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Second-law analyses applied to internal combustion engines operation

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Abstract

This paper surveys the publications available in the literature concerning the application of the second-law of thermodynamics to internal combustion engines. The availability (exergy) balance equations of the engine cylinder and subsystems are reviewed in detail providing also relations concerning the definition of state properties, chemical availability, flow and fuel availability, and dead state. Special attention is given to identification and quantification of second-law efficiencies and the irreversibilities of various processes and subsystems. The latter being particularly important since they are not identified in traditional first-law analysis. In identifying these processes and subsystems, the main differences between second- and first-law analyses are also highlighted. A detailed reference is made to the findings of various researchers in the field over the last 40 years concerning all types of internal combustion engines, i.e. spark ignition, compression ignition (direct or indirect injection), turbocharged or naturally aspirated, during steady-state and transient operation. All of the subsystems (compressor, aftercooler, inlet manifold, cylinder, exhaust manifold, turbine), are also covered. Explicit comparative diagrams, as well as tabulation of typical energy and exergy balances, are presented. The survey extends to the various parametric studies conducted, including among other aspects the very interesting cases of low heat rejection engines, the use of alternative fuels and transient operation. Thus, the main differences between the results of second- and first-law analyses are highlighted and discussed.
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Keywords: Second-law; Internal combustion engines; Availability; Exergy; Irreversibilities

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1. Introduction

Internal combustion engine simulation modeling has long been established as an effective tool for studying engine performance and contributing to evaluation and new developments. Thermodynamic models of the real engine cycle have served as effective tools for complete analysis of engine performance and sensitivity to various operating parameters [1–6].

Nomenclature

A	availability/exergy (J)
a	specific availability/exergy (J/kg)
b	flow availability/exergy (J/kg)
C	carbon
c_p	specific heat under constant pressure (J/kg K)
c_v	specific heat under constant volume (J/kg K)
E	energy (J)
F	surface (m^2)
G	mass moment of inertia (kg m^2), or Gibbs free enthalpy (J)
g	specific Gibbs free enthalpy (J/kg)
H	hydrogen
h	specific enthalpy (J/kg)
I	irreversibility (J)
m, M	mass (kg)
$\dot{m}$	mass flow rate (kg/s)
N	engine speed (rpm)
O	oxygen
p	pressure (Pa)
Q	heat (J)
R_s	specific gas constant (J/kg K)
R_{mol}	universal gas constant = 8314 J/kmol K
S	entropy (J/K), or sulfur
s	specific entropy (J/kg K)
T	absolute temperature (K)
t	time (s)
U	internal energy (J)
u	specific internal energy (J/kg)
V	volume (m^3)
W	work (J)
x	mole fraction (–)
z	number of engine cylinders (–), or fuel pump rack position (m)

Greek symbols

γ	ratio of specific heat capacities c_p/c_v
ε	second-law or exergy or exergetic efficiency
η	first-law efficiency
μ	chemical potential (J/kg)
τ	torque (Nm)
φ	crank angle (deg or rad)
ϕ	fuel–air equivalence ratio (–)
ω	angular velocity (rad/s)

Subscripts

0	restricted dead state
1	initial conditions
2	compressor outlet
3	aftercooler outlet
4	inlet manifold
5	cylinder
6	exhaust manifold
7	turbine outlet
br	brake
C	compressor
ch	chemical
cv	control volume
e	engine
em	exhaust manifold
ex	exhaust
f	fuel
fb	fuel burning
fr	friction
g	gas
i	any species, or injected
im	inlet manifold
irr	irreversibilities
L	loss, or load
m	main chamber
p	pre-chamber
TC	turbocharger
T	turbine
tot	total
v	vapor
w	wall or work

Superscripts

0	true dead state
ch	chemical
O	isooctane
thr	throttling
tm	thermomechanical
w	water

Abbreviations

°CA	degrees of crank angle
A/C	aftercooler or aftercooled
bmep	brake mean effective pressure (bar)
CI	compression ignition
CNG	compressed natural gas
CR	compression ratio
DI	direct injection
IDI	indirect injection
LFG	landfill gas

LHR	low heat rejection	SI	spark ignition
LHV	lower heating value	T/C	turbocharged or turbocharger
rpm	revolutions per minute	T/CP	turbo-compound

On the other hand, it has long been understood that traditional first-law analysis, which is needed for modeling the engine processes, often fails to give the engineer the best insight into the engine's operation. In order to analyze engine performance—that is, evaluate the inefficiencies associated with the various processes—second-law analysis must be applied [7–16]. For second-law analysis, the key concept is 'availability' (or exergy[1]). The availability content of a material represents its potential to do useful work. Unlike energy, availability can be destroyed which is a result of such phenomena as combustion, friction, mixing and throttling. The relationships needed to evaluate availability content, the transports of availability and availability destruction can be found in Refs. [7–14].

The destruction of availability—often termed irreversibility—is the source for the defective exploitation of fuel into useful mechanical work in a compression or spark ignition engine. The reduction of irreversibilities can lead to better engine performance through a more efficient exploitation of fuel. To reduce the irreversibilities, we need to quantify them. That is we need to evaluate the availability destructions-we need the second-law analysis [12,17,18].

Objectives of second-law application to internal combustion engines are:

- To weigh the various processes and devices, calculating the ability of each one of these to produce work.
- To identify those processes in which destruction or loss of availability occurs and to detect the sources for these destructions.
- To quantify the various losses and destructions.
- To analyze the effect of various design and thermodynamic parameters on the exergy destruction and losses.
- To propose measures/techniques for the minimization of destruction and losses, to increase overall efficiency.
- To propose methods for exploitation of losses—most notably exhaust gas to ambient and heat transfer to cylinder walls—now lost or ignored.
- To define efficiencies so that different applications can be studied and compared, and possible improvements measured.

Many studies have been published in the past few decades (the majority during the last 20 years), concerning second-law application to internal combustion engines—one such review paper is written by Caton [19]. The present work expands considerably upon that paper, with a different philosophy and perspective, providing details about equations used for second-law application to internal combustion engines operation, i.e. state properties, basic first-law equations, fuel chemical availability, availability equations for the engine cylinder and each engine's subsystem, entropy balance equations, second-law efficiency and basic relations for the application of the second-law analysis during transient operation. It also covers all recent publications in light of new developments such as alternative fuels and transient operation. Details about the main data, i.e. engine characteristics, modeling assumptions, etc. and—in particular—the findings of each previous study are given in this paper. Tabulation of energy and availability balances is given for many types of engines, accompanied by figures showing the effect of the most important parameters on the second-law performance of internal combustion engines.

2. Basic concepts and definitions of availability

2.1. Availability of a system

The availability of a system in a given state can be defined as the maximum useful work that can be produced through interaction of the system with its surroundings, as it reaches thermal, mechanical and chemical equilibrium. Usually, the terms associated

[1] Availability (exergy) is a special case of the more fundamental concept, available energy, introduced by Gibbs [15]. For example, see Refs. [8,16]. 67% of the published papers in the field of second-law application to internal combustion engines use the term availability over the term exergy; both terms will be used interchangeably throughout this paper.

with thermomechanical and chemical equilibration are differentiated and calculated separately.

For a closed system experiencing heat and work interactions with the environment, the following equation holds, for the thermomechanical availability [1,7–14,20–24]:

$$A^{\mathrm{tm}} = (E - U_0) + p_0(V - V_0) - T_0(S - S_0) \tag{1a}$$

where $E = E_{\mathrm{kin}} + E_{\mathrm{pot}} + U$, with E_{kin} the kinetic and E_{pot} the potential energy, p_0 and T_0 are the fixed pressure and temperature of the environment; and U_0, V_0 and S_0 are the internal energy, volume and entropy of the contents were they brought to p_0 and T_0.

Availability is an extensive property with a value greater than or equal to zero [9,12]. It is obvious that availability is a property, the value of which depends not only on the state of the system, but also on the ambient properties.

As stated above, there is no availability in a system when thermal, mechanical and chemical equilibrium exists with the environment. Thermal equilibrium is achieved when the temperature of the system is equal to the temperature of the surrounding environment. In the same way, mechanical equilibrium is achieved when there is no pressure difference between the working medium and the environment.

2.2. Chemical equilibrium

Chemical equilibrium is achieved only when there are no components of the working medium, which could interact with those of the environment to produce work. In the case of engines, all the components of the working medium must be either oxidized (e.g. fuel, CO, H), or reduced (e.g. NO, OH), in a reversible way as the system reaches the dead state (see following section for dead state definition). The only components of the system, which cannot react chemically with the atmosphere and, therefore, constitute the components of the mixture at the dead state are O_2, N_2, CO_2 and H_2O.

In addition to the work that could be obtained due to reversible reactions, some researchers propose a more general definition of chemical availability, which would also take into account the capacity to produce work because of the difference between the partial pressures of the components (when in thermal and mechanical equilibrium with the environment) and the partial pressures of the same components in the atmosphere [7–14,24]. This work could be extracted by the use of semi-permeable membranes and efficient low input pressure, high pressure ratio expansion devices (e.g. Van't Hoff's equilibrium box).

For many researchers, including the present authors, this portion of chemical availability should not be taken into account—when studying internal combustion engines applications [21,22,25–27]. For works concerning lean operation of diesel engines (especially when using a single-zone model), there are practically no partial products in the exhaust that could contain substantial chemical availability. Of course, this is unlike the case of a spark-ignition engine operating at rich conditions. An interesting situation arises when simulating diesel engine combustion using a multi-zone model. The locally-rich conditions in some of the zones are responsible for a high percentage of chemical availability, as revealed in Fig. 1, for a compression ignition engine, where the ratio of chemical to total availability at the end of the expansion stroke is shown, which can assume significant value when the fuel–air equivalence ratio ϕ increases.

Flynn et al. [21] argued that the chemical availability term is practically useless due to the inability of its recovery, at least as regards mobile applications (moving one step further they proposed that even the thermal term can only be recovered in stationary applications); Shapiro and Van Gerpen, who discussed the chemical availability term in detail in Refs. [24,28], did not disagree in principle, since they concluded that the chemical availability cannot be realized as work since it is practically unattainable in engine applications.

This is not the case, however, with fuel cells as here the fuel chemical availability is converted to useful power with almost zero thermal component in some configurations, whereas work recovery is indeed

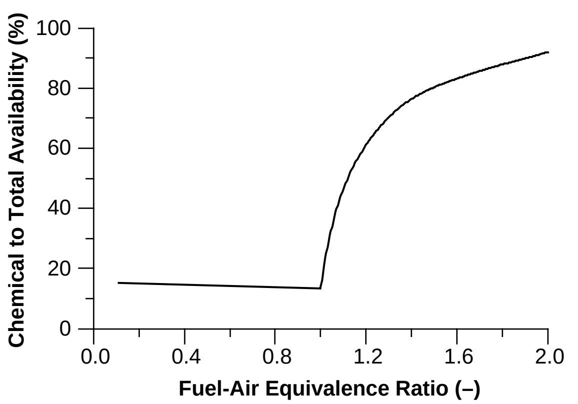

Fig. 1. Ratio of cylinder gas chemical availability to total availability at the end of expansion for a compression ignition engine at various fuel–air equivalence ratios, ϕ (adapted from Ref. [24]).

achieved during isothermal flows through semi-permeable membranes.

2.3. Dead state

The choice of a reference dead state is of paramount importance when dealing with availability calculations since this will determine what kind of equilibrium will be established with the environment and consequently, the calculated values of availability. This subject has been treated in detail in Refs. [9,21,24,29,30].

In general, a system is considered to be at the so-called 'restricted' dead state when no work potential exists between the system and the environment due to temperature or pressure differences. This is the dead state reached when calculating the thermomechanical availability. Some researchers in the field of second-law application to internal combustion engines, including the present ones, define the restricted dead state (for any given state) to have the same chemical composition as the given state (thus no work potential exists due to compositional differences); whereas some authors (e.g. Ref. [24]) define the restricted dead state to be the chemical equilibrium state of the given state's components at p_0 and T_0 (but not in chemical equilibrium with environmental components).

On the other hand, if chemical equilibrium with the environment is of concern, then we refer to the 'true' or 'unrestricted' dead state, where the chemical potentials of the system also equal those of the environment [7–14].

For engine applications the (environmental) pressure and temperature conditions of the dead state are usually taken to be $p_0 = 1.01325$ bar and $T_0 = 298.15$ K, and if chemical availability is also taken into account, then the molar composition of the environment is: 20.35% O_2, 75.67% N_2, 0.03% CO_2, 3.03% H_2O and 0.92% various other substances [9,10]. Changes in the dead state conditions are reflected by changes in the value of the system availability.

In a closed system, Eq. (1a) given above, also suggests the following for thermomechanical availability [1,7–14]:

$$A^{\mathrm{tm}} = E + p_0 V - T_0 S - G_0$$
$$= E + p_0 V - T_0 S - \sum_{\mathrm{i}} m_{\mathrm{i}} \mu_{\mathrm{i}0} \qquad (1b)$$

where G_0 is the working medium's Gibbs free enthalpy and $\mu_{\mathrm{i}0}$ is the respective chemical potential of species i, both are calculated at restricted dead state conditions, and m_{i} is the mass of species i. At the restricted dead state the system is in thermal and mechanical equilibrium with the environment. However, no chemical equilibrium exists, which means that some work recovery is possible due to the difference between the composition of the system at the restricted dead state and that of the environment. If the system at the restricted dead state is also permitted to pass into but not react chemically with, the surrounding environment, then for ideal gas mixtures, the chemical availability is defined as [9,10,12,23]

$$A^{\mathrm{ch}} = \sum_{\mathrm{i}} m_{\mathrm{i}} (\mu_{\mathrm{i}0} - \mu_{\mathrm{i}}^0) = T_0 \sum_{\mathrm{i}} R_{\mathrm{si}} m_i \ln\left(\frac{x_{\mathrm{i}}}{x_{\mathrm{i}}^0}\right) \qquad (1c)$$

with μ_{i}^0 the chemical potential of species i at the true dead state, and x_{i}, x_{i}^0 the mole fractions of species i in the mixture (restricted dead-state) and the environment (true dead state), respectively. This chemical availability is a measure of the maximum work when the system comes to equilibrium with the environmental composition.

Total, i.e. thermomechanical plus chemical availability can be calculated by adding Eqs. (1b) and (1c)

$$A = A^{\mathrm{tm}} + A^{\mathrm{ch}} = E + p_0 V - T_0 S - \sum_{\mathrm{i}} m_{\mathrm{i}} \mu_{\mathrm{i}}^0 \qquad (1d)$$

2.4. General availability balance equation

For an open system experiencing mass exchange with the surrounding environment, the following equation holds for the total availability on a time basis [7–12,23]:

$$\frac{\mathrm{d}A_{\mathrm{cv}}}{\mathrm{d}t} = \int_j \left(1 - \frac{T_0}{T_j}\right) \dot{Q}_j - \left(\dot{W}_{\mathrm{cv}} - p_0 \frac{\mathrm{d}V_{\mathrm{cv}}}{\mathrm{d}t}\right)$$
$$+ \sum_{\mathrm{in}} \dot{m}_{\mathrm{in}} b_{\mathrm{in}} - \sum_{\mathrm{out}} \dot{m}_{\mathrm{out}} b_{\mathrm{out}} - \dot{I} \qquad (2)$$

where:

(a) $\mathrm{d}A_{\mathrm{cv}}/\mathrm{d}t$ is the time rate of change in the exergy of the control volume content (i.e. engine cylinder, or exhaust manifold, etc.).
(b) $\int_j (1 - T_0/T_j)\dot{Q}_j$ is the availability term for heat transfer, with T_j the temperature at the boundary of the system, which in general, is different from the temperature level of a process (although these two temperatures are the same when applying the most usual simulation approach of internal combustion engines operation, i.e. single-zone modeling), and $\dot{Q}_j$ represents the time rate of heat transfer at the

boundary of the control volume. This equation shows that increasing the temperature of a specified energy stream also increases its availability or, the ability of the stream to produce work. This statement is very useful when studying internal combustion engines (particularly compression ignition engines), since here an increase in the fuel–air equivalence ratio ϕ results in an increase in exhaust gases temperatures due to the lean mixtures involved, and thus their potential for work production. Moreover, this equation denotes that there is actually a limitation imposed by the second-law of thermodynamics as regards operation and efficiency of thermal engines. These aspects will be discussed in more detail in Sections 7 and 8.

(c) $\dot{W}_{cv} - p_0(dV_{cv}/dt)$ is the availability term associated with (mechanical or electrical) work transfer.

(d) $\sum_{in} \dot{m}_{in} b_{in}$ and $\sum_{out} \dot{m}_{out} b_{out}$ are the availability terms associated with inflow and outflow of masses, respectively. In particular, the terms b_{in} and b_{out} in Eq. (2) refer to the flow or stream availability (or exergy) of the incoming and the outgoing cylinder mass flow rates, respectively, given by (neglecting kinetic and potential energy contribution):

$$b = b^{tm} + b^{ch} = h - T_0 s - \sum_i x_i \mu_i^0 \qquad (3)$$

with s_0 the entropy of (cylinder) flow rate were it brought to p_0 and T_0. Flow availability is defined as the maximum work output that can be obtained as the fluid passes reversibly from the given state to a dead state, while exchanging heat solely with the environment.

(e) $\dot{I}$ is the rate of irreversibility production inside the control volume due to combustion, throttling, mixing, heat transfer under finite temperature difference to cooler medium, etc. Another relation often applied is, $\dot{I} = T_0 \dot{S}_{irr}$, based on an entropy balance, with $\dot{S}_{irr}$ denoting the rate of entropy creation due to irreversibilities.

3. First-law arguments used in tandem with second-law analyses of internal combustion engines[2]

The majority of studies concerning second-law application to internal combustion engines are based on a preceding first-law mathematical modeling of the various processes inside the cylinder and its subsystems. These will be discussed briefly as they constitute the basis for the second-law analysis.

3.1. Compression ignition engines

As regards compression ignition engines, these models range from overall engine simulation to ideal cycle simulation and to the more frequently applied phenomenological filling and emptying models. Simple zero-dimensional models, accounting for the basic features of engine operation, which treat the cylinder contents as a uniform mixture, and are usually termed 'single-zone models', have been developed and continue to exist due to their simplicity, low computational cost and reasonable accuracy [1–5,25,26]. These models are termed 'zero-dimensional', in the sense that they do not involve any consideration of the flow field dimensions. Apart from the single-zone models, the urgent need to control pollutant emissions from internal combustion engines has led to the development of other more complicated models, such as two-zone [31,32], four-zone or even multi-zone models [6,33,34], which furnish increased accuracy and flexibility for such complex phenomena as the formation of nitric oxide and soot in engine cylinders.

The zero-dimensional models that have been used as a basis for the second-law balance of diesel engine operation were almost exclusively single-zone models, with the two notable exceptions of Shapiro and Van Gerpen's two-zone model [28], and Lipkea and deJoode's[3] multi-zone model [23], following the filling and emptying approach.

In a single-zone model the working fluid in the engine is assumed to be a thermodynamic system that undergoes energy and mass exchange with the surroundings, where the energy released during the combustion process is obtained by applying the first-law of thermodynamics to the system. In two-zone models, the working fluid is imagined to consist of two zones, a burned and an unburned zone. These zones are actually two distinct thermodynamic systems with energy and mass interactions between themselves and their common surroundings, the cylinder walls. The mass-burning rate (or the cylinder pressure), as a function of crank angle, is then numerically computed

[2] This section describes briefly the basic first-law modeling aspects found in second-law analyses and not in general *the* first-law operation of internal combustion engines.

[3] Lipkea and de Joode, unlike Shapiro and Van Gerpen, did not discuss the implications raised through the use of more than one zone in the application of availability balances.

by solving the simplified equations resulting from applying the first-law to the two zones. Both modeling techniques have been traditionally used in two different directions: (a) the models have been used to predict the in-cylinder pressure as a function of crank angle using an empirical heat release or mass burned profile (as a function of crank angle), or (b) the heat release rate as a function of crank angle was deduced from experimentally obtained in-cylinder pressure data [35], which was then used as an input to the in-cycle calculations. Usual assumptions include:

(a) spatial homogeneity of pressure (for two-zone models too),
(b) spatial homogeneity of temperature (for the whole cylinder or for each zone considered),
(c) working fluid is considered an ideal gas,
(d) gas properties (enthalpy, internal energy, etc.) are modeled using polynomial relations with temperature (and pressure),
(e) Heat released from combustion is distributed evenly throughout the cylinder,
(f) blow-by losses are not taken into account,
(g) enthalpy associated with pressure of injected fuel is usually not significant and hence ignored,
(h) spatially averaged, instantaneous (time resolved) heat transfer rates are used to estimate heat transfer to the cylinder walls,
(i) dissociation is usually, but not always, neglected. Especially as regards two-zone models,
(j) no heat transfer occurs between burned and unburned zones,
(k) work required to transfer fluid from the unburned zone to the burned zone is negligible.

3.2. Spark ignition engines

As regards spark ignition engines, ideal Otto cycle [36], single-zone or, usually, two-zone modeling techniques have been applied. In the latter, one of the zones is the burned one containing equilibrium products of combustion and the other is the unburned gas zone consisting of a homogeneous mixture of air, fuel and residual gas [37]. A three-zone approach has also been proposed by Caton [38]. Most of the assumptions mentioned above for compression ignition models are also applicable for spark ignition models, with the usual exception of assumption 'i', as it is logical in spark ignition engine combustion to include dissociation due to the near to stoichiometric conditions combustion.

On the other hand, only scarcely do we come across pure experimental approaches as for example those by Alkidas [22], Alasfour [39], or Parlak et al. [40], which, consequently, correspond to an overall engine analysis.

3.3. In-cylinder processes

For the simulation of combustion and heat transfer processes, which are considered the most 'delicate' ones requiring careful modeling, the following semi-empirical sub-models are usually adopted: For the combustion process in CI engines the universally accepted premixed-diffusion (a rapid premixed burning phase followed by a slower mixing-controlled burning phase) combustion models are applied in the form of simple Wiebe functions [41], or using the Watson [42] or the more fundamental Whitehouse–Way approach [43]. Experimental heat release rate patterns have also been used for evaluating the actual fuel-burning rate. For SI engines a sinusoidal or exponential [1–5,41] burning rate is usually adopted.

As regards heat transfer correlations, the global models of Annand (including both convective and radiation terms) [44] and Woschni [45] are used by most of the researchers in the field. These models deal with overall, empirical, instantaneous spatial average heat transfer coefficients, generally assumed to be the same for all surfaces (cylinder head, liner, piston crown) in the engine cylinder.

Most of the first-law models were calibrated against experimental data, a fact contributing to more credible and trustworthy exergy results. The single- or two-zone approach adopted by most of the researchers combines satisfactory accuracy with limited computer program execution time.

4. Engine modeling—general equations for state properties and first-law of thermodynamics needed for the second-law analysis

4.1. State properties

For the evaluation of specific internal energy of species i, the following relation can be applied according to JANAF Table thermodynamic data [1,5,46,47]:

$$u_{\mathrm{i}}(T) = R_{\mathrm{si}}\left[\left(\sum_{n=1}^{5}\frac{a_{\mathrm{in}}}{n}T^{n}\right) + a_{\mathrm{i6}} - T\right] \tag{4}$$

where constants a_{in} for the above polynomial relation can be found, for example, in Refs. [1,5]. Two sets of data are available for constants a_{in}, one for temperatures up to 1000 K and another for temperatures from 1000 to 5000 K. The reference temperature is 298 K. Also,

$$h_i(T) = u_i(T) + R_{si}T \tag{5}$$

The rate of internal energy change for a mixture is given by:

$$\frac{dU}{d\varphi} = \sum_i u_i \frac{dm_i}{d\varphi} + \sum_i m_i c_{vi} \frac{dT}{d\varphi} \tag{6}$$

where m_i is the mass of species i (O_2, N_2, CO_2,H_2O, N, NO, OH, H, O, etc.) and c_v is the specific heat under constant volume (a function of temperature only $c_v = du/dT$), with

$$c_{vi}(T) = R_{si}\left[\left(\sum_n a_{i,n}T^{n-1}\right) - 1\right] \tag{7}$$

with the values of m_i, dm_i, T, dT found from the corresponding first-law analysis of the cylinder contents (cf. Section 4.2).

The rate of entropy change is:

$$\frac{dS}{d\varphi} = \sum_i \frac{dm_i}{d\varphi} s_i(T, x_i p) + \sum_i \frac{m_i}{T} c_{pi} \frac{dT}{d\varphi} - \frac{V}{T}\frac{dp}{d\varphi} \tag{8}$$

with

$$s_i(T, x_i p) = s_i^{\prime}(T, p_0) - R_{si}\ln\left(\frac{x_i p}{p_0}\right) \tag{9}$$

and $s_i^{\prime}(T, p_0)$ the standard state entropy of species i, which is a function of temperature only, with x_i the molar fraction of species i in the mixture [1,5], given by the following property relation:

$$s_i^{\prime}(T, p_0) = R_{si}\left[a_{i1}\ln T + \left(\sum_{n=2}^{5} a_{in}\frac{T^{n-1}}{n-1}\right) + a_{i7}\right] \tag{10}$$

For the Gibbs free enthalpy or energy:

$$\frac{dG}{d\varphi} = \sum_i \frac{dm_i}{d\varphi}\mu_i \tag{11}$$

where $\mu_i = g_i(T,p_i)$ is the chemical potential of species i in the mixture, with

$$g_i(T, p_i) = g_i(T, x_i p) = h_i(T) - Ts_i(T, x_i p)$$
$$= h_i(T) - T\left[s_i^{\prime}(T, p_0) - R_{si}\ln\left(\frac{x_i p}{p_0}\right)\right] \tag{12}$$

For all the above expressions, it is assumed that the unburned mixture is frozen in composition and the burned mixture is always in equilibrium.

Finally, the well-known ideal gas relation is given by

$$pV = mR_sT \tag{13}$$

4.2. First-law of thermodynamics applied to the engine cylinder

The first-law of thermodynamics applied to the engine cylinder reads [1–5]:

$$\frac{dQ_L}{d\varphi} - p\frac{dV}{d\varphi} = \frac{dU}{d\varphi} - \sum_j \frac{dm_j}{d\varphi}h_j \tag{14}$$

where $dQ_L/d\varphi$ is the rate of heat loss to the cylinder walls, as described by the semi-empirical Annand or Woschni correlations, p is the pressure of cylinder contents, dm_j is the mass exchanged (positive when entering) in the step $d\varphi$ and h_j is the specific enthalpy of it. Subscript j denotes fuel injection, and exchange with the exhaust manifold, inlet manifold and crankcase (if blow-by losses are taken into account).

The ideal gas relation (Eq. (13)) can be expressed in differential form as:

$$p\frac{dV}{d\varphi} + V\frac{dp}{d\varphi} = mR_s\frac{dT}{d\varphi} + R_sT\frac{dm}{d\varphi} \tag{15}$$

The application of the first-law of thermodynamics to the engine cylinder (open cycle) can then be expressed as follows using Eq. (6) [1–5,48,49]:

$$\sum_i m_i c_{vi}\frac{dT}{d\varphi} = \frac{dQ_L}{d\varphi} - \frac{mR_sT}{V}\frac{dV}{d\varphi} + \sum_j \frac{dm_j}{d\varphi}h_j - \sum_i u_i\frac{dm_i}{d\varphi} \tag{16}$$

The volume V of the engine cylinder, needed in the previous equations, is [1–5]:

$$V = V_{cl} + \pi\left(\frac{D^2}{4}\right)x \tag{17}$$

with V_{cl} the clearance volume and x the piston displacement from its TDC position,

$$x = r(1 - \cos\varphi) + L[1 - \sqrt{1 - f^2\sin^2\varphi}] \tag{18}$$

where L is the connecting rod length, r the crank radius, $f = r/L$ and the crank angle φ is measured from the bottom dead center position (BDC). Consequently

$$\frac{dV}{d\varphi} = \frac{A\pi D^2}{4}\left[r\sin\varphi\left(1+\frac{f\cos\varphi}{\sqrt{1-f^2\sin^2\varphi}}\right)\right] \tag{19}$$

and also

$$d\varphi = 6N\,dt \tag{20}$$

with N the engine speed expressed in rpm, for transforming the various terms from time to degree crank angle (°CA) basis.

5. Engine analysis: application of exergy balance to internal combustion engines

In the following subsections, the equations will be given that deal with the exergy balance applied to the engine cylinder and its subsystems in order to evaluate the various processes irreversibilities. However, the fuel chemical availability must first be defined.

5.1. Fuel availability

In Eq. (1c) the expression for chemical availability was given, in the case, where the control mass at the restricted dead state, passes into the environment but is not permitted to chemically react with it. Chemical exergy will be enhanced in this section considering the case, where the control mass is allowed to react chemically with the environment.

The chemical exergy of a substance not present in the environment (e.g. fuel, sulfur, combustion products such as NO or OH, etc.) can be evaluated by considering an idealized reaction of the substance with other substances for which the chemical exergies are known [12]. This chemical exergy of the fuel can be expressed as follows on a molar basis [9,12]:

$$\bar{a}_{fch}(T_0,p_0) = \bar{g}_f(T_0,p_0) - \left(\sum_p x_p\bar{\mu}_p^0 - \sum_r x_r\bar{\mu}_r^0\right) \tag{21}$$

where index p denotes products (CO_2, H_2O, CO, etc.) and index r the reactants (fuel and O_2) of the (stoichiometric) combustion process, T_0 and p_0 are the dead state temperature and pressure, and the overbar denotes properties on a per mole basis.

For hydrocarbon fuels of the type C_zH_y, which are of special interest to internal combustion engines applications, Eq. (21) becomes [12]:

$$\begin{aligned}\bar{a}_{fch} &= \overline{HHV}(T_0,p_0) \\ &\quad - T_0\left[\bar{s}_f + \left(z+\frac{y}{4}\right)\bar{s}_{O_2} - z\bar{s}_{CO_2} - \frac{y}{2}\bar{s}_{H_2O(l)}\right](T_0,p_0) \\ &\quad + \left\{z\bar{a}_{CO_2,ch} + \frac{y}{2}\bar{a}_{H_2O(l),ch} - \left(z+\frac{y}{2}\right)\bar{a}_{O_2,ch}\right\}\end{aligned} \tag{22}$$

or

$$\begin{aligned}\bar{a}_{fch} &= \left[\bar{g}_{C_zH_y} + \left(z+\frac{y}{4}\right)\bar{g}_{O_2} - z\bar{g}_{CO_2} - \frac{y}{2}\bar{g}_{H_2O(l)}\right](T_0,p_0) \\ &\quad + \left\{z\bar{a}_{CO_2,ch} + \frac{y}{2}\bar{a}_{H_2O(l),ch} - \left(z+\frac{y}{4}\right)\bar{a}_{O_2,ch}\right\}\end{aligned} \tag{23}$$

with HHV the fuel higher heating value. The above relation is often approximated for liquid fuels (on a kg basis now) by (Ref. [9]):

$$a_{fch} = LHV\left(1.04224 + 0.011925\frac{y}{z} - \frac{0.042}{z}\right) \tag{24}$$

with LHV the fuel lower heating value. This approximation has been adopted by the present authors for sulfur free fuels.

Szargut and Styrylska [50], Rodriguez [51] and Stepanov [52] discuss various approximations for the chemical exergy of fossil, liquid and gaseous fuels. One such approximation for liquid fuels of the general type $C_zH_yO_pS_q$, applicable in internal combustion engines applications can be found in Ref. [52] based on the work of Szargut and Styrylska:

$$\begin{aligned}a_{fch} = LHV\Big[&1.0401 + 0.01728\frac{y}{z} + 0.0432\frac{p}{z} \\ &+ 0.2196\frac{q}{z}\left(1 - 2.0628\frac{y}{z}\right)\Big]\end{aligned} \tag{25}$$

Table 1
Tabulation of usual approximations for the ratio of fuel chemical availability to lower heating value (p_o = 1.01325 bar, T_o = 298.15 K)

Fuel	a_{fch}/LHV	Equation	Reference
n-Dodecane ($C_{12}H_{26}$)	1.0645	(24)	Moran [9]
	1.0775	(25)	Stepanov [52]
Diesel fuel ($C_{14.4}H_{24.9}$)	1.0599	(24)	Moran [9]
	1.0699	(25)	Stapenov [52]
Octane (C_8H_{18})	1.0638	(24)	Moran [9]
	1.0789	(25)	Stepanov [52]
	1.0286		Caton [53]
Gasoline (C_7H_{17})	1.0652	(24)	Moran [9]
	1.082	(25)	Stepanov [52]

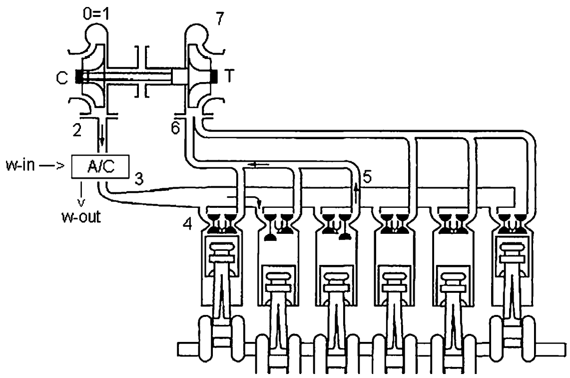

Fig. 2. Schematic arrangement of engine, manifolds, turbocharger and aftercooler for a six-cylinder internal combustion engine, showing strategic point locations used in the analysis of Section 5 ($0\equiv1$: atmosphere–compressor inlet, 2: compressor outlet–aftercooler inlet 3: inlet manifold, 4: cylinder, 5: exhaust manifold, 6: turbine inlet, 7: turbine outlet).

Flynn et al. [21] based on Rodriguez [51] and Moran [9] used an approximation for the chemical availability of the fuel, which is 1.0317 times its lower heating value. This is then used in the availability balance equations.

Caton [53] used the following relation for octane:

$$a_{\mathrm{fch}}^{\mathrm{O}} = -(\Delta G)_{T_0,p_0}^{\mathrm{O}} = 1.0286(\Delta H)_{T_0,p_0}^{\mathrm{O}} = 1.0286\,\mathrm{LHV} \tag{26}$$

Table 1 gives a summary of the most usually applied values for approximation of the chemical availability of fuels with interest for internal combustion calculations.

One interesting case is when the fuel is pre-heated before injection, as now apart from the chemical it possesses also thermal availability; however, the associated increase in its thermal availability is usually neglected as it is not greater than 0.2% of the chemical [21].

Application of the availability balance equation, Eq. (2), to the internal combustion engine subsystems, on a °CA basis, yields the relations to be given in the succeeding Subsections, as they have been proposed and used by many researchers in the past [21–24,26–28, 48,54]. Indices 1–7 refer to the strategic points locations indicated on the schematic arrangement of the engine depicted in Fig. 2, which for the general case it is considered as turbocharged and after cooled, six-cylinder one. Through definition of each control volume's availability equation, the respective irreversibilities will be identified, quantified and discussed.

5.2. Engine cylinder availability balance

For the engine cylinder, on a °CA basis, we have:

$$\frac{\mathrm{d}A_{\mathrm{cyl}}}{\mathrm{d}\varphi} = \frac{\dot{m}_4 b_4 - \dot{m}_5 b_5}{6N} - \frac{\mathrm{d}A_{\mathrm{w}}}{\mathrm{d}\varphi} - \frac{\mathrm{d}A_{\mathrm{L}}}{\mathrm{d}\varphi} + \frac{\mathrm{d}A_{\mathrm{f}}}{\mathrm{d}\varphi} - \frac{\mathrm{d}I}{\mathrm{d}\varphi} \tag{27}$$

In the above equation, $\dot{m}_4$ is the incoming flow rate from the inlet manifold, which consists of air or air plus exhaust gas (in case of operation with exhaust gas recirculation) for compression ignition engines, and mixture of fuel vapor with air and exhaust gas for spark ignited ones, whereas $\dot{m}_5$ is the outgoing one to the exhaust manifold.

Especially for (diesel) engines fitted with a pre-chamber, Eq. (27) is expanded [55] for the main chamber as

$$\frac{\mathrm{d}A_{\mathrm{m}}}{\mathrm{d}\varphi} = \frac{\dot{m}_4 b_4 - \dot{m}_5 b_5}{6N} - \frac{\mathrm{d}A_{\mathrm{w}}}{\mathrm{d}\varphi} - \frac{\mathrm{d}A_{\mathrm{mL}}}{\mathrm{d}\varphi} + \frac{\mathrm{d}A_{\mathrm{mf}}}{\mathrm{d}\varphi} + \frac{\dot{m}_{\mathrm{mp}} b_{\mathrm{mp}}}{6N} - \frac{\mathrm{d}I_{\mathrm{m}}}{\mathrm{d}\varphi} \tag{27a}$$

and for the pre-chamber as

$$\frac{\mathrm{d}A_{\mathrm{p}}}{\mathrm{d}\varphi} = \frac{\mathrm{d}A_{\mathrm{pf}}}{\mathrm{d}\varphi} - \frac{\mathrm{d}A_{\mathrm{pL}}}{\mathrm{d}\varphi} - \frac{\dot{m}_{\mathrm{mp}} b_{\mathrm{mp}}}{6N} - \frac{\mathrm{d}I_{\mathrm{p}}}{\mathrm{d}\varphi} \tag{27b}$$

with index 'm' denoting the main chamber, 'p' the pre-chamber and 'mp' flow from the main chamber to the pre-chamber.

$$\frac{\mathrm{d}A_{\mathrm{w}}}{\mathrm{d}\varphi} = (p_{\mathrm{cyl}} - p_0)\frac{\mathrm{d}V}{\mathrm{d}\varphi} \tag{28}$$

is the (indicated) work transfer, where $\mathrm{d}V/\mathrm{d}\phi$ is the rate of change of cylinder volume with crank angle taken from Eq. (19) and p_{cyl} the instantaneous cylinder pressure found from the first-law analysis of the engine processes.

$$\frac{\mathrm{d}A_{\mathrm{L}}}{\mathrm{d}\varphi} = \frac{\mathrm{d}Q_{\mathrm{L}}}{\mathrm{d}\varphi}\left(1 - \frac{T_0}{T_{\mathrm{cyl}}}\right) \tag{29}$$

is the heat transfer availability to the cylinder walls, with $\mathrm{d}Q_{\mathrm{L}}/\mathrm{d}\phi$ found from the respective heat transfer correlation used, and T_{cyl} the instantaneous cylinder gas temperature [1,7–14]. In the case of indirect injection engines, Eq. (29) is applied for both chambers of the cylinder. This availability loss is usually considered as external to the cylinder control volume, but there are some researchers, as for example Alkidas [22], who treat the heat losses as another source of irreversibility by defining an individual open thermodynamic system for the water-cooling circuit. By so doing, they usually sum up the combustion irreversibilities (see Section 5.2.1) and the exergy term for heat transfer (Eq. (29)), as will be discussed in more detail in Section 7.1, and also calculate the availability increase in both the water and oil coolant circuits. In fact, heat loss from gas to the cylinder walls contains a significant amount of availability, which is almost completely destroyed only after this is transferred to the cooling medium.

$$\frac{dA_f}{d\varphi} = \frac{dm_{fb}}{d\varphi} a_{fch} \tag{30}$$

is the burned fuel availability, with a_{fch} being the fuel (chemical) availability. The fuel burning rate $dm_{fb}/d\phi$ is calculated, for each computational step, using the combustion model chosen (i.e. Whitehouse–Way, Watson, general premixed-diffusion, Wiebe function, sinusoidal as regards SI engines, etc.). The term on the left-hand side of Eq. (27) is expressed explicitly, using Eq. (1d), as:

$$\frac{dA_{cyl}}{d\varphi} = \frac{dU}{d\varphi} + p_0 \frac{dV}{d\varphi} - T_0 \frac{dS}{d\varphi} - \sum_i \frac{dm_i}{d\varphi} \mu_i^0 \tag{31}$$

representing the rate of change in the total availability of the cylinder contents.

5.2.1. In-cylinder irreversibilities

Any system undergoing a chemical reaction experiences destruction of availability due to the (inherent) irreversibility of the reaction process. The term $dI/d\phi$ in Eq. (27) is the rate of irreversibility production within the cylinder, which consists of combustion (dominant contribution), viscous dissipation, turbulence, inlet-valve throttling and mixing of the incoming air or air–fuel mixture with the cylinder residuals. It should be noted, at this point, that since Eq. (28) was related to the indicated work, the amount of in-cylinder friction is not included in the calculated irreversibilities. It is common practice, in internal combustion engines to separate friction from the other irreversibilities contributors. By so doing, mechanical friction and consequently friction irreversibilities are computed as the difference between indicated and brake work production. This approach is applied since it is not practically feasible to calculate the amount of heat loss associated with friction from piston rings, liners, etc.

Typical values for in-cylinder irreversibilities are in the order of 20–25% for full load, four-stroke, turbocharged, diesel engine operation. Greater values are expected for spark ignition engine operation or compression ignition engine operating at low loads. For example, for lower than 20% engine loads, in-cylinder irreversibilities waste 40% or even more of the fuel chemical exergy. As it will be discussed later in the section this is mainly due to the lower gas temperatures involved.

Some researchers in the field of internal combustion engines preferred to apply an entropy balance in order to calculate irreversibilities [1,7–14,24,38,47,56–58]. By so doing, irreversibilities are linked with the entropy generation. Beretta and Keck [47] used the following relation for the entropy balance on a time basis, for a control volume (e.g. engine cylinder) open to a net mass flux $\dot{m}$ of mean specific entropy s_m

$$\dot{S} = \dot{m} s_m - \frac{Q_L}{T_L} + \dot{S}_{irr} \tag{32a}$$

with $\dot{S}_{irr}$ the rate of entropy generation due to irreversibilities inside the control volume.

Alkidas [58] calculated in-cylinder irreversibilities through the following relation, in accordance with Fig. 2,

$$\dot{I} = T_0(\dot{m}_{cyl} s_{cyl} - \dot{m}_4 s_4 - \dot{m}_{fb} s_{fb}) - \sum \dot{Q}_L \frac{T_0}{T_L} \tag{32b}$$

where T_L is the temperature under which the heat loss Q_L is transferred (from cylinder gas (L=cyl), oil or cooling water).

The contribution of combustion to the total in-cylinder irreversibilities was characterized at the beginning of this subsection as dominant. Actually, it has been computed being more than 90%. Primus and Flynn [59] calculated in-cylinder, non-combustion irreversibilities as 4.96% of the total ones, for a six-cylinder, turbocharged and aftercooled, diesel engine operating at 2100 rpm and producing 224 kW. These included thermal mixing of the incoming air with the

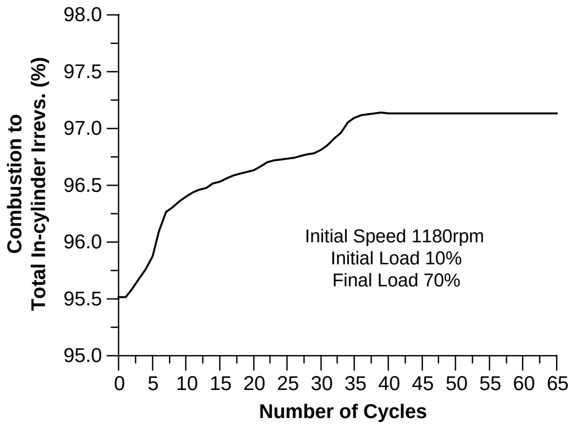

Fig. 3. Development of ratio of combustion to total in-cylinder irreversibilities during a transient event after a ramp increase in load (six-cylinder, turbocharged and aftercooled, IDI diesel engine).

cylinder residuals and intake valve throttling. Alkidas [22] working on a single-cylinder, naturally aspirated, DI diesel engine of 2.0 lt displacement volume, and using a simplified mixing model, estimated air–fuel mixing irreversibilities to be 3% of the total. Rakopoulos and Giakoumis [26], using a single-zone analysis on a six-cylinder, turbocharged and aftercooled, IDI diesel engine, calculated non-combustion, in-cylinder irreversibilities during transient conditions at 5% (maximum) of the total (decreasing magnitude with increasing load). This is depicted in Fig. 3 corresponding to a load increase in 10–70% commencing from 1180 rpm. The effect of various operating parameters on the in-cylinder irreversibilities will be enhanced in Sections 7–9 via the presentation of various research groups' results.

Some fundamental aspects of the mechanism of availability destruction due to combustion in an internal combustion engine can be summarized as follows:

(a) About 80% of the combustion irreversibilities occur during the heat transfer process between the reacting gas and the yet unburned mixture [56].
(b) An increasing combustion temperature (as, for example, is the case with increasing fuel–air equivalence ratio, ϕ in compression ignition engine lean operation) decreases the combustion irreversibilities reduced to the fuel availability. This conclusion is inter-related to the previous one since an increasing gas temperature decreases the relative amount of heat transfer from the reacting gas to the yet unburned mixture. On the other hand, the heat transfer to the cylinder walls and the exhaust gases availability increase with increasing combustion temperatures.
(c) The effect of changes of the pressure during the combustion processes (other parameters being the same) on the availability is modest [53].
(d) The amount of combustion irreversibilities can be correlated to the differential change in mixture composition, and notably nothing else. This was the result from the work conducted by Rakopoulos and Andritsakis [25], who calculated the combustion irreversibility production rate as a function of fuel reaction rate only, and reached the following very interesting equation

$$\mathrm{d}I = -\frac{T_0}{T}\sum_j \mu_j \mathrm{d}m_j \tag{33}$$

where index j includes all reactants and products. For ideal gases, $\mu_j = g_j$, for fuel, $\mu_f = a_{\mathrm{fch}}$. The above equation reveals that, after all, both heat transfer and work production inside the cylinder only indirectly influence the irreversibilities accumulation.

5.3. Availability balance of the engine subsystems

5.3.1. Turbocharger

For the compressor steady-state is assumed so that there is no accumulation term; then the availability balance equation reads [9]:

$$\frac{\dot{m}_1 b_1 - \dot{m}_2 b_2}{6N} + \frac{\dot{W}_{\mathrm{C}}}{6N} = \frac{\mathrm{d}I_{\mathrm{C}}}{\mathrm{d}\varphi} \tag{34}$$

with $\dot{m}_1 = \dot{m}_2$ the charge air flow rate.

For the turbine, accordingly [9]:

$$\frac{\dot{m}_6 b_6 - \dot{m}_7 b_7}{6N} - \dot{W}_{\mathrm{T}} = \frac{\mathrm{d}I_{\mathrm{T}}}{\mathrm{d}\varphi} \tag{35}$$

Heat losses are here usually neglected. In these equations, the terms $\dot{W}_{\mathrm{C}}$ and $\dot{W}_{\mathrm{T}}$ are evaluated from the thermodynamic analysis of the turbocharger at each degree crank angle step, via instantaneous values picked up from the turbo-machinery steady-state maps. Subscripts 1 and 2 denote compressor inlet and outlet conditions, respectively, while subscripts 6 and 7 denote turbine inlet and outlet conditions, respectively, as also shown in Fig. 2. Irreversibilities in the turbocharger are mainly fluid flow losses due to fluid shear and throttling [1] assuming around 10% of the total engine irreversibilities.

5.3.2. Aftercooler or intercooler

For the aftercooler, similarly, the availability balance equation is [9]:

$$\frac{\dot{m}_2 b_2 - \dot{m}_3 b_3}{6N} - \Delta A_{\mathrm{w}} = \frac{\mathrm{d}I_{\mathrm{AC}}}{\mathrm{d}\varphi} \tag{36}$$

where b_2 is the flow availability at the compressor outlet—aftercooler inlet, b_3 the flow availability at the aftercooler outlet–inlet manifold inlet, and

$$\Delta A_{\mathrm{w}} = \frac{1}{6N}\dot{m}\left(b^{\mathrm{w}}_{\mathrm{out}} - b^{\mathrm{w}}_{\mathrm{in}}\right) \tag{37}$$

where

$$b^{\mathrm{w}}_{\mathrm{out}} - b^{\mathrm{w}}_{\mathrm{in}} = c_{\mathrm{pw}}\left[T_{\mathrm{w-out}} - T_{\mathrm{w-in}} - T_0 \ln\left(\frac{T_{\mathrm{w-out}}}{T_{\mathrm{w-in}}}\right)\right] \tag{37a}$$

is the increase in the availability of the cooling medium having mass flow rate $\dot{m}_{\mathrm{w}}$, specific (mass) heat c_{pw}, initial temperature entering the aftercooler

$T_{w\text{–}in}$ and final temperature leaving the aftercooler $T_{w\text{–}out}$. Here, the irreversibilities account for loss of availability due to transfer of heat to a cooler medium; they can be quite large according to the temperature level of the medium to be cooled. The transfer of heat to a cooler medium is a procedure not desirable from the second-law of thermodynamics point of view. The particular one is responsible for the loss of around 0.5–1% of the fuel's chemical availability in internal combustion engine applications.

5.3.3. Inlet manifold

For the inlet manifold, the availability balance equation is [26,48]:

$$\frac{\mathrm{d}A_{\mathrm{im}}}{\mathrm{d}\varphi} = \frac{\dot{m}_3 b_3 - \sum_{j=1}^{z} \dot{m}_{4j} b_4}{6N} - \frac{\mathrm{d}I_{\mathrm{im}}}{\mathrm{d}\varphi} \tag{38}$$

where b_4 is the flow availability at the intake manifold and $j=1,\ldots,z$ is the cylinder exchanging mass with the inlet manifold found from the energy analysis at each degree crank angle step. No heat losses are taken into account in most of the cases. The term for irreversibilities $\mathrm{d}I_{\mathrm{im}}/\mathrm{d}\varphi$ accounts mainly for mixing of incoming air with the intake manifold contents, and is, usually, less than 1% of the fuel's chemical availability.

5.3.4. Exhaust manifold

For the exhaust manifold, the availability balance equation is [26,48]:

$$\frac{\mathrm{d}A_{\mathrm{em}}}{\mathrm{d}\varphi} = \frac{\sum_{j=1}^{z} \dot{m}_{5j} b_{5j} - \dot{m}_6 b_6}{6N} - \frac{\mathrm{d}I_{\mathrm{em}}}{\mathrm{d}\varphi} + \frac{\mathrm{d}A_{\mathrm{Lem}}}{\mathrm{d}\varphi} \tag{39}$$

where index 6 identifies the exhaust manifold state. The term

$$\frac{\mathrm{d}A_{\mathrm{Lem}}}{\mathrm{d}\varphi} = \frac{\mathrm{d}Q_{\mathrm{Lem}}}{\mathrm{d}\varphi}\left(1 - \frac{T_0}{T_6}\right) \tag{39a}$$

accounts for the heat losses at the exhaust manifold (considered as external to the manifold control volume, thus not included in the respective irreversibilities), where T_6 is the instantaneous temperature of the manifold contents. The term $\mathrm{d}I_{\mathrm{em}}/\mathrm{d}\varphi$ is the irreversibility rate in the exhaust manifold, which arises from throttling across the exhaust valve, mixing of cylinder exhaust gases with manifold contents and gas friction along the manifold length. It assumes values of around 1.5–3% of the fuel's chemical availability (greater values correspond to turbocharged engines). These irreversibility terms can be further isolated and computed if we assume that the exhaust manifold process can be separated, and define control volumes accordingly. For example, throttling across the exhaust valve is usually assumed to occur at constant enthalpy. The respective throttling irreversibilities are (for single-cylinder engine operation):

$$\frac{\dot{m}_5 b_5 - \dot{m}_{6'} b_{6'}}{6N} = \frac{dI_{\mathrm{em}}^{\mathrm{thr}}}{d\varphi} \tag{39b}$$

where state $6'$ corresponds to the condition of the cylinder exhaust gas downstream the exhaust valve, $\dot{m}_{6'} = \dot{m}_5$, $h_{6'} = h_5$ and the mole fraction for each species remains unaltered from 6 to $6'$. Likewise, thermal mixing between cylinder gas and exhaust manifold contents, and friction along the exhaust manifold can be evaluated.

Primus and Flynn [59] working on a six-cylinder, turbocharged and aftercooled, diesel engine operating at 2100 rpm and producing 224 kW, calculated exhaust throttling losses at 1.66%, exhaust manifold heat loss at 0.25%, fluid flow losses at 0.57% and turbine irreversibilities at 1.69% of the fuel availability. Fijalkowski and Nakonieczny [60] studied the exhaust manifold and turbine of a six-cylinder, turbocharged, diesel engine using the method of characteristics, and were able to identify and quantify the various losses in the exhaust process. They found that for the engine operating at 2000 rpm at intermediate and high loads, exhaust valve throttling accounted for 2–2.5% of the incoming (i.e. exhaust gas from cylinders) availability, heat transfer was responsible for 4–5%, friction losses for 9–11% and turbine losses (vanes and wheel) for 3%. Of the remaining amount, almost half was realized as useful turbine work with the other half thrown to the atmosphere.

5.4. Application of the availability balance to the internal combustion engine

Application of Eqs. (27)–(31) on a (diesel) engine cylinder is depicted in Fig. 4, showing the development of both rate and cumulative in-cylinder availability terms during an engine cycle.

As regards cumulative terms, these are defined after integration of the respective rate terms over an engine cycle. Especially, for steady-state operation, the cumulative value for the cylinder availability is

$$\int_0^{720} \frac{\mathrm{d}A_{\mathrm{cyl}}}{\mathrm{d}\varphi}\,\mathrm{d}\varphi = 0.$$

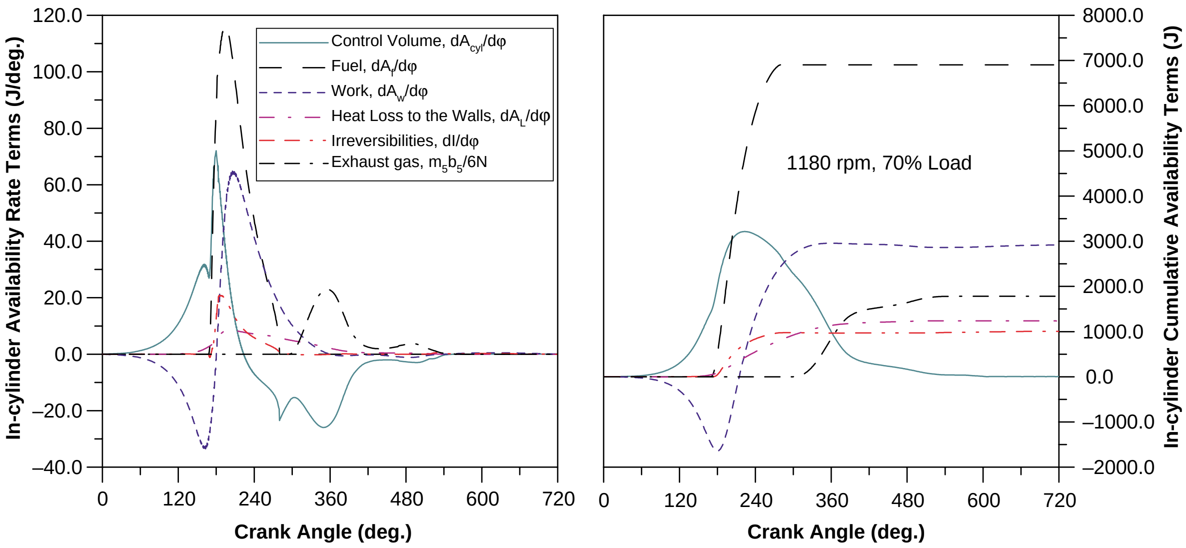

Fig. 4. Development of rate and cumulative in-cylinder availability terms during an engine cycle (six-cylinder, turbocharged and aftercooled, IDI diesel engine operating at 1180 rpm and 70% load-nomenclature corresponds to Eq. (27)).

Until the start of combustion, the availability of the cylinder contents (i.e. control volume availability) increases due to work offered by the piston during the compression process. As the working medium is trapped at a temperature lower than that of the cylinder walls, availability is transferred through heat to the working medium for the early part of the cycle. Then, the heat transfer direction is reversed as the working medium temperature rises. As the availability transfer is low during compression, it is obvious that the change of the working medium availability is almost equal to the work availability transfer, the irreversibility rate being essentially zero. At the point the fuel injection starts, a small fall is observed in the control volume availability rate pattern. This is due to the ignition delay period and the simultaneous loss of heat for evaporation of the injected fuel. After the start of combustion, things change drastically. The burning of fuel causes a considerable increase in pressure and temperature and, consequently, in cylinder availability and heat loss. The irreversibility rate increases due to combustion. Just after 200–220 °CA, when the pressure and temperature begin to fall during the expansion, there is also a fall in the control volume availability. The rate of availability becomes negative near 220 °CA. Clearly, the available energy accumulated in the cylinder contents during compression and mainly during combustion is being returned in the form of (indicated) work production, which causes the decrease in the availability of the working medium. After the opening of the exhaust valve, the control volume availability rate reaches a second minimum, due to the exhaust gas leaving the cylinder during the blow-down period. The cumulative availability term continues to decrease so that, at the end of the cycle (720 °CA), its value is zero again, as the working medium has returned to its initial state.

The previous results were based on a single-zone modeling of the compression ignition engine operation, neglecting the contribution of chemical exergy. The main conclusions are, in general, applicable for spark ignition engine operation too.

One key question is what differentiations are expected when chemical exergy is taken into account. Shapiro and Van Gerpen [28] using a two-zone model to describe the in-cylinder processes of a single cylinder, naturally aspirated SI engine, focused on this distribution between chemical and thermomechanical availability terms in the burned and unburned gas zones. They agreed that availability in each zone (one zone consists of air and the second zone of equilibrium products of combustion) is primarily due to the thermomechanical contribution. In the baseline case the fuel air ratio was stoichiometric, so that if the unburned gases were brought to the restricted dead state, the equilibrium composition would consist mainly of CO_2, H_2O and N_2. The only remaining availability would be attributed to the concentration differences between the gases in the system and the reference environment, which was computed to the non-negligible percentage of 10% of the total availability at the end of expansion. In case of rich mixtures, or high temperatures, significant amounts of species exist that are not present in the reference environment, i.e. NO, OH, CO, etc. Under these conditions, the magnitude of the chemical availability can sometimes be even larger than the magnitude of thermomechanical availability, although the general trends presented in Fig. 4 are not altered.

Caton [38] enhanced the previous analyses by adopting multiple (i.e. three) zones for the thermodynamic calculations, providing an interesting direct comparison between the multi-zone and the single-zone modelling approach. For the intake process two zones were considered, i.e. fresh charge and residual gas, both spatially homogeneous. During combustion the three zones examined were the unburned, the adiabatic core burned and the boundary layer burned zone, each one of them being spatially homogeneous. The specific entropy values during combustion are less than those for a similar single-zone simulation. This was shown to be largely a result of the higher burned gas temperatures of the multiple zone simulation, which resulted in less entropy production for specific portions of the process. The overall change of entropy for the complete combustion process was the same for both approaches. The overall cycle values for the transfers and destruction of availability were essentially identical with the values obtained from a similar single-zone simulation.

A fundamental, comparative, first- and second-law analysis, on an overall basis, was conducted by Alkidas [22,58] on an experimental single cylinder, DI diesel engine, for two different engine speeds and at two engine loads. He estimated that combustion generated irreversibilities ranged from 25–43% of the fuel chemical availability and the heat losses term (defined from integration of Eq. (29) over the engine cycle-Alkidas treated the heat losses as a source of irreversibility) ranged from 42 to 58% of the fuel availability.

Table 2 tabulates typical first- and second-law balances over an engine cycle obtained now via a single-zone model of in-cylinder processes. It refers to data available in Ref. [59], corresponding to a six-cylinder, turbocharged and aftercooled, DI diesel engine of 10 lt displacement volume, operating at 2100 rpm and producing 224 kW. First-law analysis results are based on the fact that energy is conserved in every device and process. On the other hand, second-law analysis assigning different magnitude to each energy streams' ability to produce work includes destructions and losses not to be found in the first-law balance. The typical different magnitudes between first- and second-law perspectives for the heat losses and exhaust gas to ambient terms is obvious in Table 2, while a quantification of all losses is also available (numbers in parentheses reduce the irreversibilities to the total ones) highlighting the dominance of combustion irreversibilities (21.20% of the fuel's availability[4], or 70% of the total irreversibilities). The fuel availability was 1.0338 times the LHV, consequently the brake and mechanical efficiency were different when comparing the results from the two laws. The results presented in Table 2 were confirmed by other researchers in the following years and can be considered typical as regards four-stroke, turbocharged, diesel engine operation at high load.

Table 2
Comparison of results from first- and second-law balance, and quantification of irreversibilities (six-cylinder, turbocharged and aftercooled, diesel engine operating at 224 kW and 2100 rpm) (adapted from Ref. [59])

	First-law (% of fuel energy)	Second-law (% of fuel availability)
Work	40.54	39.21
Friction	4.67	4.52
Heat transfer to the walls	17.23	13.98
Aftercooler heat transfer	5.86	1.16
Exhaust manifold heat transfer	.39	.25
Exhaust gas to ambient	31.31	12.73
Irreversibilities		
Combustion	–	21.20 (75.3)
Thermal mixing	–	0.81 (2.9)
Intake throttling	–	0.58 (2.1)
Exhaust throttling	–	1.66 (5.9)
Fluid flow	–	0.57 (2.0)
Compressor	–	1.64 (5.8)
Turbine	–	1.69 (6.0)

(numbers in parentheses denote % of total irreversibilities).

6. Second-law or exergy or exergetic efficiencies

An efficiency is defined in order to be able to compare different engine size applications or evaluate various improvements effects, either from the first- or the second-law perspective. The second-law (or exergy or availability) efficiency also found in the literature as

[4] Cf. Alkidas' results, where the combustion irreversibility term assumes values up to 43%, albeit for a single cylinder diesel engine when operating at low engine load.

effectiveness or exergetic efficiency, measures how effectively the input (fuel) is converted into product, and is usually of the form [7–14,23]:

$$\varepsilon = \frac{\text{Availability out in product}}{\text{Availability in}} = 1 - \frac{\text{loss} + \text{destruction}}{\text{Input}} \quad (40)$$

Unlike first-law efficiencies, the second-law ones weigh the variable energy terms according to their capability for work production. Moreover, a second-law efficiency includes, in addition to exergy losses (e.g. in exhaust gases) the exergy destructions (irreversibilities) too. On the other hand, because energy is conserved, first-law efficiencies reflect only energy losses. Moreover, energy losses are not representative (and typically overestimate) the usefulness of loss. And first-law efficiencies do not explicitly penalize the system for internal irreversibilities.

Variations of the above equation have been proposed for the internal combustion engine and its subsystems operation, an outline of which will be given in the following subsections.

6.1. Cylinder

For the cylinder alone, the following second-law efficiency is often defined (four-stroke engine) [9,22,23, 27,36,48]:

$$\varepsilon_1 = \frac{W_{ind}}{M_{fi} a_{fch}} \text{ or } \varepsilon_1 = \frac{W_{br}}{M_{fi} a_{fch}} \quad (41)$$

with W_{ind} the indicated and W_{br} the brake work production and M_{fi} the total mass of fuel entering the cylinder per cycle. The present authors prefer the left expression of Eq. (41) with a subsequent calculation of friction since the right expression penalizes the cylinder for the friction irreversibilities. Efficiency ε_1 can be then compared to a first-law one, such as:

$$\eta_1 = \frac{W_{br}}{M_{fi} \text{LHV}} \quad (42)$$

One could also take into account the differences between outgoing from the cylinder A_{out} and incoming A_{in} thermomechanical availability flows (J/cycle) for the ability to produce extra work, and define the following second-law efficiency [9,22,48]:

$$\varepsilon_2 = \frac{W_{br} + A_{out} - A_{in}}{M_{fi} a_{fch}} \quad (43)$$

where

$$A_{out} - A_{in} = \int_0^{720} (\dot{m}_5 b_5 - \dot{m}_4 b_4) \frac{d\varphi}{6N} \quad (44)$$

Some researchers, e.g. Lipkea and de Joode [23], added the incoming air term A_{in} to the denominator of Eq. (43), which is a more strict application of general Eq. (40), i.e.

$$\varepsilon_{2a} = \frac{W_{br} + A_{out}}{M_{fi} a_{fch} + A_{in}} \quad (45)$$

with

$$M_{fi} a_{fch} = a_{fch} \int_0^{720} \frac{dm_{fb}}{d\varphi} d\varphi = A_f \quad (46)$$

Another approach was followed by Alkidas [22], who defined the following second-law efficiency for the cylinder:

$$\varepsilon_4 = \frac{W_{br}}{W_{max}} = \frac{W_{br}}{W_{br} + I} \quad (47)$$

with the I term including irreversibilities due to combustion and heat transfer.

6.2. Turbocharger

For the compressor, an exergy efficiency or effectiveness can be defined as [7,9,11,12]:

$$\varepsilon_C = \frac{\dot{m}_C (b_2 - b_1)}{|\dot{W}_C|} \quad (48)$$

Similarly, for the turbine:

$$\varepsilon_T = \frac{\dot{W}_T}{\dot{m}_T (b_6 - b_7)} \quad (49)$$

where $\dot{W}_C$ and $\dot{W}_T$ are the instantaneous values for the compressor and turbine power, respectively, evaluated from the thermodynamic analysis of the turbocharger at each computational step via instantaneous values from the turbo-machinery steady-state maps. Both compression and expansion processes are usually assumed adiabatic, neglecting also the associated gas kinetic energy.

The turbine exergy efficiency (Eq. (49)) is a measure of how well the exhaust gas's exergy is converted into shaft work. It differs from the isentropic efficiency in as much as the latter compares the actual work developed to the work that would be developed in an isentropic expansion. In any case, both can be categorized as second-law efficiencies. The same holds for the compressor.

Table 3
Tabulation of various second-law efficiencies (six-cylinder, turbocharged and aftercooled, IDI diesel engine operating at 236 kW @1500 rpm)

Second-law efficiency	Equation
$\varepsilon_1 = 40.31\%$	(41)
$\varepsilon_2 = (40.31 + 21.38 - 2.31)\% = 59.38\%$	(43)
$\varepsilon_C = 76.38\%$	(48)
$\varepsilon_T = 87.42\%$	(49)
$\varepsilon_{tot1} = 40.31\%$	(51)
$\varepsilon_{tot2} = (40.31 + 13.45)\% = 53.76\%$	(52)

6.3. Exhaust manifold

Alkidas [22] defined the following exhaust efficiency:

$$\varepsilon_{ex} = \frac{W_{ex,max}}{E_{ex}} \tag{50}$$

which proved useful when studying low heat rejection engines. $W_{ex,max}$ stands for the maximum extractable work available from the exhaust gases (for example using a bottoming cycle), i.e. the exergy of the exhaust gases and $E_{ex} = m_{ex}(h_{ex} - h_0)$is the respective exhaust gases thermal energy.

6.4. Overall engine plant

For the whole engine plant we can define [9,27,48]:

$$\varepsilon_{tot1} = \frac{W_{br}}{A_f} \tag{51}$$

or, alternatively,

$$\varepsilon_{tot2} = \frac{W_{br} + A_{out}^{tot}}{A_f} \tag{52}$$

where

$$A_{out}^{tot} = \int_0^{720} \frac{dm_7}{d\varphi} b_7 d\varphi \tag{53}$$

is the exhaust gas to ambient flow availability, and term A_f is given by Eq. (46).

Similar to the philosophy of Alkidas' Eq. (50), which states that an exergy efficiency can be defined as the ratio of useful exergy production divided by the respective exergy consumption, Gallo and Milanez [30, 61] defined similar exergy ('exergetic' was the actual term they used) efficiencies for each process, e.g. compression, combustion, expansion, inlet. By so doing, they were able to measure the performance of each process even though there was no work production in each one of them.

Table 3 summarizes typical results for the second-law efficiencies described above for a six-cylinder, turbocharged and aftercooled, IDI diesel engine at the maximum power operating point (236 kW@1500 rpm). For the cylinder alone, 40.31% (efficiency ε_1) of the fuel's availability is converted into useful work (compared with 42.89% of the fuel's lower heating value), while this amount increases to 59.38% (efficiency ε_2) if the difference between outgoing and incoming flows is considered for its ability to produce work. The compressor and turbine efficiencies are 76.38 and 87.42%, respectively. The higher isentropic efficiency of the turbine compared to the compressor, leads to a better exergy efficiency too (Eqs. (48) and (49)). For the whole plant, $\varepsilon_{tot1} = 40.31\%$, which increases to $\varepsilon_{tot2} = 53.76\%$ if we also take into account the potential of the exhaust gases to produce useful work. The latter efficiency is proposed by the present authors for overall engine plant operation.

Similar results are expected for single-cylinder, DI diesel or SI engine operation. For example, Alkidas [22, 58] found that the second-law efficiency ε_4 (Eq. (47)) varied from 22 to 48%, while its first-law counterpart η_1 (Eq. (42)) did not exceed 40% (increasing values with increasing load), and the exhaust efficiency ε_{ex} (Eq. (50)) was less than 50%. This means that only 50% of the exhaust gases energy could be recovered as work using, for example, a bottoming cycle.

7. Review of various parameters effect on the second-law balance of fundamental modes of steady-state, in-cylinder operation

To the best of the authors' knowledge, the first studies of internal combustion engines operation that included exergy balance in the calculations were, around 1960, the works of Traupel [62], and Patterson and Van Wylen [63]. Most of the studies, however, were published from the second half of the 80s onwards, as will be discussed in the following Subsections. The most important findings of each research group will be presented and analyzed in the following sections. By so doing, we will be able to shed light to the basic results of availability analysis when applied to (various) internal combustion engines operation, and highlight the effect of the most important parameters on the engine exergy balance and mainly the term of combustion irreversibilities.

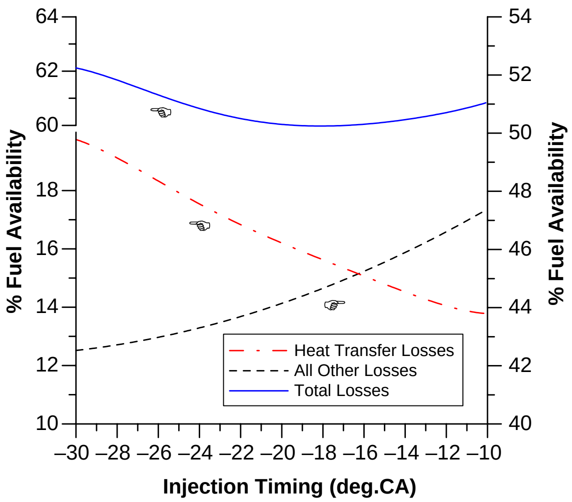

Fig. 5. Response of available energy loss terms reduced to fuel chemical availability with respect to injection timing (10 lt, six-cylinder, turbocharged and aftercooled, DI diesel engine) (adapted from Ref. [59]).

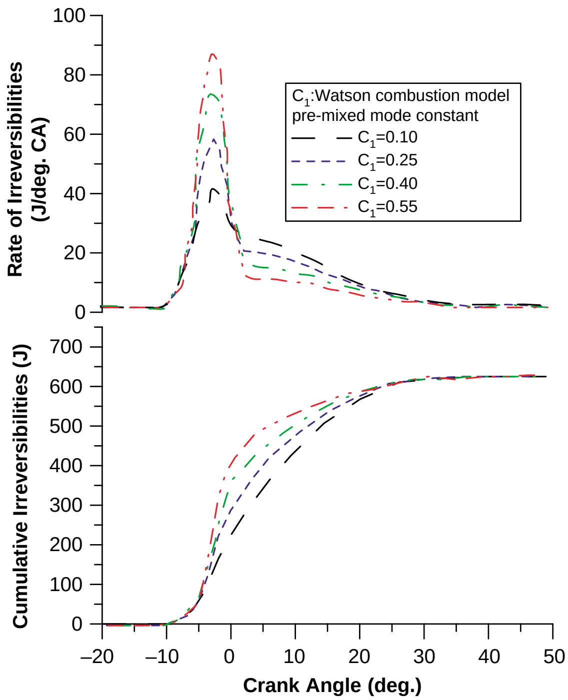

Fig. 6. Effects of premixed burning fraction on rate and cumulative irreversibility production during combustion (single-cylinder diesel engine) (adapted from Ref. [24]).

7.1. Compression ignition engines

Availability balance equations were applied to a diesel engine using a zero-dimensional modeling philosophy, where the availability equations were coupled explicitly with mathematical simulation models of the engine cycle [21,23–28,48,49,55,59, 64–73] as well as on an overall or experimental basis [22,40,57,58,74–76]. Both approaches usually included comparison between first- and second-law analyses in order for the distinctions of the second-law results to be identified and discussed as well as for extensive parametric study.

7.1.1. In-cylinder operating parameters

Fig. 5 shows the effect of one very important engine parameter, namely injection timing [59]. As is concluded, optimum injection timing exists, obtained as a result of a trade-off between the available energy lost due to heat transfer and the other losses in the system. As the injection timing is advanced the in-cylinder temperature and pressure increase, a fact reducing the combustion irreversibilities but significantly increasing the availability loss associated with the heat transfer to the cylinder walls. The combination of these effects leads to a point of minimum availability loss and, therefore, optimum injection timing. It would be interesting here, for the sake of comparison, if there was a comment available from Primus and Flynn, as to whether this optimum injection timing coincides with the one found from the first-law analysis.

The investigation of in-cylinder engine parameters on second-law balances and combustion irreversibilities was enhanced by Van Gerpen and Shapiro. They applied both single-zone [24] and two-zone models [28] and performed a detailed fundamental analysis for the closed part of the cycle. The effect of combustion duration, shape of heat release curves (both having little importance on the total amount of irreversibilities as was revealed from their analysis) and heat correlation parameters was investigated for a diesel engine of 114.3 mm bore and of equal stroke, operating at 2000 rpm. Fig. 6, adapted from this work, shows the effect of varying the heat release shape on the rate and cumulative combustion irreversibilities. Parameter C_1 that is studied in this figure represents the fraction of fuel burned in pre-mixed mode using the Watson [42] empirical heat release model. In an actual engine this would correspond to burning a fuel with different cetane number, causing changes in ignition delay and the proportion of premixed burning. Despite the great amplitude of the selected C_1 values the effects are only slight on the total irreversibilities, although the rate of combustion irreversibility production is greatly affected when increasing C_1.

The relative amount of irreversibilities decreases and the exhaust gas availability increases with

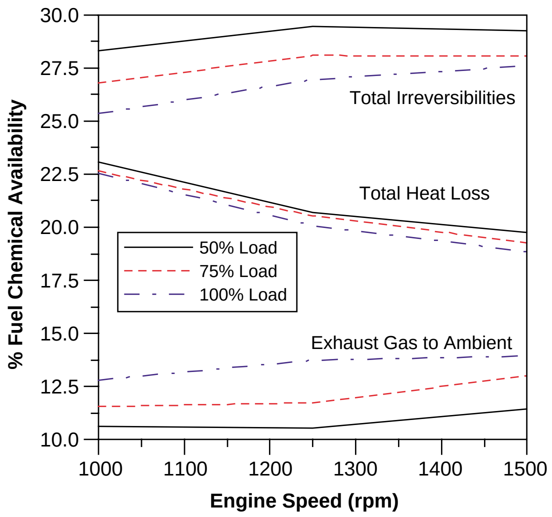

Fig. 7. Effect of speed and load on availability terms of heat losses, exhaust gas to ambient and total irreversibilities (16.62 lt, six-cylinder, turbocharged and aftercooled, IDI diesel engine in 1000–1500 rpm speed range).

increasing fuel–air ratio, ϕ up to a certain point. This holds true for both multi-cylinder, turbocharged and aftercooled [59], or for single-cylinder, naturally aspirated diesel engines [69,70]. For a diesel engine, i.e. lean operation, an increase in ϕ increases the level of temperatures inside the cylinder, thus there is lesser degradation in the fuel chemical exergy as this is now transferred to 'hotter' exhaust gases. This decreased amount of combustion irreversibilities is mainly reflected in increased amount of heat loss or exhaust gases availability; the exploitation of the latter being a key aspect of second-law application to internal combustion engines. Varying the equivalence ratio at which combustion occurs has also a significant effect on the distribution of (thermomechanical and chemical) availabilities inside the cylinder. This has already been illustrated in Fig. 1, where it is shown that the percentage of chemical to total availability increases significantly with ϕ, i.e. with richer mixtures pinpointing its significance for spark ignition engines operation.

The effect of engine speed and load on the availability balance and irreversibilities production is more complex and not always straightforward. The basic conclusions regarding the effect of speed and load on the total (i.e. cylinder and manifolds and turbocharger) irreversibilities, heat transfer and exhaust gas to ambient, are illustrated in Fig. 7 for a six-cylinder, turbocharged and aftercooled, diesel engine [73]. An increase in load causes an increase in the indicated efficiency, cylinder inlet air and exhaust gas availability terms, and compressor, turbine and exhaust manifold irreversibilities. This happens due to the increased level of pressures and temperatures that an increasing load induces. Inlet irreversibilities and mechanical friction, in comparison, decrease with increasing engine load; the same remark applies to combustion (and total irreversibilities) and cylinder heat loss. Combustion irreversibilities (reduced to the fuel availability) generally decrease with increasing load because of the fuel chemical availability being transferred to 'hotter' exhaust gases, a fact making the process more favorable from the second-law perspective. The increase in speed caused an increase in mechanical friction, combustion irreversibilities, cylinder inlet air and the amount of exhaust gases availability. The increase in speed caused a decrease in cylinder heat loss due to the lower available time for heat transactions, while the combustion irreversibilities (reduced to the indicated work) showed a maximum at about 1250 rpm (i.e. at the middle of the speed operating range of the engine).

The compression ratio plays a significant role in both first- and second-law balances, affecting combustion irreversibilities through its effect on gas temperature and pressure. However, its optimization under a second-law perspective should be seen in the light of serious changes incurred in the operational, constructional (cost) and environmental behavior of the engine, as was the conclusion reached by Rakopoulos and Giakoumis [73].

7.1.2. IDI engine operation

The implications induced by the indirect injection type of diesel engine operation were first discussed in Ref. [25], where IDI (and DI) diesel engine combustion irreversibilities were brought into focus through an in-depth analysis by Rakopoulos and Andritsakis. Furthermore, the variation of reduced combustion irreversibilities against the reacted fuel fraction for IDI diesel engines has proved to be almost independent of injection timing, load and engine speed.

Fig. 8 shows the development of the main chamber and pre-chamber cumulative availability terms during an engine cycle (i.e. control volume availability, injected fuel, heat transfer to the cylinder walls and irreversibilities) for a six-cylinder, turbocharged and aftercooled, IDI diesel engine fitted with a small pre-chamber, and operating at 1180 rpm and 70% load [55]. The main chamber contributes mostly to the total combustion irreversibilities, ranging from 70% at low loads to almost 96% at full load, steady-state conditions, aided by the higher level of pressures and

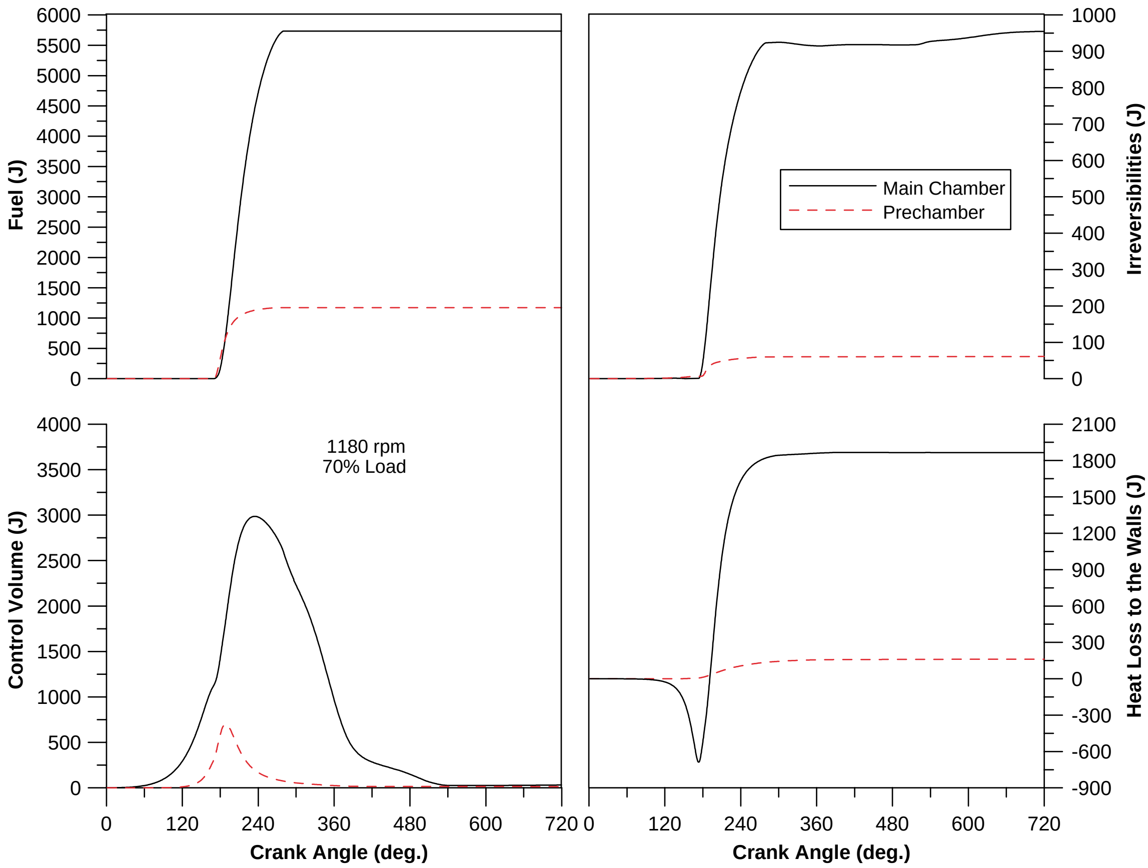

Fig. 8. Development of main chamber and pre-chamber cumulative availability terms during an engine cycle (16.62 lt, six-cylinder, turbocharged and aftercooled, IDI diesel engine).

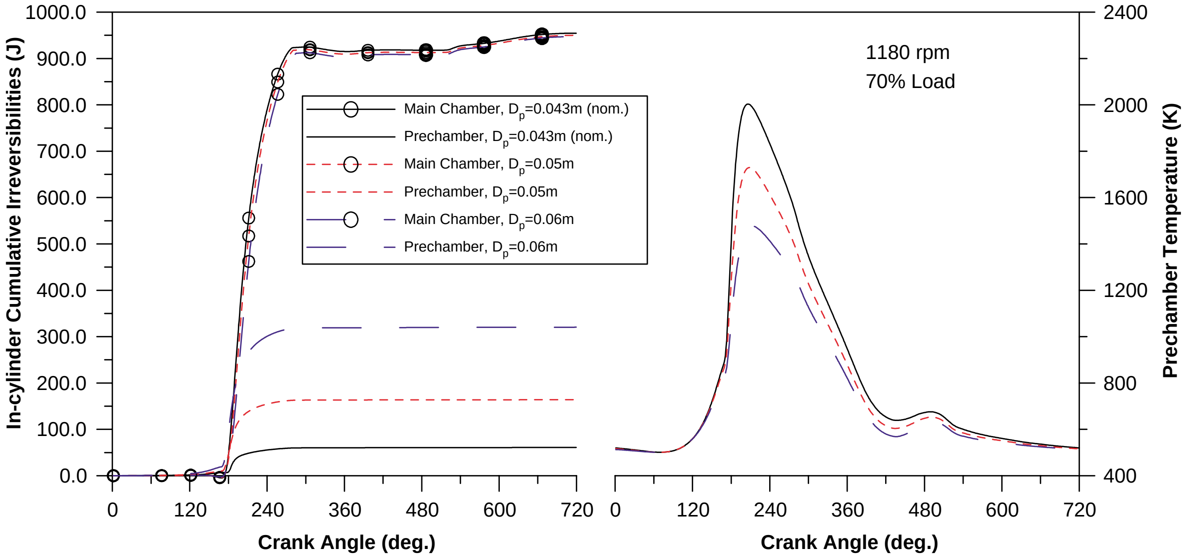

Fig. 9. Effect of pre-chamber diameter on main chamber and pre-chamber cumulative irreversibilities (16.62 lt, six-cylinder, turbocharged and aftercooled, IDI diesel engine).

temperatures in the pre-chamber and its very small volume, i.e. 1/64th of the total cylinder.

Fig. 9 shows the effect of the most prominent IDI parameter, i.e. pre-chamber volume, on the cumulative main chamber and pre-chamber irreversibilities (again for 70% engine load). The greater the pre-chamber diameter the greater the amount of fuel burned in it, a fact which corresponds accordingly to greater percentage of combustion irreversibilities (the main chamber being almost unaffected). Thus, from the 6% of the nominal case the pre-chamber irreversibilities rise to 25% of the total for a 40% increase in the pre-chamber diameter (from 43 to 60 mm), while the total irreversibilities have increased by 25%. This is due to the lower pressures and temperatures (as depicted in the right-hand sub-diagram of this figure) that are responsible for increased degradation of the fuel's chemical availability being transferred to 'colder' exhaust gases. Consequently, from the second-law perspective, an increase in the pre-chamber diameter proves unfavorable. Moreover, the static injection timing was found to only marginally affect the pre-chamber irreversibilities, although the main chamber ones increase when retarding injection. The contribution of the main chamber is expected to be lower if the engine is fitted with a swirl chamber as its pressure is almost equal to that of the main chamber.

This had already been pointed out by Li et al. [72] who conducted a comparative first- and second-law analysis on a single cylinder diesel engine fitted with a swirl chamber. They calculated energy and availability balances for the base engine as well three alternative ones (IDI with no throttling losses, adiabatic swirl chamber, and DI engine) without any major differentiations being observed as regards combustion irreversibilities (between 21.02 and 22.11% of the fuel availability for all cases examined). The swirl chamber was responsible for almost 30% of the combustion irreversibilities ($\phi = 0.64$, 2000 rpm) and the connecting passage losses accounted for 1% of the total in-cylinder irreversibilities. This can be compared to the results by Rakopoulos and Andritsakis [25], where for a six-cylinder, turbocharged and aftercooled engine, fitted with a pre-chamber of small volume and very narrow throat, throttling losses were estimated at, maximum, 0.23% of the fuel availability. Li et al. concluded that a reduction in heat transfer losses does not necessarily correspond to an equal increase in engine efficiency (due to increased exhaust gases loss), while throttling between main chamber and swirl chamber is responsible for decreasing IDI full load fuel consumption, since this is responsible for combustion deterioration in the swirl chamber and delay in the main chamber combustion process.

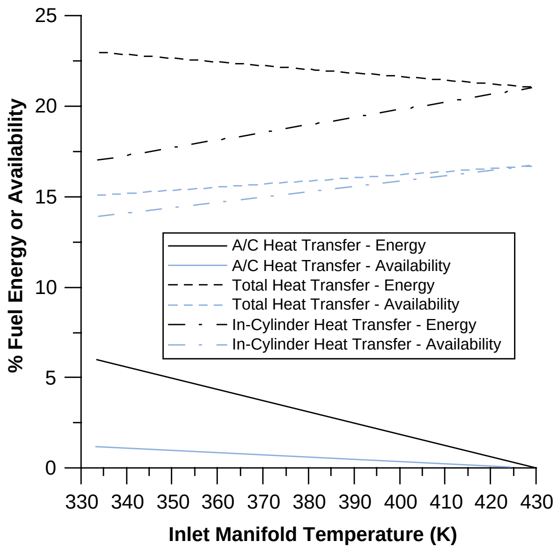

Fig. 10. Influence of intake manifold temperature on heat losses energy and availability terms (10 lt, six-cylinder, turbocharged and aftercooled, DI diesel engine) (adapted from Ref. [59]).

7.1.3. Various turbocharging schemes

For a number of years now, the majority of compression ignition engines is turbocharged and aftercooled. Therefore, the effect of various parameters associated with the turbocharging system used has been the main subject in a number of works. The examined cases ranged from operating parameters such as, for example, the intake manifold temperature up to complex turbo-compounding schemes involving bottoming cycles, etc. In principle, most of the researchers, including the present ones, agreed that turbocharging is a successful way to improve engine efficiency and, mainly, output, as (part of) the available work in the exhaust gases is exploited. A different point of view was expressed by Bozza et al. [27], working on a four-cylinder, automotive, turbocharged diesel engine, who argued that turbocharging cannot be considered as an effective method for availability recovery at the discharge of a reciprocating engine. This was attributed to the fact that further losses in the manifolds and turbocharger are induced. However, it was admitted that the more effective combustion process provoked by the increased pressures and temperatures inside the cylinder due to turbocharging had already led to reduction of the (dominant) combustion irreversibilities.

The effect of intake manifold temperature (that is affected by both turbocharging and subsequent charge air cooling) is shown in Fig. 10 regarding various heat transfer energy and exergy terms for the turbocharged diesel engine of Table 2 [59]. Even though the total energy associated with heat transfer increases by almost 10% as the intake manifold temperature is reduced, the total availability associated with heat transfer is reduced by 10%. Likewise, Zellat [57] applying the second-law balance on a large four-stroke diesel engine of 570 mm bore, concluded that cooling the charge air notably increases the combustion irreversibilities (due to the decrease in the level of temperatures inside the cylinder), a fact that was largely counterbalanced by the profits obtained from reduced thermal transfers and availability of exhaust gases to ambient. This remark was enhanced in later years especially when associated with low heat rejection engines and for the transient diesel engine operation too, as will be discussed in Section 9. Primus et al. [64] agreed that charge air cooling led to a reduction of total availability associated with heat transfer (due to the lower temperature level at the beginning of compression) thus increasing engine performance, but proposed re-optimization of the aftercooled engine for the turbocharger losses to be reduced. The latter conclusion goes along with the comments by Bozza et al. [27] regarding the increased level of irreversibilities in turbocharger and exhaust manifold that are associated with turbocharging.

Various turbocharging schemes and parameters were the main subject studied by Primus et al. in Ref. [64] and McKinley and Primus in Ref. [65]. Turbocompounding was found to increase the level of pressures (and thus associated irreversibilities) in the exhaust manifold relative to the inlet manifold, and could lead to a reduction of the cylinders' brake work when increasing the power turbine output. On the other hand, the effect of turbine area, waste gate, variable geometry turbine and resonant intake system cannot be characterized as straightforward when first- and second-law balances are applied, therefore, no clear result was reached regarding their effect.

7.1.4. Comments

- Compression ignition engine operation has focused on the (dominant) combustion process but has also included the turbocharger, aftercooler and manifolds second-law performance of the four-stroke diesel engine.
- Most of the researchers, including the present authors, have not taken into account in their analyses the term of chemical availability due to the practical difficulty in exploiting this portion of availability. The ones who have actually included the chemical availability term, have taken into account only that part which deals with the exergy due to the difference in the partial pressures of the exhaust gas species compared with their environmental counterparts.
- The use of availability analysis has revealed the different magnitude that the second-law assigns to the various energy streams, processes and efficiencies. This is particularly evident in the case of heat transfer losses and exhaust gases terms.
- The majority of works have focussed on the dominant combustion irreversibilities, which remains the most obscure and difficult availability destruction to cope with. One important aspect here comes from Flynn et al. [21], who argued that only that part of the combustion irreversibilities which is associated with the heat release placement and shape can be affected by engine development and thus improved (highlighting the inevitable of the combustion irreversibility). Other important aspects are: (a) combustion duration, heat release shape and injection timing only marginally affect combustion irreversibilities (although the latter's impact on work, heat transfer and exhaust gases availability is significant), and (b) an increasing pre-chamber volume increases the amount of total combustion irreversibilities due to the lower temperatures and pressures under which the greatest part of combustion is accomplished in the main chamber.
- A key remark is that increasing the level of combustion temperatures, as for example when increasing the equivalence ratio or compression ratio or insulating the cylinder walls, which will be discussed in the Section 8.1, results in a relative decrease in the combustion irreversibilities, since combustion becomes less irreversible as the fuel chemical availability is transferred to hotter exhaust gases. This fact denotes that such a process is, in principal, a favorable one from the second-law perspective and highlights a part of the path that has to be followed for improving engine performance. However, care has to be taken since, for example, pre-heating the air of combustion or avoiding charge air cooling seems a good option from the second-law perspective (increase in temperature level inside the cylinder), but it leads to reduced volumetric efficiency and thus overall output of the engine.
- The second part of the path is the exploitation of the increased work potential of the heat losses and exhaust gas to ambient, which are usually interconnected with a decrease in combustion

irreversibilities. Particularly, the heat losses are one term whose recovery is extremely difficult. The exhaust gas to ambient term, on the other hand, can be more easily recovered, requiring some form of bottoming (i.e. Rankine) cycle. This, however, increases both the complexity and the cost of the engine plant being economically viable only for large units. Nonetheless, such recovery would make a very powerful means of improving engine performance (output and efficiency). At the moment, the heat transfer from the hot cylinder walls to the cooling water, being at a very low temperature, destroys a great part of this available energy. In this way, the choice of various researchers who preferred to treat the availability term of heat transfer as another source of irreversibility seems justified.

- The minimization of excess air, as it has been proposed in various thermodynamic books (inherent in spark ignition engine operation), seems also a good idea, which, in the case of compression ignition engines, is limited by the combustion peculiarities and the amount of tolerable smoke emission. In spark ignition engine operation, an increase in excess air improves the ideal Otto cycle efficiency through its influence on the ratio of specific heats thus pinpointing a conflict between the two thermodynamic laws results.
- Adiabatic combustion has been proposed by many researchers as an effective and promising method for dealing with combustion irreversibilities. This, however, requires the construction of special combustion chambers to withstand the extremely high temperatures, so that consequently this should be seen through the prism of cost and development in materials science. Moreover, an increase in the NO*x* emissions is to be expected when such design choices are met.
- Turbocharging is, in general, a good way to improve engine output (not necessarily engine efficiency although this is often the case with diesel engines) since a significant amount of exhaust gas availability is utilized in order to increase engine power. The observed increase in the level of pressures and temperatures decreases the combustion irreversibilities, increases the potential for extra heat recovery, but also increases slightly the availability destruction in the manifolds.
- Second-law analysis cannot be isolated from first-law modeling. In fact, as Gyftopoulos [77] argued, it is actually misleading to separate the first- and second-law analyses and claim that one is better than the other, but, instead, use should be made of both approaches for every process study.

7.2. Spark ignition engines

All works committed so far on the availability analysis of spark ignition engines [19,28,36,38,53,63, 78–86] have dealt with naturally aspirated engines (and for the cylinder alone), so there are no results available as regards turbocharged engine operation, or specifically, turbine, compressor or manifolds irreversibilities. Most of the comments mentioned in the previous section for compression ignition engines hold true for the spark ignition engine too. The research groups have applied a single- or two- or even three-zone model for the calculation of in-cylinder properties prior to application of the exergy balance. A number of parameters were examined, the most important effects of which will be presented in the next paragraphs. A number of works on SI engine second-law operation has included alternative fuels in their analyses and as such they will be reviewed in Section 8.2.

7.2.1. In-cylinder operating parameters

An important engine parameter, affecting seriously the first-law balance, is the compression ratio. The ideal Otto cycle simulation of Lior and Rudy [36] concluded that the second-law efficiency increased with compression ratio but at a roughly double rate than its first-law counterpart, η_1. This is a very interesting finding

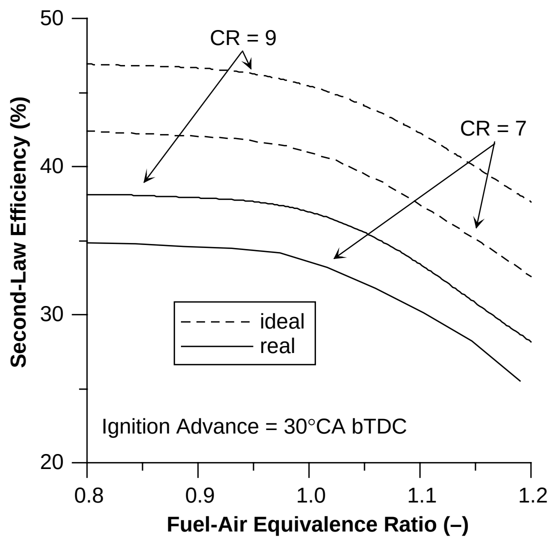

Fig. 11. Second-law efficiency ε_1 of ideal and real Otto cycle vs. fuel–air equivalence ratio, for 30 °CA ignition advance and for two compression ratios.

that pinpoints the different results obtained when first- and second-law balances are compared. The authors associated it with the inability of the energy analysis to account well for the fact that the losses in the potential to do useful work both in the combustion and exhaust processes decrease with compression ratio as well. Zhecheng et al. [78] applying the availability balance on a four-cylinder naturally aspirated SI engine confirmed this increase on the real engine cycle, and attributed it to the reduction in the loss of the exhaust gas's availability.

The equivalence ratio, ϕ and the residual fraction are both of great importance since they define the level of in-cylinder gas temperatures after combustion, affecting in this way the production of combustion irreversibilities. Moreover, if the fuel–air ratio of the mixture is rich, the gases at the restricted dead state would contain significant amounts of CO, H_2, and the presence of these gases would result in a much larger chemical availability contribution, as is illustrated in Fig. 1 [28]. The effect of ϕ on combustion irreversibilities was confirmed by Rakopoulos [80], working on a single cylinder, experimental, Ricardo SI engine. Fig. 11, from this work, shows the effect of fuel–air equivalence ratio on the second-law efficiency (ideal Otto cycle and real engine simulation) for two values of compression ratio, i.e. 7 and 9, and for a 30 °CA ignition advance. The second-law efficiency decreases as ϕ increases, a fact going along with the results from the ideal Otto cycle [36]. The real engine values lie lower than the corresponding ideal cycle ones due to

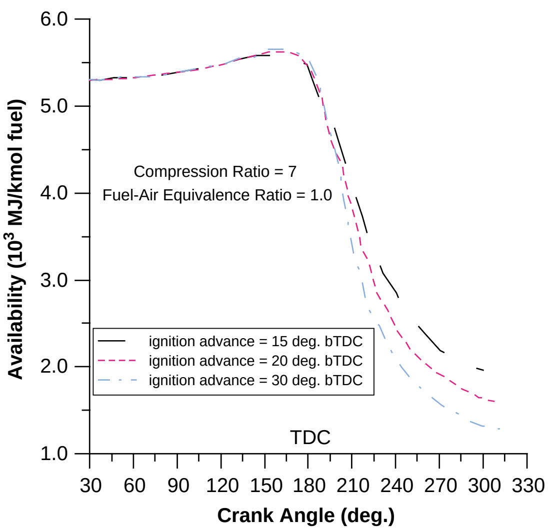

Fig. 12. Cylinder control volume availability vs. crank angle φ for various spark timings (single-cylinder, SI engine operating at 2500 rpm and wide open throttle).

Table 4
Comparison of results from first- and second-law balances, and quantification of irreversibilities (V8, 5.7 lt SI engine, operating at 2800 rpm and 3.25 bar bmep) (adapted from Ref. [83])

	First-law (% of fuel energy)	Second-law (% of fuel availability)
Work (indicated)	32.05	31.17
Heat transfer to the walls	23.29	18.77
Exhaust gas to ambient	43.98	27.88
Combustion	–	20.36 (93.7)
Intake throttling	–	1.36 (6.3)

(numbers in parentheses denote % of total in-cylinder irreversibilities).

finite burning rates, real valve timings and heat losses. Rakopoulos also concluded that the heat transferred to the combustion chamber walls is reduced when moving away from $\phi=1.05$ (either towards leaner or richer mixtures), since then top (combustion) pressures and temperatures decrease.

The combustion duration has been found to only slightly effect the amount of combustion irreversibilities [28,78]. This is also the case with compression ignition engines. Obviously, although the rate of irreversibilities production is seriously affected by the combustion duration, and hence rate, the total amount of availability destruction due to combustion remains almost unaffected.

The mass burn rate profile has been investigated too as regards its effect on the exergy balance of an automotive, eight-cylinder, SI [85]. The combustion irreversibilities were computed at about 21% of the original availability for $\phi=1$ and 1400 rpm, having only a slight dependence on the parameters of the Wiebe combustion model [41]. This conclusion goes along with the results reached by Van Gerpen and Shapiro [24] for compression ignition engines, highlighting some principles of the combustion process between SI and CI engine operation that coincide. Moreover, the instantaneous values of the availability destruction are proportional to the mass fraction burned, i.e., to the extent of reaction.

In Fig. 12, the effect of another influential engine parameter on the exergy balance is illustrated, i.e. spark timing [80]. In this figure the variation of cylinder control volume availability with crank angle φ is given for various spark timings at wide open throttle and $N=2500$ rpm engine speed. Total irreversibility due to combustion remains essentially unaltered (confirming the results by Shapiro and Van Gerpen [28]), whereas the heat transferred to the cylinder walls is increased as the spark

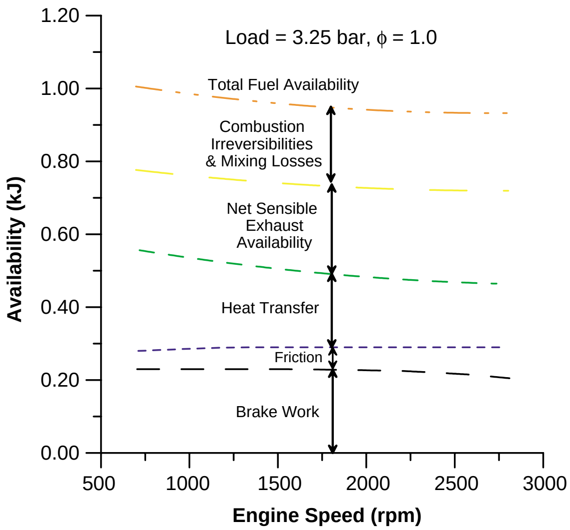

Fig. 13. Availability terms over an engine cycle as a function of engine speed for a bmep of 3.25 bar and a fuel–air equivalence ratio of 1.0 (V8, 5.7 lt SI engine) (adapted from Ref. [83]).

advance increases, since then the time period during which the walls are exposed to hot gases increases.

The effect of engine speed and load on the first- and second-law balances was studied by Caton in Ref. [83] for an automotive, eight-cylinder, SI engine. Three sets of speed and three sets of load were examined, with the start of combustion adjusted each time for maximum brake torque and fuel–air ratio, $\phi = 1$. Table 4, adapted from this work, gives a (typical) summary of first- and second-law balances for a SI engine (in this case operating at 2800 rpm engine speed and bmep = 3.25 bar), with the exhaust gases availability term possessing a very high percentage of either energy or availability of the fuel. From the parametric study conducted it was shown that: (a) the heat loss to the walls availability ranged from 15.9 to 31.5% of the fuel availability, with this fraction being lowest for the highest speeds (due to shorter available time) and highest loads, (b) the availability expelled with the exhaust gases ranged between 21.0 and 28.1% with this fraction being lowest for the lowest speeds and loads, (c) the combustion irreversibilities ranged between 20.3 and 21.4% with this fraction not varying much for the conditions of this study, and d) the availability destroyed by the mixing process of the fresh charge with the existing cylinder gases ranged between 0.9 and 2.3% of the fuel availability. In principle the effect of speed was shown to be modest, with its biggest impact being on the heat transfer availability, as is depicted in Fig. 13 (cf. the results reached by Rakopoulos and Giakoumis [73] studying engine speed and load effects on compression ignition engine operation).

7.2.2. Other SI engine configurations

Various methods for improving SI exergy efficiency have been proposed, e.g. improved combustion chamber design, improved fuel–air mixing and ignition, as well as either adiabatic combustion or use of the availability loss to drive a secondary power producing cycle, and also piston expansion past the intake volume. Some of these measures have been studied in order for their actual effect on SI engine operation to be established.

For example, Sato et al. [79] investigated the exploitation of exhaust gases as an energy source to operate an after-burner and a Stirling engine. This research group was also the first to focus on two-stroke SI engine operation. A two-zone model was used for the thermodynamic calculations of the SI engine taking into account a 10 species chemical dissociation scheme. The combustion process in the burner and Stirling engine (bore 45 mm, stroke 34 mm, speed 1450 rpm) were also modeled. From the analysis it was revealed that 39.6% of the incoming (fuel) availability was contained in the exhaust gases compared to a 19.6% work production (efficiency ε_1) at 2500 rpm and an air–fuel ratio of 13. This result seems justified taking into account both the spark ignition type of the engine and its two-stroke operation. The combustion in the catalytic burning type burner contributed 7.98 percentage points to the exploitation of available energy, increasing the exergy efficiency by 41%.

Spark ignition engine operation using the Miller cycle with late intake valve closure (LIVC) was the subject of Anderson et al. [81], who compared this engine's operation with the traditional throttled spark ignition engine from the first- and second-law perspective and for various engine loads. They used a two-zone model in their study and concluded that the second-law analysis recognized the elevated blow-down pressure as an increase in thermomechanical availability loss at high loads and identified a larger thermal loss at lighter loads. Moreover, it was found that 3% of the fuel availability is destroyed by the throttle used in a conventional SI engine.

7.3. Engine subsystems

Only a few research groups in the field of second-law application to internal combustion engines have included in their calculations the balances for the various engine subsystems (manifolds, aftercooler and turbocharger). All of these works deal with compression ignition engine operation.

Fig. 14 shows the evolution of rate and cumulative irreversibilities for inlet manifold, exhaust manifold, compressor and turbine of a six-cylinder diesel engine operating at 1180 rpm and 70% load [48,49].

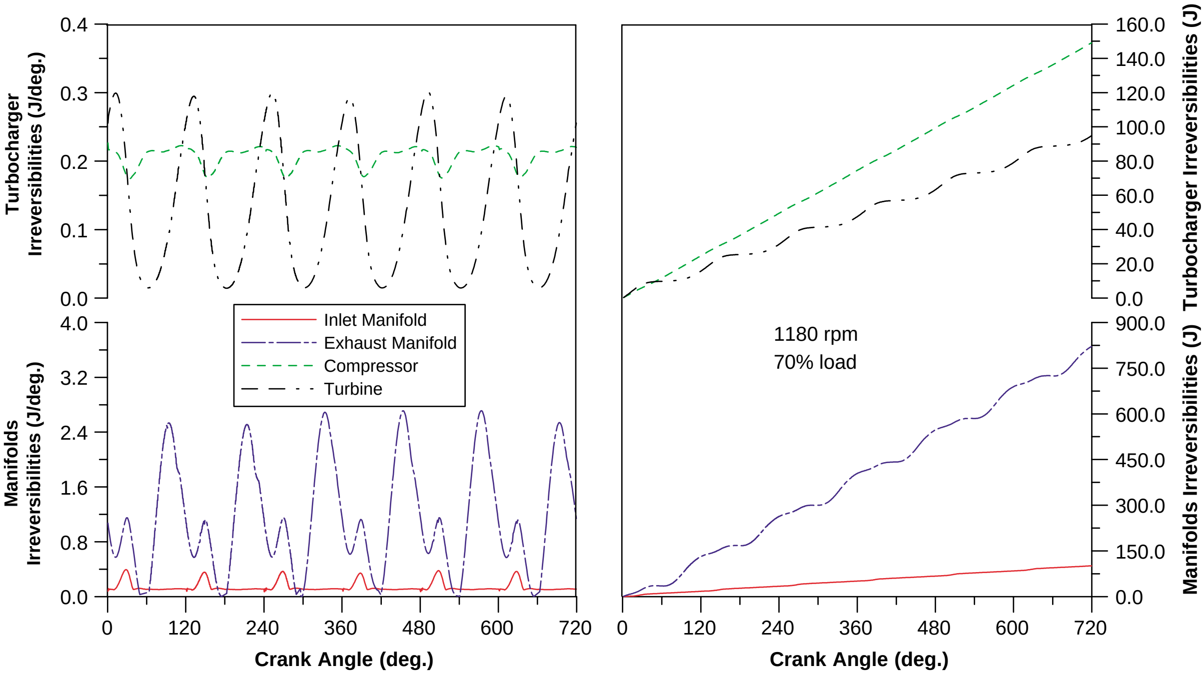

Fig. 14. Development of rate (J/°CA) and cumulative (J) irreversibilities in the manifolds and turbocharger over an engine cycle (16.62 lt, six-cylinder, turbocharged and aftercooled, IDI diesel engine operating at 1130 rpm and 70% load).

The pulsating form of the irreversibilities rate is due to the six cylinders effect. It is obvious that the exhaust manifold dominates the manifolds irreversibilities, whereas the compressor ones exhibit much lower amplitude of pulsation compared to the turbine. Apart from the combustion irreversibilities, which are the main source of availability destruction for every operating point, the throttling, friction and thermal mixing losses encountered in the turbocharger and inlet-exhaust manifolds destructions should also not be ignored, since they comprise as much as 20% (maximum) of the total irreversibilities. Exhaust manifold irreversibilities contribute as much as 10% of the total irreversibilities, thus showing one process, besides combustion, which the first-law analysis fails to describe fully.

An exhaust system optimization through the second-law was conducted by Primus in Ref. [66] for a six-cylinder, turbocharged and aftercooled, diesel engine of 14 lt displacement volume, which included detailed study of the exhaust process and extensive parametric analysis of engine, exhaust manifold and turbine data on exhaust losses. He concluded that an optimal exhaust manifold diameter exists as regards frictional and throttling losses, while increasing engine speed or engine load or turbine efficiency, or decreasing compression ratio or turbine power, results in an increase in manifold (i.e. valve throttling and friction) losses.

Another approach was adopted by Nakonieczny [87], who expanded a previous analysis of his [59], and developed an entropy generation model for the exhaust system, i.e. exhaust manifold and turbine. A 'criterion function' was developed, using the notion of entropy generation rate for the assessment of the impact of system design parameters on its performance. The function was evaluated based on results of numerical simulation of flow modeled by one dimensional gas dynamics. The computations showed that entropy production in the turbine with waste gate and in the compressor are the main components of total irreversibilities. Among the variables considered, the turbine effective area ratio has the greatest impact on the total entropy generation rate, and this is followed by the waste gate variable. Other variables, affecting the entropy production, involve the air temperature decrease in intercooler, valve overlap period, timing of exhaust valve and air pipe length.

8. Review of second-law balance of other engine configurations

8.1. Low heat rejection engines

During the last two decades there has been an increasing interest in the low heat rejection (or sometimes loosely termed 'adiabatic') engine.

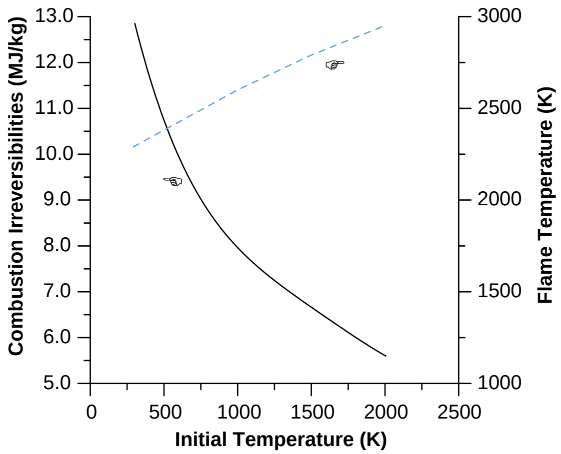

Fig. 15. Computed combustion-generated irreversibilities and flame temperature vs. initial temperature of stoichiometric reactants (adapted from Ref. [22]).

The objective of a low heat rejection cylinder is to minimize heat loss to the walls, eliminating the need for a coolant system. This is achieved through the increased level of temperatures inside the cylinder resulting from the insulation applied to the cylinder walls [1–5,33,88–91]. By so doing, a reduction can be observed (for CI engines) in ignition delay (thus combustion noise), hydrocarbons and particulate matter emissions, and also an increase in engine performance and additional exhaust energy. A major issue here is the decrease in the volumetric efficiency, hence power output, and the increase in NO*x* emissions. The low heat rejection engine has been studied by many researchers also from the second-law perspective.

The analysis of Alkidas [22,58] showed, that an increase in the combustion temperature should decrease the combustion irreversibilities significantly. This is depicted in Fig. 15, where it is shown that increasing the temperature of the reactants (i.e. through insulation of the cylinder walls) increases the flame temperature and significantly decreases the combustion irreversibilities. This is a fundamental remark concerning the application of the second-law to internal combustion engines, which was later confirmed by other researchers.

Caton [19] expanded the above remark, showing that the percentage of availability that is destroyed due to heat transfer from the gas temperature (T_g) to the wall temperature (T_w), increases as the difference ($T_g - T_w$) increases. Similar results hold true for the exhaust gases term. Consequently, increasing the cylinder wall insulation leads to an increase in the temperatures inside the cylinder, and a decrease in the combustion irreversibilities, as the fuel chemical availability is now transferred to exhaust gases of greater temperature and thus work potential. At the same time the wall insulation increases the amount of the availability terms of heat loss and exhaust gas from cylinder. Consequently, the cylinder wall insulation has proved a favorable design choice from the second-law perspective.

The importance of cylinder wall insulation on the (theoretical) recovery of the exhaust gases heat loss is prominent, since an increased insulation can significantly limit the availability destruction associated with heat transfer from the gas to the cylinder walls [21]. This availability potential could then be extracted with the use of heat transfer devices driving secondary energy extraction units. It is imperative that the engine working fluid should not be used for such devices, since its low temperature level would make a very poor work recovery, i.e. with the heat transfer from the cylinder walls to the cooling water the majority of the work potential is destroyed.

A typical tabulation of second-law results with and without insulation is illustrated in Fig. 16 for a turbo-compound diesel engine as was calculated by Primus et al.

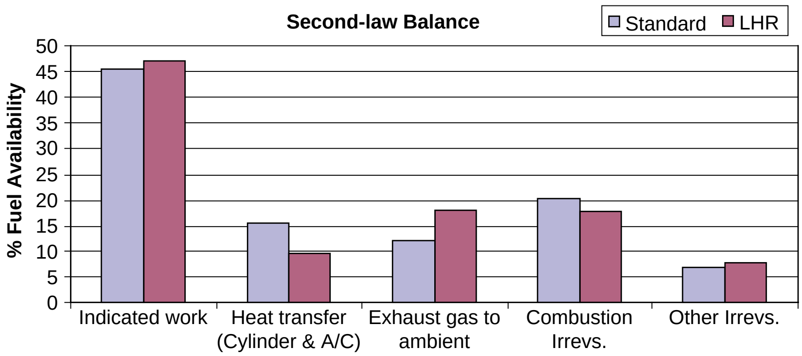

Fig. 16. Comparison of exergy terms and irreversibilities between standard and LHR case (six-cylinder, turbocharged and turbo-compound, diesel engine) (adapted from Ref. [64]).

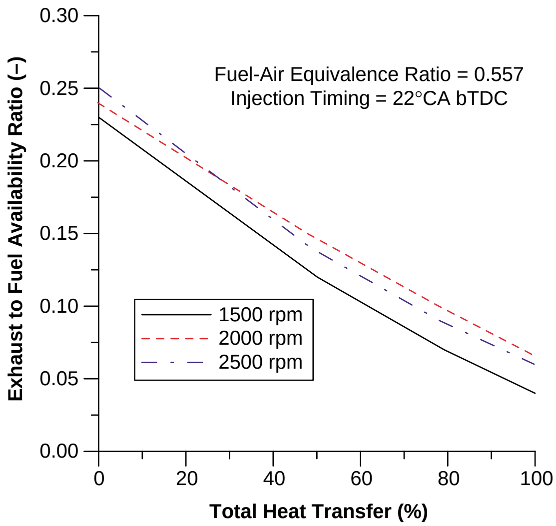

Fig. 17. Variation of exhaust gas availability to fuel availability against total heat transfer at various engine rotational speeds (single cylinder, naturally aspirated diesel engine).

[64]. This figure best highlights the effects of insulation from the second-law perspective. For the low heat rejection (LHR) engine case, a 5.08 mm insulation was applied on the piston and cylinder head face, resulting in 61% reduction of in-cylinder heat transfer (42%, if the first-law is applied). This resulted in 'only' 3.7% increase in the indicated work and also a 49% increase in the (mainly thermal) availability of exhaust gases to ambient. The latter effect is illustrated in Fig. 17 [70], showing the variation of exhaust gas availability reduced to the fuel chemical availability against total heat transfer for a single-cylinder, naturally aspirated, compression ignition engine. Obviously, the 'adiabatic' case exhibits the greatest amount of available work from exhaust gases.

The modest increase in the indicated work due to insulation can be attributed to the combined effect of the decrease in the engine volumetric efficiency and the increased exploitation of the exhaust gases energy in the turbocharger turbine in order to provide higher boost [86]. Primus et al. [64] concluded that insulating the engine reduces the exhaust manifold pressure while increasing the intake manifold one, thus decreasing the pumping losses. This effect more than offsets the decrease in engine indicated work due to the increased volumetric efficiency that the higher level of temperatures inside the cylinder creates. They emphasized also on the need for using heat recovery devices in order for the work potential of the heat transfer to the cylinder wall to be retrieved.

The second-law efficiency ε_1 is also expected to increase with insulation. This is mainly attributed to the reduced heat losses and the resulting increase in flame temperature [58]. Moreover, the heat transfer rate from the exhaust gases to the combustion chamber of the LHR engine typically ranges from 50–70% of that of the standard engine.

The basic results of Alkidas concerning low heat rejection engines were also confirmed by Bozza et al. [27], who reached the conclusion that a combined system is capable of best exploiting the increased availability potential of an adiabatic engine. The same conclusion was reached by Rakopoulos et al. as regards CI engines in Ref. [70] and SI engines in Ref. [80]; the interest for such engines emanates from their potential to do more work by utilizing the exhaust gases in a Rankine bottoming cycle or a power turbine (this was also confirmed by Zhecheng et al. [78]). However, care has to be taken as regards the corresponding decrease in the volumetric efficiency that is induced by the greater level of temperatures inside the cylinder.

A possible way to overcome the major disadvantage of cylinder insulation, i.e., decrease in volumetric efficiency can be achieved by retarding the injection timing of the LHR engine. In this way the lower volumetric efficiency can be offset as was discussed by Parlak et al. [40] for a six-cylinder, turbocharged and aftercooled, DI diesel engine.

Rakopoulos and Giakoumis [92] extended the low heat rejection engine study to investigate also the more complex case of transient (diesel engine) operation as it will be discussed in detail in Section 9.

8.2. Alternative fuels

Energy conservation and its efficient use are nowadays a major issue. The evident reduction in oil reserves combined with the increase in its price, as well as the

Table 5
Ethanol and gasoline engine first- and second-law comparisons (naturally aspirated, 0.4 lt SI engine) (adapted from Ref. [61])

	Ethanol		Gasoline
	CR = 12	CR = 8	CR = 8
First-law	% of fuel lower heating value		
Work	40.48	36.48	35.22
Heat loss	21.72	20.37	19.69
Exhaust gases	37.80	43.16	45.09
Second-law	% of fuel chemical availability		
Work	38.27	34.48	33.32
Heat loss	8.76	8.21	7.95
Exhaust gases	24.47	28.22	30.03
Irreversibilities	28.52	29.09	28.70

need for 'cleaner' fuels, have led in the past years to an increasing interest and research in the field of alternative fuels for both compression and spark ignition engines propulsion. The combustion behavior of such alternative fuels is sometimes very interesting as regards either first- or second-law balances.

8.2.1. Ethanol

The use of ethanol was studied by Gallo and Milanez in Ref. [61], who worked on a naturally aspirated spark ignition engine, and proceeded to a parametric study too. They concluded that the combustion efficiency for the ethanol fuelled engine (even when its compression ratio is the same as the gasoline one) is higher than for the gasoline version, when compared in the same range of the relative air-fuel ratios as is depicted in Table 5. From their analysis, it was shown that conflicting results may arise when studying second-law efficiencies for the various processes (inlet, exhaust, closed cycle), as a better performance in one region (e.g. exhaust) may influence another region (e.g. inlet) in an adverse way.

8.2.2. Butanol

Alasfour [39] conducted an experimental availability analysis of a spark ignition engine using a butanol-gasoline blend. A 'Hydra', single-cylinder, spark ignition, fuel-injected engine was used over a wide range of fuel–air equivalence ratios ($\phi=0.8$–1.2) at a 30% v/v butanol–gasoline blend. The availability analysis showed that 50.6% of fuel energy can be utilized as useful work (34.28% as indicated power, 12.48% from the exhaust and only 3.84% from the cooling water) and the available energy unaccounted for represents 49.4% of the total available energy. The second-law efficiency ε_1 of the gasoline–butanol blend showed a 7% decrease compared to the standard pure gasoline engine, making it an unfavorable choice through the second-law perspective.

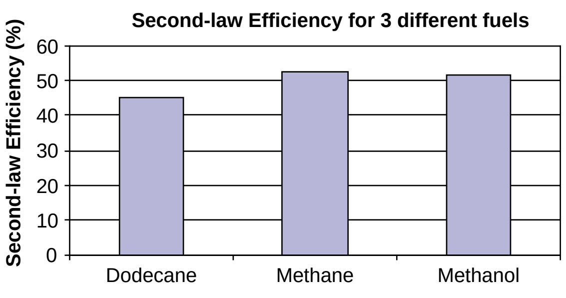

Fig. 18. Second-law efficiency ε_1 for three alternative fuels (naturally aspirated, single-cylinder, DI diesel engine operating at $\phi=0.6$ and 2000 rpm).

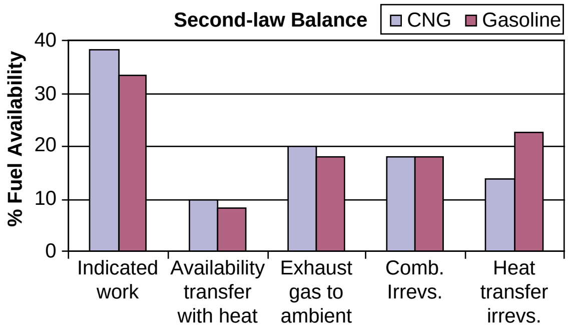

Fig. 19. Second-law balance for CNG and gasoline fuelled engines (V8, 4.7 lt, SI engine operating at 4000 rpm and wide open throttle) (adapted from Ref. [54]).

8.2.3. Methane and methanol

Rakopoulos and Kyritsis [69,93] focused on the DI diesel engine operation with methane and methanol (i.e. oxygenated) fuels compared to *n*-dodecane. They reached to the very interesting conclusion, that a decrease in combustion irreversibility is achieved when using lighter (methane) or oxygenated (methanol) fuels. This was due to the combustion characteristics of these fuels, which involve lower entropy of mixing in the combustion products. The fundamental conclusion here is that the decomposition of the lighter methane and methanol molecules during chemical reaction should create lower entropy generation than the larger *n*-dodecane molecule. A typical result from their study is given in Fig. 18, where the second-law efficiency ε_1 of the three examined fuels is depicted for $\phi=0.6$.

8.2.4. CNG

Sobiesiak and Zhang [54] focused on a naturally aspirated, SI engine, fuelled with compressed natural gas (CNG) that was modelled as methane. From their analysis, a typical result of which is reproduced in Fig. 19, they concluded that, although combustion irreversibilities are comparable for gasoline and CNG, the heat losses availability (treated here as another source of irreversibility) is lower with the CNG fueling. This was translated into increased second-law efficiency (ε_1) for the CNG engine case (38.2% compared to 33.4% for the gasoline engine).

8.2.5. Hydrogen enrichment in CNG and LFG

Rakopoulos and Kyritsis [94] continued their work on alternative fuels, this time studying hydrogen enrichment effects on the second-law analysis of natural and landfill gas (LFG) in engine cylinders. From their work it was revealed that hydrogen combustion is qualitatively different than the combustion of hydrocarbon fuels, from the second-law analysis point of view. While hydrocarbon combustion significantly increases entropy by converting molecules of relatively complicated structure to a mixture of relatively light gaseous fragments, hydrogen oxidation is the combination of two simple diatomic molecules that yields a triatomic one with significantly more structure than any of the reactants. For this reason, a monotonic decrease in combustion irreversibilities with increasing hydrogen component was calculated for the combustion of CH_4–H_2 mixtures burning in an engine chamber. The decrease in combustion irreversibilities translates to an increase in second-law efficiency for operation with H_2 enriched mixtures. The corresponding variation of exhaust gas availability with hydrogen content is non-monotonic and was computed to have a local maximum at approximately 5% (molar) hydrogen. Moreover, the presence of significant CO_2 dilution, as is the case for the landfill gas fuel, affects significantly the absolute magnitude of each of the terms of the availability balance, but not the trends observed with the increase in hydrogen composition of the fuel mixture.

8.2.6. Oxygen enrichment

A second-law study concerning combustion with oxygen-enriched air in spark ignition engine operation has been reported by Caton [95]. The percentage of oxygen enrichment examined ranged from 20 to 40%. It was shown from the analysis that the combustion irreversibilities were lower for the oxygen enriched air cases due to less mixing and reaction irreversibilities. Increasing the oxygen concentration from 21 to 32% resulted in combustion irreversibilities reduction from 20.2 to 18% (this seems a rather low percentage for SI combustion irreversibilities), respectively, for $\phi = 1$ at 2500 rpm but at the expense of decreased first-law efficiency.

8.2.7. Water addition

Özcan and Söylemez [96] investigated the effect of water addition on the exergy balance of a four-cylinder, LPG fuelled, spark ignition engine based on experimental pressure measurements converted into heat release rates in a two-zone thermodynamic model. Water injection through intake manifold was applied for water addition ranging up to water to fuel mass ratios of 0.5. It was found that water injection significantly increased the combustion irreversibility thus proving unacceptable from the second-law perspective.

9. Review of second-law balances applied to transient operation

The transient response of naturally aspirated and turbocharged (compression ignition) engines forms a significant part of their operation and is of critical importance, due to the often non-optimum performance involved. For the diesel engines used for industrial applications, such as generators, rapid loading is required together with zero (final) speed droop for the base units, as well as rapid start-up for the stand-by ones. For other less critical (in terms of speed change) applications, such as ship propulsion or pump driving, reliable governing is required as well as quick changes in the operating conditions. Rapid load changes can prove very demanding in terms of engine response and also in the reliability of fuel pumps and governors. Thus, a good interconnection and co-operation of all engine components during the transient response is vital for optimum performance. Owing to the importance of transient operation, for both automotive and stationary application it seems logical to investigate its second-law performance too. However, despite the fact that many studies concerning second-law analysis of internal combustion engines have been applied to the steady-state conditions, the respective transient case has only scarcely been dealt with and only for compression ignition engines.

For unsteady operations, the $\mathrm{d}A/\mathrm{d}\varphi$ terms given in Section 5, for the cylinder and the manifolds, do not sum up to zero (as they actually do for steady-state operation) at the end of a full cycle of the working medium. Their respective cumulative values $\int_0^{720} \mathrm{d}A/\mathrm{d}\varphi \, \mathrm{d}\varphi$ are, however, small (not more than 0.40% of the incoming fuel's availability [24]) compared to the other availability terms, especially for naturally aspirated engines. This occurs because the change in the initial conditions of the cylinder contents differentiates only moderately from cycle to cycle during the transient event.

For the turbocharger during transient operation, the following availability equation holds [27]:

$$\dot{m}_\mathrm{T}(b_6 - b_7) = \dot{m}_\mathrm{C}(b_2 - b_1) + \left(\frac{\mathrm{d}I_\mathrm{T}}{\mathrm{d}\varphi} + \frac{\mathrm{d}I_\mathrm{C}}{\mathrm{d}\varphi} + \frac{\mathrm{d}E_\mathrm{kin,TC}}{\mathrm{d}\varphi}\right) 6N \tag{54}$$

where

$$\frac{\mathrm{d}E_\mathrm{kin,TC}}{\mathrm{d}\varphi} = \frac{1}{2} G_\mathrm{TC} \frac{\mathrm{d}}{\mathrm{d}\varphi}\left(\omega_\mathrm{TC}^2\right) \tag{55}$$

is the increase in the turbocharger shaft kinetic energy.

9.1. First-law equations of transient operation

If G_{tot} represents the total system moment of inertia (engine, flywheel and load), then the conservation of energy principle applied to the total system (engine plus load) yields [1,2,4,49]:

$$\tau_e(\varphi,\omega) - \tau_{load}(\omega) - \tau_{fr}(\varphi,\omega) = G_{tot}\frac{d\omega}{dt} \tag{56}$$

where $\tau_e(\phi,\omega)$ stands for the instantaneous value of the engine torque, consisting of the gas and the inertia forces torque, $\tau_{load}(\omega)$ stands for the load torque, and $\tau_{fr}(\phi,\omega)$ stands for the friction torque.

The dynamic equation for the turbocharger is [2]:

$$\eta_{mTC}\dot{W}_T - |\dot{W}_C| = G_{TC}\frac{d\omega_{TC}}{dt} \tag{57}$$

where the turbocharger mechanical efficiency η_{mTC} is mainly a function of its speed.

To find the instantaneous fuel pump rack position z during transient operation, a second order differential equation is used [2]:

$$\frac{d^2z}{d\varphi^2} = c_1\frac{dz}{d\varphi} + c_2 z + c_3 z\omega^2 + c_4\omega^2 + c_5 \tag{58}$$

with constants c_i (i=1,…,5) derived after calibration against experimental data under transient conditions.

9.2. Second-law analysis of transient operation

The first reference regarding availability analysis of transient operation can be found in Ref. [27], where Bozza et al. extended their steady-state model to cope also with engine acceleration cases. They showed that the second-law efficiencies ε_2 and ε_3 achieved a slightly higher magnitude compared to their first-law counterparts.

A more comprehensive and extensive approach has been followed by Rakopoulos and Giakoumis, as regards naturally aspirated [49,97] and turbocharged diesel engines transient operation [26,55,92,98,99]. They applied the second-law equations to the cylinder and all subsystems of the diesel engine plant, quantifying all the processes irreversibilities and main availability terms during a transient event after a ramp increase in load. By so doing, they evaluated the response of all availability terms, during the transient event, and they also proceeded to an extensive parametric study [98] and on a direct comparison between the results given by the two thermodynamic laws for various operating parameters [99].

The naturally aspirated engine case (experimental Ricardo, single cylinder, IDI diesel engine) was studied in Refs. [49,97] as regards both load and speed (acceleration) changes, while also the effects of the magnitude of the applied change as well as the heat losses coefficient were investigated.

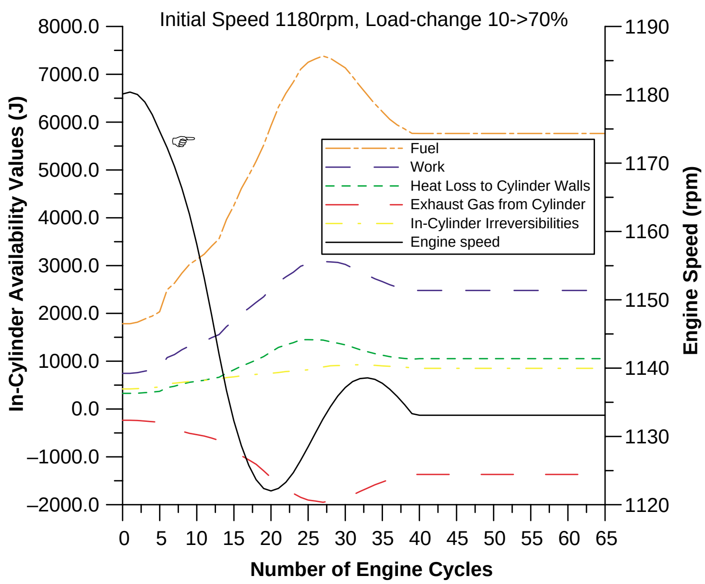

Fig. 20. Development of engine speed and in-cylinder cumulative availability terms during a transient event after a ramp increase in load (16.62 lt, six-cylinder, turbocharged and aftercooled, IDI diesel engine).

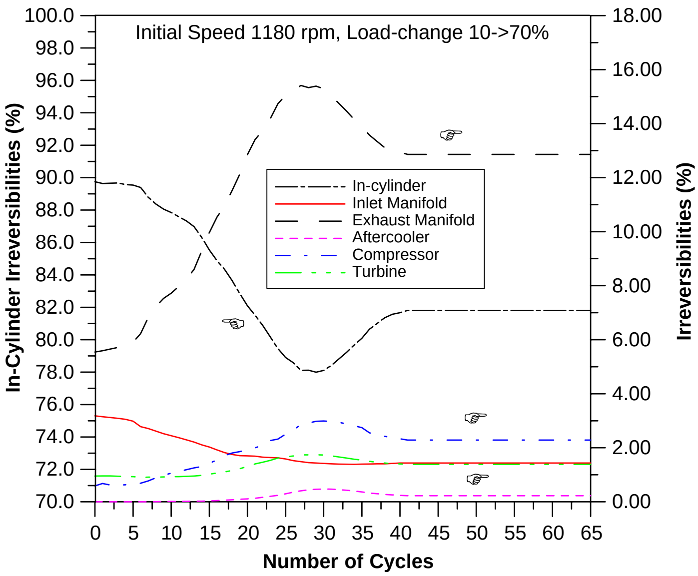

Fig. 21. Response of various engine and irreversibilities terms, reduced to the total irreversibilities, to a ramp increase in load (16.62 lt, six-cylinder, turbocharged and aftercooled, IDI diesel engine).

For the turbocharged case the engine under study was an MWM TbRHS 518S, six-cylinder, IDI, turbocharged and aftercooled diesel engine, with a speed range of 1000–1500 rpm, a maximum power output of 236 kW at 1500 rpm and a maximum brake torque of 1520 Nm at 1250 rpm. The first-law results of the engine transient response had already been validated with an extensive series of experimental tests conducted at the authors' laboratory [100], and the respective equations were solved individually for each one cylinder of the engine. In the main case examined, the initial load was 10% of the full engine load at 1180 rpm and a 650% load change was applied in 1.3 s. As can be seen in Figs. 20 and 21, the in-cylinder irreversibilities decrease, proportionally, after a ramp increase in load due to the subsequent increase in fueling. Exhaust manifold irreversibilities increased significantly during the load increase, reaching as high as 15% of the total ones, highlighting another process that needs to be studied for possible efficiency improvement. This increased amount of irreversibilities arises mainly from the greater pressures and temperatures due to turbocharging, which have already lowered the reduced magnitude of combustion irreversibilities. The inlet manifold irreversibilities, on the other hand, have a lesser and decreasing importance during the transient event. Turbocharger irreversibilities, though only a fraction of the (dominant) combustion ones, are not negligible, while the intercooler irreversibilities steadily remain of lesser importance (less than 0.5% of the total ones) during a load change. Moreover, the cycle, where each (reduced) availability term presents its peak is different for every subsystem.

The respective parametric study [92,98,99] included the effect of magnitude of the applied load, the type of load (resistance) connected to the engine, the turbocharger mass moment of inertia, the cylinder wall insulation, the aftercooler effectiveness and the exhaust manifold volume. It was made obvious that a significant amount of work potential is available during transient operation (after a ramp increase in load), the exploitation of which could increase the efficiency of the engine. The following were revealed from the parametric study:

The recovery period and the general profile of the second-law values transient response depend on the respective first-law ones, since the second-law terms are evaluated using first-law data. For the particular engine configuration, which was characterized by a high mass moment of inertia, all the second-law terms are delayed compared to the engine speed response because of the slow movement of the governor.

All the parameters that lead to slow engine speed recovery, such as large exhaust manifold volume, depicted in Fig. 22, or high turbocharger mass moment of inertia or high engine mass moment of inertia, result in similarly slow turbocharger recovery, increased fuel injected quantities and thus decreased in-cylinder irreversibilities and increased exhaust gas from cylinder or to ambient availability (reduced to the fuel

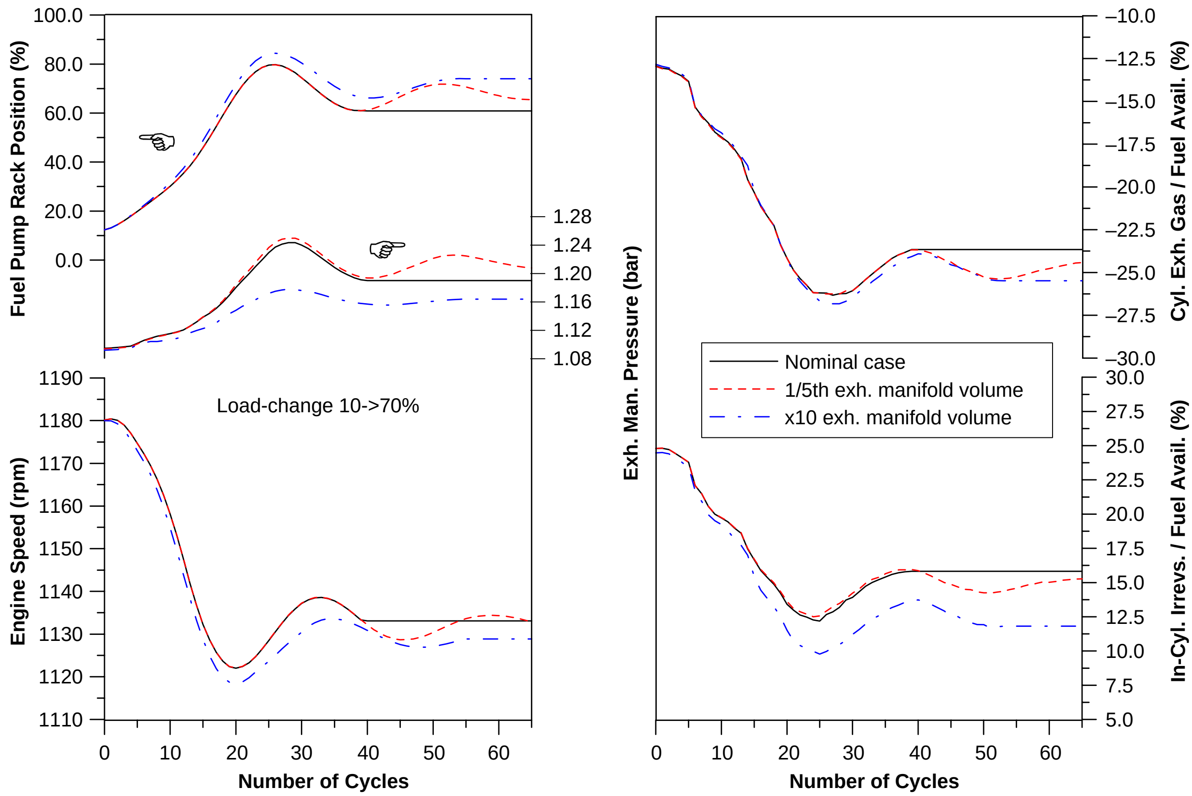

Fig. 22. Effect of exhaust manifold volume on the second-law transient response after a ramp increase in load (16.62 lt, six-cylinder, turbocharged and aftercooled, IDI diesel engine).

availability). They are, therefore, favorable from the second-law perspective since they increase the potential for work recovery, during the transient event, for example using a bottoming cycle.

The more rigid the connected to the engine load-type is, the greater the in-cylinder irreversibilities (in 'Joules') though with decreasing reduced value.

The effect of the cylinder wall temperature profile [92], after a ramp increase in load, was also studied with special reference to the low heat rejection ('adiabatic') case. As can be seen in Fig. 23, although the heat loss of energy remains almost unaffected by the applied wall temperature schedule, the engine and turbocharger second-law terms, including the various irreversibilities ones, are greatly affected especially when a low heat rejection cylinder wall is chosen. This conclusion best pinpoints the difference in energy and exergy efficiency analysis and is in accordance with the steady state results of previous researchers.

The effect of the aftercooler effectiveness in the engine first-law transient response is similarly minimal, whereas the exergy terms are significantly affected.

The contribution of each chamber of the IDI diesel engine referred to above (fitted with a pre-chamber) during transient operation after a ramp increase in load, was also studied by Rakopoulos and Giakoumis in Ref. [55], where the dominance of the main chamber compared to the pre-chamber was obvious during the whole transient operating case examined.

10. Overall-comparative results

Data and results from the analyses discussed in Sections 7–9 are summarized below. Table 6 summarizes the basic data of the previous research works in the field of second-law application to internal combustion engines. It includes, among other things, specifications of the engines studied (ignition, aspiration, number of cylinders, bore, stroke, displacement volume, power, engine speed), modeling assumptions (thermodynamic model used, combustion and heat transfer sub-models), fuels under study and basic parameters examined. The adopted approximation for the fuel chemical availability compared to the lower heating values is also

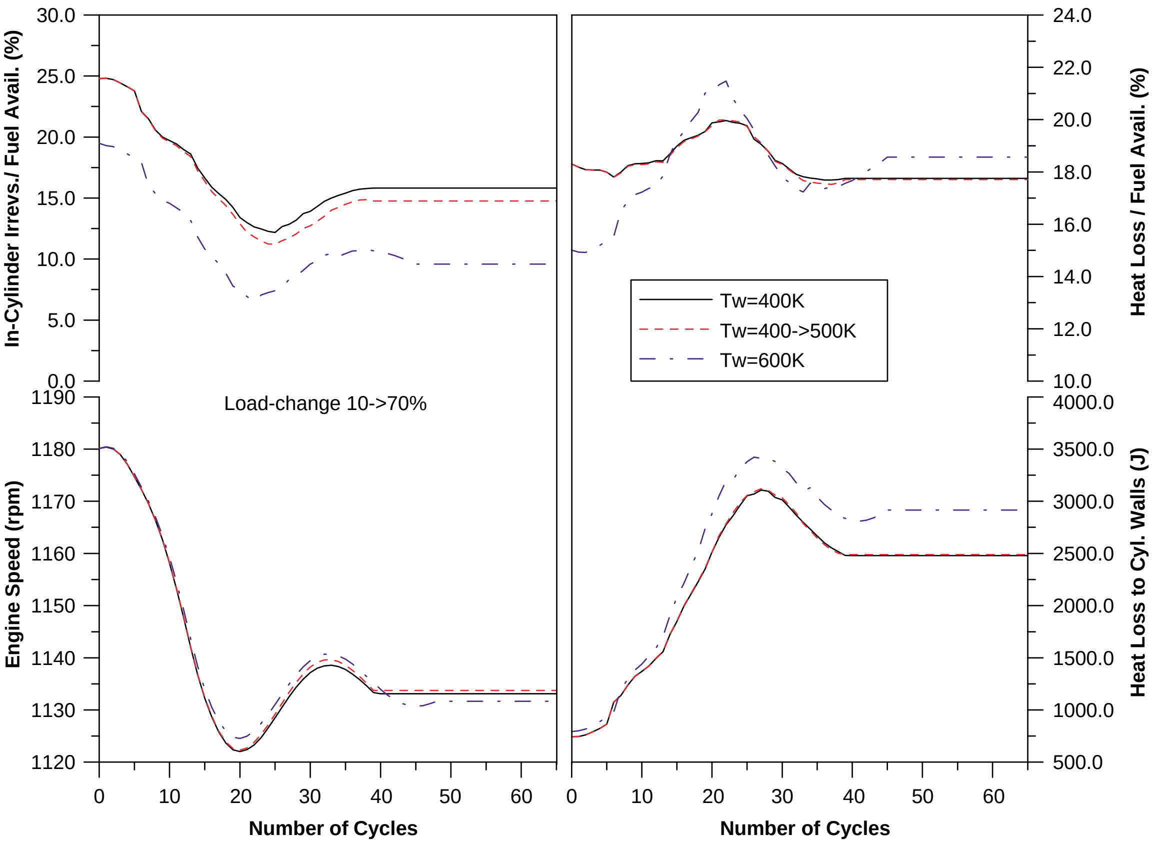

Fig. 23. Effect of cylinder wall temperature on the second-law transient response after a ramp increase in load (16.62 lt, six-cylinder, turbocharged and aftercooled, IDI diesel engine).

given (column R), and whether the particular research group included chemical availability calculations in their study (column S).

Table 7 epitomizes the parametric study conducted by all research groups, for both compression and spark ignition engine operation, giving the most important results of each examined parameter on the basic availability terms (combustion irreversibilities, exhaust gases and heat losses availability, second-law efficiencies).

Finally, Fig. 24 presents typical second-law balances for seven engine configurations, including CI and SI, naturally aspirated and turbocharged engines, and for various fuels used. This table should be used as an indication of the results of the availability balance to the cylinder-engine plant. Since we are dealing here with different engine configurations operating at different conditions, no direct comparison between the displayed results is meant to be implied. However, the reader can assume a sufficiently thorough aspect of the different results obtained when studying different engines/fuels/operating conditions.

11. Summary and conclusions

A detailed survey was presented concerning the works committed so far to the application of the second-law of thermodynamics in internal combustion engines. Detailed equations were given for the evaluation of state properties, the first-law of thermodynamics, fuel chemical availability, the second-law of thermodynamics applied to all engine subsystems and the definition of second-law efficiencies together with explicit examples.

The research in the field of the second-law application to internal combustion engines has covered so far both CI and SI four-stroke engines fundamentally, by also including most of the engine parameters effect. The review of the previous works was categorized in various Subsections, i.e. compression ignition engines (overall analyses and

Table 6
Summary of second-law research (models) in chronological order, incl. engines studied, model assumptions and parameters examined

Research group	Publication	Year	Ignition	Aspiration	Cycles	Cyls	Bore (mm)	Stroke (mm)	Displa-cement (lt)	Power (kW)	@ Speed (rpm)	Systems application	Oper. condit.	Therm. model
A	B	C	D	E	F	G	H	I	J	K	L	M	N	O
Patterson, Van Wylen	SAE	1963	SI	N-A	4	1	100	62.5	0.49	13	2800	Open cycle	St.state	Two-zone
Beretta, Keck	Combust Sci Technol	1983	–	–	4	–	–	–	–	–	–	Open system	St.state	Two–zone
Flynn et al.	SAE	1984	CI—DI	T/C	4	6	140	152	14.03	300	2100	Cylinder, manifolds, T/C	St.state	Single-zone
Primus	SAE	1984	CI—DI	T/C	4	6	140	152	14.03	268	1900	Exhaust manifold, turbine	St.state	Single-zone
Primus et al.	SAE	1984	CI—DI	T/C	4	6	140	152	14.03	185/220	2100	Cylinder, manifolds, T/C	St.state	na
Primus, Flynn	ASME	1986	CI—DI	T/C	4	6	125	136	10.01	224	2100	Cylinder, manifolds, T/C	St.state	Single-zone
Zellat	Entropie	1987	CI	T/C	4	na	570	750	191.3/ cyl	1095/cyl	338	Cylinder, manifolds, T/C	St.state	Overall
Alkidas	ASME	1988	CI—DI	N-A	4	1	130	153	2.03	3.14–33	1200/1800	Open cycle	St.state	Overall
Lior, Rudy	Energy Con-vers Mgmt	1988	SI	–	–	–	–	–	–	–	–	Open cycle	St.state	Ideal cycle
McKinley, Primus	SAE	1988	CI—DI	T/C	4	6	125	136	10.01	224	2100	Cylinder, manifolds, T/C	St.state	Single-zone
Alkidas	SAE	1989	CI—DI	N-A	4	1	130	153	2.03	3.14–33	1200/1800	Open cycle	St.state	Overall
Lipkea, deJoode	SAE	1989	CI—DI	T/C	4	6	na	na	7.60	170	2200	Cylinder, manifolds, T/C	St.state	Multi-zone
Shapiro, vanGerpen	SAE	1989	SI—CI	na	4	1	114	114.3	1.17	na	na	Closed cycle	St.state	Two-zone
Kumar et al.	Intern Comm Heat Mass Transfer	1989	CI—DI	N-A	4	1	100	100	0.79	na	2000	Closed cycle	St.state	Single-zone
van Gerpen, Shapiro	ASME	1990	CI	na	4	1	114	114.3	1.17	na	na	Closed cycle	St.state	Single-zone
Bozza et al.	SAE	1991	CI	T/C	4	4	na	na	1.37	55.6	4500	Cylinder, manifolds, T/C	St.state/ transient	Single-zone

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Table 6 (*continued*)

Research group	Publication	Year	Ignition	Aspiration	Cycles	Cyls	Bore (mm)	Stroke (mm)	Displa-cement (lt)	Power (kW)	@ Speed (rpm)	Systems application	Oper. condit.	Therm. model
A	B	C	D	E	F	G	H	I	J	K	L	M	N	O
Zhecheng et al.	SAE	1991	SI	N-A	4	4	88	82	1.99	76	5500	Closed cycle	St.state	Two-zone
Sato et al.	SAE	1991	SI	N-A	2	1	62	58	0.175	na	2500	Open cycle	St.state	Two-zone
Gallo, Milanez	SAE	1992	SI	N-A	4	1	80	79.5	0.40	na	2000–5200	Open cycle	St.state	Two-zone
Rakopoulos	Energy Convers Mgmt	1993	SI	N-A	4	1	76.2	111.2	0.51	na	2500	Closed cycle	St.state	Single-zone
Rakopoulos, Andritsakis	ASME	1993	CI—DI	N-A	4	1	85.7	82,55	0.48	na	1500–2500	Closed cycle	St.state	Single-zone
			CI—IDI	T/C	5	6	140	180	16.62		1000–1500			
Rakopoulos et al.	Heat Recov Syst CHP	1993	CI—DI	N-A	4	1	85.7	82.55	0.48	na	1500–2500	Closed cycle	St.state	Single-zone
Velasquez, Milanez	SAE	1994	CI—DI	N-A	4	1	105	109	0.94	na	3200	Open cycle	St.state	Single-zone
Li et al.	SAE	1995	CI—IDI	N-A	4	1	95	115	0.81	na	2000	Open cycle	St.state	Single-zone
Alasfour	Appl Them Eng	1997	SI	N-A	4	1	80.2	88.9	0.45	4.9	1700	Open cycle	St.state	Experimental
Rakopoulos, Giakoumis	Appl Them Eng	1997	CI	T/C	4	6	140	180	16.62	236	1500	Cylinder, manifolds, T/C	St.state	Single-zone
Rakopoulos, Giakoumis	Energy	1997	CI	N-A	4	1	76.2	111.2	0.51	na	1350–2250	Cylinder, manifolds	Transi-ent	Single-zone
Rakopoulos, Giakoumis	Energy Con-vers Mgmt	1997	CI—IDI	T/C	4	6	140	180	16.62	236	1500	Cylinder, manifolds, T/C	St.state	Single-zone
Fijalkowksi and Nako-nieczny	Proc Inst Mech Engrs	1997	CI	T/C	4	6	na	na	na	na	2200	Exhaust manifold, turbine	St.state	Method of characteristics
Anderson et al.	SAE	1998	SI—Miller	N-A	4	4	86	86	2.00	6.66	2000	Open cycle	St.state	Two-zone
Caton	ASME Conf.	1999		N-A										
		2000	SI	N-A	4	V8	101.6	88.4	5.73	$\phi = 1$	1400	Open cycle	St.state	Two-zone
Kohany, Sher	SAE	1999	SI	N-A	4	1	60.3	44.4	0.13	2.25	3600	Open cycle	St.state	Two-zone
Caton	Energy	2000	Adiab. Const. Vol.	–	–	–	–	–	–	–	–	Combus-tion	St.state	Single-zone
Caton	SAE	2000	SI	N-A	4	V8	101.6	88.4	5.73	21.9	700–2800	Open cycle	St.state	Two-zone
Kyritsis, Rakopoulos	SAE	2001	CI—DI	N-A	4	1	85.7	82.55	0.48	na	2000	Closed cycle	St.state	Single-zone

Rakopoulos, Kyritsis	Energy	2001	CI—DI	N-A	4	1	85.7	82.55	0.48	na	na	Closed cycle	St.state	Single-zone
Caton	SAE	2002	SI	N-A	4	V8	102	88.4	5.73	21.9	1400	Open cycle	St.state	Three-zone
Nakonieczny	Energy	2002	CI	T/C	4	4	110	120	4.56	52	2850	Exhaust manifold, turbine	St.state	Method of characteristics
Abdelghaffar et al.	ASME	2002	CI	N-A	4	4	91.4	127	3.33	25–152 Nm	1000–2000	Open cycle	St.state	Overall/ experimental
Sobiesiak, Zhang	SAE	2003	SI	N-A	4	V8	93	86.5	4.70	na	4000	Open cycle	St.state	Two-zone
Rakopoulos, Giakoumis	Energy	2004	CI	T/C	4	6	140	180	16.62	236	1500	Cylinder, manifolds, T/C	Transi-ent	Single-zone
Rakopoulos, Giakoumis	SAE	2004	CI	T/C	4	6	140	180	16.62	236	1500	Cylinder, manifolds, T/C	Transi-ent	Single-zone
Parlak	Energy Con-vers Mgmt	2005	CI—IDI	N-A	4	1	76.2	110	0.50	3.1–6.7	1000–2200	Open cycle	St.state	Ideal cycle / experimental
Parlak et al.	Energy Con-vers Mgmt	2005	CI—DI	T/C	4	6	105	114.9	5.94	136	2400	Open cycle	St.state	Experimental
Rakopoulos, Giakoumis	Appl Them Eng	2005	CI—IDI	T/C	4	6	140	180	16.62	236	1500	Open cycle	Transi-ent	Single-zone
Rakopoulos, Giakoumis	SAE	2005	CI—IDI	T/C	4	6	140	180	16.62	236	1500	Open cycle	St.state/ transient	Single-zone
Caton	SAE	2005	SI	N-A	4	V8	101.6	88.4	5.73	$\phi=1$	2500	Open cycle	St.state	Three-zone
Kopac, Kokturk	IJ exergy	2005	SI	N-A	na	na	na	na	na	103–135 Nm	990–3480	Open cycle	St. state	Overall
Özcan, Söylemez	IJ exergy	2005	SI	N-A	4	4	na	na	1.30	na	2000	Closed cycle	St. state	Two-zone
Rakopoulos, Giakoumis	Energy	–	CI	T/C	4	6	140	180	16.62	236	1500	Open cycle	Transi-ent	Single-zone
Rakopoulos, Kyritsis	Hydrogen energy	–	CI—SI	N-A	–	–	–	–	–	–	–	Closed cycle	St.state	Single-zone

Research group	Publication	Year	Combust. model	Heat transfer correlat.	Exper. valid. (1st-law)	a_{fch}/LHV	Chem. Avail.	2nd-law effic.	Parameters and fuels studied	Reference
A	B	C	P	Q	R	S	T	U	V	W
Patterson, Van Wylen	SAE	1963	7 Step spherical burning	Eichelberg	Yes	na	na	No	Fundamental	[63]
Beretta, Keck	Combust Sci Technol	1983	–	Woschni	–	–	–	No	–	[47]
Flynn et al.	SAE	1984	Exp. heat release rate	na	Yes	1.0317	No	No	Fundamental/cylinder wall insulation	[21]
Primus	SAE	1984	Watson	na	No	na	No	No		[66]

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Table 6 (*continued*)

Research group	Publication	Year	Combust. model	Heat transfer correlat.	Exper. valid. (1st-law)	a_{fch}/LHV	Chem. Avail.	2nd-law effic.	Parameters and fuels studied	Reference
A	B	C	P	Q	R	S	T	U	V	W
									Turbine power, efficiency, exhaust valve opening rate, CR, load, speed, ϕ	
Primus et al.	SAE	1984	na	na	Yes	1.0338	No	No	Charge air cooling, turbo-compounding, bottoming cycle	[64]
Primus, Flynn	ASME	1986	Exp. heat release rate	na	Yes	1.0338	No	No	Fundamental/ϕ, inlet manif. temper., inj. timing, exh.manif. diameter	[59]
Zellat	Entropie	1987			–	1.035	No	No	Volume, efficiency, aftercooling, turbo-compounding, insulation	[57]
Alkidas	ASME	1988			Yes	na	No	Yes	Fundamental	[22]
Lior, Rudy	Energy Convers Mgmt	1988	–	–	No	na	na	Yes	ϕ, CR	[36]
McKinley, Primus	SAE	1988	Watson	na	–	na	No	No	Waste gate, VGT, resonant intake system, turbine area	[65]
Alkidas	SAE	1989			–	1.02	No	Yes	Insulation	[58]
Lipkea, deJoode	SAE	1989	unsteady jet mixing w. one step global fuel kinetics	na	Yes	Eq. (24)	Yes	Yes	Fundamental/different engines	[23]
Shapiro, vanGerpen	SAE	1989	Watson model (CI), sinusoidal burn. rate (SI)	Annand	na	na	Yes	No	Fundamental/combustion duration, ϕ, residual fraction	[28]
Kumar et al.	Intern Comm Heat Mass Transfer	1989	arbitrary heat release [5]	turbulent/instant. local coeffs	No	na	na	No	–	[67]
van Gerpen, Shapiro	ASME	1990	Watson	Annand	na	na	Yes	No	Fundamental/combustion timing, heat release shape, heat transfer coefficients	[24]
Bozza et al.	SAE	1991	Watson	Annand	Yes	Eq. (22)	No	Yes	Ignition delay, turbocharger speed, ϕ, exhaust valve opening	[27]
Zhecheng et al.	SAE	1991	Wiebe	Woschni	Yes	na	na	No	Combustion duration, spark timing, spark plug position, insulation, CR	[78]
Sato et al.	SAE	1991	na	na	Yes	na	na	Yes	–	[79]
Gallo, Milanez	SAE	1992	Wiebe	Hohenberg	No	na	Yes	Yes	Ign. timing, comb. duration, shape of heat release curve, speed, valve overlap—ethanol	[61]
Rakopoulos	Energy Convers Mgmt	1993	polynomial	Annand	Yes	1.0338	No	Yes	CR, ϕ, ignition advance	[80]
Rakopoulos, Andritsakis	ASME	1993	W–W	Annand	Yes	Eq. (21)	No	No	Load, speed	[25]

Rakopoulos et al.	Heat Recov Syst CHP	1993	Wiebe	Annand	Yes	na	No	No	Load, speed, injection timing, insulation	[70]
Velasquez, Milanez	SAE	1994	Wiebe	Woschni	No	na	Yes	Yes	–	[71]
Li et al.	SAE	1995	Exp. heat release rate	Reynolds	Yes	1.0338	No	No	DI engine, adiabatic oper., throat	[72]
Alasfour	Appl Them Eng	1997			–	1.0338	Yes	Yes	Butanol	[39]
Rakopoulos, Giakoumis	Appl Them Eng	1997	W–W	Annand	Yes	1.0645	No	No	Speed, load, CR	[73]
Rakopoulos, Giakoumis	Energy	1997	W–W	Annand	Yes (ss)—No (tr.)	1.0645	No	No	Load/speed change magnitude, heat transfer coeffs	[97]
Rakopoulos, Giakoumis	Energy Convers Mgmt	1997	W–W	Annand	Yes	1.0645	No	Yes	Fundamental	[48]
Fijalkowksi and Nakonieczny	Proc Inst Mech Engrs	1997			No	–	na	No	–	[60]
Anderson et al.	SAE	1998	turbulent-flame entrainment process	turbulent/convection	No	Eq. (26)	na	Yes	Load, different engines	[81]
Caton	ASME Conf.	1999								[84]
		2000	Wiebe	Woschni	Yes	1.0286	No	No	Wiebe burning law parameters	[85]
Kohany, Sher	SAE	1999	Wiebe	Annand	Yes	na	na	No	Port timing	[82]
Caton	Energy	2000	adiabatic	–	–	1.0286	No	No	Fundamental/ϕ, pressure and temperature of combustion	[53]
Caton	SAE	2000	Wiebe	Woschni	Yes	1.0286	No	No	Speed, load	[83]
Kyritsis, Rakopoulos	SAE	2001	Wiebe	Annand	No	Eq. (21)	Yes	Yes	ϕ, Speed, injection timing—methane, methanol	[69]
Rakopoulos, Kyritsis	Energy	2001	Wiebe	Annand	No	Eq. (21)	Yes	Yes	Methane, methanol	[93]
Caton	SAE	2002	Wiebe	Woschni	No	1.0286	No	No	fundamental	[38]
Nakonieczny	Energy	2002			No	na	na	No	Waste gate, turbine effective area ratio, valve overlap, charge air cooling, air pipe length, IVC, EVO	[87]
Abdelghaffar et al.	ASME	2002			–	na	na	Yes	Coolant temperature	[75]
Sobiesiak, Zhang	SAE	2003	Wiebe	Woschni	Yes	na	Yes	No	CNG	[54]
Rakopoulos, Giakoumis	Energy	2004	W–W	Annand	Yes	1.0645	No	No	Fundamental	[26]
Rakopoulos, Giakoumis	SAE	2004	W–W	Annand	Yes	1.0645	No	No	Load, T/C inertia, exh.manif. volume, wall temp., A/C effectiveness, loadtype	[98]
Parlak	Energy Convers Mgmt	2005			–	na	Yes	Yes	CR, injection timing, wall insulation	[74]
Parlak et al.	Energy Convers Mgmt	2005			–	na	Yes	Yes	Cylinder wall insulation, injection timing	[40]

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Table 6 (*continued*)

Research group	Publication	Year	Combust. model	Heat transfer correlat.	Exper. valid. (1st-law)	a_{fch}/LHV	Chem. Avail.	2nd-law effic.	Parameters and fuels studied	Reference
A	B	C	P	Q	R	S	T	U	V	W
Rakopoulos, Giakoumis	Appl Them Eng	2005	W–W	Annand	Yes	1.0645	No	No	Cylinder wall insulation	[92]
Rakopoulos, Giakoumis	SAE	2005	W–W	Annand	Yes	1.0645	No	No	Injection timing, prechamber volume, load	[55]
Caton	SAE	2005	Wiebe	Woschni	Yes	1.0286	No	No	Oxygen enrichment	[95]
Kopac, Kokturk	IJ exergy	2005			–	Eq. (22)	Yes	Yes	Speed	[86]
Özcan, Söylemez	IJ exergy	2005	Wiebe exper. HRR	na	–	1.0659	No	No	Water addition, LPG	[96]
Rakopoulos, Giakoumis	Energy	2006	W–W	Annand	Yes	1.0645	No	No	T/C inertia, load-type, exh.manifold volume, wall temper, A/C effectiveness,	[99]
Rakopoulos, Kyritsis	Hydrogen energy	2006	Wiebe	Annand	No	Eq. (21)	Yes	Yes	Hydrogen enrichment—CNG, LFG	[94]

N-A, naturally aspirated; IVC, intake valve closure; W-W, Whitehouse-Way; HRR, Heat release rate; na, not available; EVO, exhaust valve opening; VGT, variable geometry turbine.

phenomenological models—direct and indirect injection), spark ignition engines, engine subsystems, low heat rejection, alternative fuels, and transient operation. Typical tables were given presenting the first- and second-law efficiency analyses of various engine configurations studied, where the different magnitude that the second-law attributes to the engine processes was highlighted. Moreover, diagrams showing the effect of some important (thermodynamic and design) parameters on the second-law performance of the engine were given.

A tabulation of the details of each work reviewed as well as a table summarizing the effect of each parameter on the engine availability balances were also provided. The latter can be used as a useful guide since it reveals that particular engine design parameters exist, the effect of which on the second-law performance of the engine can be significant, i.e. wall insulation, pre-chamber volume, aftercooling, alternative fuels, etc. Of course, even with energy analysis, first-law modeling will be needed in order for any aspects of the availability analysis to be utilized for optimization.

The second-law analysis provides a more critical and thorough insight into the engine processes by defining the term of availability destruction or irreversibilities and assigning different magnitude to the exhaust gases and heat losses terms. By so doing, it spots specific engine processes and parameters, which can improve the engine performance by affecting engine or subsystems irreversibilities and the availability terms associated with the exhaust gases (to ambient) and heat losses to the cylinder walls. Most of the analyses so far have focused on the dominant combustion irreversibilities term. It was shown that combustion duration, heat release shape, i.e. premixed burning fraction, and injection timing only marginally affect combustion irreversibilities (although the latter's impact on work, heat transfer and exhaust gases availability is significant), the combustion irreversibility production rate is a function of fuel reaction rate only, and also an increasing pre-chamber volume increases the amount of total combustion irreversibilities.

All the parameters which increase the level of pressures and (mainly) temperatures in the cylinder, i.e. fuel–air equivalence ratio, compression ratio, cylinder wall insulation, increased turbocharging, etc. lead to a reduction in the combustion irreversibilities (reduced to the fuel chemical availability).

Unfortunately, this decrease in availability destruction cannot always be realized as an increase in brake

Table 7
Summary of second-law research (models) in chronological order, incl. engines studied, model assumptions and parameters examined

Parameter	**Ignition**	**Effect** (when increasing parameter value)	**Reference**
Cylinder wall insulation	**Compression ignition engines**	Decreases combustion irreversibilities (%), increases heat transfer to the walls and exhaust gases availability (%)	[21], [40], [57], [58], [69], [74], [75], [92], [98], [99]
Injection timing		Slight effect on total irreversibilities, significant effect on availability rates (optimum value exists), slight effect on prechamber irreversibilities	[24], [27], [40], [55], [59], [69], [70], [74]
Combustion duration		Slight effect on total irreversibilities	[28]
Heat trasfer coefficients		Decreases exhaust gases availability, increases heat trasfer availability	[24], [70], [97]
Heat release shape		Affects irreversibility rate, no effect on total irreversibilities	[24]
Load (Φ)		Decreases combustion irreversibilities (%), increases exhaust gases and heat transfer availability (%), affects the distribution between chemical and thermomechanical availability, decreases prechamber irreversibilities (%), increases T/C irreversibilities (%)	[25], [27], [28], [55], [59], [66], [69], [70], [73], [98], [99]
Speed		INCREASES irreversibilities and exhaust gas availability (%), increases T/C irreversibilities (%), decreases heat loss availability, no effect on exhaust manifold irreversibilities	[25], [69], [70], [73]
Prechamber volume		Increases prechamber and total irreversibilities	[55]
Turbocompounding		Increases exhaust manifold losses, reduces cylinder brake work, increases turbine work (optimum)	[57], [64]
Aftercooling		Increases combustion irreversibilities (%), decreases cylinder heat loss availability (%)	[57], [64], [98], [99]
Inlet manifold temperature		Increases cyl. heat loss availability (%), decreases combustion irreversibilities (%)	[59]
Exhaust manifold volume		Decreases transient combustion irreversibilities (%)	[98], [99]
Turbocharger moment of inertia		Decreases transient combustion irreversibilities (%)	[98], [99]
Turbine area		Optimum value for minimizing combustion irreversibilities	[64]
Waste gate		Increases fuel economy	[64]
Variable geometry turbine		Improves fuel consumption	[64]
Resonant intake system		Slight increase in fuel economy	[65]
Methane		Decreases combustion irreversibilities	[69], [93]
Methanol		Decreases combustion irreversibilities	[69], [93]
Hydrogen enrichment		Optimum value for minimizing combustion irreversibilities	[94]
Compression ratio		Decreases combustion and turbocharger irreversibilities (%), increases cyl. heat loss and exhaust gas availabilities	[66], [74]
Ignition timing	**Spark ignition engines**	Slight effect on total combustion irreversibilities	[61], [78], [80]
Combustion duration		Slight effect on total irreversibilities	[28], [61], [78], [85]
Load		Slight effect on combustion and mixing irreversibilities, decreases heat loss availability (%), increases exhaust gases availability (%)	[80], [82]
Φ (fuel–air equivalence ratio)		Changes distribution between chemical and thermomechanical availability	[36], [80]
Speed		Decreases heat loss availability (%), increases exhaust gases availability (%), slight effect on combustion and mixing irreversibilities	[61], [83], [86]
Insulation		Decreases combustion irreversibilities (%) and cooling water availability (%), increases exhaust gas availability (%)	[78]
Spark plug position		Slight effect on engine efficiency	[78]
Compression ratio		Increases second-law efficiency	[36], [78], [80]
CNG		Decreases heat transfer irreversibilities (%)	[54]
Ethanol		Increases second-law efficiency, decreases combustion irreversibilities	[61]
Butanol		Decreases second-law efficiency	[39]
Oxygen enrichment		Decreases combustion irreversibilities (%)	[95]
Water addition		Increases combustion irreversibilities (%)	[96]

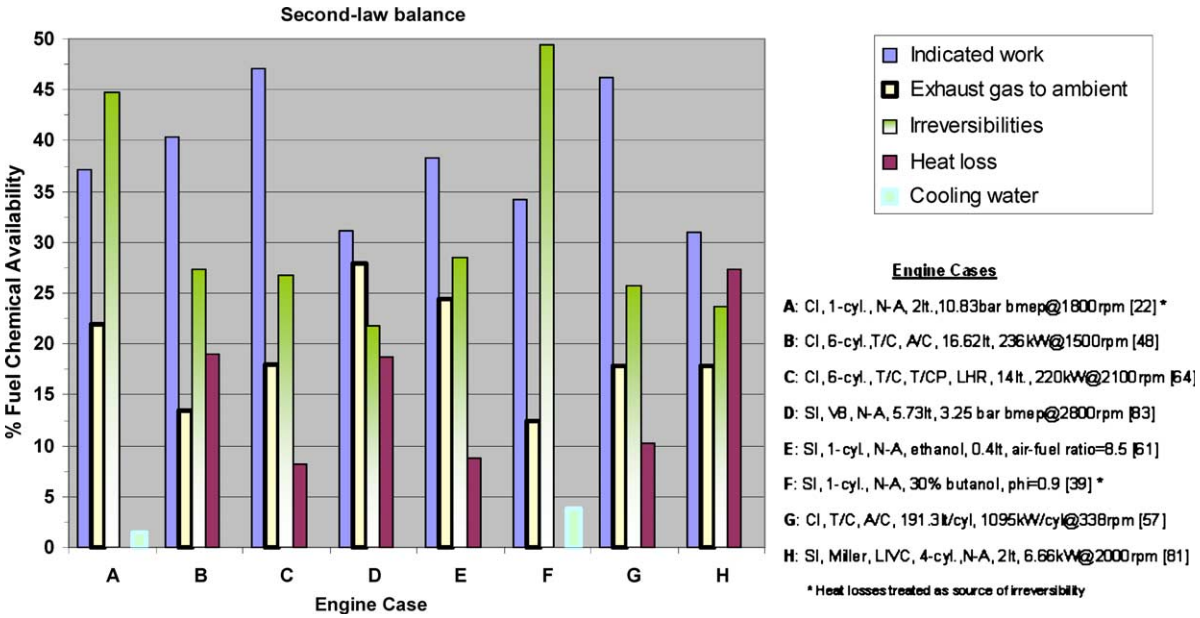

Fig. 24. Second-law balances for various engine-fuel configurations.

power. On the contrary, it is usually transformed into an increase in the heat transfer to the cylinder walls and/or increase in the exhaust gases availability. The recovery of these energy streams that are now usually ignored (e.g. through the use of heat recovery devices or bottoming cycles), is an important subject whose exploitation needs to be established and implemented. At the moment, the heat transfer from the hot cylinder walls to the cooling water, being at a very low temperature, destroys the greatest part of this available energy.

Turbocharging, on the other hand, proves a favorable second-law process increasing the amount of the exhaust gas, which is utilized in order to increase engine power.

Significant amounts of work potential through exploitation of increased heat transfer losses and exhaust gases to ambient can be realized during transient operation after a ramp increase in load.

An interesting aspect is the use/effect of alternative fuels, which seems to gain universal interest in the last years. Some interesting results have been obtained from this field when the second-law balance is applied. For example, the decomposition of lighter fuels (e.g. methane or methanol) molecules during chemical reaction creates lower entropy generation than the larger *n*-dodecane molecule. All in all, ethanol, methane, methanol, oxygen enrichment and CNG prove favorable from the second-law perspective, whereas water addition and butanol increase the (spark ignition engine) combustion irreversibilities and are, thus, not recommended. More results on the subject of alternative fuels are expected in the following years in order for the abovementioned findings to be confirmed and, possibly, enhanced.

Furthermore, it is believed that engine operation optimization based on the second-law of thermodynamics can serve as a powerful tool (together with the first-law modeling) to the engine designer.

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