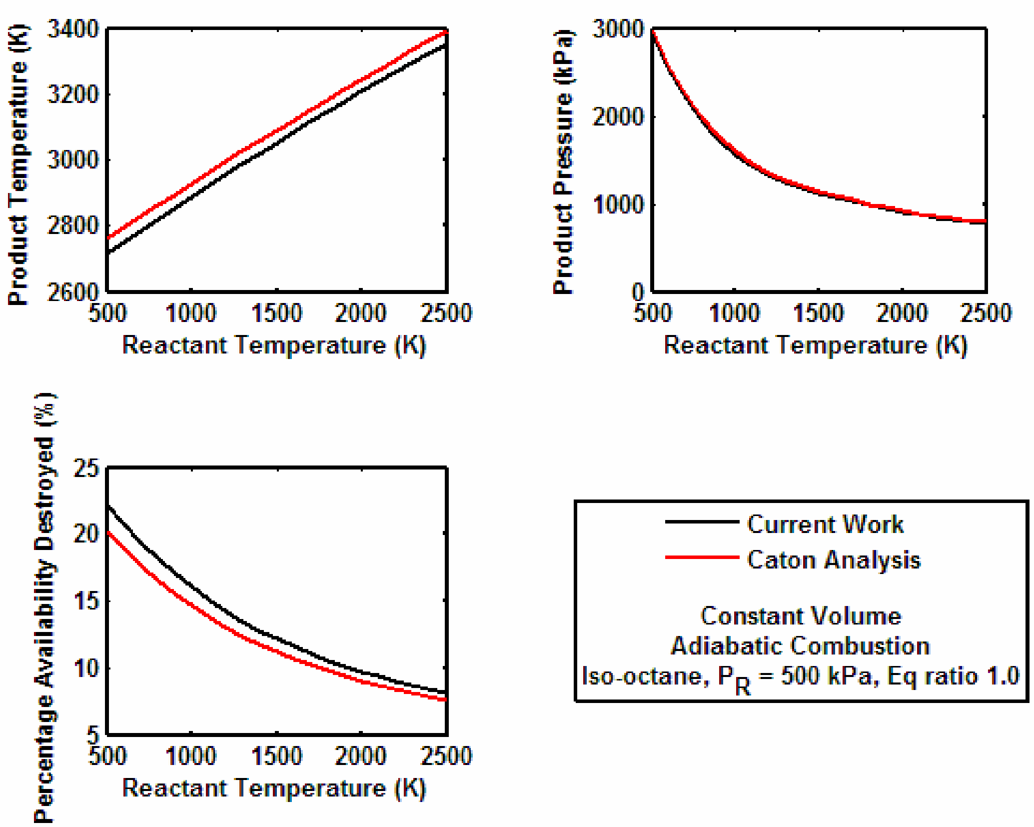


Fig. 55. Comparison of results for constant volume, adiabatic combustion of iso-octane at 500 kPa.

Fig. 55 shows a series of results for constant volume, adiabatic combustion of iso-octane for an initial reactant pressure of 500 kPa. The plot comparing the product mixture temperatures shows a small but consistent difference in the values obtained. The pressure values obtained from both studies agree much better. The curves for the fraction of availability destroyed are in the same range but significantly different in terms of the values.

Further investigations were conducted to determine the variation in the values for the percentage availability destroyed. The difference was found to be due to the difference in the product mixture temperatures obtained. The difference in the product mixture temperatures was due to the difference in the internal energies calculated for the reactant mixture, which in turn was due to the variation in the enthalpy values for iso-octane. This difference between the enthalpy values used is shown in Fig. 56.

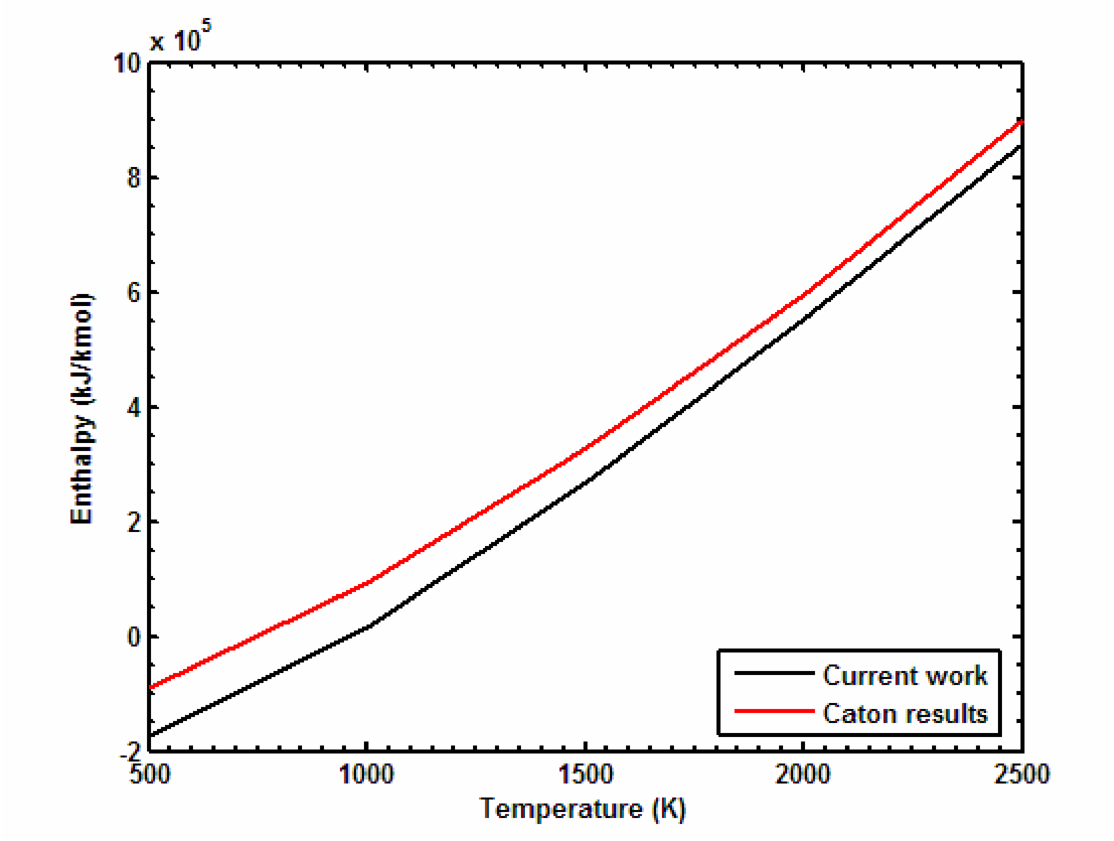


Fig. 56. Comparison of enthalpy values of iso-octane.

The differences in the values of enthalpy of iso-octane were verified to be the cause of the difference in the other values. The enthalpy values themselves differ in the two studies because the work completed by Caton [9] uses the older generation of coefficients, which were subsequently updated.

Discussion and comparison to Lutz et al. [10] analysis

The primary focus of the work conducted by Lutz et al. [10] was the comparison of the maximum theoretical efficiencies of the fuel cell to an engine operating on the Carnot cycle. However, Lutz et al. [10] also discuss the "combustion temperature", which is essentially the temperature corresponding to no change in the Gibbs energy, or in other words, the temperature at which reversible combustion takes place.

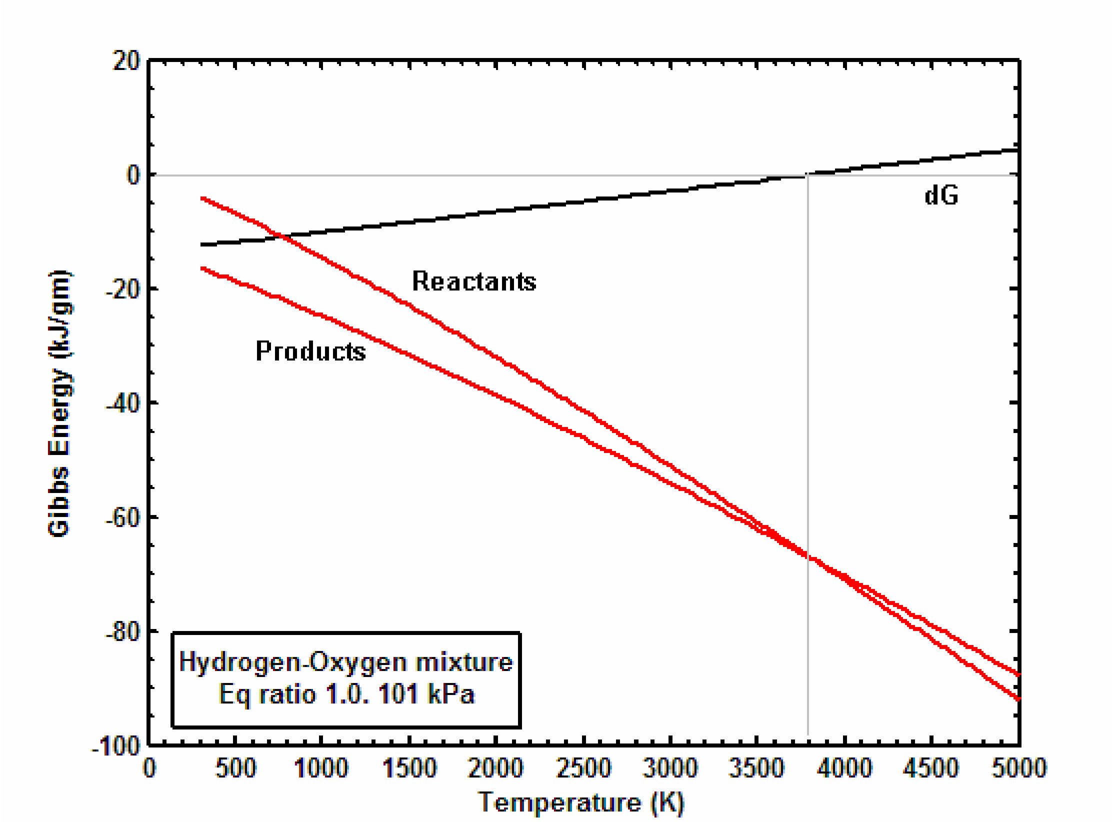


Fig. 57. Determination of "Combustion Temperature" for hydrogen oxidation, complete products of combustion.

Fig. 57 shows an attempt to determine the "combustion temperature" as obtained by Lutz et al. [10] in their analysis of the oxidation reaction of hydrogen. Using similar conditions of constant pressure oxidation in an atmosphere of pure oxygen, the value obtained for the "combustion temperature" was around 3800 K. This value is in good agreement with the value of 3802 K stated by Lutz et al. [10].

The results discussed above, however, are for complete products of combustion or in other words, water was the only product of the oxidation reaction. This is an idealization since other products of combustion such as hydrogen molecules (H_2), hydrogen atoms (H), oxygen molecules (O_2) and oxygen atoms (O) are also formed during the oxidation reaction. The analysis was therefore redone, with the equilibrium products of combustion also considered. Fig. 58 shows the curves for the reactant and product mixture Gibbs energy and the change in Gibbs energy due to the oxidation reaction.

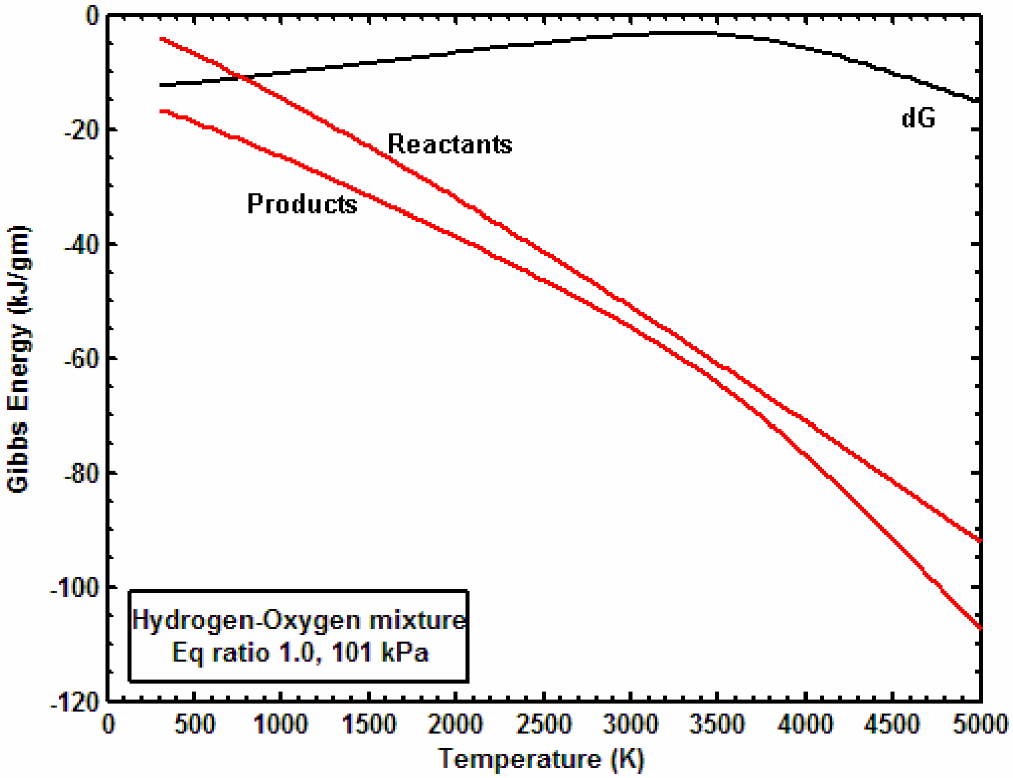


Fig. 58. Determination of the "Combustion Temperature" for hydrogen oxidation, equilibrium products of combustion.

Inclusion of the equilibrium products of combustion causes the reactant and product mixture Gibbs energy curves to not intersect, with the consequence that the change in Gibbs energy for the oxidation reaction never intersects the horizontal axis. The change in Gibbs energy initially decreases with increasing temperature, reaching closest to the horizontal axis at about 3400 K, before increasing in magnitude once again and becoming more negative.

An additional simplification still present in the analysis is assuming that the reactant mixture does not dissociate. The analysis was redone once again, relaxing all simplifications, for oxidation of hydrogen in the standard atmosphere, with equilibrium products of combustion and dissociation of the reactants considered. The Gibbs energies for the reactant and product mixtures and the change in Gibbs energy as a consequence of these are shown in Fig. 59.

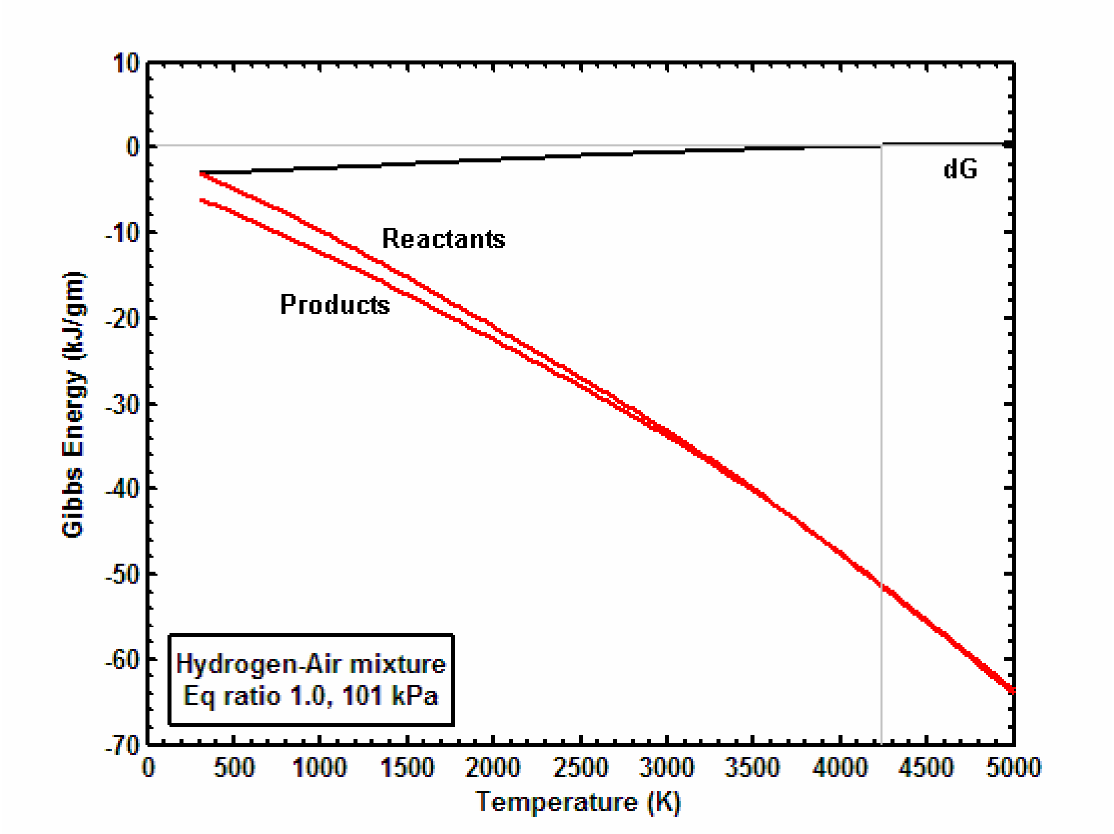


Fig. 59. Determination of “Combustion Temperature” for hydrogen oxidation, equilibrium products of combustion and dissociation of the reactant mixture.

It is evident from Fig. 59, that the Gibbs energy curves for the reactant and product mixtures do intersect and therefore, the change in Gibbs energy for the oxidation reaction intersects the horizontal axis. The zero change in Gibbs energy for the reaction now corresponds to a temperature of about 4250 K. This is significantly higher than the value of 3802 K obtained for the “combustion temperature” using the idealized assumptions in the analysis by Lutz et al. [10].

Discussion and comparison to Gyftopoulos and Beretta [15] analysis

Gyftopoulos and Beretta [15] present the fraction of availability destroyed during the combustion of various fuels for an initial temperature of 298 K and pressure of 1 atmosphere. The work considers a limited equilibrium product composition and a slightly different definition for the percentage of availability destroyed during combustion. Gyftopoulos and Beretta [15] defined the percentage of availability destroyed during combustion as

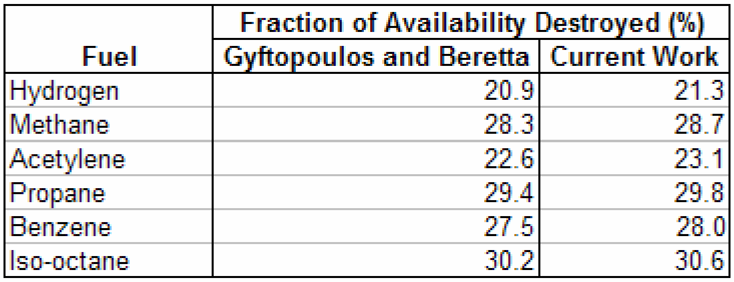
$$r_{DAC} = \frac{T_0 \Delta S}{n \Delta G} x100$$

where n is the number of moles of the fuel and ΔG is the Gibbs free energy of the fuel (per mole).

The values from the current work were computed using this definition of the fraction of availability destroyed and compared to the values provided by Gyftopoulos and Beretta [15] for both, constant pressure and constant volume combustion.

Table 1 shows the fraction of availability destroyed during constant pressure combustion of stoichiometric mixtures of fuel and air starting at a temperature of 298 K and pressure of 1 atmosphere.

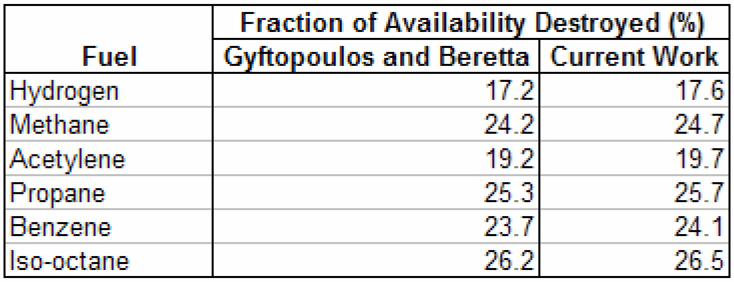
Table 1. Comparison of fraction of availability destroyed, constant pressure combustion



Fuel	Fraction of Availability Destroyed (%)	
	Gyftopoulos and Beretta	Current Work
Hydrogen	20.9	21.3
Methane	28.3	28.7
Acetylene	22.6	23.1
Propane	29.4	29.8
Benzene	27.5	28.0
Iso-octane	30.2	30.6

Table 2 shows the fraction of availability destroyed during constant volume combustion of stoichiometric mixtures of fuel and air starting at a temperature of 298 K and pressure of 1 atmosphere.

Table 2. Comparison of fraction of availability destroyed, constant volume combustion



Fuel	Fraction of Availability Destroyed (%)	
	Gyftopoulos and Beretta	Current Work
Hydrogen	17.2	17.6
Methane	24.2	24.7
Acetylene	19.2	19.7
Propane	25.3	25.7
Benzene	23.7	24.1
Iso-octane	26.2	26.5

The values computed by Gyftopoulos and Beretta [15] were based on a dry atmosphere composition and a limited number of equilibrium species being considered. This accounts for the slight difference between the two sets of values obtained for the fraction of availability destroyed.

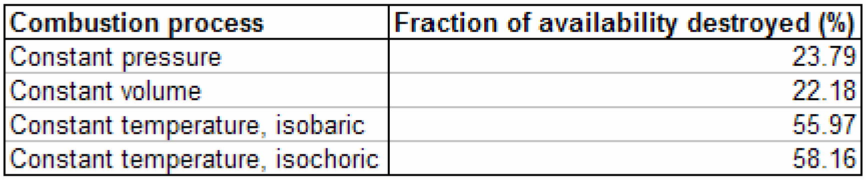
Application of results

Three combustion processes – constant pressure, constant volume and constant temperature combustion – were examined. The results from this study can be utilized to design more efficient energy conversion devices. An example of such an application is provided here.

Consider an internal combustion engine, running on iso-octane as the fuel and an equivalence ratio of 1.0. At the end of the compression stroke, a typical cylinder temperature would be 500 K and a typical pressure would be 500 kPa. The fraction of the reactant mixture availability destroyed during combustion for the various combustion processes may be evaluated.

Table 3 shows the values of the percentage of the reactant availability destroyed during the various combustion processes.

Table 3. Comparison of fraction of availability destroyed during various combustion processes



Combustion process	Fraction of availability destroyed (%)
Constant pressure	23.79
Constant volume	22.18
Constant temperature, isobaric	55.97
Constant temperature, isochoric	58.16

For the given conditions, therefore, constant volume combustion would destroy the least fraction of the reactant mixture availability. The constant temperature combustion processes (at 500 K) result in significantly higher percentage availability destruction due to combustion. This is largely because the product mixture temperature is fixed at 500 K for constant temperature combustion, while the product mixtures for constant pressure and constant volume combustion have temperatures of the order of 2500 K. Thus, it is not appropriate to compare the constant pressure and constant volume combustion processes with constant temperature combustion for the same initial temperatures.

A similar analysis can be extended to different combustion devices, allowing the availability destruction due to combustion to be quantified for different reactant mixture conditions and this allowing the selection of the optimum reactant mixture properties, finally leading to more efficient combustion devices.

Fig. 60 shows the percentage of reactant availability destroyed during constant pressure and constant volume combustion for similar initial reactant mixture conditions. Constant volume combustion is the more efficient combustion process until a reactant temperature of about 1000 K. Past this reactant temperature, the fraction of availability destroyed is lesser for constant pressure combustion, as compared to constant volume combustion.

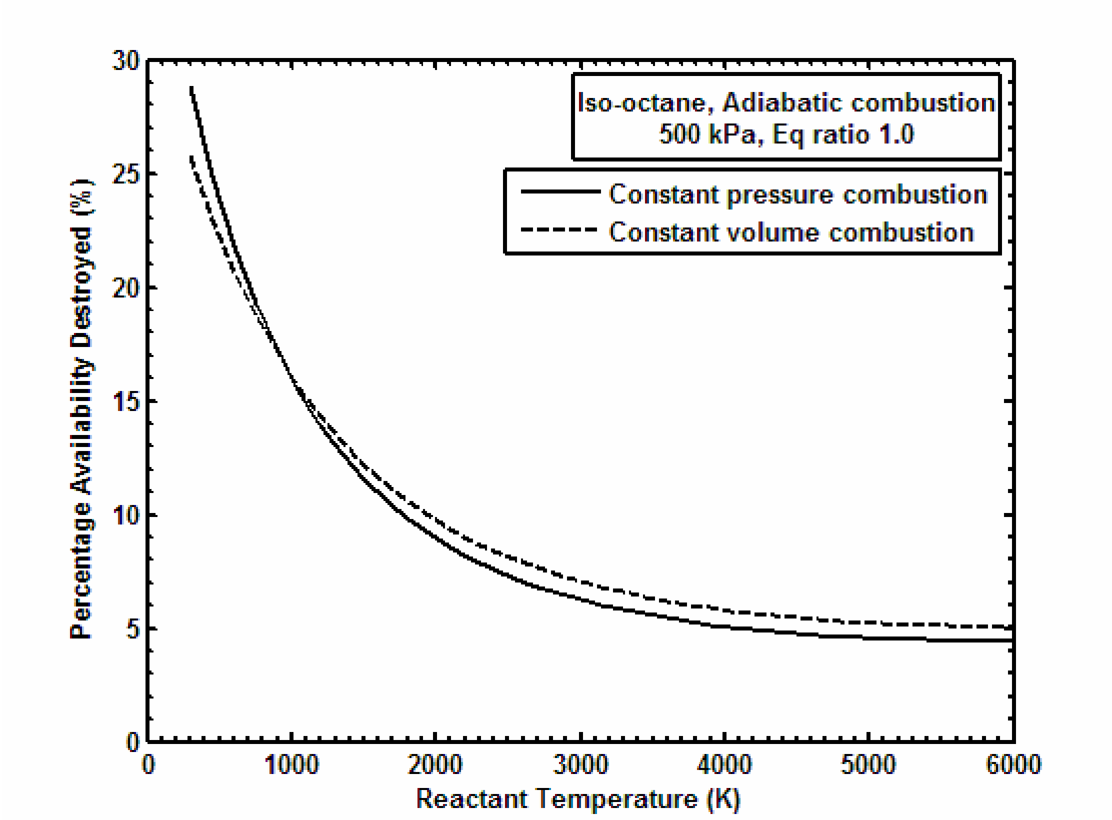


Fig. 60. Comparison of percentage of reactant availability destroyed during constant pressure and constant volume combustion.

V. SUMMARY AND CONCLUSION

A parametric examination of the availability destroyed during combustion was completed for constant pressure, constant volume and constant temperature combustion.

The effect of reactant temperature on the fraction of availability destroyed during the combustion process is significant. For constant pressure and constant volume combustion, the trend is similar – the fraction of reactant availability destroyed is greatest at lower temperatures, decreasing exponentially with increasing temperatures. This decrease in the fraction of availability destroyed at higher temperatures has led to a number of authors [7-9] concluding that it might be possible, with advances in material technology, to achieve reversible combustion. This is, however, not possible – once the dissociation effects are accounted for, it is obvious that the percentage destruction of availability reaches a minimum value before increasing again, with further increase in temperature. Thus, reversible combustion is shown to be impossible to achieve, but it also leads to the identification of a temperature corresponding to the least destruction of reactant mixture availability. Combustion losses would be least if the reactants were allowed to burn with reactant temperature equal to this temperature. For most fuels, this temperature lies outside the current materials capabilities. However, with further development of the materials, it might be possible to practically achieve these temperatures, allowing for optimal utilization of the fuel availability.

The effect of reactant mixture pressure on the fraction of availability destroyed is modest for both constant pressure and constant volume combustion.

The effect of the reactant mixture equivalence ratio on the fraction of availability destroyed is similar for both constant pressure and constant volume combustion conditions. For lean mixtures, the destruction of availability is greatest for the leanest mixtures at lower temperatures. This trend however, gets reversed with higher temperatures. For richer equivalence ratios, the trend is of greater destruction of availability for mixtures closer to stoichiometric ratio and lesser destruction of availability for richer reactant mixtures.

The fuel itself has a significant effect on the percentage of availability destroyed during the combustion process. During the analysis, it was found that combustion of hydrogen and acetylene destroyed the least fraction of availability. The fraction of availability destroyed was found to increase with increasing complexity of the structure of the fuel molecule. While the choice of fuels is often constrained by non-technical issues, the analysis is still helpful in choosing between fuels, when a choice exists between two or more potential fuels.

The chemical availability terms were analyzed and incorporated during the determination of the destruction of availability during combustion. As expected, it was found that the diffusion availability (as defined previously) was small in magnitude and did not significantly affect the total availability of the mixture. However, the reactive availability due to the species present in the mixture was significant, especially at high temperatures and often a bigger contributor to the total availability than the thermo-mechanical availability. Thus, neglecting the diffusion availability term does not change the values significantly, but the reactive availability of the mixture cannot be neglected, except under certain conditions of low temperature.

Dissociation of the reactant mixture is another effect that has been neglected in past work analyzing the combustion of fuels. This is again a significant approximation at higher temperatures. At lower reactant temperatures, the dissociation effects are negligible, but at elevated reactant temperatures, the reactant mixture is prone to dissociation and with increased temperatures, the chemical kinetics would significantly favor the dissociation process. Thus, it would not be appropriate to neglect the dissociation effects, especially since it alters the values of availability destroyed by significant amounts. Dissociation also leads to the obtaining of an efficient range of temperature for combustion leading to the least destruction of the reactant availability. Considering the dissociation of the reactant mixture allows for a more accurate estimation of the properties of the reactant mixture at the higher temperatures.

The results for constant temperature combustion differ from the constant pressure and constant volume combustion. The analyses were conducted for both, isobaric and isochoric constant temperature combustions. The results for both types of combustion were largely similar. For lower reactant temperatures, the destruction of the reactant availability is almost complete, with the fraction of availability destroyed decreasing rapidly with increasing temperatures. The fraction of availability destroyed during constant temperature tends to increase at very high temperatures. Incorporation of the dissociation effects moderates this rise, but the increases in fraction of availability destroyed persists.

The current work completes a reasonably comprehensive analysis of the various parameters affecting the efficiency of the combustion process. The results provide significant information and hints for the design and operation of combustion systems, allowing for optimal utilization of the energy contained in the fuels. The current work also allows for the comparison between the different combustion modes.

In addition, the common approximations made during the analysis of combustion processes were relaxed, allowing for a more accurate understanding of the combustion process than was possible with the simplified models.

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APPENDIX I

Atmospheric Composition

Table I.1. “Standard Wet Atmospheric” Composition used in the analyses

Species	**Percentage (Mole fractions)**
Nitrogen, N_2	0.7565
Oxygen, O_2	0.2029
Carbon dioxide, CO_2	0.0003
Water, H_2O	0.0313
Argon, Ar	0.0090

APPENDIX II

NASA Lewis Polynomial Coefficients for Fuels

Table II.1. Coefficients for use with the NASA Lewis polynomials

Fuel	Formula	Range	a1	a2	a3	a4	a5	a6	a7	b1	b2	hf
Methane	CH4	200 - 1000	-1.766851E+05	2.786181E+03	-1.202578E+01	3.917619E-02	-3.619054E-05	2.026853E-08	-4.976705E-12	-2.331314E+04	8.904323E+01	-74600
		1000 - 6000	3.730043E+06	-1.383501E+04	2.049107E+01	-1.961975E-03	4.727313E-07	-3.728815E-11	1.623737E-15	7.532067E+04	-1.219125E+02	
Acetylene	C2H2	200 - 1000	1.598112E+05	-2.216644E+03	1.265708E+01	-7.979651E-03	8.054993E-06	-2.433308E-09	-7.529233E-14	3.712619E+04	-5.244339E+01	228200
		1000 - 6000	1.713847E+06	-5.929107E+03	1.236128E+01	1.314187E-04	-1.362764E-07	2.712656E-11	-1.302066E-15	6.266579E+04	-5.818961E+01	
Ethylene	C2H4	200 - 1000	-1.163606E+05	2.554852E+03	-1.609746E+01	6.625779E-02	-7.885082E-05	5.125225E-08	-1.370340E-11	-6.176191E+03	1.093338E+02	52500
		1000 - 6000	3.408764E+06	-1.374848E+04	2.365898E+01	-2.423804E-03	4.431396E-07	-4.352683E-11	1.775411E-15	8.820429E+04	-1.371278E+02	
Ethane	C2H6	200 - 1000	-1.862044E+05	3.406192E+03	-1.951705E+01	7.565836E-02	-8.204173E-05	5.061136E-08	-1.319282E-11	-2.702933E+04	1.298140E+02	-83851
		1000 - 6000	5.025782E+06	-2.033022E+04	3.322553E+01	-3.836703E-03	7.238406E-07	-7.319183E-11	3.065469E-15	1.115964E+05	-2.039411E+02	
Propylene	C3H6	200 - 1000	-1.912462E+05	3.542074E+03	-2.114879E+01	8.901485E-02	-1.001429E-04	6.267959E-08	-1.637871E-11	-1.529962E+04	1.407641E+02	20000
		1000 - 6000	5.017620E+06	-2.086084E+04	3.644156E+01	-3.881191E-03	7.278677E-07	-7.321205E-11	3.052176E-15	1.261245E+05	-2.195716E+02	
Propane	C3H8	200 - 1000	-2.433144E+05	4.656271E+03	-2.939466E+01	1.188953E-01	-1.376308E-04	8.814824E-08	-2.342988E-11	-3.540335E+04	1.841749E+02	-104680
		1000 - 6000	6.420732E+06	-2.659791E+04	4.534357E+01	-5.020664E-03	9.471217E-07	-9.575405E-11	4.009673E-15	1.455582E+05	-2.818375E+02	
n-Butane	C4H10	200 - 1000	-3.175873E+05	6.176332E+03	-3.891562E+01	1.584654E-01	-1.860050E-04	1.199676E-07	-3.201671E-11	-4.540363E+04	2.379489E+02	-125790
		1000 - 6000	7.682322E+06	-3.256052E+04	5.736733E+01	-6.197917E-03	1.180186E-06	-1.221894E-10	5.250635E-15	1.774527E+05	-3.587919E+02	
n-Pentane	C5H12	200 - 1000	-2.768895E+05	5.834283E+03	-3.617541E+01	1.533340E-01	-1.528396E-04	8.191092E-08	-1.792328E-11	-4.665375E+04	2.265544E+02	-146760
		1000 - 6000	-2.530779E+06	-8.972593E+03	4.536223E+01	-2.626990E-03	3.135136E-06	-5.318729E-10	2.886897E-14	1.484617E+04	-2.516550E+02	
Benzene	C6H6	200 - 1000	-1.677341E+05	4.404500E+03	-3.717378E+01	1.640510E-01	-2.020812E-04	1.307915E-07	-3.444284E-11	-1.035455E+04	2.169853E+02	82880
		1000 - 6000	4.538576E+06	-2.260503E+04	4.694007E+01	-4.206677E-03	7.907994E-07	-7.968302E-11	3.328212E-15	1.391465E+05	-2.868751E+02	
n-Hexane	C6H14	200 - 1000	-5.815927E+05	1.079098E+04	-6.633947E+01	2.523715E-01	-2.904345E-04	1.802202E-07	-4.617224E-11	-7.271545E+04	3.938284E+02	-166920
		1000 - 6000	-3.106626E+06	-7.346088E+03	4.694132E+01	1.693964E-03	2.068997E-06	-4.212142E-10	2.452346E-14	5.237503E+02	-2.549968E+02	

Table II.1. Continued

Fuel	Formula	Range	a1	a2	a3	a4	a5	a6	a7	b1	b2	hf
n-Heptane	C7H16	200 - 1000	-6.127433E+05	1.184085E+04	-7.487189E+01	2.918466E-01	-3.416795E-04	2.159285E-07	-5.655853E-11	-8.013409E+04	4.407213E+02	-187780
		1000 - 6000	9.135632E+06	-3.923320E+04	7.889781E+01	-4.654252E-03	2.071774E-06	-3.442539E-10	1.976835E-14	2.050708E+05	-4.851104E+02	
n-Octane	C8H18	200 - 1000	-6.986647E+05	1.338501E+04	-8.415166E+01	3.271937E-01	-3.777210E-04	2.339837E-07	-6.010893E-11	-9.026223E+04	4.939222E+02	-208750
		1000 - 6000	6.365407E+06	-3.105365E+04	6.969162E+01	1.048060E-02	-4.129622E-06	5.543226E-10	-2.651436E-14	1.500969E+05	-4.169896E+02	
Iso-Octane (l	C8H18	165.79 - 380	1.419158E+05	-2.937251E+03	4.168835E+01	-8.436942E-02	2.894148E-04	-2.200564E-07	7.234226E-11	-2.479399E+04	-1.930220E+02	-259160
Iso-Octane	C8H18	200 - 1000	-1.688759E+05	3.126903E+03	-2.123503E+01	1.489152E-01	-1.151180E-04	4.473216E-08	-5.554882E-12	-4.468061E+04	1.417456E+02	-224010
		1000 - 6000	1.352765E+07	-4.663370E+04	7.795313E+01	1.423730E-02	-5.073594E-06	7.248233E-10	-3.819190E-14	2.541178E+05	-4.933887E+02	
Methanol	CH3OH	200 - 1000	-2.416643E+05	4.032147E+03	-2.046415E+01	6.903698E-02	-7.598933E-05	4.598208E-08	-1.158707E-11	-4.433261E+04	1.400142E+02	-200940
		1000 - 6000	3.411571E+06	-1.345500E+04	2.261408E+01	-2.141029E-03	3.730051E-07	-3.498846E-11	1.366073E-15	5.636082E+04	-1.277814E+02	
Ethanol	C2H5OH	200 - 1000	-2.342791E+05	4.479181E+03	-2.744817E+01	1.088679E-01	-1.305309E-04	8.437346E-08	-2.234559E-11	-5.022229E+04	1.764829E+02	-234950
		1000 - 6000	4.694818E+06	-1.929798E+04	3.447584E+01	-3.236166E-03	5.784948E-07	-5.564600E-11	2.226226E-15	8.601623E+04	-2.034802E+02	
Carbon	C	200 - 1000	6.495031E+02	-9.649011E-01	2.504675E+00	-1.281448E-05	1.980134E-08	-1.606144E-11	5.314483E-15	8.545763E+04	4.747924E+00	716680
		1000 - 6000	-1.289136E+05	1.719529E+02	2.646044E+00	-3.353069E-04	1.742093E-07	-2.902818E-11	1.642182E-15	8.410598E+04	4.130047E+00	
		6000 - 2000	4.432528E+08	-2.886018E+05	7.737108E+01	-9.715282E-03	6.649595E-07	-2.230079E-11	2.899389E-16	2.355273E+06	-6.405123E+02	
Hydrogen	H2	200 - 1000	4.078323E+04	-8.009186E+02	8.214702E+00	-1.269714E-02	1.753605E-05	-1.202860E-08	3.368093E-12	2.682485E+03	-3.043789E+01	0
		1000 - 6000	5.608128E+05	-8.371505E+02	2.975365E+00	1.252249E-03	-3.740716E-07	5.936625E-11	-3.606994E-15	5.339824E+03	-2.202775E+00	
		6000 - 2000	4.966884E+08	-3.147547E+05	7.984122E+01	-8.414789E-03	4.753248E-07	-1.371873E-11	1.605462E-16	2.488434E+06	-6.695728E+02	
Carbon	CO	200 - 1000	1.489045E+04	-2.922286E+02	5.724527E+00	-8.176235E-03	1.456903E-05	-1.087746E-08	3.027942E-12	-1.303132E+04	-7.859241E+00	-110535
Monoxide		1000 - 6000	4.619197E+05	-1.944705E+03	5.916714E+00	-5.664283E-04	1.398815E-07	-1.787680E-11	9.620936E-16	-2.466261E+03	-1.387413E+01	
		6000 - 2000	8.868663E+08	-7.500378E+05	2.495475E+02	-3.956351E-02	3.297772E-06	-1.318410E-10	1.998938E-15	5.701421E+06	-2.060705E+03	

APPENDIX III

Change in Gibbs Energy for oxidation of fuels

Table III.1. Values for change in Gibbs energy for various fuels

FUEL	FORMULA	CHANGE IN GIBBS ENERGY* (kJ/kg)
Hydrogen	H_2	113372
Carbon	C	32836
Carbon monoxide	CO	9184
Methane	CH_4	49914
Acetylene	C_2H_2	47108
Propane	C_3H_8	47036
Benzene	C_6H_6	40734
Iso-octane (g)	C_8H_{18}	45750
Methanol	CH_3OH	21500
Ethanol	C_2H_5OH	28400
Hydrogen atom	H	315055
Hydroxyl radical	OH	8762
Oxygen atom	O	14483
Nitrogen atom	N	32520
Nitrogen oxide	NO	2896

* Values calculated from Fundamentals of Engineering Thermodynamics, Fourth edition, Moran M J and Shapiro H N.

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