Exergy calculations based on a fixed standard reference environment versus the actual ambient conditions: Gas turbine and fuel cell examples

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Abstract: Two approaches for calculating exergy values were compared: One based on the actual local temperature, pressure and relative humidity, and one based on fixed reference conditions of 25ºC, 1 atm and 70% relative humidity. In the former exergy values represent the actual potential of the system, while the latter is chosen by some commercial software. The objective was to investigate to which degree the choice of environment influences on the results of the exergy analysis. For power plants and chemical conversion, the effects were modest with respect to overall efficiency (which however can be assessed without exergy). Details of the exergy analysis were, however, influenced by the choice of environment. Irreversibilities (exergy destruction) and flow exergies were more affected, and the distribution of exergy losses between irreversibility and discharge was different. For elevations above sea level, the flow exergies can get negative values.

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1 Introduction

Exergy analysis can be used to evaluate and compare energy systems. An important outcome of such analyses is the identification and quantification of thermodynamic losses. This knowledge can guide designers to optimize the systems. Exergy is the reversible work obtainable when bringing a flow or a system into equilibrium with the surrounding environment, that is, the maximum work obtainable. Alternatively, this can be regarded as the minimum work required to bring a flow or system to a certain state.

The local atmosphere is often the obvious surroundings, although the ocean and the Earth's crust also can be relevant. The definition of the environment has been discussed and different views have been held (reviews by e.g. Szargut et al. (1988), Gallo and Milanez (1990), Ertesvåg (2007) and Torio et al. (2009)). The state of the atmospheric air is determined by the temperature, pressure and relative humidity. These properties change with local climate, seasons, time of the day and weather conditions, and with elevation. In some parts of the World, the temperature can be −50 °C, while other regions experience above +50 °C. The saturation pressure of water vapour follows an exponential relation with temperature, and therefore, the local moisture content shows great variation. At sea level, the atmospheric pressure varies around the normal value of 1.013 bar with 0.05-0.10 bar due to weather conditions. At locations 3000 m above sea level, the normal pressure is 0.70 bar, and for an aircraft at 15000 m, the pressure is approximately 0.12 bar (ISO, 1975).

Although the state of the environment changes with time and location, it is important to note that it is not influenced by the processes that are analysed.

From one point of view, it seems obvious that "equilibrium with environment" should mean the instantaneous local conditions.

An alternative approach is to conduct exergy analyses on the basis of a fixed standard reference environment, pre-defined and independent of the actual ambient conditions. The standard reference conditions can, for instance, be 25 °C, 1 atm and 70% relative humidity (RH), as used for tabulated data e.g. by Szargut et al. (1988), or 15 °C, 1 atm and 60% RH, as prescribed for gas-turbine testing (ISO, 1989). The latter approach of a fixed, standard reference is followed by some authors. It is also implemented in some commercially available software, either as the only alternative or as the default option. With this approach, both the development of the simulator code and the operational calculations become simpler.

Quite a few investigations have been made on the effects of changing ambient temperatures for a variety of thermal systems. Examples include Ertesvåg et al. (2005), Utlu and Hepbasli (2008), Aljundi (2009), Alasfour et al. (2011), Acır et al. (2012), Anozie and Odejobi (2013). Also some investigations have been made on systems with changed ambient pressure (altitude), for instance Turgut et al. (2007) and Turan (2012), and with changed ambient humidity, Saravanan et al. (2008), Alasfour et al. (2011). In these studies, the exergy calculations were made with respect to a varying local environment. In some other analyses, exergy calculations are made with respect to a fixed environmental state, even when changes are investigated (Agudelo et al., 2009; Benjumena et al., 2009). The question that can then be raised is: Which consequences do such choices have for the results of the analysis? For relevant conditions deviating from those of the chosen environment, will there be notable or significant differences in the results of the two approaches? The aim of this study was to shed some light on these issues.

The studies by Rosen and Dincer (2004) of a coal-fired power plant, and by Etele and Rosen (2001) and Rosen (2009) of a turbojet engine, seem to be the only investigations published in archival journals of the effect of the choice of environment for exergy calculations. Rosen and Dincer (2004) concluded that the main results of energy and exergy analyses are usually not significantly sensitive to reasonable variations in the dead-state properties. A coal-fired (actually carbon fired) electric power plant was used as the illustrative case. The base case at

ambient temperature of 15 ºC was also analysed with exergy calculated with respect to dead state temperatures of 5 ºC and 25 ºC.

Etele and Rosen (2001) investigated the effects of the state of the environment on exergy losses of a turbojet, and the study was continued by Rosen (2009). They considered two fixed environments, air state at sea level and at 15000 m, and the ambient conditions varying between these two states. It was concluded that the exergy loss results were significantly affected by the choice of environment, with differences up to 28% for individual components.

The present study was explicitly triggered by the observation that a commercial simulator applied a fixed reference environment for its exergy calculations and that no other options were available. Later we found that this simulator was not unique in that matter.

Here, exergy analyses are conducted for some systems at different ambient conditions. Each case is analysed both on the basis of the actual local environment and on the basis of a fixed reference environment, and the results are compared. The systems chosen for this study were a general combustor, two gas turbine (GT) cycles and a simplified fuel cell system. The purpose of the analyses of these well-known systems was to investigate the effect of the choice of environment for exergy calculations. All systems were analysed with a range of ambient temperatures, relative humidity and pressure. A preliminary discussion was presented at ECOS 2011 (Ertesvåg, 2011).

The present study differs from the existing above mentioned three studies by investigating the effects of atmospheric humidity, the effects of ambient pressure (altitudes) for stationary power plants, and of the effects of a wider range of ambient temperature. Moreover, the chemical exergies were calculated with a full dependency on the chosen environment, which means that the sensitivity of chemical exergy to the choice of environmental conditions was included in the results.

The aim of the study was to investigate the differences between exergy calculations made with respect to the local ambient conditions and those made with respect to a fixed environment.

In the following, the theory of exergy calculations is reviewed for the purpose of the study. General aspects of exergy calculations with respect to the two approaches are outlined. Then the exemplary systems are studied, the results are discussed and some conclusions are made.

2 Theory

The theory of exergy is well know from publications and textbooks. Here, some key expressions are shown for later reference in the paper.

The molar exergy of a material flow can be split into chemical exergy and thermomechanical flow exergy,

$$\varepsilon = \varepsilon^{\text{ch}} + \varepsilon^{\text{tm}} = \varepsilon^{\text{ch}} + (h - h_0) - T_0(s - s_0), \tag{1}$$

where subscripts ch and tm, respectively, denote chemical and thermomechanical exergy, h and s are the molar enthalpy and entropy, respectively, of the flowing matter, while

$h_0 = h(T_0, p_0)$ and $s_0 = s(T_0, p_0)$. Here, potential and kinetic energy (exergy) are left out. The exergy is determined relative to the environmental state of temperature T_0 and pressure p_0.

For some purposes, a decomposition of the thermomechanical exergy into temperature and pressure components (Kotas, 1986) can be useful

$$\varepsilon^{\text{tm},T} = (h(T, p) - h(T_0, p)) - T_0(s(T, p) - s(T_0, p)) \tag{2}$$

and

$$\varepsilon^{\text{tm},p} = (h(T_0, p) - h(T_0, p_0)) - T_0(s(T_0, p) - s(T_0, p_0)). \tag{3}$$

For the chemical exergy, a reference composition of the atmosphere has to be defined. Since the dry-air composition is very close to invariant, the environment can be defined by the relative humidity (RH), φ.

The molar chemical exergy of an atmospheric gas is expressed as

$$\varepsilon_i^{\text{ch}} = -RT_0 \ln X_i^e, \tag{4}$$

where R is the universal gas constant and X_i^e is the atmospheric mole fraction of the gas. This is equal to the work obtained from a reversible, isothermal (at T_0) expansion from atmospheric pressure (p_0) to the atmospheric partial pressure $(p_i^e = X_i^e p_0)$. For a substance $C_aH_bO_c$, the chemical exergy at a certain state can be expressed (Szargut et al., 1988; Ertesvåg, 2007) as

$$\varepsilon_i^{\text{ch}} = -\Delta G^{\text{ref}} + (T_{\text{ref}} - T_0)(-\Delta S^{\text{ref}}) + W_1 + W_2 + \sum_{j \neq i} \nu_j \varepsilon_j^{\text{ch}}, \tag{5}$$

where ΔG^{ref} and ΔS^{ref} are the Gibbs-energy and entropy differences for the reaction where the substance reacts to products found in the atmosphere, superscript ref denotes that data are taken at a standard reference state $(T_{\text{ref}}, p_{\text{ref}})$, ν_j are the reaction coefficients of the involved species (negative for reactants) and the terms of Eq. (5) are expressed[1] as

$$W_1 = -\sum_j \nu_j \int_{T_{\text{ref}}}^{T_0} c_{p,j}(T)(1 - \frac{T_0}{T})dT, \tag{6}$$

$$W_2 = -T_0 R \sum_j \nu_{j,\text{gas}} \ln \frac{p_0}{p_{\text{ref}}}. \tag{7}$$

The subscript "gas" here denotes that only the gaseous species of the reaction follow this expression. A solid or liquid, incompressible fuel has no contribution to the term in Eq. (7). It has been shown (Ertesvåg, 2007) that the chemical exergies of atmospheric gases, H_2 and hydrocarbons have significant variation with the ambient conditions.

For an ideal mixture, the molar chemical exergy can be expressed as

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[1] It can be noticed that the minus signs of Eqs. (6)-(7) by an error were left out in Ertesvåg (2007). In the calculations, however, the signs were correct.

$$\varepsilon_{\text{mix}}^{\text{ch}} = \sum_i X_i \varepsilon_i^{\text{ch}} + RT_0 \sum_i X_i \ln X_i. \tag{8}$$

Here, the molar chemical exergy of each individual component is expressed from either Eq. (4) or Eq. (5), and X_i is its mole fraction in the mixture. The rate of flow exergy of a stream (No. k) is the product of the molar flow rate n_k and the molar flow exergy of the stream, $E_k = n_k \varepsilon_k$. For a steady-state steady-flow (sub-)system, an exergy balance can be put up and the irreversibility (exergy destruction) can be calculated when all involved streams are known.

The environment is the non-immediate surroundings of the process or system, and its state is not affected by energy or mass exchange with the system. The conditions of the environment are defined by temperature T_0, pressure p_0 and relative humidity φ^e. When the system is in equilibrium with the environment, it is said to be in dead state.

Two approaches for defining the state of the environment will be compared in the following. In the first, the actual local ambient state will be used. Hence, T_0, p_0 and φ^e, respectively, will be equal to the temperature, pressure and RH of the ambient air, T_{amb}, p_{amb} and φ_{amb}. The local ambient conditions can have seasonal, diurnal and weather variations, but are not affected by the system that is investigated.

In the alternative approach, the state of the environment will be defined to be a fixed reference state, T_{fix}, p_{fix} and φ_{fix}. Here, the temperature and pressure were taken equal to those of the chemistry standard reference state (25 ºC, 1 atm) for which tabulated quantities are available, for instance as used in Eq. (5), and the RH was set to 70% following Szargut et al. (1988). However, the fixed reference state could be chosen in accordance with some other standard state, such as industrial standards (e.g. ISO (1989) specifies a standard of 15 ºC, 1 atm, 60% RH).

3   General considerations on exergy and irreversibility

3.1   *Assumptions and procedures*

Dry air had a composition (molar basis) of 78.0840 % N_2, 20.9415% O_2, 0.0375 % CO_2, 0.9370% Ar. All air flows were composed of this dry air together with an amount of water vapour specified in terms of the relative humidity and temperature. The dry air composition was based on the ISO (and US) standard atmosphere (ISO, 1975; Linde, 1999) with the following modifications, cf. Ertesvåg (2007): CO_2 is increased on the cost of O_2, and all other minor components were represented by Ar. Enthalpy and entropy differences for gases and gas mixtures were calculated by integrating temperature functions of species specific heats (Moran and Shapiro, 1998; Sonntag and Van Wylen, 1982). For the GT and SOFC systems, the latter reference was used since these had temperatures above 1000 K.

Chemical exergies for varying environmental conditions were calculated with the model described above. The values and sources of thermochemical data used by Ertesvåg (2007) were also used here: molar masses, specific heats, water/steam saturation pressures, specific

volumes, enthalpies and entropies, enthalpies of formation and absolute entropies. The lower heating values (LHV) were calculated with reference to the chosen environmental temperature. The ambient and fixed reference temperatures gave a difference in LHV, however small cf. Ertesvåg (2007), ISO (1996).

All systems presented here were assumed to be steady-state, steady flow and were computed in a spreadsheet. When required, iterative solutions were obtained with the "solver" function of the spreadsheet (MS Office Excel 2010).

A Base Case was defined for each system at an air temperature 25 ºC, pressure 1.01325 bar (1 atm) and 70% relative humidity (RH). The state of the ambient air was then varied from −30 ºC to 55 ºC for three series of 10%, 70% and 90% RH, respectively. For each of these cases, the appropriate calculations based on elements, mass and energy were made. Next, the exergy analysis was conducted on the basis of the actual ambient conditions. Calculations were then repeated for the same case using the fixed reference conditions (25 ºC, 1 atm, 70% RH). Finally, the two approaches of exergy analysis for each case were compared.

For presentation purposes, a relative deviation was defined as

$$\mathrm{RD}_A = (A_{\mathrm{fix}} - A_{\mathrm{amb}}) / A_{\mathrm{amb}} . \tag{9}$$

Here, A is any relevant exergetic quantity, e.g. a rate of flow exergy or an efficiency. The subscript "fix" denotes that it is determined on the basis of the fixed reference state (25 ºC, 1 atm, 70% RH), and "amb" denotes that the quantity A is determined with respect to the actual ambient state (T_{amb}, p_{amb}, φ_{amb}).

The moisture content of air can be specified as a partial pressure, as a humidity ratio (mass of vapour divided by mass of dry air) or as a relative humidity. Within the range of conditions investigated here, the humidity ratio and partial pressure show variations over 3-4 orders of magnitude, and these quantities cannot be held constant within a variation of temperature. On the other hand, most realistic cases have relative humidities within one order of magnitude.

3.2 *Irreversibility*

The entropy production of a (sub-)system with given condition will not be affected by the choice of environment. The irreversibility then depends linearly on the environmental temperature. Furthermore, the ratios of irreversibilities of different subsystems will be proportional to the ratios of entropy productions, and hence, not affected by the environmental temperature.

The relative deviation (Eq. (9)) of an irreversibility rate I can be expressed as

$$\mathrm{RD}_I = T_{\mathrm{fix}} / T_{\mathrm{amb}} - 1 . \tag{10}$$

For a fixed reference temperature of 25 ºC, this relation produces a nearly linear (slightly concave) curve from 22.6% to −9.1%, as shown in Fig. 1, when the ambient temperature is varied from −30 ºC to 55 ºC. The relation is also shown for a fixed reference temperature of 5 ºC. The deviation increased by 1% for each 3 K of reduced ambient temperature.

3.3 *Flow exergy components*

Temperature component of thermomechanical exergy

The thermomechanical exergy for an air flow is shown in Fig. 2 for air-flow temperatures varying from –100 ºC to 800 ºC for two air-flow pressures (1 atm and 25 atm), Eq. (2). The composition of the air was constant and equal to that at the ambient conditions of 0 ºC, 1 atm and 70% RH. The exergy calculations were made with respect to ambient conditions ("amb") and with respect to the fixed reference of 25 ºC, 1 atm ("fix"). The relative differences were the largest near the ambient and fixed-reference temperatures. However, even at 800 ºC (1 atm) the relative deviation was 8%. A relative deviation of 50% between the two approaches was seen at approximately –100 ºC and 90 ºC.

Pressure component of thermomechanical exergy

The pressure component (Eq. (3)) depends both on the temperature and pressure of the environment. For the cases shown in Fig. 2, the ambient pressure was 1 atm. For the flow at a pressure of 25 atm, the pressure component thermomechanical exergy was 7310 kJ/kmol and 7979 kJ/kmol, respectively, in the "amb" and "fix" approaches.

Fig. 3 shows the variation of the thermomechanical exergy of a flow at varied pressure and a constant environmental temperature of 25 ºC, Eq. (3). The ambient air pressure was 0.7 bar. This corresponded to an elevation of 3012 m according to the ISO (1975) standard atmosphere. The two curves represent the exergy calculated with respect to the ambient pressure of 0.7 bar ("amb") and with respect to the fixed reference pressure of 1 atm ("fix"). It can be noted that in the latter approach, the exergy of a gas flow at ambient pressure is negative.

Chemical exergy

Chemical exergy for various temperature, pressure and relative humidity was investigated by Ertesvåg (2007) for atmospheric gases and some fuels. The variations were considerable for hydrogen and atmospheric gases. Also for light hydrocarbons, the variations were significant.

Fig. 4 shows the relative deviation of chemical exergy according to Eq. (9) for solid carbon and liquid n-dodecane at ambient conditions of 1 atm, 70% relative humidity and varied temperature. Hydrogen and methane from Ertesvåg (2007) were included in the graph for comparison. Notice that the relative deviation defined by Ertesvåg (2007) is different from Eq. (9). The former focused on the deviation from the standard reference conditions, whereas the present focus on deviation from the ambient conditions. The chemical exergy of solid carbon was not affected by the pressure or humidity of the atmosphere. The effects for dodecane were modest: RD was reduced by approximately 0.2 % points at 0.35 bar atmospheric pressure and by approximately 0.1 % points at 10% RH.

4 Exemplary process calculations

4.1 *Combustor*

The changes of chemical exergy over a combustor for hydrogen, CO and some light hydrocarbons were investigated previously by Ertesvåg (2007). The inflows are separate streams of fuel and atmospheric air, while the exit is the flue gas mixture. All three flows are at ambient temperature and pressure, and the air has the ambient humidity.

For dodecane the change was not more than approximately 0.3% below the chemical exergy of the fuel at stoichiometric combustion. The relative deviation (Eq.(9)) of the change at varied ambient temperature followed that of the fuel chemical exergy. Ambient moisture had only small effects, while reduced ambient pressure lowered the value of the relative deviation. For ambient conditions of 0.3 bar, 25 ℃, 70% relative humidity, the relative deviation was − 0.2% for stoichiometric, complete combustion.

For a carbon combustor, the change of chemical exergy showed almost no variation. The change at 1 atm, 25 ℃, 70% and stoichiometric combustion was 96.2% of the fuel chemical exergy. The change was not affected by ambient pressure or humidity. Moreover, unlike the fuel chemical exergy, there was almost no effect of the ambient temperature on the change over the combustor.

4.2 *Simple gas-turbine power plant cycle*

The flow sheet of the simple gas turbine cycle is shown in Fig. 5. Atmospheric air (1) is compressed (2), heated (3) by the exhaust, ducted to the combustor where it is mixed with fuel (4). After combustion, the exhaust (5) is expanded through the turbine to atmospheric pressure (6), cooled by the air flow in the regenerator and rejected (7) to the atmosphere.

For the power plant, the fuel (4), pure methane, was available at pressure 60 bar and throttled into the combustor. The fuel temperature was set equal to the air temperature ($T_4 = T_1$). Pressure losses, except throttling of the fuel, were neglected. Hence, stream Nos. 1, 6 and 7 had atmospheric pressure and, stream Nos. 2, 3 and 5 had the pressure of the compressor outlet. All units were assumed adiabatic, and combustion was assumed complete. The pressure ratio was set to 20, and the isentropic efficiencies of compressor and turbine were set to 0.85. The turbine inlet temperature (T_5) was fixed to 1210 ℃, and the effectiveness of the recuperative heat exchanger was set to 70%.

The non-specified temperatures and flows of the system were solved iteratively from the energy balance: First the air flow (per kg of fuel), then the temperatures of stream 6 and of stream 7. The relative residues of the energy balances were 10^{-7} or less. The compositions and exergy flows of all streams, and the irreversibilities of the four units, were determined.

Table 1 shows results for the Base Case. The air excess ratio for this case was λ=3.33. When varying the atmospheric temperature from −30 ℃ to 55 ℃ and the relative humidity from 10% to 90%, the work produced per mole of fuel varied from 120% to 88% of that obtained in the Base Case. In the same variation, the chemical exergy based on actual ambient conditions

showed a variation of 102.5%-99.1%. The exergy efficiency, $\psi = W / E_4$, for the cases of 10% and 90% RH are presented in Fig. 6a. Results for 70% fell between the series shown and was left out for clarity. The relative deviation (RD) for the exergy efficiency is shown for all cases in Fig. 6b. The deviation increased by 0.1% for each 4 K of reduced ambient temperature. The relative deviations of the irreversibilities followed closely Eq. (10), although not exactly, since different references also have a small effect on the fuel heating value and hence, mass flows.

Fig. 7 shows the distribution of the supplied exergy into produced power, irreversibilities of the individual units, and discharge with exhaust for the case of air conditions 1 atm, 0 ℃ and 10% RH. The two approaches for exergy calculation are compared. The main difference was the shift from irreversibility to discharged exergy.

The model was also tested with varying ambient pressure, from 0.6 to 1.05 bar, corresponding to elevations from 4200 m above sea level to 300 m below (ISO, 1975). The air temperature and relative humidity were kept constant at 25 ℃ and 70%, respectively. Compared to air pressure at 1 atm, this gave no or very small changes in results for power and for irreversibilities. Lower pressure gave a weak reduction in methane chemical exergy (0.3% over the range). The main changes in the series of calculations were the exergies of the air inflow and exhaust for the approach of a fixed reference environment. Here, the exhaust flow exergy was reduced from 26.5% of the fuel chemical exergy at 1.05 bar to 20.8% at 0.6 bar. For the same range, the air-inflow exergy of this approach became negative with a value of 5.0% of the chemical exergy. This was because a flow at a pressure lower than that of the (here, fixed) environmental pressure requires work to be brought into mechanical equilibrium with the environment. In comparison, the exergy calculations with respect to the ambient conditions gave a modest change of 0.2 %-points in the exhaust flow exergy from 1.05 to 0.6 bar. In this approach the air-inflow exergy was, of course, zero for all cases.

The choice of compressor and turbine efficiencies has a notable effect on the overall efficiency. When reducing the isentropic efficiencies from 0.85 to 0.80, the overall exergy efficiency was reduced by 6–8 %-points. However, the relative deviation of the exergy efficiency was not visibly altered when plotted in a graph like Fig. 6b.

4.3 *Gas-turbine cycle for a turboshaft engine*

The gas-turbine model above could, with small modifications, be used for a turboshaft aircraft engine. When modeling an aircraft engine, the fuel was pure dodecane ($C_{12}H_{26}$), which here represented jet fuel. The turbine is a power-shaft engine with no exhaust thrust (e.g. helicopter engine).

Data for enthalpy, entropy, specific heat and specific volume of dodecane were found in the NIST Webbook (Lindstrom and Mallard). The LHV and chemical exergy depending on the environmental conditions were calculated according to Ertesvåg (2007). The fuel was assumed to have the temperature and pressure of ambient air and pumped to 1.2 times the compressor outlet pressure, $p_4 = 1.2 p_2$. The fuel was assumed incompressible and the pump work was modelled as $v_{\text{fuel}}(p_4 - p_1)$, where v_{fuel} is the specific volume of the liquid fuel. The pressure ratio of the compressor was set to 10, the isentropic efficiencies of compressor and turbine were set to 0.87, and the turbine inlet temperature (T_5) was fixed to 1260 ℃. The

remaining assumptions were equal to those of the power-plant gas turbine. This reproduced with close approximation the turboshaft engine data of McDonald et al. (2008).

The comparison of results from the two approaches of exergy calculations came out very similar to those of the methane-fuelled power-plant gas turbine above. Since the chemical exergy showed some lesser variation with the dead state conditions, the exergy efficiency showed a correspondingly lesser variation with the choice of environment.

Fig. 8 shows the flow exergies of the air inlet (1) and exhaust (7) in % of the fuel chemical exergy for a series of calculations following the conditions of the ISO (1975) standard atmosphere from sea level (15 ºC, 1 atm) to 6923 m (-30 ºC, 0.415 bar), while keeping RH constant at 70%. In this series the fixed reference environment was set to the sea-level conditions (15 ºC, 1 atm, 70% RH). For the approach where the dead state equalled the ambient conditions, the air had zero exergy and the ratio of the exhaust exergy to the fuel chemical exergy was close to constant. For the approach with the fixed reference environment, the exhaust exergy was decreasing with elevation and the air flow exergy got an increasing, negative value.

4.4 *Solid-oxide fuel cell (SOFC) fuelled with hydrogen*

For the purpose of this study, a simplification of the SOFC system analysed by Bedringås et al. (1997) was set up, Fig. 9. The fuel is pure hydrogen. Fuel and air is preheated separately and fed to the fuel cell (FC). The product gas, still containing some of the fuel, is ducted to an afterburner (AB) in which complete combustion was assumed. The flue gas is used to preheat the fuel and air flows in recuperative heat exchangers (Pre1 and Pre2).

The air-fuel ratio was set to 100 kg/kg, and the temperature of fuel was set equal to the air temperature ($T_1 = T_2$). The state of the inflow air (2) was equal to the specified (varied) state and composition of the ambient air. The temperatures of inflows ($T_3 = T_4$) and outflow (T_5) of the FC were fixed to 1100 K and 1250 K, respectively. The conversion fraction of fuel in the FC was set to 85%, while the remaining fuel was burned in the AB. Heat loss from the FC was assumed 2% of the LHV of the converted fuel, while any other heat losses were neglected. All pressure losses were neglected as pressures were set to 1.01325 bar (1 atm).

The non-specified temperatures (streams 6, 7 and 8) of the system were solved iteratively from the energy balances for the AB, Pre1 and Pre2. The relative residues were 10^{-7} or less.

The exergy lost by heat loss from the FC was calculated together with the FC irreversibility, while the exergy lost by the exhaust (8) was calculated from Eq. (1). Table 2 shows results for the Base Case of the SOFC system: temperature, energy (for a flow: thermal enthalpy and LHV, $H_k = n_k (h - h_0 + h_{LHV})_k$) and exergy flows. For this case, the specified air-fuel mass ratio corresponded to an air excess ratio $\lambda = 2.88$.

While varying the ambient (inlet) air temperature and composition, the air excess ratio was changed, as well as the calculated temperatures and enthalpies of the flows. The flow exergies for each case depended on the chosen reference. Fig. 10a shows the the exergy efficiency, $\psi = W / E_1^{ch}$, taken as the electric power production divided by the chemical exergy of the fuel. The corresponding relative deviation (RD) is shown in Fig. 10b. The deviation increased

by 1% for each 15 K of reduced ambient temperature. The irreversibilities of the preheaters and the afterburner gave RDs according to Eq.(10), while the FC exergy loss and irreversibility gave a somewhat lesser deviation.

The power output of the system decreased with increasing air temperature. So did also the fuel chemical exergy and with a relatively stronger tendency, however, only in the "amb" approach (since the chemical exergy is fixed in the "fix" approach). This led to an increasing efficiency in the "amb" approach, whereas in the "fix" approach, the efficiency decreased.

Calculations with a lower FC fuel conversion (80%) gave around 5 %-points lower efficiency for 70% RH and ambient temperatures from –30 ℃ to 55 ℃. The RDs of the exergy efficiencies were, however, not visibly different from those of Fig. 10b. Similarly, reducing the heat loss (to 0.5% of converted LHV) increased the efficiency by around 1.3 %-points, but with no visible change of the RD as plotted in Fig. 10b.

5 Discussion

5.1 *Main observations*

The aim of this study was to investigate the effects and impact of the choice of properties for the environment in exergy calculations. Two approaches for exergy calculations have been compared: First, the environment was specified by the actual ambient conditions, that is temperature, pressure and relative humidity of the local atmosphere. Second, a fixed reference state and composition of the atmosphere was used, specifically 25 ℃, 1 atm and 70% relative humidity. The two approaches are denoted "amb" and "fix", respectively.

For systems where work or electric energy is the useful output, and a fuel is the input, the overall results were little or moderately affected by the choice of environment. The coal-fired power plant investigated by Rosen and Dincer (2004) also gave this result. The same can be said about systems where a fuel is converted to other chemical substances, such as the combustor (Sect. 4.1). The reason is that the exergy of work and electricity is invariant to the environment, while the chemical exergies of fuels show moderate or little variation. Carbon-rich fuels give less variation than hydrogen-rich fuels.

Although the overall exergy efficiency of the power plant did not change significantly, it can be seen from Rosen and Dincer (2004) that some material streams of their system had differences in flow exergy of several percent between the two approaches. For instance, from the reported flow exergy values of the high-pressure steam, a relative deviation (according to Eq.(9)) of 4.1% could be calculated for a fixed reference environment of 25 ℃.

For all systems, the details of the exergy analysis may be considerably affected by the choice of environment for the calculations. In particular, the irreversibilities (see Sect. 3.2) of the units depend on the chosen environmental temperature.

The distribution of the exergy losses between irreversibility and discharge depends on the choice of environment. At ambient temperatures below the fixed reference, the "fix" approach gives higher irreversibilities than the "amb" approach, whereas the exergy lost with exhaust

discharge becomes lower. This is seen in Fig. 7 for the GT system for an air temperature of 0 °C. For the air temperature of −30 °C, the "fix" approach gave an exhaust flow exergy discharge 8.0 %-ponts less than the in the "amb" approach (18.6% vs. 26.6% of the chemical exergy). For temperatures above the fixed reference, the situation is the opposite: At 55 °C the "fix" approach gave an exergy discharge 3.5 %-points larger than in the "amb" approach.

Another aspect of the "fix" approach is the exergy of the inlet air. At ambient pressures below the fixed reference, the pressure component of flow exergy is negative. This is, of course, due to the calculation rather than to physical realities. The temperature component of air flow exergy is positive at ambient temperatures both above and below the fixed reference. For the GT system case of −30 °C air temperature, the inflow air had a flow exergy rate corresponding to 0.8% of the rate of fuel chemical exergy. For 0 °C (shown in Fig. 2), the amount was 0.2%. Intuitively, this positive inflow quantity should be addable to the other inflow (fuel) as a utilizable resource for the system. In a second thought, however, we will keep in mind that in a simple process of compression and heating, the exergy of a flow at sub-environmental temperature first has to be reduced to zero in a process requiring exergy. Hence, in the "fix" approach, this positive exergy flow is not a resource but rather something that has a cost. Again, it is due to the calculation rather than to physical realities.

The deviations or discrepancies of the results between the two approaches of exergy calculations can be divided into groups according to their degree of graveness:
- The main quantities had only numerical deviations. For instance, the exergy efficiency of a gas turbine at 0 ºC, 1 atm, 70% RH was 39.8% (amb) or 40.0% (fix), and the combustor irreversibility was 26.9 (amb) or 29.5 % (fix) of the fuel chemical exergy, in the two approaches. Although different, these figures are of the same magnitude and the same sign.
- Some quantities had numerical deviations, although of a larger magnitude. Such figures have different magnitudes, and will usually be regarded as significantly different.
- Some quantities had opposite signs, or had zero vs. non-zero values. For instance the gas at elevated locations (lower pressure) had a negative exergy inflow of the air inlet, and close to zero exergy outflow of the exhaust for the "fix" approach.

It may be argued that the influence of the environment is obvious. Apparently, this does not prevent the use of a fixed environment in commercial software. Moreover, the existing literature can be cited for the argument that it does not matter for power plants.

5.2 *Importance of deviations and discrepancies*

The criteria for "acceptable" errors or discrepancies vary from one circumstance to another. In some instances, a 10-20% deviation, or even more, is regarded as fully acceptable for engineering design. Other instances have very low tolerance for calculation errors. An example of small amounts of potential importance is seen in the ISO (1996) standard for natural gas. The industry has found necessary to specify a correction of the heating value at a temperature deviating from the defined standard temperature. For instance, at 0 ºC, the LHV should be corrected by 0.03% compared to the value at 25 ºC. Another example is the large efforts done by industry to increment the efficiency of gas turbines with a few tenths of a percent. On this background, it can be stated that in certain cases, the small amounts, changes or deviations are important.

When quantities have different magnitude, or in particular, different signs, the use of the fixed reference for optimization and evaluation of sub-processes will be unnecessary challenging and can be misleading. Also when results are just numerically different, using the fixed reference will give an inaccurate impression of the improvement potentials. The use of a non-ambient chosen environment move exergy losses from irreversibilities to discharge flows, or vice versa.

For the systems where the mean (overall) indicators are little or moderately affected by the choice of exergy environment, the same information can often be provided from a simpler energy analysis, see for instance Arrieta and Lora (2005) or Basrawi et al. (2011). For a power plant, the exergy efficiency is close to its energy (thermal) efficiency. As soon as the exergy method gives something more than an energy analysis, this added value is affected by the choice of environment.

Interpretation and presentation of exergy results can sometimes be a challenge. When the non-ambient fixed environment is chosen, the interpretation has to take the discrepancies into consideration. For a skilled scientist, this may not be a big issue. However, the pedagogical challenge of explaining that a negative exergy inflow in reality is a neutral or positive contribution, should not be underestimated. Moreover, the need for these additional descriptions can disturb and confuse the main message of the exergy analysis.

A question raised is whether it is more convenient to use an entropy analysis, since this is independent of the state of the environment. To some extent, the point can be made: Entropy production inside a process unit does not depend on the environment, as opposed to the corresponding irreversibility. However, the entropy analysis still has to be interpreted, explained and presented. This very soon involves some relation to "what can be achieved" – that is, some sort of exergy consideration. Moreover, when the system analysed interact with the environment, like the exemplary systems above, the environment is brought into the problem – and we are back to the same questions regarding ambient or fixed reference conditions.

5.3 *Calculations and accuracy*

In the calculations, quite a few compositions, mass flows and temperatures were specified prior to the calculation and hence, can be regarded as accurate. In most cases, the remaining quantities were solved directly. In the simulations of the Brayton cycles and SOFC system, iterative solutions were made, with maximum errors as specified in each section. The relative residues were 10^{-7} or (usually) less than that.

The specific heat functions of Sontag and Van Wylen (1982) were given with a maximum error ranging from less than 0.2% (CH_4, CO_2) to 0.43% (N_2, H_2O, CO). Based on data from the NIST Webbook (Lindstrom and Mallard), the relative uncertainties of LHV and ΔG^{ref} (Eq. (5)) were estimated to 0.02% for H_2, 0.04% for CH_4 and 0.08% for CO. For dodecane the uncertainty of the LHV was 0.6%, while uncertainty data for entropy (and hence, ΔG^{ref}) were not available.

These estimates indicate the accuracy of the calculations. Without doing a detailed error analysis for each case, it can readily be observed that the deviations between the two

approaches for exergy calculations are greater than the uncertainties of the calculated quantities.

Another aspect is the robustness of the relative deviation. It was seen that parameter variations that gave considerable changes in the results of each case, hardly affected the relative deviation for the two approaches of exergy calculation. An example is the reduction of isentropic efficiencies for the gas turbine compressor and expander. This reduced the exergy efficiency, whereas the relative deviation of the exergy efficiency was not visibly altered.

6 Conclusions

Effects of the choice of environment for exergy calculations were investigated. The first approach was to define the environment by the actual and varying ambient conditions. The alternative approach was to select a fixed reference state and composition of the atmosphere, for use in all cases, regardless of the local conditions.

The effects of ambient temperature on the chemical exergies of solid carbon and liquid dodecane are modest and less than for methane, although with the opposite sign. For dodecane, the ambient pressure and relative humidity have small effects, whereas no effets for carbon.

Power-plant efficiencies, which involve work/electricity and consumed fuel, are only affected by moderate numerical values. Carbon-rich fuels give less variation than hydrogen-rich fuels. The deviation of efficiency was increased by 0.1% for each 4 K of reduced ambient temperature for the gas turbine, while for the fuel cell, the increase was 1% for 15 K.

It was found that details of the exergy analysis are considerably affected by the choice of environment for the calculations. In particular, the irreversibilities of the systems and units depend on the chosen environmental temperature. The deviation was 1% for each 3 K of ambient temperature. Although the ratios of irreversibilities of different units are unaltered, the choice of environment will change the distribution between irreversibility and discharged exergy.

The exergy of entrained or discharged flows can be strongly influenced by the choice of environment. For low ambient pressures, flow exergies are reduced and can become negative when a fixed environment is chosen.

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Nomenclature

Latin symbols

c_p	molar heat capacity
h	molar enthalpy
I	irreversibility rate
n	molar flow rate
p	pressure
R	universal gas constant
RD	relative deviation
s	molar entropy
T	temperature
v	specific volume
W	work rate or electric power
W_1, W_2	terms in Eq. 5
X	mole fraction

Greek symbols

ΔG	Gibbs-energy difference for reaction
ΔS	entropy difference for reaction
ε	molar flow exergy
E	rate of flow exergy/exergy transfer
λ	air excess ratio
ν	reaction coefficient
φ	relative humidity
ψ	exergy efficiency

Subscripts

0	environmental state
amb	actual (local) ambient conditions
fix	fixed reference environmental state
i,j	indices for chemical species
k	index for mass flow stream
mix	mixture
ref	reference state

Superscripts

ch	chemical exergy
e	environment(al)
ref	reference state
tm	thermomechanical exergy

Abbreviations

LHV	lower heating value
RH	relative humidity

Fig. 1 Relative deviation (Eq.(9)) of irreversibility at two different values of the fixed standard reference temperatures and varied ambient temperature.

Fig. 2. Thermomechanical flow exergy for air at varying gas flow temperature and two gas pressures evaluated with respect to the actual ambient temperature of $0^{\circ}C$ ("amb") and on the basis of the fixed reference conditions ("fix").

Fig. 3. Thermomechanical flow exergy for air at varying gas flow pressures at a constant temperature of $25\ ^{\circ}C$, evaluated with respect to the actual ambient pressure of 0.70 bar ("amb") and on the basis of the fixed reference conditions ("fix").

Fig. 4. Relative deviation (Eq.(9)) of chemical exergies of hydrogen, methane, solid carbon and liquid dodecane at ambient conditions of 1 atm, 70 relative humidity and varying temperatures.

Fig. 5. Flow sheet of gas turbine system.

Fig. 6. GT system (a) Exergy efficiency and (b) its Relative deviation (cf. Eq.(9)) as functions of atmospheric air temperature and RH.

Fig. 7. GT with air of $0\ ^{\circ}C$, 1 atm, 10% RH. Distribution of exergy into net power, irreversibility rates of the compressor, combustor, turbine and regenerator, respectively, and exhaust flow exergy discharge rate, in fractions (%) of the fuel chemical exergy for the two approaches of exergy calculation.

Fig. 8. Turboshaft GT. Flow exergies of air inlet (E_1) and exhaust (E_7) as fractions of the fuel chemical exergy at different elevations of ISO standard atmosphere.

Fig. 9. Flow sheet of simplified solid-oxide fuel cell (SOFC) system.

Fig. 10. SOFC (a) Exergy efficiency and (b) its Relative deviation (cf. Eq. (9)) as functions of atmospheric air temperature and RH.

Tables

Table 1. Data and results for the GT Base Case (air 25 ºC, 1 atm, 70% relative humidity, pressure ratio of 20).

	T (ºC)	H/n_4 (kJ/mol)	H/H_{LHV} (%)	E/n_4 (kJ/mol)	$E/E_{ch,4}$ (%)
1: Air	25	0	0.0	0	0
2: Air from compress.	478.6	439.0	54.7	411.6	49.5
3: Air to combustor	541.2	503.0	62.7	451.3	54.3
4: Fuel	25.0	802.3	100.0	841.6	101.2
5: Gas to turbine	1210.0	1305.3	162.7	1052.9	126.6
6: Gas from turbine	568.0	560.9	69.9	258.2	31.1
7: Exhaust	509.4	496.9	61.2	217.7	26.2
Net work		305.4	38.1	305.4	36.7
Irrev. compressor				27.3	3.3
Irrev. combustor				240.0	28.9
Irrev. turbine				50.3	6.0
Irrev. recuperator				0.9	0.1

Table 2. Flow data for the SOFC Base Case (air 25 ºC, 1 atm, 70% relative humidity).

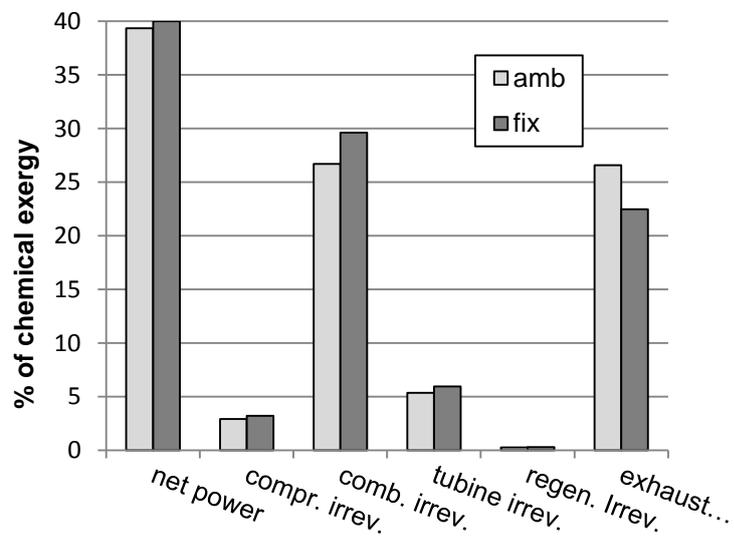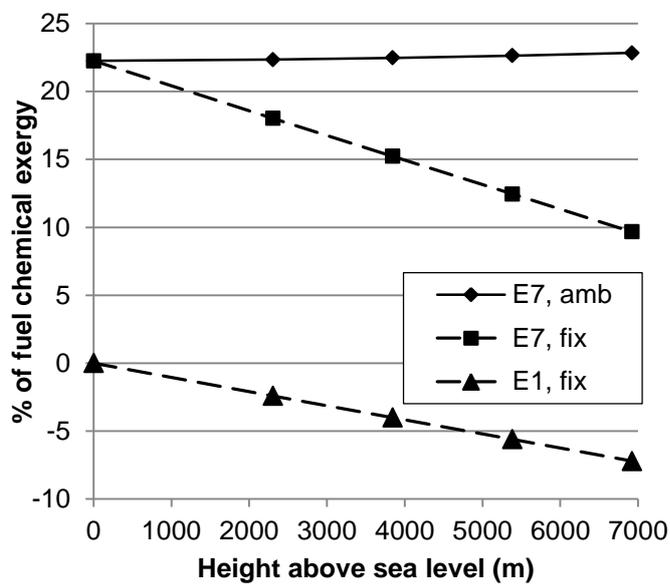|	T (ºC)	H/n_1 (kJ/mol)	H/H_{LHV} (%)	E/n_1 (kJ/mol)	E/E_1 (%)
1: Fuel	25	241.8	100	236.1	100.0
2: Air inlet	25	0	0	0	0
3: Heated fuel	826.9	265.5	109.8	248.4	105.2
4: Heated air	826.9	176.6	73.0	92.3	39.1
5: gas from FC	976.9	270.8	112.0	167.9	71.1
6: from AB	1115.0	270.8	112.0	163.0	69.1
7: Flue gas	1027.7	247.1	102.2	144.6	61.2
8: Exhaust	333.8	70.6	29.2	25.4	10.7
Electricity		167.2	69.0	167.2	70.8
Irreversibility Pre1				6.2	2.6
Irreversibility Pre2				26.9	11.4
Loss/irreversibility FC		4.1	1.7	5.6	2.4
Irreversibility AB				4.9	2.1

FIGURES
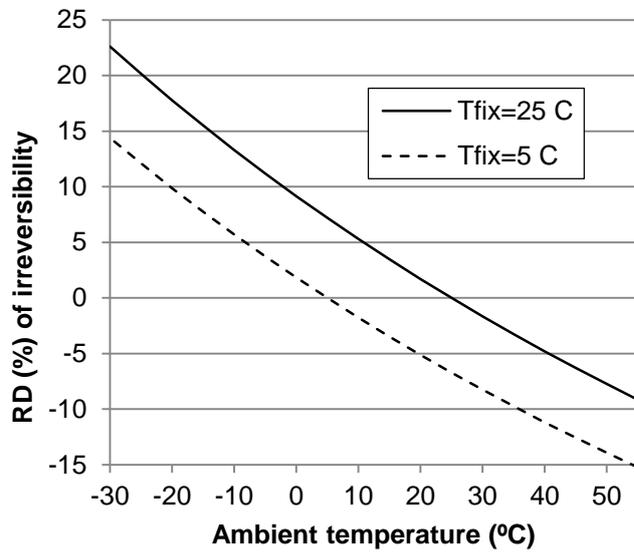
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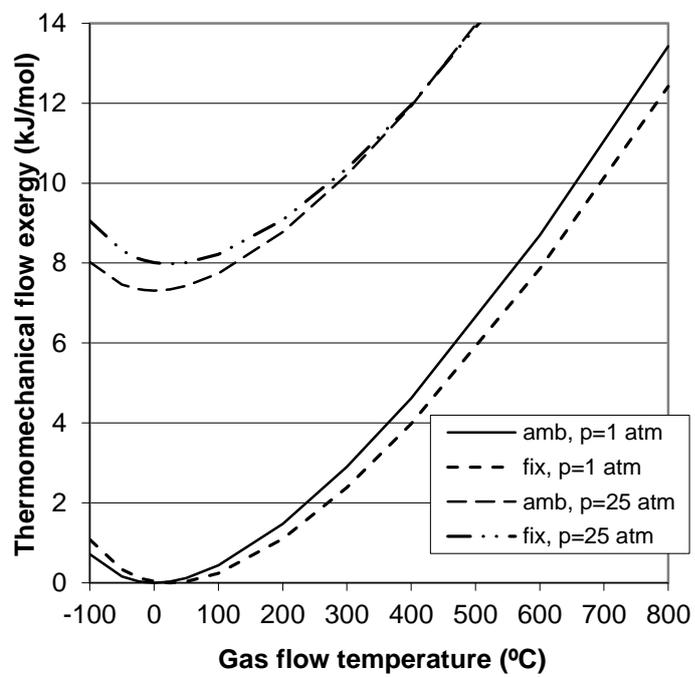
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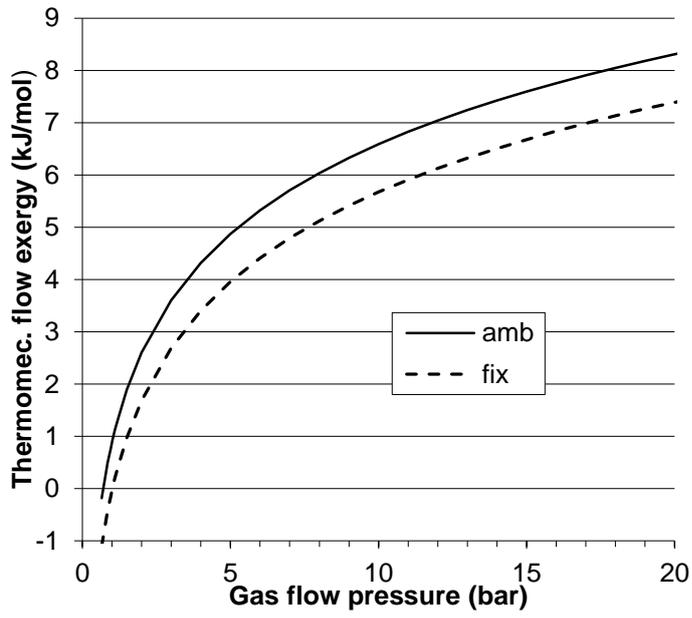
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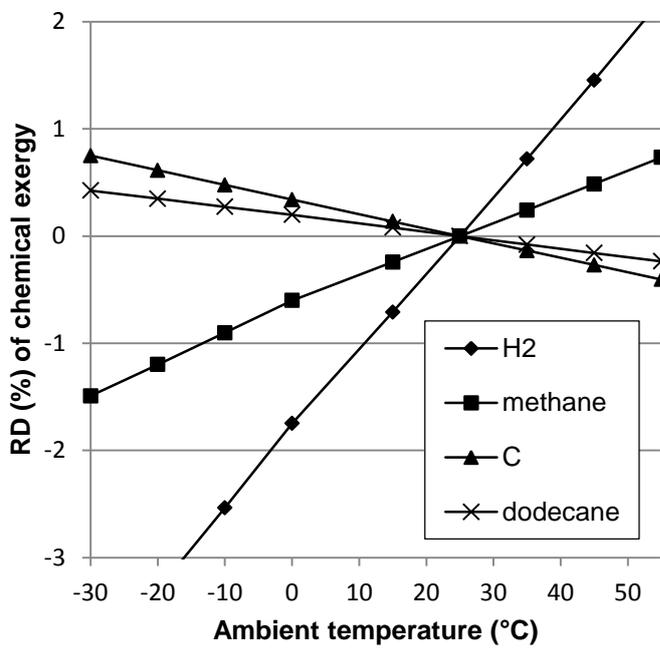
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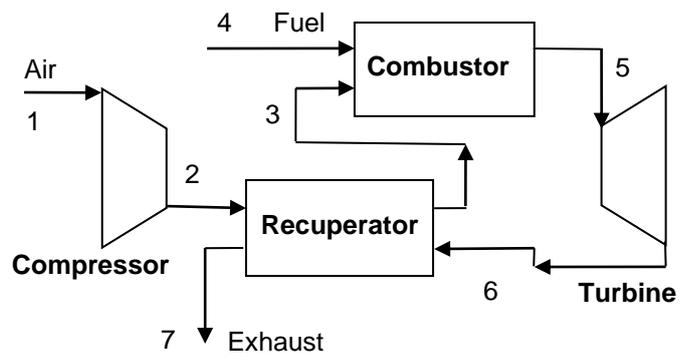
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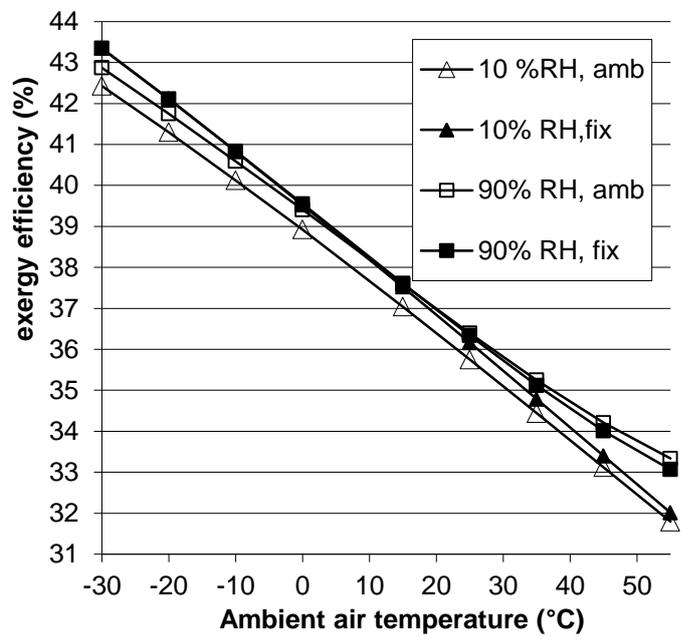
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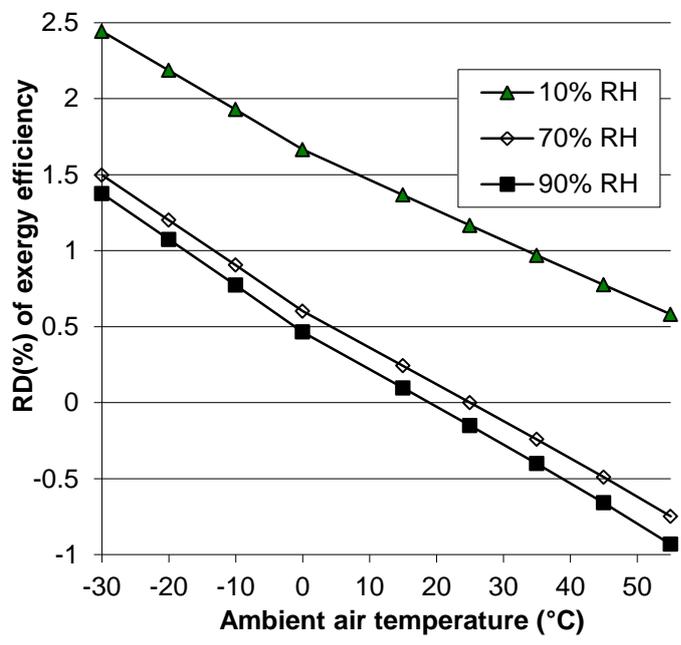
Fig.6b

Fig.7

Fig.8

Fig.9

Fig.10a

Fig.10b