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# **A Submodel for Calculating Exergy Linked to AspenPlus**



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## Abstract

Process simulations provide an opportunity to design and optimize processes so that they are in mass- and energy balance, but they don't directly provide information where thermodynamic losses occur. Other analysis tools that are based on the second law of thermodynamics are needed to provide this information. One of these analysis tools is exergy analysis. In this report two methods for calculating both physical and chemical exergy values of streams are presented. The data for these methods are obtained from AspenPlus simulation software. In the first of these methods, AspenStreams, the physical exergy at environmental conditions of a stream is calculated by copying a stream that either enters or exits a process into an additional stream and changing the pressure and temperature of this stream into the values of the environment. The benefit is that any property method in AspenPlus can be used to calculate the enthalpy and entropy values of the streams in environmental conditions. The drawback is that generating the additional streams is hard to automate. In the second approach, called AspenData, the physical exergy of a stream is calculated using the stream's molar concentration together with a mixing rule and multiplying this corrected molar concentration with the specific enthalpy and entropy of each species. The benefit here is that no additional streams are needed, but the precision of the calculation depends on the precision of the mixing rule. The chemical exergy of both methods is calculated using the Standard Chemical Exergy approach. Both of the methods were tested on a oxyfuel power plant. The results of these calculations show that both methods provided the same results, and hence for oxyfuel processes, the AspenData approach can be seen as the more efficient one. Although the methods presented in this report are applied on Excel Worksheets, the methods could be written as part of AspenPlus code. In general the methods presented in this report could be applied also to other types of process simulation software. The only necessity is that stream enthalpies, entropies and molar concentrations are provided.

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## 0.1 Introduction

The problem of global climate change has brought forward the question of reducing significantly greenhouse gases, especially CO<sub>2</sub>, emissions into the atmosphere. One option to accomplish this is CO<sub>2</sub> capture and storage (CCS). This way fossil fuels, especially coal, could be used as a fuel in power production and with no or limited emissions to the atmosphere. The problem is that the costs of power production would increase and research is needed to find a suitable and trustworthy storage place for the CO<sub>2</sub>. The sequestration could be done with pumping the gas into oil wells or salt aquifers or with mineral carbonation. The capturing could be done with three major technologies: post-combustion capture systems, pre-combustion capture systems and oxyfuel combustion capture systems. These systems are currently being developed both by experimental and modeling research.

Steady-state process simulations provide the opportunity to design and optimize processes so that they are in mass- and energy balance. AspenPlus Asp [2011] from AspenTech is a market-leading process modeling tool for conceptual design, optimization, and performance monitoring for the chemical, polymer, specialty chemical, metals and minerals, and coal power industries. Aspen Plus includes a large database of pure component and phase equilibrium data for conventional chemicals, electrolytes, solids, and polymers.

Although process simulation software provide information of mass and energy flows, they don't directly provide information where thermodynamic losses occur. Other analysis tools that are based on the second law of thermodynamics are needed to provide this information. One of these analysis methods is exergy analysis. Exergy analysis is a technology based on the second law of thermodynamics. It is used to compare, improve and optimize process designs. Exergy analysis provides efficiencies that measure how far is the process studied from ideal and in which parts of the process exergy losses occur. Exergy analysis can not recommend how the process could be improved, but if changes to the process are made, exergy analysis can show if the changes were thermally beneficial or not. Exergy is defined as the maximum theoretical useful work obtained if a system S is brought into thermodynamic equilibrium with the environment by means of processes in which the S interacts only with this environment (Sciubba and Wall [2010]).

There is a lot of books on exergy analysis. In the book of Szargut et al. [1988] detailed methods for calculating exergy, both physical and chemical, are provided. The book of Szargut et al. [1988] is the basis for this report. Also in the book from Brodyansky et al. [1994], although not in the same depth, calculation methods are presented and used in different application areas. In Kotas [1985] the focus is more on thermal plants and processes and more on physical, not chemical, exergy, but an extensive amount of examples and calculation methods are presented. Calculation of physical exergy in thermal plants and energy systems is the focus also in the

book from Ahrendts [1980]. More recently the book from Dincer and Rosen [2007] focuses on exergy analysis of different applications ranging from thermal systems to different countries, regions and economic sectors. In their book the basic principles of thermoeconomics, exergetic life cycle assessment and exergy of industrial ecology are discussed.

In this report exergy analysis has been performed on a oxyfuel combustion process, although in general the tools used could also be used in other CCS technologies. Figure 1 shows a block diagram of a oxyfuel power plant concept. During oxyfuel combustion, a combination of oxygen (typically greater than 95% purity) and recycled flue gas, i.e. not air, is used for combustion of the fuel. A gas consisting mainly of  $\text{CO}_2$  and  $\text{H}_2\text{O}$  is generated. This flue gas has a  $\text{CO}_2$  concentration high enough for sequestration, although typically the  $\text{CO}_2$  is purified and liquefied in a subprocess called in a  $\text{CO}_2$  Separation and Purification Unit ( $\text{CO}_2\text{SEP}$ ). The recycled flue gas is used to control flame temperature and make up the volume of the missing  $\text{N}_2$  to ensure there is enough gas to carry the heat through the boiler.  $\text{O}_2$  is separated from air in a subprocess called Air Separation Unit (ASU). The  $\text{CO}_2\text{SEP}$  and ASU are the major contributors to an efficiency penalty of about 7-12 %-points compared to a power plant without CCS.

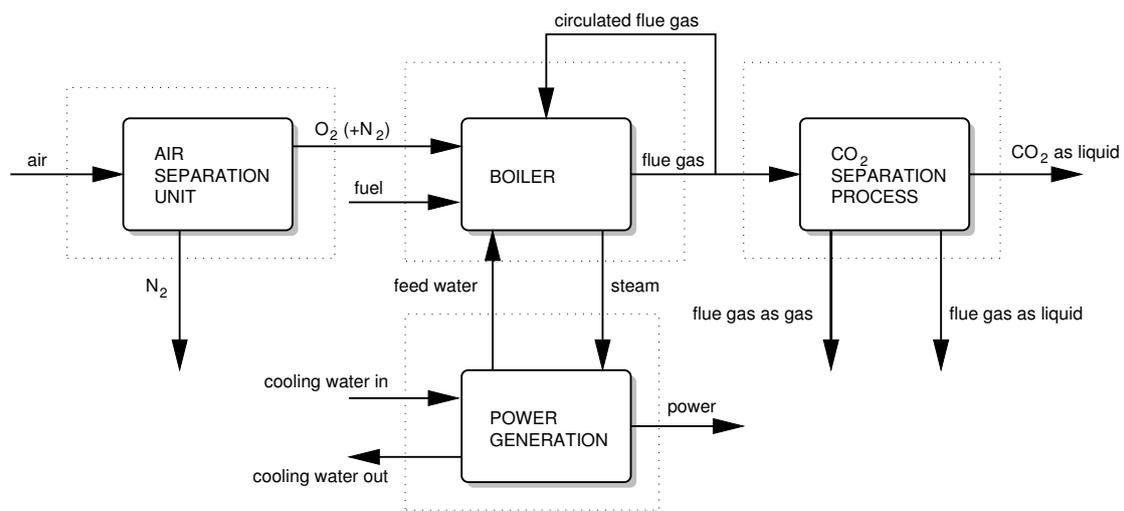


Figure 1: Oxyfuel power plant concept

### 0.1.1 Objective of this report

The objective of this report is to provide two exergy calculation methods linked to data obtained from AspenPlus process simulation software. Although the two approaches are partly general, they have been tested on a oxyfuel combustion

power plant. The exergy efficiency of the overall oxycombustion power plant are calculated using both methods.

### **0.1.2 Outline of the report**

In Chapter 0.2 the basic definitions of energy, exergy, entropy, anergy and Gibbs free energy are given. Additionally a short introduction how the environment in exergy analysis is defined and what is meant by exergy loss and exergy efficiency.

## 0.2 Basic definitions

### 0.2.1 Energy

According to Dincer and Rosen [2007] even though the concept of energy is so familiar to us today that it seems intuitively obvious to understand, yet we often have difficulty defining it precisely. Dincer and Rosen [2007] try to define it by saying that energy is a scalar quantity that cannot be observed directly but can be recorded and evaluated by indirect measurements. The absolute value of energy of a system is difficult to measure, whereas the energy change is relatively easy to evaluate.

The definitions found in [Wikipedia, 2012a] define energy as a physical quantity that describes the amount of work that can be performed by a force, and as a quantity that is often understood as the ability a physical system has to produce changes on another physical system. The changes are produced when energy is transferred from a system to another. A system can transfer energy by means of three ways, namely: physical or thermodynamical work, heat transfer, or mass transfer.

Energy can not be produced nor destroyed, but it can be transformed to other forms although in some transformations (heat-work) this is not possible without losses.

### 0.2.2 Exergy

Exergy is defined as the maximum theoretical useful work obtained if a system S is brought into thermodynamic equilibrium with the environment by means of processes in which S interacts only with this environment (Sciubba and Wall [2010]). According to Szargut et al. [1988] “Exergy is the amount of work obtainable when some matter is brought to a state of thermodynamic equilibrium with the common components of the natural surroundings by means of reversible processes, involving interaction only with the above mentioned components of nature”.

Exergy is a combination property of a system and its environment because unlike energy it depends on the state of both the system and environment. For a fixed environment exergy is a state property. The exergy of a system in equilibrium with the environment is zero.

Excluding nuclear, magnetic, electrical and interfacial effects, the exergy  $E$  of a stream of substance can be divided into four components: kinetic exergy  $E_k$ , potential exergy  $E_p$ , physical exergy  $E_{ph}$  and chemical exergy  $E_{ch}$  [Szargut et al., 1988] as defined by Equation 1.

$$E = E_k + E_p + E_{ph} + E_{ch} \quad (1)$$

<b>Energy</b>	<b>Exergy</b>
Dependent on properties of only matter or energy flow, and independent of environment properties	Dependent on properties of both a matter or energy flow and the environment
Has values different from zero when in equilibrium with the environment	Equal to zero when in dead state by virtue of being in complete equilibrium with the environment
Conserved for all processes	Conserved for reversible processes and not conserved for real processes (where it is partly or completely destroyed due to irreversibilities)
Can be neither destroyed nor produced	Can be neither destroyed nor produced in a reversible process, but is always destroyed (consumed) in an irreversible process
Appears in many forms (e.g., kinetic energy, potential energy, work, heat) and is measured in that form	Appears in many forms (e.g., kinetic exergy, potential exergy, work, thermal exergy) and is measured on the basis of work or ability to produce work
A measure of quantity only	A measure of quantity and quality

Table 1: Comparison of energy and exergy (obtained from Dincer and Rosen [2007])

*Kinetic exergy* is equal to the kinetic energy, when the velocity is considered relative to the surface of the earth.

*Potential exergy* is equal to the potential energy when it is evaluated with respect to the average level of the earth in the locality of the process under consideration.

*Physical exergy* is the work obtainable by taking the substance through reversible physical processes from its initial state (temperature  $T$ , pressure  $p$ ), to the state determined by the environment (temperature  $T_0$  and pressure  $p_0$ ).

*Chemical exergy* is the work that can be obtained by taking a substance having the parameters  $T_0$ ,  $p_0$  to the state of thermodynamic equilibrium with the datum level components of the environment.

The sum of physical and chemical exergy can be called the *thermal exergy*  $E_{th}$ .

$$E_{th} = E_{ph} + E_{ch} \quad (2)$$

### 0.2.3 Energy versus exergy

Table 1 obtained from Dincer and Rosen [2007](page 13) shows a comparison between energy and exergy.

## 0.2.4 Entropy

According to Dincer and Rosen [2007] entropy is a thermodynamic property, which is a measure of the amount of molecular disorder within a system. A system possessing a high degree of molecular disorder has a high entropy. Entropy has the following characteristics [Dincer and Rosen, 2007]:

- The entropy of a system is a measure of its internal molecular disorder.
- A system can only generate, not destroy, entropy.
- The entropy of a system can be increased or decreased by energy transports across the system boundary.

According to Wikipedia [2012b] entropy is a thermodynamic property that is a measure of the energy not available for useful work in a thermodynamic process, such as in energy conversion devices, engines, or machines. Such devices can only be driven by convertible energy, and have a theoretical maximum efficiency when converting energy to work. During this work entropy accumulates in the system, but has to be removed by dissipation in the form of waste heat.

## 0.2.5 Anergy

Rant [1964] defined that exergy is the part of energy that can be fully converted into any other kind of energy. Rant [1964] called *anergy* the part that can not be converted to other kinds of energy. According to Szargut et al. [1988] this is an error, because for example lowering the temperature of a substance having a lower temperature than the environment decreases the energy, but increases the exergy. Hence anergy can only be defined as a difference between energy  $E$  and exergy  $Ex$  as shown in Equation 3.

$$A = E - Ex \quad (3)$$

## 0.2.6 Environment in Exergy analysis

Because exergy of a system or species is calculated with respect to the environment, it is important to define the reference environment.

In theory the reference environment should be such that it is in stable equilibrium, with all parts at rest relative to one another. No chemical reactions can occur between the environmental components. The reference environment acts as an infinite system, and is a sink and source for heat and material. It experiences only internally reversible processes in which its intensive state remains unaltered. The exergy of the reference environment is zero and the exergy of a stream or

system is zero when it is in equilibrium with the reference environment. [Dincer and Rosen, 2007],(pp.27)

Unfortunately the natural environment does not have the theoretical characteristics of a reference environment. The natural environment is not in equilibrium, and its intensive properties exhibit spatial and temporal variations. Many chemical reactions in the natural environment are blocked because the transport mechanisms necessary to reach equilibrium are too slow at ambient conditions. Thus, the exergy of the natural environment is not zero; work could be obtained if it were to come to equilibrium. Consequently, models for the reference environment are used which try to achieve a compromise between the theoretical requirements of the reference environment and the actual behavior of the natural environment. [Dincer and Rosen, 2007],(pp.29).

There are five classes of reference-environment models:

- *Natural-environment-subsystem models*: The main idea of these models is to try to simulate realistically subsystems of the natural environment. These models include Baehr and Schmidt [1963], Gaggioli and Petit [1977] and Rodriguez [1980].
- *Reference-substance models*: These models resemble the models of the previous class *Natural-environment-subsystem models*, although the main idea here is to select reference species from which other species are made from. The reference species have zero exergy in the natural environment. The model of Szargut et al. [1988] belongs to this group. The problem with this model is that the reference species are chosen arbitrarily mainly based on economic value or industrial importance of the reference species. A model that does not try to simulate the natural environment is the one from (Sussman [1980] and Sussman [1981]).
- *Equilibrium models*: Ahrendts [1980] proposed a model that tries to satisfy the equilibrium characteristics of the reference environment by pooling together and calculating an equilibrium composition for a given temperature considering all materials present in the atmosphere, oceans and a layer of the crust of the earth. The problem with this model is that exergy values calculated with the model are strongly dependent on the considered thickness of earth's crust. Additionally because there are no technical processes available to obtain the work from these materials, the exergy values obtained with the model have little practical benefit for real processes.
- *Constrained-equilibrium models*: Ahrendts [1980] developed the previous model by introducing a constraint for equilibrium by excluding the possibility of formation of nitric acid ( $\text{HNO}_3$ ) and its compounds. Interestingly

with a crust thickness of 1 m and with temperature of 25°C, the model was similar to the natural environment.

- *Process-dependent models*: Bosnjakovic [1963] presented a model that has only components that participate in the process being studied. These components are in stable equilibrium at the temperature and total pressure of the natural environment. The problem with this approach is that these models are case-specific and thus exergy values calculated for one process differ from exergy values of another process having different components.

In this work the model presented by Szargut et al. [1988] is used as a base for calculations.

### 0.2.7 Gibbs free energy

According to Wikipedia [2012c] Gibbs defined what he called the available energy of a body as such: The greatest amount of work which can be obtained from a given quantity of a certain substance in a given initial state, without increasing its total volume or allowing heat to pass to or from external bodies, except such as at the close of the processes are left in their initial condition. The initial state of the body, according to Gibbs, is supposed to be such that “the body can be made to pass from it to states of dissipated energy by reversible processes”.

According to de Swaan Arons et al. [2004] the concept of chemical exergy has a distinct advantage over the standard Gibbs energy of formation. Whereas the latter is zero for the elements at standard conditions, the chemical exergy has a zero value for compounds or elements in equilibrium with and as they occur in our natural environment. Thus the standard chemical exergy of a compound clearly represents the amount of work available with respect to the environment in which we live and work. The chemical exergy can be simply calculated from the Gibbs energy of formation. The only difference between the two concepts is that their zero values are defined for different reference substances.

### 0.2.8 Exergy loss

There are two types of exergy losses, internal losses due to irreversibilities in process units and external losses due to effluent flows having exergy that is not utilized. Exergy loss is additive, so the exergy losses for an entire plant equals the sum of exergy losses determined from its components parts.

## 0.2.9 Exergy balance

The exergy balance of a control volume at steady state can be written with Equation 4.

$$\text{Exergy}_{in} = \text{Exergy}_{output\ in\ product} + \text{Exergy}_{emitted\ in\ waste} + \text{Exergy}_{destruction} \quad (4)$$

Exergy emitted in waste can be seen as external exergy losses.

## 0.2.10 Exergy efficiency

Exergy efficiency is a dimensionless value between 0 and 1 showing how effectively the input is converted to the product. Equation 5 can be used to calculate exergy efficiency.

$$\begin{aligned} \psi &= \text{Exergy}_{output\ in\ product} / \text{Exergy}_{input} \\ &= 1 - (\text{Exergy}_{loss} / \text{Exergy}_{input}) \\ &= 1 - [(\text{Exergy}_{waste\ emission} + \text{Exergy}_{destruction}) / \text{Exergy}_{input}] \end{aligned} \quad (5)$$

## 0.3 General calculation of exergy

### 0.3.1 Physical Exergy

Physical exergy [J] of a substance having temperature  $T_1$  and pressure  $p_1$  is calculated with Equation 6 assuming that the environment has a temperature of  $T_0$  and pressure  $p_0$ .

$$Ex_{ph} = H_1 - H_0 - T_0(S_1 - S_0) \quad (6)$$

Specific physical exergy [ $\frac{J}{kg}$ ] or [ $\frac{J}{mol}$ ] can be calculated with Equation 7.

$$ex_{ph} = h_1 - h_0 - T_0(s_1 - s_0) \quad (7)$$

In Equations 6 and 7  $H$  [J] and  $h$  [ $\frac{J}{kg}$ ] or [ $\frac{J}{mol}$ ] is the enthalpy of the substance and  $S$  [ $\frac{J}{K}$ ] and  $s$  [ $\frac{J}{kg \cdot K}$ ] or [ $\frac{J}{mol \cdot K}$ ] is the entropy of the substance.  $T_0$  has to be given in Kelvins [K].

### Physical exergy of an ideal gas with constant heat capacity

When the substance is an ideal gas having a constant heat capacity  $c_p$  [ $\frac{J}{kg*K}$ ] or [ $\frac{J}{mol*K}$ ], Equation 8 is obtained.  $R$  is the gas constant [ $\frac{J}{kg*K}$ ] or [ $\frac{J}{mol*K}$ ].

$$ex_{ph}^{idealgas} = c_p \left[ (T - T_0) - T_0 \ln \frac{T}{T_0} \right] + RT_0 \ln \frac{p}{p_0} \quad (8)$$

### Physical exergy difference between two states

With Equation 9 the difference of physical exergy between two states can be calculated.

$$ex_{ph,1} - ex_{ph,2} = h_1 - h_2 - T_0(s_1 - s_2) \quad (9)$$

### 0.3.2 Chemical Exergy

Chemical exergy can be calculated according to Equation 10 at temperature  $T_0$  and pressure  $p_0$ .

$$ex_{ch} = \sum_{i=1}^n z_i (\mu_i - \mu_{i,0}) \quad (10)$$

where  $z_i$  = the mass (or mole) fraction of the  $i$ th component  
 $\mu_i$  is the chemical potential of species  $i$  of the substance  
 $\mu_{i,0}$  is the chemical potential of species  $i$  in the environment

Equation 10 can be formulated with activities with temperature  $T_0$  and pressure  $p_0$ . The chemical potential can be calculated with activities using equations

$$\mu_i = \mu_i^0 + RT_0 \ln \alpha_i \quad (11)$$

$$\mu_{i,0} = \mu_i^0 + RT_0 \ln \alpha_{i,0} \quad (12)$$

$$\mu_i - \mu_{i,0} = RT_0 \ln \frac{\alpha_i}{\alpha_{i,0}} \quad (13)$$

where  $\mu_i^0$  is the chemical potential of a pure substance in the standard state (temperature  $T_0$  and pressure  $p_0$ )

$a_i$  is the activity of species  $i$  of the substance

$a_{i,0}$  is the activity of species  $i$  in the environment .

Thus the chemical exergy of a substance using activities can be calculated with Equation 14.

$$ex_{ch} = RT_0 \sum_{i=1}^n z_i \ln \frac{\alpha_i}{\alpha_{i0}} \quad (14)$$

### Reference species in atmospheric air

The gaseous reference species in the environment are assumed to be ideal gases and constant (except for  $H_2O$ ). The reference species are  $O_2$ ,  $N_2$ ,  $CO_2$ ,  $H_2O$ ,  $D_2O$ ,  $Ar$ ,  $He$ ,  $Ne$ ,  $Kr$  and  $Xe$ . For ideal gases Equation 14 can be modified to Equation 15.

$$ex_{ch} = RT_0 \sum_i y_i \ln \frac{y_i}{y_{i,0}} \quad (15)$$

where  $y_i, y_{i,0}$  = mole fraction of the component in the fluid under consideration and in the environment.

For a pure substance ( $y_i = 1$ ) in normal standard conditions, Equation 15 can be written with Equation 16.

$$ex_{ch} = -RT_0 \ln y_{i,0} \quad (16)$$

With partial pressures this can be written with Equations 17 and 18.

$$ex_{ch} = -RT_0 \ln \frac{p_{i,0}}{p_n} \quad (17)$$

$$ex_{ch} = RT_0 \ln \frac{p_n}{p_{i,0}} \quad (18)$$

### Standard Chemical Exergy

According to Szargut et al. [1988] (page 56) exergy balances could be more easily found if values of the chemical exergy were tabulated. For this reason he introduced the notion of *Standard Chemical Exergy*. It is related to the substance in the standard state at normal temperature and pressure ( $T_0 = 298.15$  K and  $p_0 = 1$  bar). In (Bilgen [2009] and Szargut et al. [2005]) different Standard Chemical Exergies of different chemical reference species are tabulated. These tables include the standard chemical exergy for elements of gaseous reference species, elements for reference substances dissolved in seawater and elements for solid reference substances.

In Figure 2 [Szargut et al., 1988](page 57) the calculation method for chemical exergy is presented.

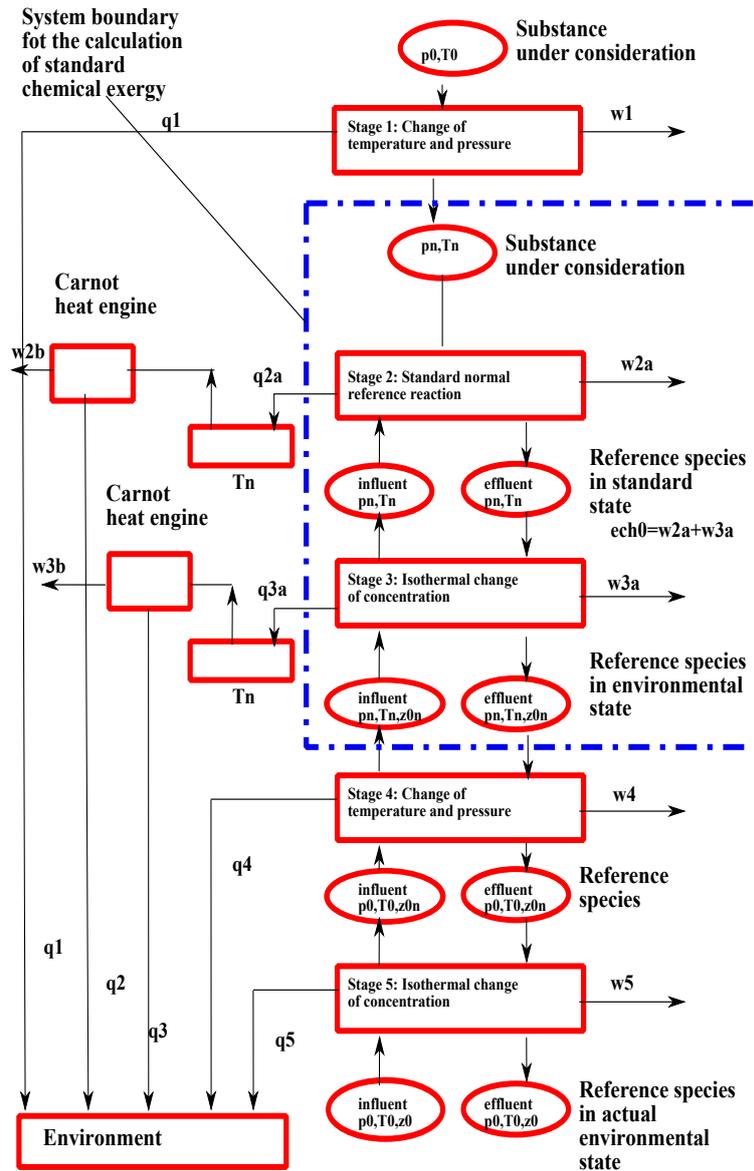


Figure 2: Model for calculating chemical exergy with introduction of standard chemical exergy (adopted from Szargut et al. [1988]).

In *Stage 1* the substance under consideration first has the temperature and pressure of the real environment  $T_0$  and  $p_0$  (i.e the reference temperature and pressure of physical exergy). Work  $w_1$  is the maximum work obtainable from changing the temperature and pressure reversibly from this state ( $T_0$  and  $p_0$ ) to the

normal standard state ( $T_n = 298.15$  K and  $p_n = 1$  bar). This work can be calculated with Equation 19. This work is typically quite small because the temperatures and pressures of the environment are in most cases not too far from the standard temperatures and pressures.

$$w_1 = h_0 - h_n - T_0(s_0 - s_n) \quad (19)$$

In *Stage 2* a normal standard reference reaction is used as can be seen in Equation 20. Besides the substance under consideration, only reference species in the standard state take part.

$$w_{2a} = \Delta_r G^0 \quad (20)$$

where  $\Delta_r G^0$  = standard normal free energy change (increase) for the reference reaction

An auxiliary heat source permits the reversible reaction to be accomplished at the normal temperature  $T_n$ . A reversible Carnot machine assures reversible heat exchange between the normal standard state and the real environment.

$$w_{2b} = q_{2a} \left( \frac{T_n - T_0}{T_n} \right) \quad (21)$$

Equation 22 shows how  $q_{2a}$  can be calculated.

$$q_{2a} = \Delta_r H^0 - \Delta_r G^0 = T_n \Delta_r S^0 \quad (22)$$

where  $\Delta_r H^0, \Delta_r S^0$  are the standard normal enthalpy change (increase) and standard normal entropy change for the reference reaction.

In *Stage 3* the reversible work of changing the concentration of a reference species from the environment to the concentration needed in the reaction of Stage 2 is calculated. This can be calculated with Equation 23.

$$w_{3a} = \sum_k n_k e_{ch,k}^0 - \sum_j n_j e_{ch,j}^0 \quad (23)$$

where  $n_j, n_k$  = numbers of moles of the influent and effluent species  
 $e_{ch,j}^0$  and  $e_{ch,k}^0$  = standard chemical exergy of influent and effluent species, related to 1 mol

An auxiliary heat source permits this isothermal change to be accomplished at the normal temperature  $T_n$ . A reversible Carnot machine assures reversible heat exchange between the normal standard state and the real environment.

$$w_{3b} = q_{3a} \left( \frac{T_n - T_0}{T_n} \right) = -w_{3a} \left( \frac{T_n - T_0}{T_n} \right) \quad (24)$$

In *Stage 4* the reversible work of changing the temperature and pressure of influent and effluent reference species from the real temperature  $T_0$  and pressure  $p_0$  to the normal standard temperature  $T_n$  and pressure  $p_n$  are calculated. This can be calculated with Equation 19.

In *Stage 5* the reversible work of changing the concentration of a reference species isothermally from the real environmental concentration to the normal standard environment is calculated with Equation 25, which is an extension of Equation 15.

$$w_5 = RT_0 \sum_j n_j \ln \frac{y_{0,j}}{y_{0,n,j}} - RT_0 \sum_k n_k \ln \frac{y_{0,k}}{y_{0,n,k}} \quad (25)$$

So altogether the chemical exergy of a substance is the sum of all the work obtainable from Figure 2.

$$e_{ch} = w_1 + w_{2a} + w_{2b} + w_{3a} + w_{3b}w_4 + w_5 \quad (26)$$

The standard chemical exergy is given by Equation 27.

$$e_{ch}^0 = w_{2a} + w_{3a} = \Delta_r G^0 + \sum_k n_k e_{ch,k}^0 - \sum_j n_j e_{ch,j}^0 \quad (27)$$

where  $\Delta_r G^0$  = standard normal free energy change (increase) for the reference reaction

$n_j, n_k$  = numbers of moles of the influent and effluent species

$e_{ch,j}^0$  and  $e_{ch,k}^0$  = standard chemical exergy of influent and effluent species, related to 1 mol.

Because the calculation of standard chemical exergy by Equation 27 is inconvenient except for calculation of the standard chemical exergy of some pure chemical elements having simple reference reactions, Equation 28 can be used to calculate the standard chemical exergy of other chemical elements and compounds.

$$e_{ch}^0 = \Delta_f G^0 + \sum_{el} n_{el} e_{ch,el}^0 \quad (28)$$

where  $\Delta_f G^0$  = standard normal free energy of formation

$n_{el}$  = number of moles of the elements in the compound under consideration

$e_{ch,el}^0$  = standard chemical exergy of the elements

Values for  $\Delta_f G^0$  can be found in thermodynamic tables or with software that has access to these tables.

## Reference species dissolved in seawater

Because the atmosphere has only 10 appropriate reference chemical species that are needed to calculate the standard chemical exergy of elements, for compounds having elements not included in these ten elements other reference species are needed. The solid species most commonly found on the surface of earth could be such reference species, but the problem here according to Szargut et al. [1988] is that the chemical composition of the earth's surface is not well-defined and exact calculations providing consistent results of the thermodynamic functions of such solid reference species is difficult. For this reason Morris and Steward [1984] proposed that ions or compounds dissolved in seawater could be used as the reference species for some elements. Unfortunately the theory of thermodynamic functions is only sufficiently accurate for monocharged and/or bicharged ions. In some situations the concentration in seawater of some un-ionized molecules containing the chemical element under consideration is big enough that this species can be used as a reference species. The following ionic and molecular reference species dissolved in seawater are (according to Szargut et al. [2005]):

- $\text{Cl}^-$ ,  $\text{AgCl}_2^-$ ,  $\text{B}(\text{OH})_3$  aq,  $\text{BiO}^+$ ,  $\text{Br}^-$ ,  $\text{CdCl}_2$  aq,  $\text{Cs}^+$ ,  $\text{Cu}^{+2}$ ,  
 $\text{HPO}_4^{-2}$ ,  $\text{HAsO}_4^{-2}$ ,  $\text{HgCl}_4^{-2}$ ,  $\text{IO}_3^-$ ,  $\text{K}^+$ ,  $\text{Li}^+$ ,  $\text{MoO}_4^{-2}$ ,  
 $\text{Na}^+$ ,  $\text{Ni}^{+2}$ ,  $\text{PbCl}_2$  aq,  $\text{Rb}^+$ ,  $\text{SO}_4^{-2}$ ,  $\text{SeO}_4^{-2}$ ,  $\text{WO}_4^{-2}$ ,  $\text{Zn}^{+2}$ .

The calculation scheme of standard chemical exergy of reference species dissolved in seawater is shown in Figure 3, which resembles steps 2 and 3 in Figure 2. 1 mol of the element under consideration together with additional elements present in the reference species go into the standard electrochemical cell with hydrogen electrode. If the reference ion is positive a hydrogen ion in monomolar ideal solution is delivered to the cell. If the reference ion is negative, the hydrogen ion flows away from the cell. Hydrogen gas in the standard normal state flows away from the cell in the first case and flows into the cell in the second case. In stage 3 occurs the isothermal change of concentration between the monomolar ideal solution and the conventional seawater. Equation 29, developed by Morris and Steward [1984], can be used to calculate the standard chemical exergy of elements dissolved in seawater.

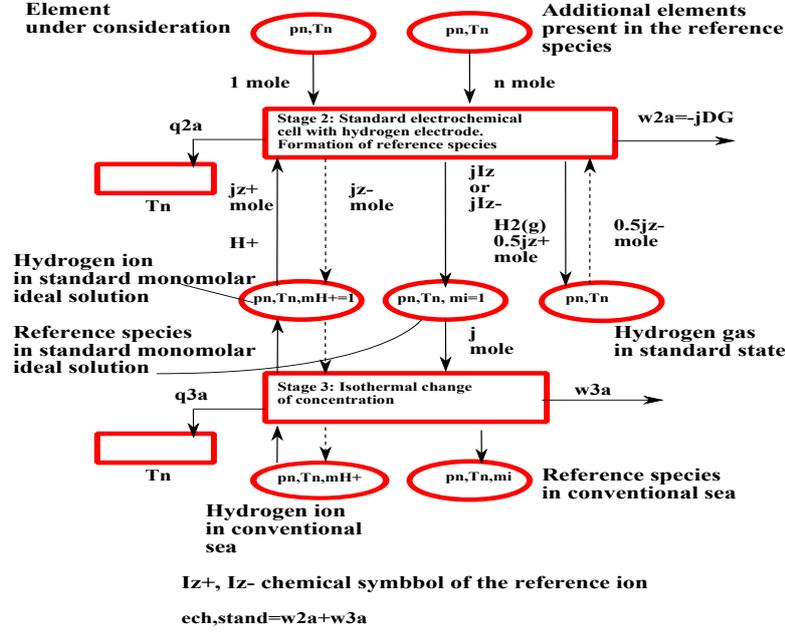


Figure 3: Calculation scheme of standard chemical exergy in the case of reference species dissolved in seawater (adopted from Szargut et al. [1988]).

$$e_{ch,n}^0 = j(-\Delta_f G^0 + 0.5ze_{ch,H_2}^0 - \sum_k \nu_k e_{ch,k}^0 - RT_n[2.303z(pH) + \ln m_n \gamma]) \quad (29)$$

where

$j$  number of reference ions or molecules derived from one molecule of the element under consideration,

$\Delta_f G^0$  formation Gibbs energy of the reference species,

$z$  number of elementary positive charges of the reference ion,

$\nu_k$  number of molecules of additional elements present in the molecule of reference substance,

$e_{ch,H_2}^0, e_{ch,k}^0$  standard chemical exergy of hydrogen gas and of the  $k$ -th additional

element,

$m_n$  conventional standard molarity of the reference substance in seawater,  
 $\gamma$  activity coefficient (molarity scale) of the reference substance in seawater,  
 $pH$  exponent of the concentration of hydrogen ion in seawater (=8,1)

The activity coefficient of single ion can be calculated by means of the Debye-Huckel (Equation 30) or from some advanced thermodynamic property databases.

$$-\log\gamma = \frac{Az_i^2\sqrt{I}}{1 + a_iB\sqrt{I}} \quad (30)$$

where

$A = 0.51 \text{ kg}^{0.5}\text{mol}^{-0.5}$  for water at 298.15 K,

$B = 3.287\text{E}9 \text{ kg}^{0.5}\text{m}^{-1}\text{mol}^{-0.5}$  for water at 298.15 K,

$a_i$  effective diameter of the ion,

$I$  ionic strength of the electrolyte.

The ionic strength of the electrolyte results can be calculated with Equation 31.

$$I = 0.5 \sum_i m_i z_i^2 \quad (31)$$

where

$m_i$  is the molarity of the ion,  $\frac{\text{mol}}{\text{kgH}_2\text{O}}$ ,

$z_i$  is the number of elementary electric charges of the ion.

### Solid reference species

Eventhough a big portion of elements can be calculated based on reference species existing in air and in seawater, some elements need reference species appearing in the external layer of the continental part of Earth's crust. The problem here is that exact calculations of the chemical exergy of the components in the Earth's crust is impossible because the Earth's crust is an extremely complicated mixture of solid solutions. Therefore only approximations of the chemical exergies of the reference species can be obtained based on the conventional standard mole fraction as shown in Equation 32. In the work presented in Szargut et al. [1988] there are 13 elements based on reference species existing on the external layer of the continental part of Earth's crust. In the work of Szargut et al. [2005], 53 such elements were presented.

$$e_{ch,i}^0 = RT_n \ln x_{i,n} \quad (32)$$

With Equation 28 the standard chemical exergy of any substance can be calculated if the standard chemical exergies of all the elements comprising the substance and the Gibbs formation energy are known.

## Mixtures

The chemical exergy of a substance molecule in a mixture is smaller than in its pure state, as it will require work to separate the mixture in its pure constituents, the exergy of separation. For a mixture the partial exergy of a substance can be defined similarly as partial enthalpy, partial entropy and partial free energy. The partial molar chemical exergy can be expressed in terms of the activity  $a_i$  of the component  $i$  of the solution as shown in Equation 33. For an ideal solution the activity of a substance is equal to the molar fraction of the substance in the solution.

$$\bar{e}_{ch,i} = e_{ch,i} + RT_0 \ln a_i \quad (33)$$

With Equations 34 and 35 the total chemical exergy of a solution build up from the different components can be calculated.

$$e_{ch} = \sum_i n_i \bar{e}_{ch,i} \quad (34)$$

$$e_{ch} = \sum_i n_i e_{ch,i} + RT_0 \sum_i \ln a_i \quad (35)$$

If a solution contains only one dissolved species, the standard chemical exergy  $e_{ch}^a$  of the species dissolved in ideal monomolar solution (molarity = 1 mol/kg H<sub>2</sub>O)  $e_{ch}^a$  for aqueous solutions can be calculated with Equation 36.

$$E_{ch}^0 = n_i(e_{ch,i}^a + RT_n \ln m_i \gamma_i) + n_{H_2O}(e_{ch,H_2O} + RT_n \ln x_{H_2O} \gamma_{H_2O}) \quad (36)$$

where  $n_i$  = number of moles of the dissolved species  
 $m_i, \gamma_i$  = molarity and activity coefficient of the dissolved species  
 $x_{H_2O}, \gamma_{H_2O}$  = mole fraction and activity coefficient of H<sub>2</sub>O  
 $e_{ch}^a$  can be calculated with Equation 37.

$$e_{ch}^a = e_{ch}^0 + \Delta_f G_{aq}^0 - \Delta_f G^0 \quad (37)$$

where  $\Delta_f G_{aq}^0$  = standard free energy of formation of the species dissolved in ideal monomolar solution  
 $\Delta_f G^0$  = standard free energy of formation of pure substance.

## Electrolyte solutions

The chemical exergy of electrolyte solutions can be calculated with Equations 34 or 35, where the chemical exergy of an ionic substance in the solution can be calculated with Equation 33. The standard chemical exergy of an ionic species

can be calculated with Equation 29. A more detailed description of the calculation of chemical exergy in electrolyte solutions can be found in Marin and Turégano [1986].

## 0.4 Exergy with AspenPlus streams

In this section two approaches for calculating the exergy values of streams are presented. In the first approach, called AspenStreams, a stream either entering or exiting a process is copied to an additional stream which is then transformed into the pressure and temperature of the environment. This way the physical exergy of the original stream can be easily obtained using Equation 7 and importantly, with any of the property methods available in AspenPlus. The chemical exergy of the stream is calculated using the Standard Chemical Exergy approach and assuming ideal behavior of the components (using Equation (35)).

In the second approach, called AspenData, the physical exergy of a stream is calculated using the stream's molar concentration together with a mixing rule and multiplying this corrected molar concentration with the specific enthalpy and entropy of each species. The benefit here is that no additional streams are needed, but the precision of the calculation depends on the precision of the mixing rule. The chemical exergy of the stream is calculated using the Standard Chemical Exergy approach and assuming ideal behavior of the components (using Equation (35)).

### 0.4.1 Chemical exergy of pure substances

Before using either of the exergy calculating methods, a mutual step for calculating the chemical exergy of pure substances at the pressure and temperature of the environment ( $25^{\circ}\text{C}$  and 1 bar in the examples of this report) is needed. These pure substances are substances that can be found in oxyfuel combustion processes. For the Excel-worksheet application presented in this report, it is also important that these pure substances are ordered in the same way as these substances are presented in the AspenPlus components list, but for a general approach this is not necessary.

The chemical exergies important in oxyfuel combustion processes are presented in Table 2. Here the enthalpies and entropies of the substances are obtained from AspenPlus using the Peng-Robinson Equation Of State (PREOS). The chemical exergies are calculated with Szargut's Standard Chemical Exergy approach, which was shortly presented in Section 0.3.2.

The values of pure substances that are reference species (Argon,  $\text{N}_2$ ,  $\text{O}_2$ ,  $\text{H}_2$  and C) contained in atmosphere can be found either with Equation 17 or directly from

Substance	T	R	M	h	h	s	s	exph	exch	DELTA G <sup>0</sup>
	[K]	[J/(mol*K)]	[kg/kmol]	[J/kg]	[J/kmol]	[J/(kg*K)]	[J/(kmol*K)]	[J/kg]	[kJ/mol]	[kJ/mol]
ARGON	298.15	8.314	39.948	1.30E-11	5.21E-10	3.27E-14	0.0000	0.00E+00	11.69258	
H2O	298.15	8.314	18.015	-1.60E+07	-2.88E+08	-9319.91	-167 900.0000	0.00E+00	0.934833	
N2	298.15	8.314	28.013	-2.72E+02	-7.63E+03	3.120666	87.4205	0.00E+00	0.720062	
O2	298.15	8.314	31.999	-2.94E+02	-9.42E+03	2.674305	85.5746	0.00E+00	3.974677	
NO2	298.15	8.314	46.006	7.19E+05	3.31E+07	-1326.1	-61 007.6700	0.00E+00	55.51227	51.178
NO	298.15	8.314	30.006	3.01E+06	9.02E+07	413.9688	12 421.5900	0.00E+00	88.96057	86.613
S	298.15	8.314	32.080	5.66E+06	1.82E+08	-175.303	-5 620.2130	0.00E+00	609.6	
SO2	298.15	8.314	64.059	-4.64E+06	-2.97E+08	170.326	10 910.8800	0.00E+00	313.4821	-300.093
SO3	298.15	8.314	80.058	-5.36E+06	-4.29E+08	-2380.27	-190 560.0000	0.00E+00	244.5507	-371.011
H2	298.15	8.314	2.016	2.73E+02	5.51E+02	53.22358	107.2881	0.00E+00	236.09	
C	298.15	8.314	12.011	4.34E-11	5.21E-10	1.09E-13	0.0000	0.00E+00	410.24	
CO	298.15	8.314	28.010	-3.95E+06	-1.11E+08	3190.566	89 369.0400	0.00E+00	277.0352	-137.180
CO2	298.15	8.314	44	-8.94E+06	-3.94E+08	65.92509	2 900.7040	0.00E+00	19.85138	-394.363
COAL	298.15	8.314							29.778	[MJ/kg]
ASH	298.15	8.314							0	

Table 2: Enthalpies, entropies and chemical exergies of pure substances relevant for oxyfuel combustion processes.

Szargut et al. [1988] on page 56. The pure substances that are reference species dissolved in seawater (only S in this case) can be found in Szargut et al. [1988]. The standard chemical exergies of pure substances that are not reference species, but can be built up from the reference species (in this case H<sub>2</sub>O, NO<sub>2</sub>, NO, SO<sub>2</sub>, SO<sub>3</sub>, CO and CO<sub>2</sub>), can be obtained with Equation 28. The chemical exergy of coal is calculated according to Szargut et al. [1988] using Equation 38.

$$\begin{aligned} e_{ch}^{coal} &= (C_l + L * z_w) * \beta + (e_{ch,S} - C_S) * z_S + e_{ch,a} * z_a + e_{ch,w} * z_w \\ &= (C_R - 9 * L * z_{H_2}) * \beta + (e_{ch,S} - C_S) * z_S + e_{ch,a} * z_a + e_{ch,w} * z_w \quad (38) \end{aligned}$$

where  $C_F, C_L$  = the gross and net calorific value of moist fuel,  
 $C_S$  = calorific value of sulfur  
 $L$  = enthalpy of water vaporization

$z_{H_2}, z_w$  = hydrogen and water mass fractions in moist fuel

$z_S, z_a$  = sulfur and ash mass fractions in moist fuel

$e_{ch,S}, e_{ch,a}$  = standard chemical exergy of sulfur and ash

$e_{ch,S}^0 - C_S^0 = 9683$  kJ/kg S

$\beta = 1.0437 + 0.1896 * \frac{z_{H_2}}{z_C} + 0.0617 * \frac{z_{O_2}}{z_C} + 0.0428 * \frac{z_{N_2}}{z_C}$

The chemical exergy of ash is neglected in this report.

#### 0.4.2 Physical exergy of streams at environmental conditions calculated by copying entering and exiting AspenPlus streams: AspenStreams

As mentioned, in this approach the physical exergy at environmental conditions of a stream is calculated by copying a stream that either enters or exits a process into an additional stream and changing the pressure and temperature of this stream into the values of the environment by either heating or cooling and compressing or expanding it. The only data needed from AspenPlus is the enthalpy, entropy and molar concentration of the stream in question.

##### A simple example

In order to describe this approach, a simple example is presented. Figure 4 shows the flowsheet of this simple Rankine cycle power plant together with the additional steam needed to calculate the physical exergy values of entering and exiting streams. In the example 1  $\frac{kg}{s}$  of C (stream CIN) as the fuel is burned with 15  $\frac{kg}{s}$  (stream AIRIN) (molar fractions of 21% O<sub>2</sub>, 78% N<sub>2</sub> and 1% argon). The flue

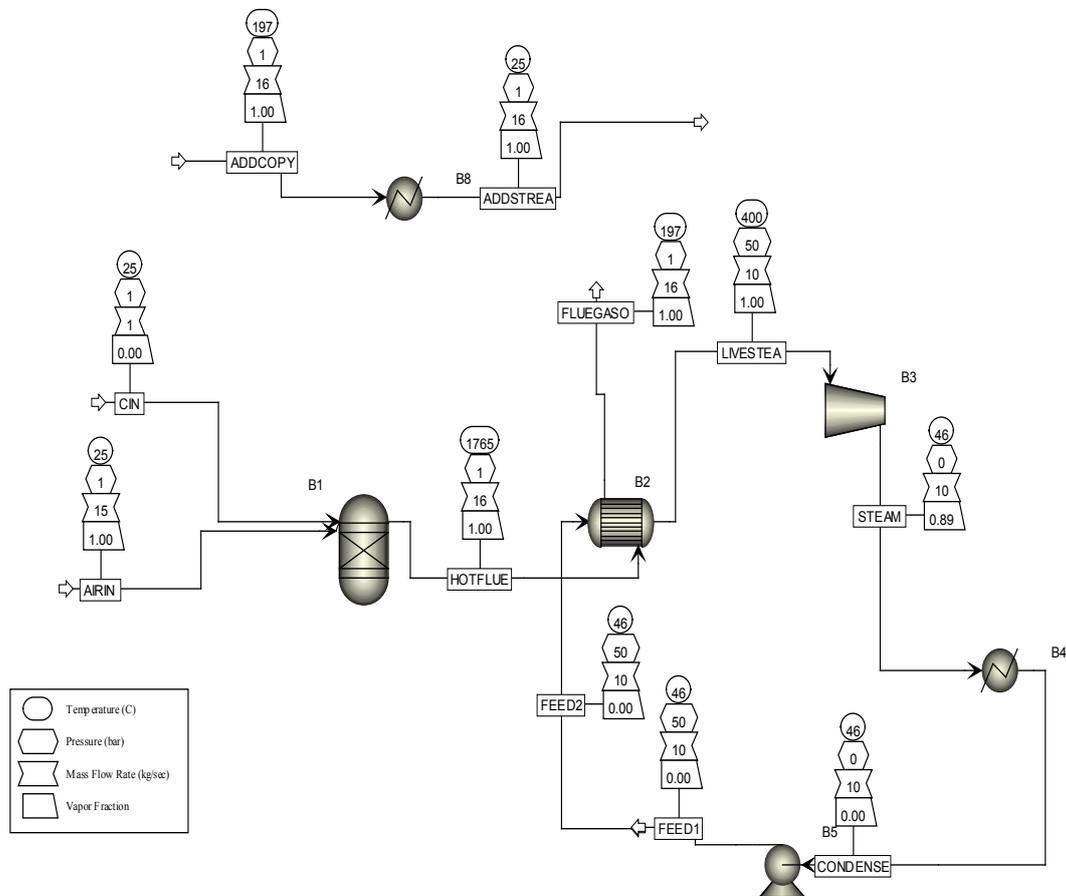


Figure 4: the flowsheet of the simple example

gas produces  $10 \frac{kg}{s}$  live steam (LIVESTEA) having a pressure of 50 bars and 400 °C. This steam is used to produce electricity in a turbine having an isentropic efficiency of 80%. The steam is condensed at 0.1 bar pressure before pumped back to 50 bars.

Altogether there are two streams (AIRIN and CIN) entering and one stream exiting (FLUEGASO) the process. Additionally electricity and heat is produced.

Equations 39 and 40 show how exergy and technical exergy losses are calculated in this case. Equations 41 and 42 show how are the exergy efficiency and technical exergy efficiency calculated. Exergy efficiency considers the difference between total (physical and chemical) exergy, while the technical exergy uses only valuable exergy products. This way the exergy efficiency shows the internal process losses. Table 3 shows the results.

$$E_{loss}^{Tot} = E_{in}^{Tot} - E_{out}^{Tot} - W_{out} - Q_{out} \quad (39)$$

$$E_{loss}^{Tech} = E_{in}^{Fuel} - W_{out} \quad (40)$$

$$E_{eff}^{Tot} = 1 - \frac{E_{loss}^{Tot}}{E_{in}^{Tot}} \quad (41)$$

$$E_{eff}^{Tech} = 1 - \frac{E_{loss}^{Tech}}{E_{in}^{Fuel}} \quad (42)$$

As can be seen from results, the technical exergy efficiency is substantially less than the total exergy efficiency. This is because the total exergy efficiency considers as losses only the losses that occurs in the process. So all streams exiting or entering the process are considered to have exergy potential left that could be utilized. As an example the heat exiting the process at 46 °C is assumed to have exergy potential. In the technical exergy efficiency this heat is also considered to be a loss. The same is true for both physical and chemical exergy of the flue gas stream (FLUEGASO).

### 0.4.3 Exergy calculated using AspenPlus enthalpy and entropy data: AspenData

In this approach the physical exergy of a stream is calculated using the stream's molar concentration together with a mixing rule and multiplying this corrected molar concentration with the specific enthalpy and entropy of each species. Also here the only data needed from AspenPlus is the enthalpy, entropy and , molar concentration of the stream in question. The benefit is that no additional streams are needed, but the precision of the calculation depends heavily on the precision of the mixing rule. In this report the mixing is based on Equation 35, where the activities are the molar concentrations, so ideal mixtures are assumed. Generally the mixing rule should be based on the chosen property method and property model.

#### A simple example

The simple case is used to present this approach. Exergy losses, technical exergy losses, exergy efficiency and technical exergy efficiency are calculated with Equations 39, 40, 41 and 42, respectively. Table 4 shows the results.

ExPhin	W	0.00E+00
ExPhout	W	5.83E+05
ExCheIn	W	3.42E+07
ExChOut	W	1.23E+06
ExTOTIn	W	3.42E+07
ExTOTOOut	W	1.81E+06
Wout	W	8.67E+06
Qoout	W	9.69E+06
ExLossTot	W	1.403407E+07
ExLossTech	W	2.54815E+07
EffTot		58.98 %
EffTech		25.40 %

		1	1	-1
Name		AIRIN	CIN	FLUEGASO
Small		1.00E-30	1.00E-30	1.00E-30
Tref	K	298.15	298.15	298.15
h	J/KMOL	-7.73E-10	5.21E-10	-5.79E+07
h0	J/KMOL	-7.73E-10	5.21E-10	-6.33E+07 From the additional stream
s	J/KMOL-K	4.83E+03	1.31E-12	2.03E+04
s0	J/KMOL-K	4.83E+03	1.31E-12	6.24E+03 From the additional stream
smix	J/KMOL-K	0.00E+00	0.00E+00	0.00E+00 Always zero with this additional stream approach
s0ToT	J/KMOL-K	4.83E+03	1.31E-12	6.24E+03
ExPh	J/KMOL	0.00E+00	0.00E+00	1.13E+06
ExChBase	kJ/MOL	1.51E+00	4.10E+02	4.07E+00
ExCHMix	kJ/MOL	-1.41E+00	0.00E+00	-1.69E+00
ExCHTot	kJ/MOL	1.06E-01	4.10E+02	2.38E+00
<b>ExTot</b>	<b>kW</b>	<b>5.50E+01</b>	<b>3.42E+04</b>	<b>5.84E+05</b>
ExPhin	kW	0.00E+00	0.00E+00	0.00E+00
ExPhout	kW	0.00E+00	0.00E+00	5.83E+02
ExChein	kW	5.50E+01	3.42E+04	0.00E+00
ExCheout	kW	0.00E+00	0.00E+00	1.23E+03

Table 3: Results of the simple case exergy analysis with the approach that uses additional AspenPlus streams (AspenStreams)

ExPhin	W	0.00E+00
ExPhout	W	0.00E+00
ExCheIn	W	3.42E+07
ExChOut	W	1.23E+06
ExTOTIn	W	3.42E+07
ExTOTOut	W	1.23E+06
Wout	W	8.67E+06
Qoout	W	9.69E+06
ExLossTot	W	1.461704E+07
ExLossTech	W	2.54815E+07
EffTot		57.27 %
EffTech		25.40 %

Name		1      1      -1		
		AIRIN	CIN	FLUEGASO
Small		1.00E-30	1.00E-30	1.00E-30
Tref	K	298.15	298.15	298.15
h	J/KMOL	-7.73E-10	5.21E-10	-5.79E+07
h0	J/KMOL	-7.93E+03	5.21E-10	-6.33E+07
s	J/KMOL-K	4.83E+03	1.31E-12	2.03E+04
s0	J/KMOL-K	8.62E+01	1.31E-12	5.39E+02
smix	J/KMOL-K	-1.41E+00	0.00E+00	-1.69E+00
s0ToT	J/KMOL-K	8.48E+01	1.31E-12	5.37E+02
ExPh	J/KMOL	0.00E+00	0.00E+00	0.00E+00
ExChBase	kJ/MOL	1.51E+00	4.10E+02	4.07E+00
ExCHMix	kJ/MOL	-1.41E+00	0.00E+00	-1.69E+00
ExCHTot	kJ/MOL	1.06E-01	4.10E+02	2.38E+00
<b>ExTot</b>	<b>kW</b>	<b>5.50E+01</b>	<b>3.42E+04</b>	<b>1.23E+03</b>
ExPhin	kW	0.00E+00	0.00E+00	0.00E+00
ExPhout	kW	0.00E+00	0.00E+00	0.00E+00
ExChein	kW	5.50E+01	3.42E+04	0.00E+00
ExCheout	kW	0.00E+00	0.00E+00	1.23E+03

Table 4: Results of the simple case exergy analysis with the approach that uses AspenPlus enthalpy and entropy data (26 AspenData)

Component	[%]
C	74
H <sub>2</sub>	6
O <sub>2</sub>	10
Ash	10
moisture	10

Table 5: Fuel composition

## 0.5 Oxyfuel case

In this section, the two exergy calculation approaches have been applied in a oxyfuel power plant process. The process consumes  $24 \frac{kg}{s}$  of coal (Table 5 gives the ultimate analysis of the coal) and produces  $152.2 MW$  electricity for sale. Air Separation Unit produces  $23.6 \frac{kg}{s}$  gas of which of  $22.9 \frac{kg}{s}$  is O<sub>2</sub> and the rest is argon. The fluegas flow to the CO<sub>2</sub> separation unit is  $86.3 \frac{kg}{s}$ , from which  $63.7 \frac{kg}{s}$  is CO<sub>2</sub>. From this CO<sub>2</sub>  $62.2 \frac{kg}{s}$  exists as liquid after the final condenser that operates at 100 bar and 12 °C. The purity of the existing liquid CO<sub>2</sub> is 87%. Figure 5 shows the flowsheet done with AspenPlus.

The results of the exergy analysis using the two approaches presented in 0.4 are shown in Table 6. As can be seen from the results, both calculation methods provide similar results. Assuming that Peng Robison Equation of State (PREOS) is an appropriate property method choice, the results for oxyfuel combustion processes show that method AspenData is accurate enough and because no additional streams are needed, it can be considered as the more efficient and hence better method.

The exergy analysis shows that a substantial exergy loss occurs in the oxyfuel process. In the total exergy efficiency (using Equations 39 and 41) it is assumed that all streams, and both the chemical and physical exergy, entering and exiting are considered. So this efficiency only shows the internal exergy losses. Interestingly the exergy losses mainly occurs in the power plant, and for example ASU does not destroy too much exergy. This is partly due to the assumption that all streams are “products”, including f.ex. the nitrogen exiting ASU has a lot of chemical exergy. Technically this chemical exergy is not so easily utilized and for this reason the technical exergy losses are also shown in Table 6. Here only the valuable inputs and valuable outputs are considered. In ASU this means that valuable inputs are electricity, and valuable output is oxygen (both physical and chemical exergy). In the power plant valuable inputs are fuel and oxygen (both physical and chemical exergy) and valuable output is electricity. In the CO<sub>2</sub> separation process, valuable

## POWER PLANT

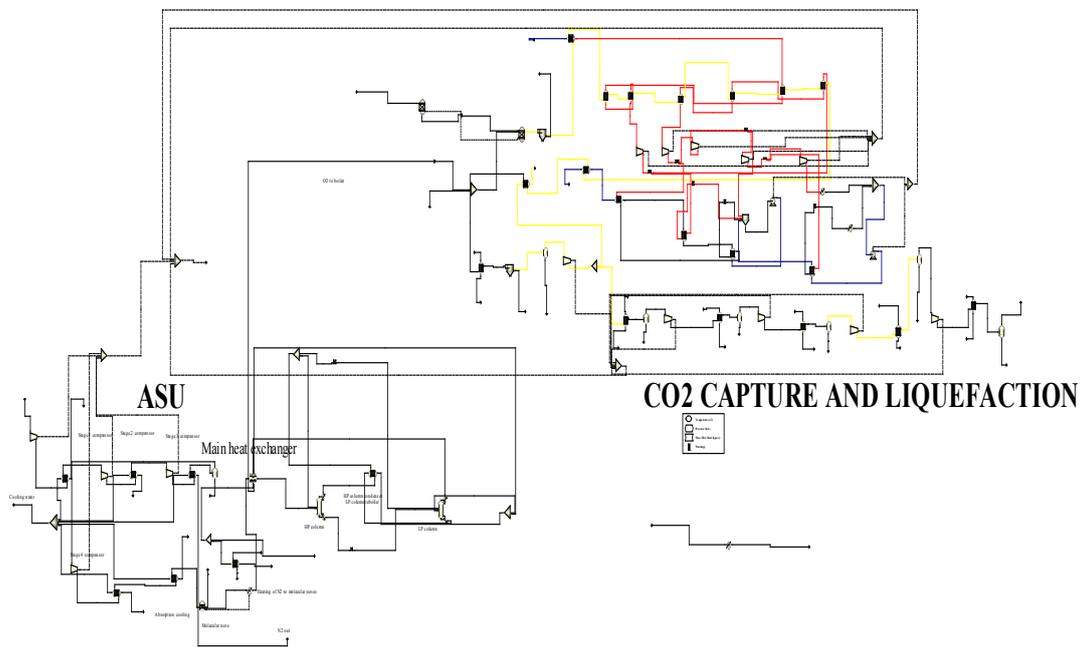


Figure 5: The flowsheet of the oxyfuel combustion process including ASU and CO<sub>2</sub> separation unit

	<b>Total Exergy Losses [MW]</b>	
	AspenData	AspenStreams
ASU	18.4	18.4
Power Plant	518.8	518.8
CO <sub>2</sub> Sep	25.4	25.4
TOTAL	562.4	562.4
	bfseriesTotal Exergy Efficiency[%]	
ASU	32.0	32.0
Power Plant	27.2	27.2
CO <sub>2</sub> Sep	93.5	93.5
TOTAL	49.3	49.3
	bfseriesTechnical Exergy Losses [MW]	
	AspenData	AspenStreams
ASU	18.4	18.4
Power Plant	518.8	518.8
CO <sub>2</sub> Sep	25.3	25.3
TOTAL	562.5	562.5
	bfseriesTechnical Exergy Efficiency[%]	
ASU	0.0	0.0
Power Plant	27.4	27.4
CO <sub>2</sub> Sep	0.0	0.0
TOTAL	21.3	21.3

Table 6: Results of the exergy analysis of the oxyplant using both methods (AspenData and AspenStreams)

input is electricity and valuable output is the physical and chemical exergy of CO<sub>2</sub> exiting as liquid. For the overall process the only valuable input is the fuel and outputs are electricity and liquefied CO<sub>2</sub>.

## 0.6 Conclusions and future work

In this report, the main focus has been to present two methods for performing exergy analysis using AspenPlus simulation software. The other objective is to test these methods on a oxyfuel power plant process. Although the methods presented in this report are applied on Excel Worksheets, the methods could decently easily be written as part of AspenPlus code. In general the methods presented in this report could be applied also to other types of process simulation software. The only necessity is that stream enthalpies, entropies and molar concentrations are

provided.

In the first approach, called AspenStreams, the physical exergy at environmental conditions of a stream is calculated by copying a stream that either enters or exits a process into an additional stream and changing the pressure and temperature of this additional stream into the values of the environment by either heating or cooling and compressing or expanding it. The chemical exergy is calculated using the Standard Chemical Exergy approach by Szargut (Szargut et al. [1988]).

In the second approach, called AspenData, the physical exergy of a stream is calculated using the stream's molar concentration together with a mixing rule and multiplying this corrected molar concentration with the specific enthalpy and entropy of each species. The benefit here is that no additional streams are needed, but the precision of the calculation depends on the precision of the mixing rule. The chemical exergy is calculated using the Standard Chemical Exergy approach by Szargut (Szargut et al. [1988]).

In the oxyfuel case, both approaches give the same results, so it can be concluded, that the AspenData approach is more convenient in oxyfuel combustion processes. This is at least when Peng-Robinson Equation of State is used as the property method providing the enthalpies and entropies.

In the future, the AspenData method could be incorporated into AspenPlus code or to have an external program calling data from AspenPlus and after the calculations sending this data back to AspenPlus. Another important continuation would be to incorporate other mixing rule that preferably would be based on the property methods available. It would be beneficial to test the methods also in other Carbon Capture and Storage (CCS) applications. And most importantly, it would be very important to use the exergy analysis methods as part of valuating different CCS processes. This is for the reason that only with second law studies, the real losses can be found.

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