

Jaroslav KOZACZKA*, Pavel KOLAT**

EXERGY IN TECHNOLOGICAL SUBSTANCE EXCHANGE PROCESSES

EXERGIE V TECHNOLOGICKÝCH PROCESECH VÝMĚNY LÁTKY

Abstract

The exergy concept applied to technological substance exchange processes has been presented and discussed in detail. The special behavior of the thermal and substantial parts of exergy flows has been taken into account in analyzing simple drying/wetting and CO₂-absorption/desorption processes. In the exergy analysis of drying certain practical simplifications and approximations have been introduced, which can be advantageous for the mechanical engineer in preparing project brief foredesign. CO₂-absorption processes are important for the so-called CCS new power technologies, especially the post-combustion ones. All the analyzes presented focus on the thermodynamic effectivity, which can be used in exergy rating of complex systems independent on their structure.

Abstrakt

Koncept exergie byl aplikován na látkové výměny v technologických procesech a byla provedena jejich podrobná diskuze. Zvláštní chování tepelných a podstatných částí exergetických toků byla vzata v úvahu při analýze jednoduchých sušení/zvlhčování a CO₂-absorbčních a desorbčních procesů. V exergetické analýze sušení některé praktické zjednodušení a aproximace byly zavedeny, což může být výhodné pro strojní inženýry, při před-projektové přípravě. CO₂-absorpční procesy jsou důležité pro moderní energetické technologie CCS, zejména po spalovacím procesu. Všechny předložené analýzy se zaměřují na termodynamickou efektivitu, a mohou být použity v exergetickém hodnocení komplexních systémů, nezávisle na jejich struktuře.

1 INTRODUCTION

In power engineering and especially in process & chemical engineering systems the very important processes are the so-called technological exchange unit operations. They are the heat and substance (mass) transfer phenomena applied to achieve certain temperatures and/or chosen specie concentrations. Thus, the technological exchange processes can be parted into three main groups due to their goal in the engineering practice. They are: heat exchange, heating up (or cooling down), drying (wetting) and absorption. The first group is the most important in every engineering branch and hitherto very good described and analyzed from the thermodynamics point of view. Drying and absorption, however, are not that widely known and applied in thermodynamic analyzes, especially using the *Second Law* and the exergy method. The goal of investigations (the presented contribution is a part of them) led within the project is the universal (or generalized) method of modeling and exergy analysis of main processes that can be used for building whole complex systems modeled, analyzed and rated in the same way. The homogeneity of the proposed approach is its main advantage and the right use of the exergy method, which allows analyzes taking into account not only *First Law* (balancing), but also *Second Law* (process run possibility) and the natural environment with constant intensities during the time of analysis. The following discussion is dedicated to the generalized exergy analysis and rating of main technological substance exchange processes with the so-called thermodynamic effectivity quotient.

* Prof. Ing., Dr. (Prof. dr hab. inž), AGH – University of Science and Technology, Faculty of Mechanical Engineering and Robotics, Department of Power Engineering and Environmental Protection, Mickiewicza 30, 30-059 Kraków, Poland – corresponding author (kozaczka@agh.edu.pl)

** Prof. Ing., DrSc., VŠB – Technical University of Ostrava, Faculty of Mechanical Engineering, Department of Power Engineering, 17 listopadu 15, 708 33 Ostrava-Poruba, Czech Republic

2 TECHNOLOGICAL DRYING AND WETTING PROCESSES

The technological substance exchange processes run in general in counter-current and concurrent vessels. Drying and wetting processes, however, can be showed in the same manner the heating up and cooling down ones, Figure 1.

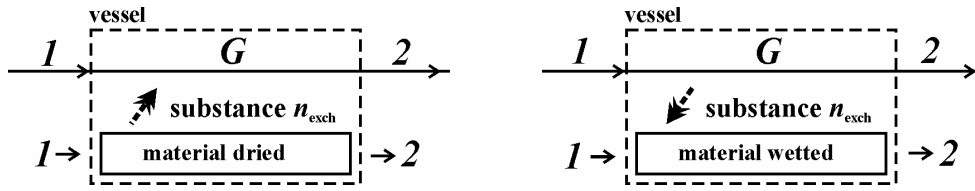


Fig. 1 Drying (to the left) and wetting (to the right) as technological substance exchange processes in a vessel (apparatus)

The exergy balance for processes showed in Figure 1 will be to

$$E_{I,MD,1} + E_{I,G,1} = E_{I,MD,2} + E_{I,G,2} + T_0 \Delta S_{irr}$$

and

$$E_{I,MHU,1} + E_{I,G,1} = E_{I,MHU,2} + E_{I,G,2} + T_0 \Delta S_{irr}$$

with subscripts *MD* for „material dried“, *MW* for „material wetted“ and *G* for gas stream. From above two balances yields their another form

$$-(E_{I,MD,2} - E_{I,MD,1}) - (E_{I,G,2} - E_{I,G,1}) = T_0 \Delta S_{irr} \quad \text{or} \quad -\Delta E_{I,MD} - \Delta E_{I,G} = T_0 \Delta S_{irr} \quad (01)$$

and

$$-(E_{I,MW,2} - E_{I,MW,1}) - (E_{I,G,2} - E_{I,G,1}) = T_0 \Delta S_{irr} \quad \text{or} \quad -\Delta E_{I,MW} - \Delta E_{I,G} = T_0 \Delta S_{irr} \quad (02)$$

Moisture (or humidity) changes in processes presented in Figure 1 should be, however, strictly described. For simplicity it can be assumed an adiabatic–isobaric process in both cases. There can be differentiated between a simplified isothermal drying (and wetting) and a non–isothermal one. This is because the two substances exchanging media (gaseous agent and dried/wetted material) are not in contact, just like in absorption processes).

2.1 Isothermal Process Conditions

In this case temperature changes of the material dried (or wetted) and of the gaseous medium are in general negligible. Only moisture contents changes: in the dried material diminishes, in the wetted one rises. In the gas working medium it rises in the drying process or diminishes in the wetting one. The moisture contents will be defined as

$$x = \frac{M_{\text{moisture}}}{M_{\text{dry air}}} \left[\frac{\text{kg moisture}}{\text{kg dry air}} \right] \equiv x^{mc}$$

and very often instead of the symbolic *x* will be used *d*, *X* or *Y* (the last one especially in the process & chemical engineering, e.g. [1]). The last symbolic refers to the appropriate usage in the substance exchange analysis for gaseous phase, although as a quotient of appropriate mole numbers. Because of the assumed process isothermal conditions the relative humidity φ of the gas medium changes with the moisture contents *x* in a very good known way. To differentiate the moisture contents from the molar fraction — both of them are usually denoted by *x* — the first one will be marked by the symbolic x^{mc} (the superscript *mc* is for „moisture contents“).

The dried material can be moistened by any liquid, but in following it will be assumed the only moisture is water (in fact the most general medium for power engineers), the same refers to wet-

ting processes. The assumption makes the exergy analyzes easier because in the natural environment the molar concentration of water (in the hydrosphere) will be assumed to $x_{\text{water},0}=1$, e.g. [2]–[3] and other authors which means, the natural atmosphere is the dry air. The last assumption can be seen as a somewhat controversial one, but there is not any evidence for a certain humidity value in a unique atmospheric air. In opposite to works of JAN SZARGUT who assumed his own natural environment relative humidity value of $\phi_0=0.6$ (other researchers gave sometimes their own, but even different ones), either the *Zeroth Law of Thermodynamics* will be taken into account as a main assumption for the classical thermodynamics (R.H. FOWLER, 1931; Los Angeles, 1932) and there will be not tried to apply the equilibrium (i.e. classical) thermodynamics methods to the non–equilibrium processes (natural environment as a non–equilibrium system). In thermodynamic analyzes, especially according to the proposed method the exergy changes are important but not exergy absolute numerical values. They can vary up to assumed natural environment state, i.e. T_0, p_0 , and eventually $\phi_0 \neq 0$.

In general the exergy change is a sum of a thermal exergy change caused by the temperature change, a mechanical one caused by the pressure change and the chemical exergy change, cause by the change of the chemical potential, i.e.

$$\Delta E_1 = \Delta E_{1,T} + \Delta E_{1,p} + \Delta E_{1,\mu}$$

because the exergy of enthalpy E_1 (of a flow system in general) is a parameter of state, e.g. [2], [4]. At isothermal–isobaric conditions above balance equations will be to

$$-\Delta E_{1,MD} - \Delta E_{1,G,\mu} = T_0 \Delta S_{\text{irr}} \quad \text{and} \quad -\Delta E_{1,MW} - \Delta E_{1,G,\mu} = T_0 \Delta S_{\text{irr}}$$

The chemical substance changes (chemical reactions) are excluded, so that the whole chemical exergy change is due to the moisturizing substance (water H_2O) concentration change. For water with assumed $x_{\text{water},0}=1$ there is no need to differentiate the whole molar concentration change below or above the $x_{\text{water},0}$ value (just like below or above T_0). The same refers to species not represented in the natural environment, for which the so–called apparent natural environment concentration always equals to 1, either (they could be synthesized using the devaluation chemical reaction according to the classical contribution of JAN SZARGUT). Because for the concentration change from x_1 to x_2 the chemical concentration exergy change of a gaseous medium is

$$\Delta E_{1,G,\mu}^x = n_{\text{G,H}_2\text{O},2} \bar{R} T_0 \ln x_2 - n_{\text{G,H}_2\text{O},1} \bar{R} T_0 \ln x_1 \quad \text{and} \quad \Delta E_{1,G,\mu}^0 = (n_{\text{G},2} x_2 - n_{\text{G},1} x_1) \bar{e}_{\mu,\text{H}_2\text{O}}^0$$

It is to emphasize that the subscript *H2O* refers to the water steam and the subscript *water* to the liquid H_2O . For water the chemical zero exergy equals to zero, but for the water steam it is $\bar{e}_{\mu,\text{H}_2\text{O}}^0 = 10.38647 \text{ kJ/mol}$ for $T=283.15 \text{ K}$, $\bar{e}_{\mu,\text{H}_2\text{O}}^0 = 9.78333 \text{ kJ/mol}$ for $T=288.15 \text{ K}$, $\bar{e}_{\mu,\text{H}_2\text{O}}^0 = 9.18381 \text{ kJ/mol}$ for $T=293.15 \text{ K}$, $\bar{e}_{\mu,\text{H}_2\text{O}}^0 = 8.80795 \text{ kJ/mol}$ for $T=296.15 \text{ K}$, $\bar{e}_{\mu,\text{H}_2\text{O}}^0 = 8.58785 \text{ kJ/mol}$ for $T=298.15 \text{ K}$ (standard chemical exergy) and $\bar{e}_{\mu,\text{H}_2\text{O}}^0 = 8.36824 \text{ kJ/mol}$ for $T=300 \text{ K}$. The zero exergy for water steam has been determined using the devaluation reaction according to JAN SZARGUT and that is why its apparent molar fraction in the natural environment equals to 1, just like for the water (liquid), [2]. The total change of the chemical exergy for the concentration change from x_1 to x_2 in the gaseous medium yields

$$\Delta E_{1,G,\mu} = \Delta E_{1,G,\mu}^0 + \Delta E_{1,G,\mu}^x$$

the above two balances according to Equations (01)–(02) are

$$-\Delta E_{1,MD} - n_{\text{G,H}_2\text{O},2} \bar{R} T_0 \ln x_{\text{H}_2\text{O},\text{G},2} + n_{\text{G,H}_2\text{O},1} \bar{R} T_0 \ln x_{\text{H}_2\text{O},\text{G},1} - (n_{\text{G,H}_2\text{O},2} - n_{\text{G,H}_2\text{O},1}) \bar{e}_{\mu,\text{H}_2\text{O}}^0 = T_0 \Delta S_{\text{irr}} \quad (03)$$

for a drying process, and

$$-\Delta E_{1,MW} - n_{\text{G,H}_2\text{O},2} \bar{R} T_0 \ln x_{\text{H}_2\text{O},\text{G},2} + n_{\text{G,H}_2\text{O},1} \bar{R} T_0 \ln x_{\text{H}_2\text{O},\text{G},1} - (n_{\text{G,H}_2\text{O},2} - n_{\text{G,H}_2\text{O},1}) \bar{e}_{\mu,\text{H}_2\text{O}}^0 = T_0 \Delta S_{\text{irr}} \quad (04)$$

for a wetting one. Thus, for the exergy change determination of the drying (or wetting) gaseous medium the water steam, molar flows and their molar concentrations in a total gas flow at the start ($n_{G,H_2O,1}$ and $x_{H_2O,G,1}$) and at the end of the process ($n_{G,H_2O,2}$ and $x_{H_2O,G,2}$) are needed.

Molar fractions x can be determined knowing the moisture contents x^{mc} for dry air ($\mu_{air}=29$ kg/kmol) and water steam ($\mu_{H_2O}=18$ kg/kmol) pseudo-binary mixture (the humid air) from

$$x_{H_2O} = \frac{n_{H_2O}}{n_{air} + n_{H_2O}} = \frac{x^{mc}}{\frac{\mu_{H_2O}}{\mu_{air}} + x^{mc}} = \frac{x^{mc}}{0.622 + x^{mc}}$$

The next problem is determining the exergy change of the moisture (or simply water, according to the assumption made) in the material dried or wetted. In the first case the appropriate exergy change will be equal to the evaporating exergy at the process temperature, and in the second one the appropriate condensation exergy at the process temperature, either. In the drying process the evaporation exergy change of the mass $M_{H_2O,MD}$ equals to

$$\Delta E_{I,MD} = M_{H_2O,MD} \Delta e_{I, \text{evap}} = M_{H_2O,MD} (i'' - i' - T_0 s'' + T_0 s') = M_{H_2O,MD} \cdot \left(1 - \frac{T_0}{T}\right) \cdot r \quad (05)$$

where i'' , i' , s'' , s' and r are enthalpies, entropies and evaporation heat ($r=i''-i'$) at the process temperature T (usually equal or higher than T_0), which can be taken from thermodynamic tables for water steam, e.g. [5]. The appropriate determination of the exergy change of the wetted material, i.e. for the water condensing in it, yields

$$\Delta E_{I,MW} = M_{H_2O,MD} \Delta e_{I, \text{cond}} = M_{H_2O,MW} (i'' - i' - T_0 s'' + T_0 s') = M_{H_2O,MW} \cdot \left(1 - \frac{T_0}{T}\right) \cdot r \quad (06)$$

The last step in determining the so-called thermodynamic transition as a base for formulating the generalized exergy rating quotient, the thermodynamic effectivity, is stating the behavior of every term of the balance equation. For certain numerical values it can be made very simply within the computer program (the term can be less or greater than zero), but for general analysis a special discussion is needed. In drying processes the mole number of the gaseous medium rises and there rise the water steam concentrations in it, either. Thus, the Equation (03) will be to

$$-\Delta E_{I,MD} - \left| n_{G,H_2O,2} \bar{R} T_0 \ln x_{H_2O,G,2} - n_{G,H_2O,1} \bar{R} T_0 \ln x_{H_2O,G,1} \right| - \left| (n_{G,H_2O,2} - n_{G,H_2O,1}) \bar{e}_{\mu,H_2O}^0 \right| = T_0 \Delta S_{\text{irr}} \quad (07)$$

or

$$-\Delta E_{I,MD} - \left| \Delta E_{I,G,\mu}^x \right| - \left| \Delta E_{I,G,\mu}^0 \right| = T_0 \Delta S_{\text{irr}} \quad (08)$$

The water evaporation exergy will diminish the total exergy of the dried material, so the Equation (05) will be to

$$\Delta E_{I,MD} = M_{H_2O,MD} (r - T_0 s'' + T_0 s') = M_{H_2O,MD} \left(1 - \frac{T_0}{T}\right) \cdot r \equiv -\left| \nabla E_{I,MD} \right| \quad (09)$$

and the Equation (08) finally to

$$\left| \nabla E_{I,MD} \right| - \left| \Delta E_{I,G,\mu}^x \right| - \left| \Delta E_{I,G,\mu}^0 \right| = T_0 \Delta S_{\text{irr}}$$

The thermodynamic transition formula yields

$$\left| \nabla E_{I,MD} \right| \rightarrow \left| \Delta E_{I,G,\mu}^x \right| + \left| \Delta E_{I,G,\mu}^0 \right| + T_0 \Delta S_{\text{irr}} \quad (10)$$

and the thermodynamic effectivity of the drying process according to the presented one in Figure 1

$$\varepsilon_{\text{dry}} = \frac{|\Delta E_{I,G,\mu}^x| + |\Delta E_{I,G,\mu}^0|}{|\nabla E_{I,MD}|} \quad (11)$$

The same procedure made for the wetting process presented in Figure 1, either, leads to the thermodynamic transition formula

$$|\nabla E_{I,G,\mu}^x| + |\nabla E_{I,G,\mu}^0| \rightarrow |\Delta E_{I,MD}| + T_0 \Delta S_{\text{irr}}$$

and the thermodynamic effectivity quotient (for processes above T_0)

$$\varepsilon_{\text{dry}} = \frac{|\Delta E_{I,MW}|}{|\nabla E_{I,G,\mu}^x| + |\nabla E_{I,G,\mu}^0|}$$

2.2 Non–Isothermal Process Conditions

In the technological practice processes showed schematically in Figure 2 run in adiabatic–isobaric but usually in non–isothermal conditions. In drying processes the gaseous agent cools down, but its moisture contents and, obviously, the relative humidity rises. The temperature of the dried material rises, especially in drum vessels, where a loose material is lead against the gaseous agent flow (counter–current case). Following discussions, however, will be limited to the cases presented in Figure 1, emphasizing the drying processes as a much more often applied one in the technological practice. Hence, Equations (05)–(06) can be applied with a mean dried (or wetted) material temperature in a process. The problem is, how to determine the exergy changes of the gaseous agent, while its temperature and humidity changes simultaneously. There can be adopted an approximate method, the idea of which has been presented in [6].

In the case of drying the total exergy change of the gaseous stream is

$$\Delta E_{I,G} = \Delta E_{I,G,T} + \Delta E_{I,G,\mu}^x + \Delta E_{I,G,\mu}^0 = I_{G,2} - I_{G,1} - T_0 (S_{G,2} - S_{G,1}) = \Delta I_G - T_0 \Delta S_G$$

Knowing temperatures and relative humidities φ (or moisture contents x^{mc}) of the gas agent at the start and at the end of a drying process, i.e. $T_1, T_2, \varphi_1, \varphi_2$ (or $x_1^{\text{mc}}, x_2^{\text{mc}}$), the enthalpy change can be determined using the MOLLIER i – x^{mc} (i.e. i – x) diagram. Even the very good known analytical formulas can be applied.

Excluding for the following approximations the gaseous stream G exergy change due to the water steam zero exergy, the enthalpy change of the gaseous stream equals exactly to

$$\Delta I_G = M_{\text{dry air}} \Delta i_{G,1+x}$$

with

$$\Delta i_{G,1+x} = c_{p,\text{air}} (T_{G,2} - T_{G,1}) + x^{\text{mc}} c_{p,\text{H}_2\text{O}} (T_{G,2} - T_{G,1})$$

In fact, the above expression is not exact because x^{mc} changes in a process. It can be, however, used the mean value, e.g. the arithmetic one. But because the x^{mc} values are very low, the above expression can be further simplified and approximated to get

$$\Delta i_{G,1+x} \cong (c_{p,\text{air}} + x_1^{\text{mc}} c_{p,\text{H}_2\text{O}}) (T_{G,2} - T_{G,1})$$

The moisture contents value at the start of a process has been taken into account, because it is usually very good known. Thus,

$$\Delta I_G \cong M_{\text{dry air}} \left[(c_{p,\text{air}} + x_1^{\text{mc}} c_{p,\text{H}_2\text{O}}) (T_{G,2} - T_{G,1}) \right] \quad (12)$$

Determination of the entropy change of the gas agent is much more complicated. From the very good known exact formula

$$\Delta S_{G,1+x} = c_{p,\text{air}} \ln \frac{T_{G,2}}{T_{G,1}} - R_{\text{air}} \ln \frac{p_{\text{air},2}}{p_{\text{air},1}} + x^{\text{mc}} c_{p,\text{H}_2\text{O}} \ln \frac{T_{G,2}}{T_{G,1}} - x^{\text{mc}} R_{\text{H}_2\text{O}} \ln \frac{p_{\text{H}_2\text{O},2}}{p_{\text{H}_2\text{O},1}}$$

can be stated that the first and third terms of the right hand side describe entropy change of the gaseous agent G due to the temperature change, and the second and fourth term the entropy change due to the moisture contents change (in general heat transfer and substance transfer, respectively). Pressures p_{air} and $p_{\text{H}_2\text{O}}$ are partial dry air and moisture (H_2O) pressures in the humid gas. Just like in the case of the enthalpy change some simplifications and approximations can be undertaken (the x^{mc} numerical values and their changes are very small in comparison to the dry air content, and there are usually known quantities at the start of a process), e.g.

$$\Delta S_{G,1+x} \cong (c_{p,\text{air}} + x_1^{\text{mc}} c_{p,\text{H}_2\text{O}}) \ln \frac{T_{G,2}}{T_{G,1}} - (R_{\text{air}} + x_1^{\text{mc}} R_{\text{H}_2\text{O}}) \ln \frac{p_{\text{air},2}}{p_{\text{air},1}} \quad (13)$$

with

$$c_{p,G} = c_{p,\text{air}} + x_1^{\text{mc}} c_{p,\text{H}_2\text{O}} \quad \text{and} \quad R_G = R_{\text{air}} + x_1^{\text{mc}} R_{\text{H}_2\text{O}} \quad (14)$$

cf. Equation (12), and hence

$$\Delta S_G = M_{\text{dry air}} \Delta S_{G,1+x} = M_{\text{dry air}} \left(c_{p,G} \ln \frac{T_{G,2}}{T_{G,1}} - R_G \ln \frac{p_{\text{air},2}}{p_{\text{air},1}} \right)$$

The expression above can be made more convenience for calculations after some further simplifications. From the very good known humid gas units conversion equation

$$x^{\text{mc}} = \frac{\mu_{\text{H}_2\text{O}}}{\mu_{\text{air}}} \frac{p_{\text{H}_2\text{O}}}{p - p_{\text{H}_2\text{O}}}$$

with $p = p_{\text{air}} + p_{\text{H}_2\text{O}}$ yields for the partial pressure p_{air}

$$p_{\text{air}} = \frac{0.622 p}{0.622 + x^{\text{mc}}}$$

because $\mu_{\text{H}_2\text{O}}/\mu_{\text{air}} = 18/29 \approx 0.622$. Setting the quantity into the last term of the right hand side of Equation (13) one gets

$$R_G \ln \frac{p_{\text{air},2}}{p_{\text{air},1}} = R_G \ln \frac{0.622 + x_1^{\text{mc}}}{0.622 + x_2^{\text{mc}}} = R_G \ln \frac{R_{\text{air}} + x_1^{\text{mc}} R_{\text{H}_2\text{O}}}{R_{\text{air}} + x_2^{\text{mc}} R_{\text{H}_2\text{O}}} \quad (15)$$

Evaluating the natural logarithm into series according to the formula

$$\ln z = \frac{z-1}{z} + \frac{(z-1)^2}{2z^2} + \frac{(z-1)^3}{3z^3} + \dots +$$

the convergence is achieved for $z > 0.5$. The pressures ratio in technological driers lies usually in the range between 0.9 and 1. Hence, there can be taken into account only the first term of the series, i.e.

$$\ln z = \ln \frac{p_{\text{air},2}}{p_{\text{air},1}} = \frac{\frac{p_{\text{air},2}}{p_{\text{air},1}} - 1}{\frac{p_{\text{air},2}}{p_{\text{air},1}}} = \frac{p_{\text{air},2} - p_{\text{air},1}}{p_{\text{air},2}} = 1 - \frac{p_{\text{air},1}}{p_{\text{air},2}} \quad (16)$$

Comparing the formula with Equations (15)–(16) yields

$$\ln \frac{p_{\text{air},2}}{p_{\text{air},1}} = 1 - \frac{R_{\text{air}} + x_2^{\text{mc}} R_{\text{H}_2\text{O}}}{R_{\text{air}} + x_1^{\text{mc}} R_{\text{H}_2\text{O}}} = \frac{R_{\text{H}_2\text{O}}(x_1^{\text{mc}} - x_2^{\text{mc}})}{R_{\text{air}} + x_1^{\text{mc}} R_{\text{H}_2\text{O}}}$$

and setting into Equation (15)

$$R_G \ln \frac{p_{\text{air},2}}{p_{\text{air},1}} = (R_{\text{air}} + x_1^{\text{mc}} R_{\text{H}_2\text{O}}) \frac{R_{\text{H}_2\text{O}}(x_1^{\text{mc}} - x_2^{\text{mc}})}{R_{\text{air}} + x_1^{\text{mc}} R_{\text{H}_2\text{O}}} = R_{\text{H}_2\text{O}}(x_1^{\text{mc}} - x_2^{\text{mc}})$$

Hence, the entropy change of the gaseous agent is to

$$\Delta S_G \approx M_{\text{dry air}} c_{p,G} \ln \frac{T_{G,2}}{T_{G,1}} - M_{\text{dry air}} R_{\text{H}_2\text{O}}(x_1^{\text{mc}} - x_2^{\text{mc}})$$

and with Equations (12) and (14),

$$\Delta I_G \approx M_{\text{dry air}} c_{p,G} (T_{G,2} - T_{G,1})$$

its exergy change approximately to

$$\Delta E_{I,G} \approx M_{\text{dry air}} \left[c_{p,G} (T_{G,2} - T_{G,1}) - T_0 R_G \ln \frac{T_{G,2}}{T_{G,1}} + T_0 R_{\text{H}_2\text{O}} (x_1^{\text{mc}} - x_2^{\text{mc}}) + (x_2^{\text{mc}} - x_1^{\text{mc}}) \bar{e}_{\mu,\text{H}_2\text{O}}^0 \right]$$

Furthermore the above equation can be parted into the thermal and chemical (concentration) exergy change, i.e.

$$\Delta E_{I,G} = \Delta E_{I,G,T} + \Delta E_{I,G,\mu}^x + \Delta E_{I,G,\mu}^0$$

where

$$\Delta E_{I,G,T} = M_{\text{dry air}} \left[c_{p,G} (T_{G,2} - T_{G,1}) - T_0 R_G \ln \frac{T_{G,2}}{T_{G,1}} \right] \quad (17)$$

$$\Delta E_{I,G,\mu}^x = M_{\text{dry air}} T_0 R_{\text{H}_2\text{O}} (x_1^{\text{mc}} - x_2^{\text{mc}}) = M_{\text{dry air}} T_0 R_{\text{H}_2\text{O}} (x_1^{\text{mc}} - x_2^{\text{mc}}) \quad (18)$$

$$\Delta E_{I,G,\mu}^0 = M_{\text{dry air}} (x_2^{\text{mc}} - x_1^{\text{mc}}) \bar{e}_{\mu,\text{H}_2\text{O}}^0 \quad (19)$$

The chemical (concentration) exergy change does not depend on any algebraic sign inversion point value of the moisture contents (it has been assumed $x_{\text{H}_2\text{O},0}=1$), but in drying processes there is not always $x_2^{\text{mc}} > x_1^{\text{mc}}$. In each case of the non-isothermal drying it should be tested. That is why the whole exergy change of the gaseous agent due to the moisture change can be parted into two parts, namely

$$\Delta E_{I,G,\mu}^x = \left| \Delta E_{I,G,\mu}^{x(1>2)} \right| - \left| \nabla E_{I,G,\mu}^{x(1<2)} \right| - \left| \nabla E_{I,G,\mu}^{0(1>2)} \right| + \left| \Delta E_{I,G,\mu}^{0(1<2)} \right|$$

according to Equations (18)–(19). The thermal exergy change, however, depends on the natural environment temperature T_0 . Because for the analyzed non-isothermal drying processes there is always

$T_{G,2} < T_{G,1}$, the exergy change can be parted up to the range of the temperature change below or above T_0 , namely

$$\Delta E_{I,G,T} = -|\nabla E_{I,G,T}^>| + |\Delta E_{I,G,T}^<|$$

Thus, the exergy balance for an adiabatic–isobaric non–isothermal drying process according to Equation (01) yields

$$-\Delta E_{I,MD} + |\nabla E_{I,G,T}^>| - |\Delta E_{I,G,T}^<| - |\Delta E_{I,G,\mu}^{x(1>2)}| + |\nabla E_{I,G,\mu}^{x(1<2)}| + |\nabla E_{I,G,\mu}^{0(1>2)}| - |\Delta E_{I,G,\mu}^{0(1<2)}| = T_0 \Delta S_{irr}$$

The exergy change of the dried material that warms up while the gaseous agent cools down consists of two parts: heating up the whole material and the following moisture evaporation. In the case of assumed non–isothermal conditions such simplifications have to be made, i.e. the additional assumption that the moisturizing substance does not evaporate while raising its temperature T_{MD} : the water turns into water steam at the end. Thus

$$\begin{aligned} \Delta E_{I,MD} = M_{MD} \Delta b & \left[c_{p,H_2O} (T_{MD,2} - T_{MD,1}) - R_{H_2O} T_0 \ln \frac{T_{MD,2}}{T_{MD,1}} + \left(1 - \frac{T_0}{T}\right) \cdot r \right] + \\ & + M_{MD} (1 - \Delta b) \left[c_{p,MD} \left(T_{MD,2} - T_{MD,1} - T_0 \ln \frac{T_{MD,2}}{T_{MD,1}} \right) \right] \end{aligned}$$

where r is the evaporation heat of water at T or at the mean temperature of the dried material, e.g. at $(T_{MD,1} + T_{MD,2})/2$, $\Delta b = b_2 - b_1$ the moisture concentrations change in the dried material (b — mass fraction kg/kg) and $c_{p,MD}$ the mean specific heat of the dried material. From the mass balance it is obviously

$$M_{MD} \Delta b = M_{dry\ air} (x_2^{mc} - x_1^{mc})$$

In a common drying process with $T_{MD,2} > T_{MD,1}$, i.e. in the case of warming up the dried material in a drier, the above exergy change can be treated as a thermal exergy change. Taking into account the possible process below the natural environment temperature T_0 it is

$$\Delta E_{I,MD} = |\Delta E_{I,MD}^>| - |\nabla E_{I,MD}^<|$$

Finally, the exergy balance will be to

$$-|\Delta E_{I,MD}^>| + |\nabla E_{I,MD}^<| + |\nabla E_{I,G,T}^>| - |\Delta E_{I,G,T}^<| - |\Delta E_{I,G,\mu}^{x(1>2)}| + |\nabla E_{I,G,\mu}^{x(1<2)}| + |\nabla E_{I,G,\mu}^{0(1>2)}| - |\Delta E_{I,G,\mu}^{0(1<2)}| = T_0 \Delta S_{irr}$$

Hence, the thermodynamic transition formula yields

$$|\nabla E_{I,MD}^<| + |\nabla E_{I,G,T}^>| + |\nabla E_{I,G,\mu}^{x(1<2)}| + |\nabla E_{I,G,\mu}^{0(1>2)}| \rightarrow |\Delta E_{I,MD}^>| + |\Delta E_{I,G,T}^<| + |\Delta E_{I,G,\mu}^{x(1>2)}| + |\Delta E_{I,G,\mu}^{0(1<2)}| + T_0 \Delta S_{irr}$$

and the thermodynamic effectivity rating quotient

$$\varepsilon_{dry} = \frac{|\Delta E_{I,MD}^>| + |\Delta E_{I,G,\mu}^{x(1>2)}| + |\Delta E_{I,G,T}^<| + |\Delta E_{I,G,\mu}^{0(1<2)}|}{|\nabla E_{I,MD}^<| + |\nabla E_{I,G,T}^>| + |\nabla E_{I,G,\mu}^{x(1<2)}| + |\nabla E_{I,G,\mu}^{0(1>2)}|}$$

and for the most common case of processes above T_0

$$\varepsilon_{dry}^> = \frac{|\Delta E_{I,MD}^>| + |\Delta E_{I,G,\mu}^{x(1>2)}| + |\Delta E_{I,G,\mu}^{0(1<2)}|}{|\nabla E_{I,G,T}^>| + |\nabla E_{I,G,\mu}^{x(1<2)}| + |\nabla E_{I,G,\mu}^{0(1>2)}|}$$

In fact the variety of the drying (or wetting) processes is very high, so it cannot be presented only one unique calculation approach. Nevertheless it has been undertaken such a trial knowing the thermodynamic effectivity advantage can be observed especially while analyzing complex power engineering and chemical engineering systems. The clear, simple and thermodynamically correct solution is needed to fulfill the goal. The special analysis of processes with humid air (or gas in general) can be reached because of its very special characteristics: the moisture contents values used in balancing these processes are much lower than the dry air (or gas in general) contents, i.e.

$$M_{\text{dry air}} \gg x^{\text{mc}} M_{\text{dry air}}$$

2.3 Numerical Example I

In a drying process of $M_{\text{MD}}=1000$ kg special bricks their moisture changes by $\Delta b=0.40$ (in fact $\Delta b=-0.40$, because the mass fraction of moisture b diminishes) but the temperature $t_{\text{MD}} = 27$ °C (or $T_{\text{MD}}=300$ K) does not change ($dT_{\text{MD}}=0$). The hot air at $t_{\text{G},1}=130$ °C and $x_1^{\text{mc}} = 0.04040$ kg/kg (it refers to the heated up atmospheric air gained by $t_0=15$ °C and $\varphi_0=0.8$). The parameters of the air after the process are $t_{\text{G},2}=50$ °C and $x_2^{\text{mc}} = 0.0117$ kg/kg (or $\varphi_2=0.5$). The mass stream of the dry air is $M_{\text{dry air}}=14700$ kg (in a certain time interval).

Appropriate thermo-physical data are:

$$c_{\text{p,air}}=1.01 \text{ kJ}/(\text{kg}\cdot\text{K}), \quad c_{\text{p,H}_2\text{O}}=1.89 \text{ kJ}/(\text{kg}\cdot\text{K}),$$

With $\bar{R} = 8.314$ kJ/(kmol·K), there is further

$$R_{\text{air}}=8.314/29=0.2867 \text{ kJ}/(\text{kg}\cdot\text{K}) \quad \text{and} \quad R_{\text{H}_2\text{O}}=8.314/18=0.4619 \text{ kJ}/(\text{kg}\cdot\text{K})$$

Hence, using Equations (13) there is

$$c_{\text{p,G}} = 1.01 + 0.0404 \cdot 1.89 = 1.0864 \frac{\text{kJ}}{\text{kg}\cdot\text{K}}; \quad R_{\text{G}} = 0.2867 + 0.0404 \cdot 0.4619 = 0.3053 \frac{\text{kJ}}{\text{kg}\cdot\text{K}}$$

From Equation (17) the thermal exergy change is to ($T_0=273+t_0$)

$$\Delta E_{\text{I,G,T}} = 14700 \cdot \left[1.0864 \cdot (50 - 130) - 288 \cdot 0.3053 \cdot \ln \frac{273 + 50}{273 + 130} \right] = -991592.5 \text{ kJ}$$

Because $T_{\text{G}} > T_0$ and $\Delta E_{\text{I,G,T}} < 0$ it is obviously $\Delta E_{\text{I,G,T}} = -|\nabla E_{\text{I,G,T}}|$. Further, from Equations (18)–(19) the approximate substantial exergy change equals to

$$\Delta E_{\text{I,G},\mu}^{\text{x}} = 14700 \cdot 288 \cdot 0.4619 \cdot (0.0404 - 0.0117) = 56122.8 \text{ kJ}$$

Because there is $x_1^{\text{mc}} > x_2^{\text{mc}}$, the above exergy change is $\Delta E_{\text{I,G},\mu}^{\text{x}} = |\Delta E_{\text{I,G},\mu}^{\text{x}(1>2)}|$, while the substantial exergy change due to the water steam zero exergy contents

$$\Delta E_{\text{I,G},\mu}^0 = \frac{14700}{18} \cdot (0.0117 - 0.0404) \cdot 9783.33 = -229304.9 \text{ kJ}$$

i.e. $\Delta E_{\text{I,G},\mu}^0 = -|\nabla E_{\text{I,G},\mu}^{0(1>2)}|$. In the above expression the water steam contents change in a gas stream equals to $14700 \cdot (0.0117 - 0.0404) / 18$ kmol H_2O and the zero exergy of the water steam at $T_0=288$ K is 9783.33 kJ/kmol.

The bricks temperature in a process is assumed to be unchanged so that the only exergy change will be due to the moisture evaporation. It is the case of the isothermal exergy change in a solid state material, so according to Equation (05) with $r_{27}=2437.3$ kJ/kg (taken from [5]) will be to

$$\Delta E_{I,MD} = M_{MD} \Delta b \left(1 - \frac{T_0}{T_{MD}} \right) \cdot r_{27} = -1000 \cdot 0.40 \cdot \left(1 - \frac{288}{300} \right) \cdot 2437.3 = -38996.8 \text{ kJ}$$

The exergy change of the material dried due to the evaporation of its moisture is negative, it can be treated as an exergy diminished in the process, i.e. $\Delta E_{I,MD} = -|\nabla E_{I,MD}|$. Thus, the thermodynamic effectivity of the drying process is (cf. Chapter 2.1. above)

$$\varepsilon_{\text{dry}} = \frac{|\Delta E_{I,G,\mu}^{x(1>2)}|}{|\nabla E_{I,G,T}^>| + |\nabla E_{I,MD}| + |\nabla E_{I,G,\mu}^{0(1>2)}|} = \frac{56122.8}{991592.5 + 38996.8 + 229304.9} = 0.0445$$

In the example the atmospheric air heating process (from $t_0=15$ °C to $t_{G,1}=130$ °C) has not been taken into account. It can be evaluated in the same manner as for classical technological heat exchange process. The determined exergy changes — i.e. their absolute values) — can be then added to the numerator (ΔE_I) and denominator (∇E_I) of the above expression for the thermodynamic effectivity. Thus, the appropriate exergy rating quotient for the whole system heating up and drying can be obtained, according to the method developed.

The thermodynamic effectivity numerical value of the process is very low which means, drying processes are thermodynamically highly inefficient. This statement, very good known in the unit operations analysis, has been proved above quantitatively.

2.4 Numerical Example II

The special air drying process is in fact a technological heat exchange process in a non-membrane vessel (i.e. adiabatic mixing) with a simultaneous substance exchange one. The wet hot air is led to the process to exchange heat (cooling down) and eventually to exchange moisture (in fact very low values that practically do not affect the mass or substance change of the two streams: dry air as a gaseous stream and water as a liquid stream). The goal of such a process is lowering the moisture contents in air by lowering its dew-point (saturation point). E.g. the humid air (dry air stream of $\dot{M}_{\text{dry air}} = 1.72$ kg/s) at $t_{\text{air},1}=40$ °C and $\varphi_1=1$ (i.e. saturated air) is led to the drier filled with RASCHIG rings and using the counter-current water stream of $\dot{M}_{\text{water}} = 2.5$ kg/s at $t_{\text{water},1}=8$ °C. At the end of the process the humid air parameters are $t_{\text{air},2}=15$ °C and obviously $\varphi_2=1$ (i.e. saturated air) and the cooling water end temperature is $t_{\text{water},2}=28.4$ °C. Thus, after following heating up the air stream will be obtained, the moisture contents and thus the relative humidity will be lower. The humid air stream pressure is approximately equal to 1 atm.

Using simplifications presented in this Chapter, approximate values of the gaseous stream $c_{p,G}$ and its gas constant R_G will be determined according to Equations (14). First, however, appropriate moisture contents at the start should be calculated. The water steam saturation pressure at 40 °C is $p_{s,40}=7.33 \cdot 10^3$ N/m². Thus,

$$x_1^{\text{mc}} = \frac{\mu_{\text{H}_2\text{O}}}{\mu_{\text{air}}} \frac{\varphi_1 p_{s,40}}{p - \varphi_1 p_{s,40}} = 0.622 \cdot \frac{1 \cdot 7.33 \cdot 10^3}{101.3 \cdot 10^3 - 1 \cdot 7.33 \cdot 10^3} = 0.0485 \frac{\text{kg H}_2\text{O}}{\text{kg dry air}}$$

Hence,

$$c_{p,G} = 1.01 + 0.0485 \cdot 1.89 = 1.1017 \frac{\text{kJ}}{\text{kg} \cdot \text{K}} \quad \text{and} \quad R_G = 0.2867 + 0.0485 \cdot 0.4619 = 0.3091 \frac{\text{kJ}}{\text{kg} \cdot \text{K}}$$

and from Equations (17)–(18)

$$\Delta E_{1,G,T} = 1.72 \cdot \left[1.1017 \cdot (15 - 40) - 283 \cdot 0.3091 \cdot \ln \frac{273 + 15}{273 + 40} \right] = -34.8486 \text{ kJ}$$

where by the natural environment temperature has been assumed to be equal to the inlet water temperature of $t_0 = 11 \text{ }^\circ\text{C}$ (i.e. $T_0 = 283 \text{ K}$). Hence,

$$\Delta E_{1,G,T} = -|\nabla E_{1,G,T}|$$

because the resulting thermal exergy change is negative (less than zero). For the substantial exergy change yields with saturation pressure at $15 \text{ }^\circ\text{C}$ $p_{s,15} = 1.705 \cdot 10^3 \text{ N/m}^2$ and

$$x_2^{\text{mc}} = \frac{\mu_{\text{H}_2\text{O}}}{\mu_{\text{air}}} \frac{\varphi_1 p_{s,15}}{p - \varphi_1 p_{s,15}} = 0.622 \cdot \frac{1 \cdot 1.705 \cdot 10^3}{101.3 \cdot 10^3 - 1 \cdot 1.701 \cdot 10^3} = 0.0106 \frac{\text{kg H}_2\text{O}}{\text{kg dry air}}$$

$$\Delta E_{1,G,\mu}^x = 1.72 \cdot 283 \cdot 0.3091 \cdot (0.0485 - 0.0106) = 5.7023 \text{ kJ} \quad \text{i.e.} \quad \Delta E_{1,G,\mu}^x = |\Delta E_{1,G,\mu}^{x(1>2)}|$$

The exergy change due to the zero exergy in the cooled/dried air will be to

$$\Delta E_{1,G,v}^{0(1>2)} = \frac{1.72}{18} \cdot (0.0106 - 0.0485) \cdot 10386.47 = -37.6152 \text{ kJ} \quad \text{i.e.} \quad \Delta E_{1,G,\mu}^{0(1>2)} = -|\nabla E_{1,G,\mu}^{0(1>2)}|$$

The cooling water exergy change at assumed unchanged water stream value will be to

$$\Delta E_{1,\text{water},T} = \Delta I - T_0 \Delta S = \dot{M}_{\text{water}} \left[c_{p,\text{water}} (T_{\text{water},2} - T_{\text{water},1}) - c_{p,\text{water}} T_0 \ln \frac{T_{\text{water},2}}{T_{\text{water},1}} \right]$$

because for the isobaric process there is

$$ds = \frac{dq}{T} = \frac{di}{T} = c_p \frac{dT}{T} \quad \text{and} \quad \Delta s = c_p \int \frac{dT}{T} = c_p \ln \frac{T_2}{T_1}$$

Thus,

$$\Delta E_{1,\text{water},T} = 2.5 \cdot 4.19 \cdot \left[(28.4 - 8) - 281 \cdot \ln \frac{273 + 28.4}{273 + 8} \right] = 7.4006 \text{ kJ}$$

i.e.

$$\Delta E_{1,\text{water},T} = |\Delta E_{1,\text{water},T}|$$

Putting in order results for particular exergy changes the thermodynamic transition is

$$|\nabla E_{1,G,T}| + |\Delta E_{1,G,\mu}^{0(1>2)}| \rightarrow |\Delta E_{1,\text{water},T}| + |\Delta E_{1,G,\mu}^{x(1>2)}| + T_0 \Delta S_{\text{irr}}$$

and the thermodynamic effectivity

$$\varepsilon_{\text{dry}} = \frac{|\Delta E_{1,\text{water},T}| + |\Delta E_{1,G,\mu}^{x(1>2)}|}{|\nabla E_{1,G,T}| + |\Delta E_{1,G,\mu}^{0(1>2)}|} = \frac{7.4006 + 5.7023}{34.8486 + 37.6152} = 0.1808$$

3 TECHNOLOGICAL GAS ABSORPTION PROCESSES

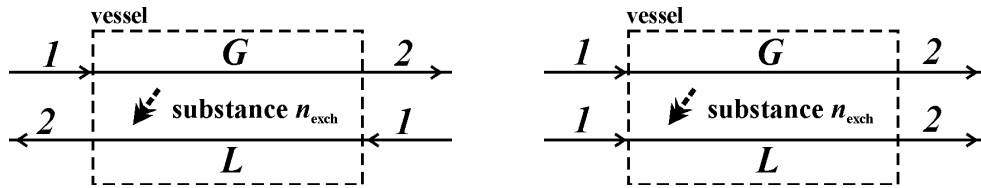


Fig. 2 Absorption in counter-current (*to the left*) and concurrent flow (*to the right*) as a technological substance exchange process in a vessel (apparatus)

The exergy balance for the basic substance exchange process as presented in Figure 2 above with only one absorbate (e.g. in following discussions CO₂) can be written down as

$$\Delta E_{1,\text{CO}_2,\text{L}} + \Delta E_{1,\text{CO}_2,\text{G}} = T_0 \Delta S_{\text{irr}}$$

because amounts of the absorbent (liquid) n_{L} and gaseous inerts n_{G} do not change in the process, [7]. For simplicity an isothermal–adiabatic process without chemical reactions is considered. Using fundamentals of the chemical thermodynamics one can assume that species in the condensed phase are no miscible ones. Thus, the total exergy change of the absorbent (liquid) flow will only consist of the CO₂ amount change in it, i.e. of the chemical zero exergy:

$$\Delta E_{1,\text{CO}_2,\text{L}} = \Delta E_{1,\text{CO}_2,\text{L}}^0 = n_{\text{L}} (X_{\text{CO}_2,2} - X_{\text{CO}_2,1}) \cdot \bar{e}_{\mu,\text{CO}_2}^0 \quad (20)$$

According to [2] there is $\bar{e}_{\mu,\text{CO}_2}^0 = 19.09745$ kJ/mol at $T_0 = 283.15$ K, $\bar{e}_{\mu,\text{CO}_2}^0 = 19.42469$ kJ/mol at $T_0 = 288.15$ K, $\bar{e}_{\mu,\text{CO}_2}^0 = 19.77192$ kJ/mol at $T_0 = 293.15$ K, $\bar{e}_{\mu,\text{CO}_2}^0 = 19.98438$ kJ/mol at $T_0 = 296.15$ K, $\bar{e}_{\mu,\text{CO}_2}^0 = 20.10915$ kJ/mol at $T_0 = 298.15$ K (standard chemical exergy) and $\bar{e}_{\mu,\text{CO}_2}^0 = 20.23393$ kJ/mol at $T_0 = 300$ K.

In the gaseous phase the concentration part of the exergy change should be taken additionally into calculations, namely

$$\begin{aligned} \Delta E_{1,\text{CO}_2,\text{G}} = \Delta E_{1,\text{CO}_2,\text{G}}^0 + \Delta E_{1,\text{CO}_2,\text{G}}^x = n_{\text{G}} (Y_{\text{CO}_2,2} - Y_{\text{CO}_2,1}) \cdot \bar{e}_{\mu,\text{CO}_2}^0 + \\ + n_{\text{G}} \left(y_{\text{CO}_2,2} \bar{R} T_0 \ln \frac{y_{\text{CO}_2,2}}{y_{\text{CO}_2,0}} - y_{\text{CO}_2,1} \bar{R} T_0 \ln \frac{y_{\text{CO}_2,1}}{y_{\text{CO}_2,0}} \right) \end{aligned} \quad (21)$$

where $y_{\text{CO}_2,0}$ is the CO₂ mole concentration in the natural (reference) environment and T_0 its temperature, [2]. The appropriate molar concentrations into molar loads (or mole ratios) can be converted using following formulas

$$y_{\text{CO}_2} = \frac{Y_{\text{CO}_2}}{1 + Y_{\text{CO}_2}} \quad \text{and} \quad Y_{\text{CO}_2} = \frac{y_{\text{CO}_2}}{1 - y_{\text{CO}_2}} \quad (22)$$

whereas they are valid for the binary mixture.

The extreme (minimum) value of the CO₂ concentration exergy change is reached at the concentration $y_{\text{CO}_2,\text{extr}} = 1.1036 \cdot 10^{-4}$ ($y_{\text{CO}_2,0} = 0.0003$). With the converting formula it corresponds to the mole ratio value of $Y_{\text{CO}_2,\text{extr}} = 1.1037 \cdot 10^{-4}$ (which could be expected, because for low concentrations the molar fraction approximately equals to the molar load, i.e. $y_{\text{CO}_2} \approx Y_{\text{CO}_2}$). Thus, the concentration change of CO₂ in the gaseous phase should be parted according to the scheme

$$Y_{\text{CO}_2,1} \rightarrow Y_{\text{CO}_2,\text{extr}} \rightarrow Y_{\text{CO}_2,2} \quad (\text{or} \quad y_{\text{CO}_2,1} \rightarrow y_{\text{CO}_2,\text{extr}} \rightarrow y_{\text{CO}_2,2})$$

Thus, Equation (21) can be rearranged, if an extreme point exists in the range of the appropriate concentration change:

$$\begin{aligned} \Delta E_{1,\text{CO}_2,\text{G}} = \Delta E_{1,\text{CO}_2,\text{G}}^0 + \Delta E_{1,\text{CO}_2,\text{G}}^x = n_{\text{G}} (Y_{\text{CO}_2,2} - Y_{\text{CO}_2,1}) \cdot \bar{e}_{\mu,\text{CO}_2}^0 + \\ + n_{\text{G}} \left(y_{\text{CO}_2,2} \bar{R} T_0 \ln \frac{y_{\text{CO}_2,2}}{y_{\text{CO}_2,0}} - y_{\text{CO}_2,\text{extr}} \bar{R} T_0 \ln \frac{y_{\text{CO}_2,2}}{y_{\text{CO}_2,0}} \right) + n_{\text{G}} \left(y_{\text{CO}_2,\text{extr}} \bar{R} T_0 \ln \frac{y_{\text{CO}_2,1}}{y_{\text{CO}_2,0}} - y_{\text{CO}_2,1} \bar{R} T_0 \ln \frac{y_{\text{CO}_2,1}}{y_{\text{CO}_2,0}} \right) \end{aligned}$$

Because Y_{CO_2} (or y_{CO_2}) gets lower in the absorption process (X_{CO_2} is getting greater), the general exergy balance can be rearranged for the absorption into so-called „thermodynamic transition”

$$|\Delta E_{1,\text{CO}_2,\text{L}}^0| - |\nabla E_{1,\text{CO}_2,\text{L}}^0| - |\nabla E_{1,\text{CO}_2,\text{G}}^{x>}| + |\Delta E_{1,\text{CO}_2,\text{G}}^{x<}| \rightarrow T_0 \Delta S_{\text{irr}}$$

where the superscript $>$ means concentration exergy change above and superscript $<$ the change below the appropriate exergy minimum point ($y_{\text{CO}_2,\text{extr}}$). According to the general algorithm presented in [2] the thermodynamic effectivity quotient for the absorption process will be to

$$\varepsilon_{\text{abs}} = \frac{|\Delta E_{1,\text{CO}_2,\text{L}}^0| + |\Delta E_{1,\text{CO}_2,\text{G}}^{x<}|}{|\nabla E_{1,\text{CO}_2,\text{G}}^0| + |\nabla E_{1,\text{CO}_2,\text{G}}^{x>}|}$$

The typical gas absorption process is presented in Figure 3.

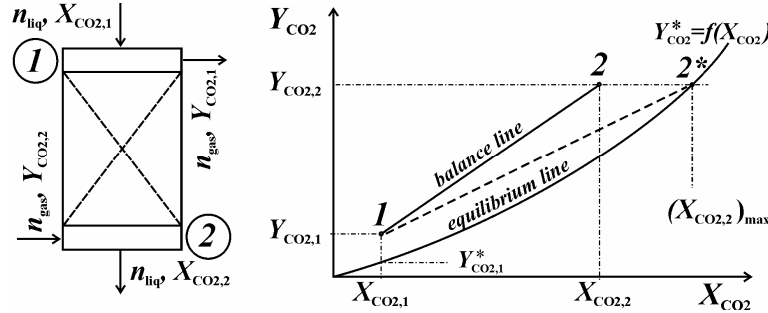


Fig. 3 Balance and equilibrium lines for the absorption process of CO_2 (the case of more convex equilibrium line will not be considered)

In the case of the basic desorption process the value of Y_{CO_2} (or y_{CO_2}) will get higher and the CO_2 load in the absorbent (liquid) will get lower. The appropriate „thermodynamic transition” will be to

$$-|\nabla E_{1,\text{CO}_2,\text{L}}^0| + |\Delta E_{1,\text{CO}_2,\text{G}}^0| - |\nabla E_{1,\text{CO}_2,\text{G}}^{x<}| + |\Delta E_{1,\text{CO}_2,\text{G}}^{x>}| \rightarrow T_0 \Delta S_{\text{irr}}$$

and the desorption thermodynamic effectivity

$$\varepsilon_{\text{des}} = \frac{|\Delta E_{1,\text{CO}_2,\text{G}}^0| + |\Delta E_{1,\text{CO}_2,\text{G}}^{x>}|}{|\nabla E_{1,\text{CO}_2,\text{L}}^0| + |\nabla E_{1,\text{CO}_2,\text{G}}^{x<}|}$$

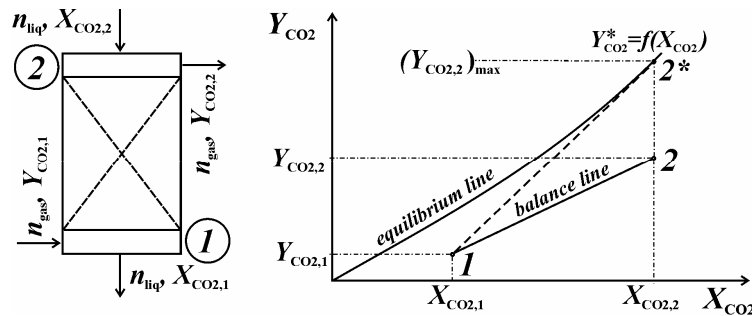


Fig. 4 Balance and equilibrium lines for the desorption process of CO_2 (the case of more convex equilibrium line will not be considered)

The last thermodynamic effectivity quotient refers to the „classical” desorption process presented in Figure 4. The desorption, however, can be realized by heating up the CO_2 -rich absorbent (liquid) with water steam. The equilibrium point changes (e.g. temperature change from ca. 20 °C to 80 °C) and the CO_2 will be free. Thus, water steam will condense giving up heat to the absorbent flow; they both reach their end equilibrium temperature (e.g. 80 °C). The CO_2 molar load in the

absorbent flow decreases from $X_{\text{CO}_2,1}$ (bottom l of the desorption unit) to $(X_{\text{CO}_2,2})_{\text{max}}$, which is the equilibrium value. The rest of CO_2 , i.e. $n_{\text{CO}_2,2}=n_L[(X_{\text{CO}_2,2})_{\text{max}}-X_{\text{CO}_2,1}]$ will appear in the head 2. The appropriate „thermodynamic transition”

$$-\left|\nabla E_{\text{I,H}_2\text{O,T}}\right| + \left|\Delta E_{\text{I,L,T}}\right| + \left|\Delta E_{\text{I,CO}_2,\text{G}}^0\right| \rightarrow T_0 \Delta S_{\text{irr}}$$

where $\nabla E_{\text{I,H}_2\text{O,T}}$ is the thermal exergy change of the water steam from its initial state (bottom l) to the thermal equilibrium with absorbent flux in the head 2. $\Delta E_{\text{I,L,T}}$ is the thermal exergy change of the absorbent flux while heating up with the water steam. Finally, $\Delta E_{\text{I,CO}_2,\text{G}}^0 = n_{\text{CO}_2} \cdot \bar{e}_{\text{H,CO}_2}^0$ is the chemical exergy of the free CO_2 flux in the device head. The thermodynamic effectivity for such a desorption process yields

$$\varepsilon'_{\text{des}} = \frac{\left|\Delta E_{\text{I,CO}_2,\text{G}}^0\right| + \left|\Delta E_{\text{I,L,T}}\right|}{\left|\nabla E_{\text{I,H}_2\text{O,T}}\right|}$$

In fact, the last case has been simplified — the exergy change caused by mixing of water steam and absorbent and the (very low) contents of CO_2 in the last one were not taken into account.

3.1 Numerical Example III

The molar (or volume) CO_2 concentration at the start is $y_1=0.1$ (bottom of the vessel), and at the end of an absorption process $y_2=0.003$ (head of the vessel). In the liquid phase (water) the concentration at the start was $c_2=25 \text{ mg/l}$ (head, subscript 2). The gas volume stream is $1000 \text{ m}^3/\text{h}$ in standard conditions ($V_{\text{norm}}=22.4 \text{ m}^3/\text{kmol}$), the process pressure $p=15.5 \text{ at}$ and process temperature $t_0=25 \text{ }^\circ\text{C}$ (the example from [8], pp. 331–333).

First, the equilibrium concentration in water in bottom (subscript l) should be determined. The equilibrium line is

$$Y^* = \frac{kX}{1+(1-k)X} \quad \text{with } k = \frac{H}{p}$$

The HENRY’s constant for water– CO_2 solutions at $25 \text{ }^\circ\text{C}$ equals to $H=1.64 \cdot 10^3 \text{ at}$, hence the equilibrium line according to the last expression can be constructed. With $Y^*=f(X)$ there is

X_{CO_2}	$1.025 \cdot 10^{-5}$	$1 \cdot 10^{-4}$	$2 \cdot 10^{-4}$	$4 \cdot 10^{-4}$	$6 \cdot 10^{-4}$	$8 \cdot 10^{-4}$	$1 \cdot 10^{-3}$
$Y_{\text{CO}_2}^*$	$1.12 \cdot 10^{-3}$	$1.11 \cdot 10^{-2}$	$2.24 \cdot 10^{-2}$	$4.57 \cdot 10^{-2}$	$7 \cdot 10^{-2}$	$9.6 \cdot 10^{-2}$	$1.23 \cdot 10^{-2}$

The appropriate units conversion results according to Equation (22) are

$$Y_{\text{CO}_2,2} = \frac{0.003}{1-0.003} = 0.003 \frac{\text{kmol}}{\text{kmol}} \quad Y_{\text{CO}_2,1} = \frac{0.1}{1-0.1} = 0.11 \frac{\text{kmol}}{\text{kmol}}$$

and

$$X_{\text{CO}_2,2} = \frac{c_2 / \mu_{\text{CO}_2}}{\rho_2 / \mu_{\text{water}}} = \frac{0.025 \cdot 18}{44 \cdot 997} = 1.025 \cdot 10^{-5} \frac{\text{kmol}}{\text{kmol}}$$

For $Y_{\text{CO}_2,1}=0.11$ the equilibrium value in water $X_{\text{CO}_2,1}^*=9.06 \cdot 10^{-4} \text{ kmol/kmol}$. The minimal liquid (water) flow, which refers to the equilibrium process, can be determined from the substance balance

$$L_{\text{min}}(X_{\text{CO}_2,1}^* - X_{\text{CO}_2,2}) = G(Y_{\text{CO}_2,1} - Y_{\text{CO}_2,2})$$

Hence, the numerical value of L_{\min} is to

$$L_{\min} = \frac{1000 \cdot (0.11 - 0.003)}{22.4 \cdot (0.000906 - 0.00001025)} = 44.6 \cdot \frac{0.107}{0.00089574} = 5328 \frac{\text{kmol}}{\text{h}}$$

and there will be assumed the „real” liquid flow as

$$L = 2L_{\min} = 2 \cdot 5328 = 10658 \frac{\text{kmol}}{\text{h}}$$

From the CO_2 balance in water the end molar load $X_{\text{CO}_2,1}$ at the bottom of the vessel can be determined

$$X_{\text{CO}_2,1} = \frac{G(Y_{\text{CO}_2,1} - Y_{\text{CO}_2,2})}{L} + X_{\text{CO}_2,2} = \frac{44.6 \cdot 0.107}{10656} + 0.00001025 = 0.0004581 \frac{\text{kmol}}{\text{kmol}}$$

Thus, the operation line crosses the points $X_{\text{CO}_2,1} = 4.581 \cdot 10^{-4}$; $Y_{\text{CO}_2,1} = 0.11$ and $X_{\text{CO}_2,2} = 1.025 \cdot 10^{-5}$; $Y_{\text{CO}_2,2} = 0.003$. To avoid any misunderstanding in the meaning of particular terms and quantities, the whole calculation procedure has been presented.

To calculate exergy changes molar fractions in the gas phase are needed. Using Equation (22) it follows

$$y_{\text{CO}_2,2} = \frac{Y_{\text{CO}_2,2}}{1 + Y_{\text{CO}_2,2}} = \frac{0.003}{1 + 0.003} = 0.00299$$

and

$$y_{\text{CO}_2,1} = \frac{Y_{\text{CO}_2,1}}{1 + Y_{\text{CO}_2,1}} = \frac{0.11}{1 + 0.11} = 0.09910$$

The result means, there is no an extreme concentration value of $y_{\text{CO}_2,\text{extr}} = 1.1036 \cdot 10^{-4} = 0.00011$ in the whole range of CO_2 concentration changes. There is always $y_{\text{CO}_2} > y_{\text{CO}_2,\text{extr}}$ (superscript $>$ in the appropriate exergy change term, while $\Delta E_{1,\text{CO}_2,\text{G}}^{x<} = 0$).

From Equation (20) there is

$$\Delta E_{1,\text{CO}_2,\text{L}}^0 = L(X_{\text{CO}_2,2} - X_{\text{CO}_2,1}) \cdot \bar{e}_{\mu,\text{CO}_2}^0 = 10658 \cdot (0.0004581 - 0.00001024) \cdot 20109.15 = 95986.84 \frac{\text{kJ}}{\text{h}}$$

$$\nabla E_{1,\text{CO}_2,\text{G}}^0 = G(Y_{\text{CO}_2,2} - Y_{\text{CO}_2,1}) \cdot \bar{e}_{\mu,\text{CO}_2}^0 = 44.6 \cdot (0.11 - 0.00001025) \cdot 20109.15 = 98734.77 \frac{\text{kJ}}{\text{h}}$$

and in the same way, Equation (21)

$$\begin{aligned} \nabla E_{1,\text{CO}_2,\text{G}}^{x>} &= \overline{GR}T_0 \left(y_{\text{CO}_2,2} \ln \frac{y_{\text{CO}_2,2}}{y_{\text{CO}_2,0}} - y_{\text{CO}_2,1} \ln \frac{y_{\text{CO}_2,1}}{y_{\text{CO}_2,0}} \right) = \\ &= 44.6 \cdot 8.3143 \cdot 298 \cdot \left(0.00299 \cdot \ln \frac{0.00299}{0.0003} - 0.0991 \cdot \ln \frac{0.0991}{0.0003} \right) = -62813.03 \frac{\text{kJ}}{\text{h}} \end{aligned}$$

Hence, the thermodynamic effectivity of the absorption process under consideration equals to

$$\varepsilon_{\text{abs}} = \frac{|\Delta E_{1,\text{CO}_2,\text{L}}^0| + |\Delta E_{1,\text{CO}_2,\text{G}}^{x<}|}{|\nabla E_{1,\text{CO}_2,\text{G}}^0| + |\nabla E_{1,\text{CO}_2,\text{G}}^{x>}|} = \frac{95986.84 + 0}{98734.77 + 62813.03} = \underline{0.5942}$$

4 CONCLUSIONS

The main technological substance exchange processes have been presented: the drying/wetting and CO₂-absorption. In the exergy analysis of processes with humid air some simplifications and approximations have been proposed that make the calculations easier. The approach could be proved in two numerical examples. The most important analysis, however, is the determination of the thermodynamic effectivity quotient for the CO₂-absorption. This rating quotient suits very good for exergy analyzes of complex systems, independent on their inner structure. A very similar analysis can be made for the CO₂-desorption processes, Figure 5, so the CO₂-absorption/desorption subsystem of the modern power engineering system can be fully taken into account.

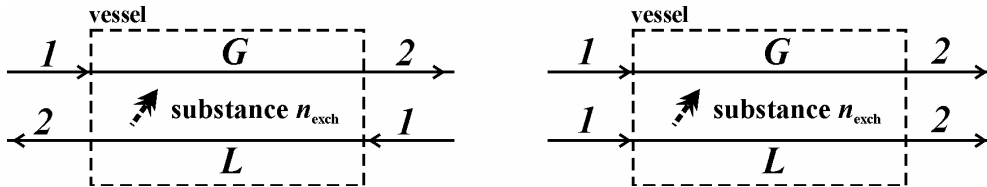


Fig. 5 Desorption in counter-current (to the left) and concurrent flow (to the right) as a technological substance exchange process in a vessel (apparatus)

Worked out within the research project:

Evaluation, Verification and Interpretation of the Environmental Loads of the Czech Republic – INTERVIRON 2B06068

REFERENCES

1. KEEY R.B.: *Introduction to Industrial Drying Operations*, Pergamon Press, Oxford – New York – Toronto – Sydney – Paris – Frankfurt 1978, →rus.: КЕЙ Р.Б.: *Введение в технологию промышленной сушки*, Наука и техника, Минск 1983
2. KOZACZKA J.: *Thermodynamic Analysis of Energy Conversion Processes*, Problems of Mechanical Engineering and Robotics Nr 8, Faculty of Mechanical Engineering and Robotics, AGH – University of Science and Technology, Kraków 2002, ISBN 83–913400–0–7
3. KOZACZKA J.: *The Natural Surroundings in Thermodynamic Analyzes*, International Conference: Power Engineering and Environment – 2007 Modern Energy Technologies and Renewable Energy Resources, VŠB–TUO, Czech Republic, 26.–27.09.2007, Sborník přednášek konference, pp.145–149, CD–ROM Energetika a životní prostředí – 2007, ISBN 978–80–248–1586–2
4. KOZACZKA J.: *Exergie als Zustandsgröße und die Exergiebilanz mit Berücksichtigung von Begrenzungen der Energiewandlungsprozesse*, Kwartalnik AGH Mechanika 17(1998)4, S.571–576
5. ELSNER N., FISCHER S., KLINGER J.: *Thermophysikalische Stoffeigenschaften von Wasser*, VEB Deutscher Verlag für Grundstoffindustrie, Leipzig 1982
6. SAZHIN B.S. → САЖИН Б.С.: *Основы техники сушки*, Химия, Москва 1984
7. KOZACZKA J.: *Thermodynamic Analysis and Rating of Modern Power Engineering Systems*, Vědecké spisy Fakulty strojní, Habilitační a inaugurační spisy, sv. 41, VŠB – Technická univerzita Ostrava, Fakulta strojní, Ostrava říjen 2007, ISBN 978–80–248–1594–7
8. FLOAREA O., SMIGELSCHI O.: *Calcul de operații și utilaje din industria chimică*, Editura Tehnică, București 1966, →rus.: ФЛОРЕА, О., СМИГЕЛЬСКИЙ О.: *Расчеты по процессам и аппаратам химической технологии*, Издательство Химия, Москва 1971