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THERMODYNAMICS OF THE CO₂-ABSORPTION/DESORPTION SECTION IN THE
INTEGRATED GASIFYING COMBINED CYCLE — II. ANALYSIS

TERMODYNAMIKA ABSORPČNÍ/DESORPČNÍ CO₂ SEKCE INTEGROVANÉHO
ZPLYŇOVACÍHO OBĚHU – II. ANALÝZY

Abstract

The thermodynamic analysis of the absorption/desorption section of the ICGC-cycle has been presented using the Second Law with special emphasis on the thermodynamic effectivity concept and usability for complex systems investigations. Essential problems have been discussed based on the classical bibliographical items on the subject. Numerical calculations have been accomplished using results obtained in the first part, which contained absorption and desorption modeling approach oriented onto thermodynamic analyzes. Additionally the special properties of dilute solutions, especially the CO₂/water system, have been presented and the problem of the solute chemical concentration exergy change suggested.

Abstrakt

Termodynamická analýza absorpční/desorpční sekce IGCC oběhu je prezentována za použití druhého zákona se zdůrazněním na koncept termodynamické efektivity a vhodnosti pro výzkum komplexních systémů. Podstatné problémy byly diskutovány na základě klasických bibliografických podkladů. Numerické výpočty byly doplněny za použití výsledků z první části, která obsahovala absorpční a desorpční modelový přístup orientovaný na termodynamickou analýzu. Speciální vlastnosti ředěného roztoku hlavně CO₂/voda systému byly prezentovány a byl uvažován problém exergie pro chemickou koncentraci daného roztoku.

1 INTRODUCTION

The exergy balance for the basic substance exchange process with only one solute (CO₂) can be written down as

$$E_{\text{CO}_2, \text{liq}, \text{input}} + E_{\text{CO}_2, \text{gas}, \text{input}} = E_{\text{CO}_2, \text{liq}, \text{output}} + E_{\text{CO}_2, \text{gas}, \text{input}} + T_0 \Delta S_{\text{irr}} \quad \text{and} \quad -\Delta E_{\text{CO}_2, \text{liq}} - \Delta E_{\text{CO}_2, \text{gas}} = T_0 \Delta S_{\text{irr}}$$

because amounts of the liquid absorbent (solvent) n_{liq} and gaseous inerts n_{gas} do not change in the process. Using fundamentals of the chemical thermodynamics one can assume that species in the condensed phase are not miscible ones, with except of the CO₂, which can be absorbed and desorbed. The total exergy change of the gas flow will consist of the CO₂ amount change in it, i.e. of the chemical zero exergy and of the compositional one between state 1 (start) and state 2 (end):

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$$\Delta \dot{E}_{\text{CO}_2, \text{gas}} = \Delta \dot{E}_{\text{CO}_2, \text{gas}}^0 + \Delta \dot{E}_{\text{CO}_2, \text{gas}}^x = \dot{n}_{\text{gas}}^{\text{abs}} (Y_{\text{CO}_2, 2} - Y_{\text{CO}_2, 1}) \cdot \bar{e}_{\mu, \text{CO}_2}^0 + \dot{n}_{\text{gas}}^{\text{abs}} \bar{R} T_0 \left(y_{\text{CO}_2, 2} \ln \frac{y_{\text{CO}_2, 2}}{y_{\text{CO}_2, 0}} - y_{\text{CO}_2, 1} \ln \frac{y_{\text{CO}_2, 1}}{y_{\text{CO}_2, 0}} \right) \quad (1)$$

(see [1]: the extraction process analysis). 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.

The change of the concentration chemical exergy can be divided into two parts, if only the appropriate minimum value point (or exergy change inversion point) exists in the range of the molar concentration change [1]–[2]. There is to examine the function (y_{CO_2} is the mole fraction in gaseous phase, x_{CO_2} the appropriate fraction in liquid)

$$f(y_{\text{CO}_2}) = \frac{\bar{e}_{\mu, \text{CO}_2}^x}{\bar{R} T_0} = y_{\text{CO}_2} \ln \frac{y_{\text{CO}_2}}{y_{\text{CO}_2, 0}}$$

the derivative of it is

$$f'(y_{\text{CO}_2}) = 1 + \ln \frac{y_{\text{CO}_2}}{y_{\text{CO}_2, 0}}$$

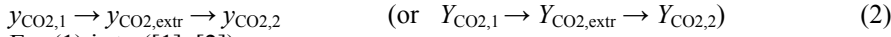
Setting above formula equal to zero and the solution yields

$$y_{\text{CO}_2} = y_{\text{CO}_2, \text{extr}} = \exp(\ln y_{\text{CO}_2, 0} - 1) = \frac{y_{\text{CO}_2, 0}}{e}$$

with the value of e as the base of natural logarithms ($e = 2.71828$). The appropriate molar exergy value is

$$\bar{e}_{\mu, \text{CO}_2, \text{extr}}^x = y_{\text{CO}_2, \text{extr}} \bar{R} T_0 \ln \frac{y_{\text{CO}_2, \text{extr}}}{y_{\text{CO}_2, 0}} = \frac{y_{\text{CO}_2, 0}}{e} \bar{R} T_0 \ln \frac{y_{\text{CO}_2, 0}}{e \cdot y_{\text{CO}_2, 0}} = -\frac{\bar{R} T_0}{e} y_{\text{CO}_2, 0}$$

The extreme (minimum) value of the CO₂ concentration exergy change is reached at the concentration $y_{\text{CO}_2, \text{extr}} = 1.10364 \cdot 10^{-4} = 0.000110364$ ($y_{\text{CO}_2, 0} = 0.0003$). With the converting formula it corresponds to the mole ratio value of $Y_{\text{CO}_2, \text{extr}} = 1.10376 \cdot 10^{-4} = 0.000110376$ (the equality could be expected, because for low concentrations the molar fraction approximately equals to the molar ratio, i.e. $y_{\text{CO}_2} \approx Y_{\text{CO}_2}$). If also the CO₂ mole fraction changes according to the scheme



Eq. (1) is to ([1]–[2]):

$$\Delta \dot{E}_{\text{CO}_2, \text{gas}} = \Delta \dot{E}_{\text{CO}_2, \text{gas}}^0 + \Delta \dot{E}_{\text{CO}_2, \text{gas}}^x = \dot{n}_{\text{gas}}^{\text{abs}} (Y_{\text{CO}_2, 2} - Y_{\text{CO}_2, 1}) \cdot \bar{e}_{\mu, \text{CO}_2}^0 + \dot{n}_{\text{gas}}^{\text{abs}} \bar{R} T_0 \left[y_{\text{CO}_2, 2} \ln \frac{y_{\text{CO}_2, 2}}{y_{\text{CO}_2, 0}} - y_{\text{CO}_2, \text{extr}} \right] + \dot{n}_{\text{gas}}^{\text{abs}} \bar{R} T_0 \left[y_{\text{CO}_2, \text{extr}} - y_{\text{CO}_2, 1} \ln \frac{y_{\text{CO}_2, 1}}{y_{\text{CO}_2, 0}} \right]$$

The subscript l has been used in above relations again as the start and 2 as the end state of the molar fraction changing process.

Chemical exergy change of the solute CO₂ in solvent H₂O can be determined in the same way as for gas phase, and in fact for technological substance exchange processes its numerical value is the same as the value for the gas flux, namely

$$\Delta \dot{E}_{\text{CO}_2, \text{liq}}^0 = \dot{n}_{\text{liq}}^{\text{des}} (X_{\text{CO}_2, 1} - X_{\text{CO}_2, 2}) \cdot \bar{e}_{\mu, \text{CO}_2}^0$$

Similarly can be the chemical concentration change of the solute in the liquid (solvent) determined. The special behavior of this change, however, should be taken into account.

There are known only two significant elaborations dealing with thermodynamic analysis of absorption/desorption processes, [3]–[4], besides contributions of the co-authors in different journals and occasions, e.g. [5]–[7]. They do analyze the processes but without making any use of the solution properties. In fact they do apply the 2. Law Analysis, in particular the exergy one, but only with respect to the heat involved in different absorption/desorption configurations. The separation (useful

or technical) work they determine in the ordinary way, just like it could be presented e.g. in [1]. Conclusions of such in fact selective analyses could help improving these processes and technologies, but not their operation in a complex system. The in [3] presented method of thermodynamic analysis using the exergy concept is somehow similar to the procedure worked out taking advantage of the „thermodynamic transition” or „thermodynamic effectivity” concepts. The very significant difference, however, is that the method does not take into account special behavior of the chemical concentration exergy change, i.e. it does not refer to its extreme (minimum) point, at which the algebraic sign inversion occurs. It depends very closely on the molar concentration of the particular specie in the assumed natural environment, [1]–[2].

For thermodynamic analyses using the thermodynamic effectivity rating quotient, which should be formulated in the same way for all kinds of processes, the already mentioned references are practically worthless. They can be only an inspiration in searching for a proper solution. The thermodynamic effectivity quotient is in fact a proof for the correctness of process calculations: it should be less than one (or in limit equal to one). If not, the *2. Law of Thermodynamics* is not fulfilled, i.e. the process cannot run at all, e.g. [8]. By modeling CCS systems such a case happened especially while analyzing an absorption/desorption section. It was the reason why the problem of solution thermodynamics with respect to exergy method has been investigated thoroughly, and presented in Chapter 5.

2 PROCESSES IN THE ABSORPTION/DESORPTION SECTION

The general schema of the absorption/desorption section is showed in Fig. 1. The additional energy supplies have not been presented: they are the additional useful work if the absorption runs at greater pressure than the desorption, but both at the same temperature (the so-called isothermal absorption with the expanding desorption unit), or the heat exergy, if the absorption and desorption run at the same pressure but different temperatures (usually $t_{\text{abs}} > t_{\text{des}}$). In the last case the supplied heat exergy for cooling down the liquid flux in the segment from desorption to absorption equals to zero, because the heat is taken at the natural environment temperature. Assuming almost full regeneration of the useful work in the section, i.e. that the liquid turbine work is almost equal to the pumping work, only a small useful work amount should be supplied. The same can be assumed for the heat: only a small amount of it should complete the losses due to the regeneration imperfectness.

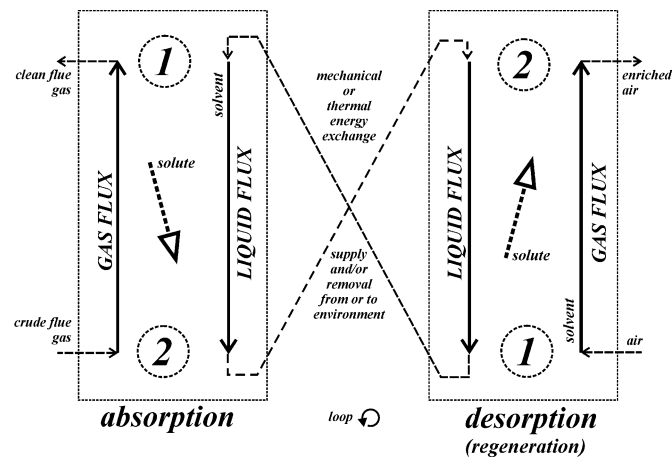


Fig. 1 Scheme of the absorption/desorption (regeneration) section.

The CO₂-absorption/desorption section operation can be presented at the Y, X -diagram, Fig. 2, where the appropriate equilibrium line and both, the absorption and desorption lines are showed. The $X_1 \equiv X_{\text{CO}_2,1}$ and $X_2 \equiv X_{\text{CO}_2,2}$ values are the same, as can be seen from Fig. 1.

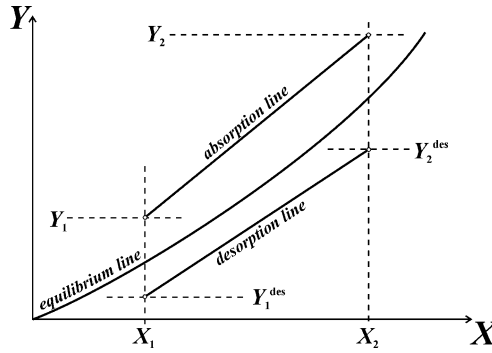


Fig. 2 Equilibrium, absorption and desorption lines in X, Y –diagram.

The essential problem, which occurred analyzing the coupled absorption/desorption section in [3]–[7] was that of the particular terms algebraic signs. The absorption and desorption units could not be analyzed separately but always as a system regarding heat energies or work. To overcome these difficulties, the very explicit analysis direction has been assumed. It has been proved correct in many tests. The direction is from the bottom (index 2 for absorption and index 1 for desorption in Fig. 1) to the head (index 1 for absorption and index 2 for desorption in Fig. 1) of the counter–current substance exchange process, i.e. the particular fluxes are

absorption	bottom \rightarrow head	gas: 2 \rightarrow 1	liquid: 1 \rightarrow 2
desorption	bottom \rightarrow head	gas: 2 \rightarrow 1	liquid: 1 \rightarrow 2

The assumption is even justified in a subjective selection of advantages and expenditures in the processes: in the absorption the reducing of a specie in gas flux is the main purpose, and in the coupled desorption one (the so–called regeneration), the reducing of the specie in liquid flux. It is to emphasize that the indices for vessel's bottom and head are not to be mislead with indices 1 and 2 for the start (input) or end (output) of the analyzed process. It is one of common mistakes in process calculations using methods of the chemical engineering. In [3] the rating quotient of chemical concentration exergy change of the CO_2 absorbing air in the desorption unit and the appropriate change of the CO_2 desorbing crude flue gas has been taken as the exergy efficiency, i.e.

$$\eta_{\text{ex}} = \frac{\Delta \dot{E}_{\text{CO}_2, \mu}^{\text{abs}}}{\Delta \dot{E}_{\text{CO}_2, \mu}^{\text{des}}} = \frac{\dot{n}_{\text{CO}_2, \text{gas}}^{\text{abs}} \Delta \bar{e}_{\mu, \text{CO}_2}^{\text{x,abs}}}{\dot{n}_{\text{CO}_2, \text{gas}}^{\text{des}} \Delta \bar{e}_{\mu, \text{CO}_2}^{\text{x,des}}}$$

but the exergy changes in the numerator and denominator have been determined between following states (Fig. 1):

$$\Delta \bar{e}_{\mu, \text{CO}_2}^{\text{x,abs}} = \bar{e}_{\mu, 1}^{\text{x,abs}} - \bar{e}_{\mu, 2}^{\text{x,abs}} \quad \text{and} \quad \Delta \bar{e}_{\mu, \text{CO}_2}^{\text{x,des}} = \bar{e}_{\mu, 2}^{\text{x,des}} - \bar{e}_{\mu, 1}^{\text{x,des}}$$

hence, the above net exergy efficiency yields

$$\eta_{\text{ex}} = \frac{\Delta \dot{E}_{\text{CO}_2, \mu}^{\text{abs}}}{\Delta \dot{E}_{\text{CO}_2, \mu}^{\text{des}}} = \frac{\dot{n}_{\text{CO}_2, \text{gas}}^{\text{abs}} \Delta \bar{e}_{\mu, \text{CO}_2}^{\text{x,abs}}}{\dot{n}_{\text{CO}_2, \text{gas}}^{\text{des}} (\bar{e}_{\mu, \text{CO}_2, 2}^{\text{x,des}} - \bar{e}_{\mu, \text{CO}_2, 2}^{\text{x,abs}})}$$

The obvious requirement that the rating quotient varied in the only logical range between zero and one could be guaranteed by taking into account additional energy supply to the section. The heat exergy is much greater than the chemical concentration one and it appeared always in the denominator of the rating quotient. Such a formulation using in fact the subjective selection of expenditures and advantages is quite profitable in analyzing the absorption/desorption section alone, but taking into account that it is a particular element of a complex system, e.g. the *IGCC* one, the same analysis approach should be applied, i.e. the thermodynamic effectivity concept [1]–[2].

Another approach has been presented in [4], where the exergy rating quotient for the absorption process was formulated as

$$v_{ex} = \frac{\dot{E}_{1, gas} + \dot{E}_{2, liq}}{\dot{E}_{2, gas} + \dot{E}_{1, liq}} \quad \text{or in general} \quad v_{ex, \Sigma} = \frac{\sum \dot{E}_{out}}{\sum \dot{E}_{in}}$$

In the last formulation all input and output exergy flows have been taken into account. Also this approach does not suit the worked out general exergy rating procedure using the thermodynamic effectivity concept, [1]–[2].

In usual cases the absorption is considered as the main process, and the desorption is only as a solvent regeneration unit. It is because the last process can be accomplished in different ways, e.g. using the solvent expansion, the true substance exchange or even solvent distillation process. The two first mentioned methods are being the most useful for CO₂–absorption/desorption unit.

3 ABSORPTION WITH EXPANDING DESORPTION UNIT

The numerical results for the absorption/desorption unit of that kind have been obtained from the simplified model, intended for thermodynamic analyzes. They are contained in the Tab. 1. The natural environment temperature is assumed to be equal $T_0=293.15$ K.

Tab. 1 Results for 25 °C ($H_A=165$ MPa) isothermal conditions.

<i>absorption unit</i>		<i>desorption unit</i>	
$Y_{CO_2,2}$	0.422	$Y_{CO_2,1}^{des} = Y_{CO_2}^{air}$	0.00030009
$y_{CO_2,2}$	0.29676512	$y_{CO_2,1}^{des} = y_{CO_2}^{air}$	0.0003
\dot{n}_{gas}^{abs} [kmol/h]	141.3	\dot{n}_{gas}^{des} [kmol/h]	7.691634
$\dot{n}_{liq}^{abs} = \dot{n}_{liq}^{des}$ [kmol/h]	15324.897	$\dot{n}_{liq}^{des} = \dot{n}_{liq}^{abs}$ [kmol/h]	15324.897
$t_{abs} = t_{des}$ [°C]	25	$t_{des} = t_{abs}$ [°C]	25
p_{abs} [MPa]	2.65	p_{des} [MPa]	0.1
$X_{CO_2,2}$	0.00384667	$Y_{CO_2,2}^{des}$	7.511657585
$x_{CO_2,2}$	0.0037041823	$y_{CO_2,2}^{des}$	0.882502379
$X_{CO_2,1}$	0.000077111482		
$x_{CO_2,1}$	0.000071055		
$Y_{CO_2,1}$	0.01316759		
$y_{CO_2,1}$	0.012996458		

For the liquid flux, the chemical zero exergy change between bottom (2) and head (1) equals to

$$\begin{aligned} \Delta \dot{E}_{CO_2, liq}^0 &= \dot{n}_{liq}^{abs} (X_{CO_2,2} - X_{CO_2,1}) \cdot \bar{e}_{\mu, CO_2}^0 = 15324.897 \cdot 10^3 \cdot (0.003847 - 0.0000771) \cdot 19.77192 = \\ &= 1142186319 \frac{kJ}{h} = 317.2740 kW = \left| \Delta \dot{E}_{CO_2, liq}^0 \right| \end{aligned}$$

and for the gaseous phase to

$$\begin{aligned} \nabla \dot{E}_{CO_2, gas}^0 &= \dot{n}_{gas}^{abs} (Y_{CO_2,1} - Y_{CO_2,2}) \cdot \bar{e}_{\mu, CO_2}^0 = 141.3 \cdot 10^3 \cdot (0.01318 - 0.422) \cdot 19.77192 = \\ &= -1142184661 \frac{kJ}{h} = -317.2735 kW = -\left| \nabla \dot{E}_{CO_2, gas}^0 \right| \end{aligned}$$

The same numerical result in both cases has been expected.

The chemical concentration exergy change can be calculated after the condition according to Eq. (2) has been proved. From the above results matrix follows

$$Y_{CO_2,2}=0.422 \rightarrow Y_{CO_2,1}=0.01318$$

or

$$y_{\text{CO}_2,2}=0.296765 \rightarrow y_{\text{CO}_2,1}=0.0129965$$

where $y_{\text{CO}_2,\text{extr}}=0.000110364$: it means the extreme exergy point has not been crossed. Thus, assuming $T_0=293.15$ K,

$$\begin{aligned} \Delta \dot{E}_{\text{CO}_2,\text{gas}}^x &= \dot{n}_{\text{gas}}^{\text{abs}} \bar{R} T_0 \left(y_{\text{CO}_2,1} \ln \frac{y_{\text{CO}_2,1}}{y_{\text{CO}_2,0}} - y_{\text{CO}_2,2} \ln \frac{y_{\text{CO}_2,2}}{y_{\text{CO}_2,0}} \right) = \\ &= 141.3 \cdot 10^3 \cdot 0.0083143 \cdot 293.15 \cdot \left(0.0129965 \ln \frac{0.0129965}{0.0003} - 0.296765 \ln \frac{0.296765}{0.0003} \right) = \\ &= -6880283888 \frac{\text{kJ}}{\text{h}} = -191.1190 \text{ kW} = -\left| \nabla \dot{E}_{\text{CO}_2,\text{gas}}^{x>} \right| \end{aligned}$$

Thus, thermodynamic effectivity for the absorption process equals to

$$\varepsilon_{\text{abs}} = \frac{\Delta \dot{E}_{\text{CO}_2,\text{liq}}^0}{\nabla \dot{E}_{\text{CO}_2,\text{gas}}^0 + \left| \nabla \dot{E}_{\text{CO}_2,\text{gas}}^{x>} \right|} = \frac{317.2740}{317.2735 + 191.1190} = \underline{0.6241}$$

According to Chapter 2 and Fig. 1 the process is analyzed from the bottom to the head, i.e. for the gas flux there is: $2 \rightarrow 1$ and for the liquid flux: $1 \rightarrow 2$

The desorbing medium is atmospheric air, for which the chemical exergy equals to zero, and which contains the carbon dioxide molar fraction of $y_{\text{CO}_2,0}=0.0003$. According to the data matrix there is $y_{\text{CO}_2,2}^{\text{des}}=0.882502$ and $y_{\text{CO}_2,1}=0.0003$, thus, there is no $y_{\text{CO}_2,\text{extr}}$ exergy algebraic sign inversion point in the range between $y_{\text{CO}_2,1}$ and $y_{\text{CO}_2,2}^{\text{des}}$, hence

$$\begin{aligned} \Delta \dot{E}_{\text{CO}_2,\text{gas}}^x &= \dot{n}_{\text{gas}}^{\text{des}} \bar{R} T_0 \left[y_{\text{CO}_2,1} \ln \frac{y_{\text{CO}_2,1}}{y_{\text{CO}_2,0}} - y_{\text{CO}_2,2}^{\text{des}} \ln \frac{y_{\text{CO}_2,2}^{\text{des}}}{y_{\text{CO}_2,0}} \right] = 7.69163410^3 \cdot 0.0083143 \cdot 293.15 \times \\ &\times \left(0 - 0.882502 \ln \frac{0.882502}{0.0003} \right) = -1321354418 \frac{\text{kJ}}{\text{h}} = -36.7043 \text{ kW} = -\left| \nabla \dot{E}_{\text{CO}_2,\text{gas}}^{x>} \right| \end{aligned}$$

and the appropriate thermodynamic effectivity

$$\varepsilon_{\text{des}} = \frac{\left| \Delta \dot{E}_{\text{CO}_2,\text{liq}}^0 \right|}{\left| \nabla \dot{E}_{\text{CO}_2,\text{gas}}^0 \right| + \left| \nabla \dot{E}_{\text{CO}_2,\text{gas}}^{x>} \right|} = \frac{317.2739}{317.2739 + 36.7043} = \underline{0.8963}$$

The chemical zero exergy change in the process is the same as in the coupled absorption unit. In accordance to statements made in Chapter 2, the analysis has been provided again from the bottom to the head of the vessel, i.e. for the liquid flux it has been taken the direction $1 \rightarrow 2$ and for the gaseous one $2 \rightarrow 1$.

The pumping work can be determined from the known relations, namely

$$N_{\text{pmp}} = \frac{\dot{V} \cdot \Delta p}{0.85 \cdot 3600}$$

whereas the efficiency has been assumed to be 85%. Setting numerical values it yields:

$$N_{\text{pmp}} = \frac{18 \cdot 15324 \cdot 10^{-3} \cdot 2.55 \cdot 10^6}{0.85 \cdot 3600} = 229.8600 \text{ kW}$$

The recovered turbine work at its efficiency of 95% equals to

$$N_{\text{trb}} = \frac{\dot{V} \cdot \Delta p}{0.95 \cdot 3600} \quad \text{and} \quad N_{\text{trb}} = \frac{18 \cdot 15324 \cdot 10^{-3} \cdot 2.55 \cdot 10^6}{0.95 \cdot 3600} = 205.6642 \text{ kW}$$

The thermodynamic effectivity of the pump/turbine section is therefore to

$$\varepsilon_{\text{pt}} = \frac{N_{\text{trb}}}{N_{\text{pmp}}} = \frac{205.6642}{229.8600} = \underline{0.8947}$$

Thus, the thermodynamic effectivity of the whole absorption/desorption section equals to

$$\varepsilon_{\text{abs/des}}^{\text{net}} = \frac{|\Delta\dot{E}_{\text{CO}_2,\text{liq}}^0| + |\Delta\dot{E}_{\text{CO}_2,\text{gas}}^0|}{|\nabla\dot{E}_{\text{CO}_2,\text{gas}}^0| + |\nabla\dot{E}_{\text{CO}_2,\text{gas}}^{\text{x>}}| + |\nabla\dot{E}_{\text{CO}_2,\text{liq}}^0| + |\nabla\dot{E}_{\text{CO}_2,\text{liq}}^{\text{x>}}|} = \frac{317.2740 + 317.2739}{317.2735 + 191.1190 + 317.2735 + 36.7043} = \underline{0.7358}$$

and regarding additional pumping work supply and turbine work recovered,

$$\varepsilon_{\text{abs/des}} = \frac{|\Delta\dot{E}_{\text{CO}_2,\text{liq}}^0| + |\Delta\dot{E}_{\text{CO}_2,\text{gas}}^0| + N_{\text{trb}}}{|\nabla\dot{E}_{\text{CO}_2,\text{gas}}^0| + |\nabla\dot{E}_{\text{CO}_2,\text{gas}}^{\text{x>}}| + |\nabla\dot{E}_{\text{CO}_2,\text{liq}}^0| + |\nabla\dot{E}_{\text{CO}_2,\text{liq}}^{\text{x>}}| + N_{\text{pmp}}} = \frac{317.2740 + 317.2739 + 205.6642}{317.2735 + 191.1190 + 317.2735 + 36.7043 + 229.8600} = \underline{0.7693}$$

With determined thermodynamic effectivity quotient for the absorption and desorption process their appropriate mathematical weights can be determined. For the last thermodynamic effectivity quotient yields

$$\varepsilon_{\text{abs/des}}^{\text{net}} = \gamma_{\text{abs}} \cdot \varepsilon_{\text{abs}} + \gamma_{\text{des}} \cdot \varepsilon_{\text{des}} + \gamma_{\text{pt}} \cdot \varepsilon_{\text{pt}}$$

with

$$\gamma_{\text{abs}} = \frac{317.2735 + 191.1190}{317.2735 + 191.1190 + 317.2735 + 36.7043 + 229.8600} = 0.4655$$

$$\gamma_{\text{des}} = \frac{317.2735 + 36.7043}{317.2735 + 191.1190 + 317.2735 + 36.7043 + 229.8600} = 0.3241$$

and

$$\gamma_{\text{pt}} = \frac{229.8600}{317.2735 + 191.1190 + 317.2735 + 36.7043 + 229.8600} = 0.2105$$

Hence,

$$\varepsilon_{\text{abs/des}} = \gamma_{\text{abs}} \varepsilon_{\text{abs}} + \gamma_{\text{des}} \varepsilon_{\text{des}} + \gamma_{\text{pt}} \varepsilon_{\text{pt}} = 0.4655 \cdot 0.6241 + 0.3241 \cdot 0.8963 + 0.2105 \cdot 0.8947 = \underline{0.7693}$$

The result can be interpreted that the absorption process is of a little bit greater significance in the analyzed section, but the almost unexpected role of the pumping and expanding work.

4 ABSORPTION WITH CLASSICAL PLATES DESORPTION UNIT

The next solution of the section under consideration is the absorption unit with a classical desorption column as the regeneration unit. The results of an appropriate model determination are presented in Tab. 2. The section runs at isothermal conditions, but the process temperatures are clearly different: 25 °C for the absorption and 50 °C for the desorption.

Tab. 2 Results for 25 °C (absorption, $H_A=165$ MPa) and 50 °C (desorption, $H_A=307.75$ MPa).

absorption unit		desorption unit	
$Y_{\text{CO}_2,2}$	0.422	$Y_{\text{CO}_2,1}^{\text{des}} = Y_{\text{CO}_2}^{\text{air}}$	0.00030009
$y_{\text{CO}_2,2}$	0.296765	$y_{\text{CO}_2,1}^{\text{des}} = y_{\text{CO}_2}^{\text{air}}$	0.0003
$\dot{n}_{\text{gas}}^{\text{abs}}$ [kmol/h]	141.3	$\dot{n}_{\text{gas}}^{\text{des}}$ [kmol/h]	149.0135
$\dot{n}_{\text{liq}}^{\text{abs}} = \dot{n}_{\text{liq}}^{\text{des}}$ [kmol/h]	203292.447	$\dot{n}_{\text{liq}}^{\text{des}} = \dot{n}_{\text{liq}}^{\text{abs}}$ [kmol/h]	203292.447
t_{abs} [°C]	25	t_{des} [°C]	50
p_{abs} [MPa]	0.2	p_{des} [MPa]	0.2
$X_{\text{CO}_2,2}$	0.0002881	$Y_{\text{CO}_2,2}^{\text{des}}$	0.391073
$x_{\text{CO}_2,2}$	0.003704	$y_{\text{CO}_2,2}^{\text{des}}$	0.281131
$X_{\text{CO}_2,1}$	0.000001803	t_{des}	0.9944
$x_{\text{CO}_2,1}$	0.000001803		
$Y_{\text{CO}_2,1}$	0.00990		

$y_{\text{CO}_2,1}$	0.009803
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The zero exergy change of the two CO₂ exchanging fluxes in the absorption unit are
 $\nabla \dot{E}_{\text{CO}_2, \text{gas}}^0 = \dot{n}_{\text{gas}}^{\text{abs}} (Y_{\text{CO}_2,1} - Y_{\text{CO}_2,2}) \cdot \bar{e}_{\mu, \text{CO}_2}^0 = 141.3 \cdot 10^3 \cdot (0.00990 - 0.422) \cdot 19.77192 =$
 $= -1151313870 \frac{\text{kJ}}{\text{h}} = -319.8094 \text{ kW}$

for the gaseous one, and

$$\Delta \dot{E}_{\text{CO}_2, \text{liq}}^0 = \dot{n}_{\text{liq}}^{\text{abs}} (X_{\text{CO}_2,2} - X_{\text{CO}_2,1}) \cdot \bar{e}_{\mu, \text{CO}_2}^0 = 203292447 \cdot 10^3 \cdot (0.0002881 - 0.00000180) \cdot 19.77192 =$$

$$= 1150966612 \frac{\text{kJ}}{\text{h}} = 319.7129 \text{ kW}$$

for the solvent flux (output minus input).

Setting numerical values presented in the above results table for the gaseous phase, namely
 $y_{\text{CO}_2,2} = 0.296765 \quad \rightarrow \quad y_{\text{CO}_2,1} = 0.00980285$

there can be stated that the exergy change inversion point $y_{\text{CO}_2, \text{extr}} = 0.000110364$ is not crossed, and the appropriate concentration exergy change equals to (subscript 2 for the start and subscript 1 for the end, Fig. 1)

$$\Delta \dot{E}_{\text{CO}_2, \text{gas}}^{\text{x>}} = \dot{n}_{\text{gas}}^{\text{abs}} \bar{R} T_0 \left(y_{\text{CO}_2,1} \ln \frac{y_{\text{CO}_2,1}}{y_{\text{CO}_2,0}} - y_{\text{CO}_2,2} \ln \frac{y_{\text{CO}_2,2}}{y_{\text{CO}_2,0}} \right) =$$

$$= 141.3 \cdot 10^3 \cdot 0.008314329315 \cdot \left(0.00980285 \ln \frac{0.00980285}{0.0003} - 0.296765 \ln \frac{0.296765}{0.0003} \right) =$$

$$= -6931254559 \frac{\text{kJ}}{\text{h}} = -192.5348 \text{ kW} \equiv -|\nabla \dot{E}_{\text{CO}_2, \text{gas}}^{\text{x>}}|$$

There is always $y_{\text{CO}_2} > y_{\text{CO}_2, \text{extr}}$ (superscript > in the appropriate exergy change term, while $\Delta \dot{E}_{\text{CO}_2, \text{gas}}^{\text{x<}} = 0$).

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

$$\varepsilon_{\text{abs}} = \frac{|\Delta \dot{E}_{\text{CO}_2, \text{liq}}^0|}{|\nabla \dot{E}_{\text{CO}_2, \text{gas}}^0| + |\nabla \dot{E}_{\text{CO}_2, \text{gas}}^{\text{x>}}|} = \frac{319.7129}{319.8094 + 192.5348} = \underline{0.6240}$$

with particular exergy changes

$$\nabla \dot{E}_{\text{CO}_2, \text{gas}}^0 = -319.8094 \text{ kW} \quad \Delta \dot{E}_{\text{CO}_2, \text{liq}}^0 = 319.7129 \text{ kW} \quad \Delta \dot{E}_{\text{CO}_2, \text{gas}}^{\text{x>}} = -192.5348 \text{ kW} \equiv -|\nabla \dot{E}_{\text{CO}_2, \text{gas}}^{\text{x>}}|$$

In fact, zero exergy changes of the both CO₂ exchanging media (water and flue gas) should be the same: the slightly difference results from the calculation device accuracy, but it can also be a proof for the procedure correctness.

To determine thermodynamic effectivity for the desorption process it will be proceeded in a similar way. It becomes

$$\Delta \dot{E}_{\text{CO}_2, \text{liq}}^{0, \text{des}} = \dot{n}_{\text{liq}}^{\text{des}} (X_{\text{CO}_2,2} - X_{\text{CO}_2,1}) \cdot \bar{e}_{\mu, \text{CO}_2}^0 = 203292447 \cdot 10^3 \cdot (0.00000180 - 0.0002881) \cdot 19.77192 =$$

$$= 1151328365 \frac{\text{kJ}}{\text{h}} = 319.8134 \text{ kW}$$

for the solvent, and

$$\nabla \dot{E}_{\text{CO}_2, \text{gas}}^{0, \text{des}} = \dot{n}_{\text{gas}}^{\text{des}} (Y_{\text{CO}_2,1} - Y_{\text{CO}_2,2}) \cdot \bar{e}_{\mu, \text{CO}_2}^0 = 149.0135 \cdot 10^3 \cdot (0.00030009 - 0.391073) \cdot 19.77192 =$$

$$= -1151328365 \frac{\text{kJ}}{\text{h}} = -319.8134 \text{ kW}$$

for the solute. The concentration exergy changes are (the reduction of CO₂ molar fractions will not be made)

$$\Delta \dot{E}_{\text{CO}_2, \text{gas}}^{\text{x}} = \dot{n}_{\text{gas}}^{\text{des}} \bar{R} T_0 \left[y_{\text{CO}_2,1}^{\text{des}} \ln \frac{y_{\text{CO}_2,1}^{\text{des}}}{y_{\text{CO}_2,0}} - y_{\text{CO}_2,2}^{\text{des}} \ln \frac{y_{\text{CO}_2,2}^{\text{des}}}{y_{\text{CO}_2,0}} \right] = 149.0135 \cdot 10^3 \cdot 0.008314329315 \times$$

$$\times \left(0.00003 \ln \frac{0.00003}{0.0003} - 0.281131 \ln \frac{0.281131}{0.0003} \right) = -6986870423 \frac{\text{kJ}}{\text{h}} = -194.0797 \text{ kW} = |\nabla \dot{E}_{\text{CO}_2, \text{gas}}^{\text{x>}}|$$

Hence, for the separate desorption process, for which the solvent temperature should be increased, there is

$$\varepsilon_{\text{des}} = \frac{|\Delta \dot{E}_{\text{CO}_2, \text{liq}}^{0, \text{des}}|}{|\nabla \dot{E}_{\text{CO}_2, \text{gas}}^{0, \text{des}}| + |\nabla \dot{E}_{\text{CO}_2, \text{gas}}^{x, \text{des}}|} = \frac{319.8134}{319.8134 + 194.0797} = 0.6223 \quad (3)$$

The simple absorption process can be realized without any heat interference into its physical rule. In fact, the substance exchanging media should be taken at the process temperature and pressure. At the assumed $T_0=293.15$ K and $T_{\text{abs}}=298.15$ K, the solvent (in the considered case the water) should be heated up (by 5 K) and eventually the crude flue gas should be cooled down, if it is supplied with the gasifying process temperature (*IGCC*-cycle). For all that, however, the crude flue gas heat surplus can be recovered and led to another particular system process, e.g. to the desorption one. The most forthright case will be taken into account in following analyzes.

The considered absorption/desorption section includes a heat recovery unit and additional heat supply and removing sources. The liquid flux is the same in both units, i.e.

$$\dot{n}_{\text{liq}}^{\text{abs}} = \dot{n}_{\text{liq}}^{\text{des}} = 203292.447 \text{ kmol/h}$$

Assuming the intensity of the heat regeneration $t_{\text{hex}}=0.98$, yields

$$t_{\text{hex}} = \frac{\dot{Q}}{\dot{Q}_{\infty}} = \frac{\dot{n}_{\text{liq}}^{\text{abs}} \bar{c}_{\text{liq}} (t_{\text{des}} - t'_{\text{abs}})}{\dot{n}_{\text{liq}}^{\text{abs}} \bar{c}_{\text{liq}} (t_{\text{des}} - t_{\text{abs}})} = \frac{t_{\text{des}} - t'_{\text{abs}}}{t_{\text{des}} - t_{\text{abs}}}$$

and (Fig. 3)

$$t'_{\text{abs}} = t_{\text{des}} - t_{\text{hex}} (t_{\text{des}} - t_{\text{abs}}) \quad \text{i.e.} \quad t'_{\text{abs}} = 50 - 0.98 \cdot (50 - 25) = 26.25^{\circ}\text{C}$$

From the heat balance there is further

$$(t_{\text{des}} - t'_{\text{abs}}) = (t'_{\text{des}} - t_{\text{abs}}) \quad \text{i.e.} \quad t'_{\text{des}} = 25 + (50 - 26.25) = 48.75^{\circ}\text{C}$$

Hence, the heat supplied by the regeneration exchanger to the desorption process equals to

$$\dot{Q}_{+, \text{rec}}^{\text{des}} = \dot{n}_{\text{liq}}^{\text{des}} \bar{c}_{\text{liq}} (t'_{\text{des}} - t_{\text{abs}}) = 203292447 \cdot 4.1805 \cdot (48.75 - 25) = 201842717 \frac{\text{kJ}}{\text{h}} = 56067422 \text{ kW}$$

Additional heat amount, i.e.

$$\dot{Q}_{+, \text{add}}^{\text{des}} = \dot{n}_{\text{liq}}^{\text{des}} \bar{c}_{\text{liq}} (t_{\text{des}} - t'_{\text{des}}) = \frac{203292447 \cdot 4.1805}{0.95} (50 - 48.75) = 1118242203 \frac{\text{kJ}}{\text{h}} = 310.6228 \text{ kW}$$

should be supplied (the efficiency of this heat supply has been estimated to be ca. 95%).

Appropriate exergies are

$$\begin{aligned} \dot{E}_{Q+, \text{rec}}^{\text{des}} &= \dot{n}_{\text{liq}}^{\text{des}} \bar{c}_{\text{liq}} \int_{T_{\text{abs}}}^{T'_{\text{des}}} \left(1 - \frac{T_0}{T}\right) dT = \dot{n}_{\text{liq}}^{\text{des}} \bar{c}_{\text{liq}} (T'_{\text{des}} - T_{\text{abs}}) - \dot{n}_{\text{liq}}^{\text{des}} \bar{c}_{\text{liq}} T_0 \ln \frac{T'_{\text{des}}}{T_{\text{abs}}} = \\ &= 203292447 \cdot 4.1805 \cdot \left[(321.90 - 298.15) - 293.15 \cdot \ln \frac{321.90}{298.15} \right] = 1089310040 \frac{\text{kJ}}{\text{h}} = 302.5861 \text{ kW} \end{aligned}$$

and approximately

$$\dot{E}_{Q+, \text{add}}^{\text{des}} \approx \left(1 - \frac{T_0}{T_{\text{des}}}\right) \cdot \dot{Q}_{+, \text{add}}^{\text{des}} = \left(1 - \frac{293.15}{323.15}\right) \cdot 1118242203 = 1038132944 \frac{\text{kJ}}{\text{h}} = 28.8370 \text{ kW}$$

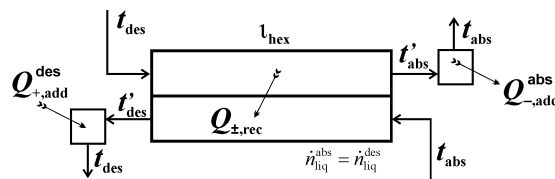


Fig. 3 Scheme of the absorption/desorption heat recovery unit.

The same procedure will be applied to the heat, carried away to cool down the liquid to the absorption temperature. For the recovered heat it follows

$$\dot{Q}_{-,\text{rec}}^{\text{abs}} = \dot{n}_{\text{liq}}^{\text{abs}} \bar{c}_{\text{liq}} (t_{\text{des}} - t'_{\text{abs}}) = 203292447 \cdot 4.1805 \cdot (50 - 26.25) = 2018427177 \frac{\text{kJ}}{\text{h}} = 56067422 \text{ kW}$$

and

$$\begin{aligned} \dot{E}_{Q-,\text{rec}}^{\text{abs}} &= \dot{n}_{\text{liq}}^{\text{abs}} \bar{c}_{\text{liq}} \int_{T_{\text{abs}}}^{T_{\text{des}}} \left(1 - \frac{T_0}{T}\right) dT = \dot{n}_{\text{liq}}^{\text{abs}} \bar{c}_{\text{liq}} (T_{\text{des}} - T_{\text{abs}}) - \dot{n}_{\text{liq}}^{\text{abs}} \bar{c}_{\text{liq}} T_0 \ln \frac{T_{\text{des}}}{T_{\text{abs}}} = \\ &= 203292447 \cdot 4.1805 \cdot \left[(323.15 - 299.40) - 293.15 \cdot \ln \frac{323.15}{299.40} \right] = 1166065114 \frac{\text{kJ}}{\text{h}} = 323.9070 \text{ kW} \end{aligned}$$

The additional heat to remove and its exergy are equal to (appropriate efficiency is assumed to 97%)

$$\dot{Q}_{-,\text{add}}^{\text{abs}} = \dot{n}_{\text{liq}}^{\text{abs}} \bar{c}_{\text{liq}} (t'_{\text{abs}} - t_{\text{abs}}) = \frac{203292447 \cdot 4.1805}{0.97} (26.25 - 25) = 1095185663 \frac{\text{kJ}}{\text{h}} = 304.2182 \text{ kW}$$

$$\dot{E}_{Q-,\text{add}}^{\text{abs}} \approx \left(1 - \frac{T_0}{T_{\text{abs}}}\right) \cdot \dot{Q}_{-,\text{add}}^{\text{abs}} = \left(1 - \frac{293.15}{298.15}\right) \cdot 1095185663 = 183663536 \frac{\text{kJ}}{\text{h}} = 5.1018 \text{ kW}$$

Hence, the thermodynamic effectivity of the heat recovery and additional supply/removing becomes to (according to the concept's rules)

$$\varepsilon_{\text{hex}} = \frac{\dot{E}_{Q-,\text{rec}}^{\text{abs}} + \dot{E}_{Q-,\text{add}}^{\text{abs}}}{\dot{E}_{Q+,\text{rec}}^{\text{des}} + \dot{E}_{Q+,\text{add}}^{\text{des}}} = \frac{323.9070 + 5.1018}{302.5861 + 28.8370} = 0.9927$$

The net thermodynamic effectivity of the absorption/desorption section, i.e. the rating quotient without taking into account the heat recovery, supply and removing, equals to

$$\varepsilon_{\text{abs/des}}^{\text{net}} = \frac{|\Delta \dot{E}_{\text{CO}_2,\text{liq}}^0| + |\Delta \dot{E}_{\text{CO}_2,\text{liq}}^{0,\text{des}}|}{|\nabla \dot{E}_{\text{CO}_2,\text{gas}}^0| + |\nabla \dot{E}_{\text{CO}_2,\text{gas}}^{x>} + |\nabla \dot{E}_{\text{CO}_2,\text{gas}}^{0,\text{des}}| + |\nabla \dot{E}_{\text{CO}_2,\text{gas}}^{x>,\text{des}}|} = \frac{319.7129 + 319.8134}{319.8094 + 192.5348 + 319.8134 + 194.0797} = 0.6232$$

This rating quotient is in fact non-important, because it does not give any special section characteristics.

The total thermodynamic effectivity, however, regards the heat recovery unit, and it is

$$\begin{aligned} \varepsilon_{\text{abs/des}} &= \frac{|\Delta \dot{E}_{\text{CO}_2,\text{liq}}^0| + |\Delta \dot{E}_{\text{CO}_2,\text{liq}}^{0,\text{des}}| + \dot{E}_{Q-,\text{rec}}^{\text{abs}} + \dot{E}_{Q-,\text{add}}^{\text{abs}}}{|\nabla \dot{E}_{\text{CO}_2,\text{gas}}^0| + |\nabla \dot{E}_{\text{CO}_2,\text{gas}}^{x>} + |\nabla \dot{E}_{\text{CO}_2,\text{gas}}^{0,\text{des}}| + |\nabla \dot{E}_{\text{CO}_2,\text{gas}}^{x>,\text{des}}| + \dot{E}_{Q+,\text{rec}}^{\text{des}} + \dot{E}_{Q+,\text{add}}^{\text{des}}} = \\ &= \frac{319.7129 + 319.8134 + 323.9070 + 5.1018}{319.8094 + 192.5348 + 319.8134 + 194.0797 + 302.5861 + 28.8370} = 0.7134 \end{aligned}$$

There is

$$\varepsilon_{\text{abs/des}} = \gamma_{\text{abs}} \cdot \varepsilon_{\text{abs}} + \gamma_{\text{des}} \cdot \varepsilon_{\text{des}} + \gamma_{\text{hex}} \cdot \varepsilon_{\text{hex}}$$

with

$$\gamma_{\text{abs}} = \frac{319.8094 + 192.5348}{319.8094 + 192.5348 + 319.8134 + 194.0797 + 302.5861 + 28.8370} = 0.3774$$

$$\gamma_{\text{des}} = \frac{319.8134 + 194.0797}{319.8094 + 192.5348 + 319.8134 + 194.0797 + 302.5861 + 28.8370} = 0.3785$$

$$\gamma_{\text{hex}} = \frac{302.5861 + 28.8370}{319.8094 + 192.5348 + 319.8134 + 194.0797 + 302.5861 + 28.8370} = 0.2441$$

and

$$\varepsilon_{\text{abs/des}} = 0.3774 \cdot 0.6240 + 0.3785 \cdot 0.6223 + 0.2441 \cdot 0.9927 = 0.7134$$

4.1 Absorption with Classical Plates Desorption Unit at Greater Gas Flux

The same procedure will be repeated to see, how the greater gaseous flux does affect the thermodynamic effectivity quotients. Because of the same liquid flux, the energy terms (heat exergies) will be also the same, Fig. 2. The appropriate results matrix is shown below as Tab. 3.

To determine thermodynamic effectivity for the desorption process by $k_{des}=2$:

$$\nabla \dot{E}_{CO_2,liq}^{0,des} = \dot{n}_{liq}^{des} (X_{CO_2,1} - X_{CO_2,2}) \cdot \bar{e}_{\mu,CO_2}^0 = 203292447 \cdot 10^3 \cdot (0.0000018\theta - 0.0002881\delta) \cdot 19.77192 = -1151328365 \frac{kJ}{h} = -319.8134 \text{ kW}$$

for the solvent, and

$$\Delta \dot{E}_{CO_2,gas}^{0,des} = \dot{n}_{gas}^{des} (Y_{CO_2,2}^{des} - Y_{CO_2,1}^{des}) \cdot \bar{e}_{\mu,CO_2}^0 = 238.4216376 \cdot 10^3 \cdot (0.24445647 - 0.0003000\theta) \cdot 19.77192 = 1150966249 \frac{kJ}{h} = 319.7128 \text{ kW}$$

for the solute. The concentration exergy changes are (the reduction of CO₂ molar fractions will not be made)

Tab. 3 Results for 25 °C (absorption, $H_A=165$ MPa) and 50 °C (desorption, $H_A=307.75$ MPa) at greater gas flux ($k_{des}=2$) — for the absorption unit the same as in Tab. 2.

<i>desorption unit</i>	
$Y_{CO_2,1}^{des} = Y_{CO_2}^{air}$	0.00030009
$y_{CO_2,1}^{des} = y_{CO_2}^{air}$	0.0003
\dot{n}_{gas}^{des} [kmol/h]	238.4216376
$\dot{n}_{liq}^{des} = \dot{n}_{liq}^{abs}$ [kmol/h]	203292.447
t_{des} [°C]	50
p_{des} [MPa]	0.2
$Y_{CO_2,2}^{des}$	0.244456547
$y_{CO_2,2}^{des}$	0.196436386
t_{des}	0.994415668

$$\Delta \dot{E}_{CO_2,gas}^x = \dot{n}_{gas}^{des} \bar{R} T_0 \left[y_{CO_2,2}^{des} \ln \frac{y_{CO_2,2}^{des}}{y_{CO_2,0}} - y_{CO_2,1}^{des} \ln \frac{y_{CO_2,1}^{des}}{y_{CO_2,0}} \right] = 238.4216376 \cdot 10^3 \cdot 0.0083143 \cdot 293.15 \times$$

$$\times \left(0.196436386 \ln \frac{0.196436386}{0.0003} - 0.0003 \ln \frac{0.0003}{0.0003} \right) = 7401965523 \frac{kJ}{h} = 205.6102 \text{ kW} = \left| \Delta \dot{E}_{CO_2,gas}^{x>} \right|$$

Hence, for the separate desorption process, for which the solvent temperature should be increased, there is

$$\varepsilon_{des} = \frac{\left| \Delta \dot{E}_{CO_2,liq}^{0,des} \right|}{\left| \nabla \dot{E}_{CO_2,gas}^{0,des} \right| + \left| \nabla \dot{E}_{CO_2,gas}^{x>,des} \right|} = \frac{319.8134}{319.7128 + 205.6102} = \underline{0.6088}$$

The numerical value is lower than the previously determined thermodynamic effectivity for the process, Eq. (3). Thus, the rating quotients that are calculated for the whole absorption/desorption section both, the net value and the total one regarding the heat recovery section will be also lower. Thus, the net (i.e. without additional energy supply) thermodynamic effectivity of the section is to

$$\varepsilon_{abs/des}^{net} = \frac{\left| \Delta \dot{E}_{CO_2,liq}^{0,des} \right| + \left| \Delta \dot{E}_{CO_2,liq}^{0,abs} \right|}{\left| \nabla \dot{E}_{CO_2,gas}^{0,des} \right| + \left| \nabla \dot{E}_{CO_2,gas}^{x>,des} \right| + \left| \nabla \dot{E}_{CO_2,gas}^{0,abs} \right| + \left| \nabla \dot{E}_{CO_2,gas}^{x>,abs} \right|} =$$

$$= \frac{319.8134 + 319.7129}{319.8134 + 205.7128 + 319.7128 + 192.5348} = \underline{0.6162}$$

and with the same heat exergies, as for the previous case above, it yields

$$\varepsilon_{abs/des} = \frac{\left| \Delta \dot{E}_{CO_2,liq}^{0,des} \right| + \left| \Delta \dot{E}_{CO_2,liq}^{0,des} \right| + \dot{E}_{Q-,rec}^{abs} + \dot{E}_{Q+,add}^{abs}}{\left| \nabla \dot{E}_{CO_2,gas}^{0,des} \right| + \left| \nabla \dot{E}_{CO_2,gas}^{x>,des} \right| + \left| \nabla \dot{E}_{CO_2,gas}^{0,des} \right| + \left| \nabla \dot{E}_{CO_2,gas}^{x>,des} \right| + \dot{E}_{Q+,rec}^{des} + \dot{E}_{Q+,add}^{des}} =$$

$$= \frac{319.7129 + 319.8134 + 323.9070 + 5.1018}{319.8134 + 192.5348 + 319.7129 + 205.7128 + 302.5861 + 28.8370} = \underline{0.7074}$$

5 CONCENTRATION EXERGY CHANGES IN DILUTE SOLUTIONS

The natural environment for exergy and exergy change determination has been supposed to be the dry atmospheric air, pure water as the liquid specie and somehow average solid species compositions, [1]–[2]. For the zero exergy calculation the method of the so-called devaluation chemical reaction — elaborated by Jan Szargut — has been used (applying modifications by Wolfgang Fratzscher). In the method it has been assumed that the condensed phase species are represented in the natural environment at the molar fraction equal to one. It is typical for the chemical thermodynamics, where these species are not miscible. The only except is the case, the rare species are not represented in the atmosphere and hydrosphere (its only component is water H₂O!): then the approach proposed by Jan Szargut should be applied, [1]–[2].

The dilute solution, especially the CO₂(solute)/H₂O(solvent) system, however, should be treated in another way. The species CO₂ and H₂O are represented in the natural environment, but all the natural environment parameters are fixed for all possible cases. It means, the exergy change inversion point is the same as for gas phase (atmospheric air), i.e.

$$x_{\text{CO}_2,0} = y_{\text{CO}_2,0} \quad \text{and hence} \quad x_{\text{CO}_2,\text{extr}} = y_{\text{CO}_2,\text{extr}}$$

(the character x is for molar fraction in liquid, the character y the molar fraction in the gas).

This somehow strange assumption seems to be fully motivated because all the natural environment parameters are fixed, just like the natural environment is fixed in the time of analysis. Hence, for chemical concentration exergy change the same procedure as presented in previous Chapters could be applied, namely

$$\Delta \dot{E}_{\text{CO}_2,\text{liq}}^x = \dot{n}_{\text{liq}}^{\text{abs}} \bar{R} T_0 \left(x_{\text{CO}_2,2} \ln \frac{x_{\text{CO}_2,2}}{x_{\text{CO}_2,0}} - x_{\text{CO}_2,1} \ln \frac{x_{\text{CO}_2,1}}{x_{\text{CO}_2,0}} \right)$$

and, if the exergy change inversion point is crossed, i.e. if

$$x_{\text{CO}_2,1} \rightarrow x_{\text{CO}_2,\text{extr}} \rightarrow x_{\text{CO}_2,2}$$

it becomes

$$\begin{aligned} \Delta \dot{E}_{\text{CO}_2,\text{liq}}^x &= \dot{n}_{\text{liq}}^{\text{abs}} \bar{R} T_0 \left[x_{\text{CO}_2,2} \ln \frac{x_{\text{CO}_2,2}}{x_{\text{CO}_2,0}} - x_{\text{CO}_2,\text{extr}} \right] + \dot{n}_{\text{liq}}^{\text{abs}} \bar{R} T \left[x_{\text{CO}_2,\text{extr}} - x_{\text{CO}_2,1} \ln \frac{x_{\text{CO}_2,1}}{x_{\text{CO}_2,0}} \right] = \\ &= \dot{n}_{\text{liq}}^{\text{abs}} \bar{R} T_0 \left[x_{\text{CO}_2,2} \ln \frac{x_{\text{CO}_2,2}}{x_{\text{CO}_2,0}} - \frac{x_{\text{CO}_2,0}}{e} \right] + \dot{n}_{\text{liq}}^{\text{abs}} \bar{R} T \left[\frac{x_{\text{CO}_2,0}}{e} - x_{\text{CO}_2,1} \ln \frac{x_{\text{CO}_2,1}}{x_{\text{CO}_2,0}} \right] \end{aligned}$$

There can be applied another approach to the exergy changes in dilute solution. Instead of real numerical values for the natural environment molar fraction in the liquid, i.e. $x_{\text{CO}_2,0} = y_{\text{CO}_2,0} = 0.0003$, an apparent appropriate value can be taken into account. The apparent CO₂ contents (or molar fraction) in the solvent H₂O at the presupposed natural environment corresponds to the equilibrium value. The assumed natural environment contents of CO₂ (molar fraction) in the atmosphere is 0.0003, thus, applying the Henry's Law, it becomes

$$X^* = \frac{1}{\frac{H_A}{pY} + \frac{H_A}{p} - 1} \quad \text{with} \quad Y_{\text{CO}_2,0} = \frac{y_{\text{CO}_2,0}}{1 - y_{\text{CO}_2,0}}$$

The symbol y (or Y) is applied to the gaseous phase flow, while the symbol x (or X) to the liquid flow. There can be assumed following Henry's constant values from experimental data: 106 MPa for $T_0 = 283.15$ K, 124 MPa for $T_0 = 288.15$ K, 144 MPa for $T_0 = 293.15$ K, 165 MPa for $T_0 = 298.15$ K (standard chemical temperature) and 174.2 MPa for $T_0 = 300$ K. For the natural environment temperature of 293.15 K and pressure $p_0 = 1$ bar, yields

$$X_{\text{CO}_2,0}^* = \frac{1}{\frac{144}{0.1 \cdot \frac{0.0003}{1 - 0.0003}} + \frac{144}{0.1} - 1} = 0.0000002083$$

and hence the apparent natural environment CO₂ molar fraction in H₂O

$$x_{\text{CO}_2,0}^* = \frac{X_{\text{CO}_2,0}^*}{1 + X_{\text{CO}_2,0}^*} = 0.0000002083$$

Tab. 4 Apparent exergy change inversion points in liquid for a CO₂/H₂O–system.

T_0	H_A	$x_{\text{CO}_2,0}$	$x_{\text{CO}_2,\text{extr}}=x_{\text{CO}_2,0}/e$
283.15 K	106 MPa	0.000000283019	0.000000104117
288.15 K	124 MPa	0.0000002419	0.000000089003
293.15 K	144 MPa	0.0000002083	0.000000076642
298.15 K	165 MPa	0.0000001818	0.000000066882
300 K	174.2 MPa	0.0000001722	0.000000063355

Appropriate numerical values for another natural environment temperatures T_0 and $p_0=1$ bar can be determined. In the Tab. 4 appropriate $x_{\text{CO}_2,0}$ and $x_{\text{CO}_2,\text{extr}}=x_{\text{CO}_2,0}/e$ values for chosen temperatures T_0 and actual natural environment pressure $p_0=0.1$ MPa are compiled.

As a result appropriate thermodynamic effectivity quotient can be formulated and its numerical value calculated. The process thermodynamic transition is in general [1]–[2]

$$\Sigma|E_j^-| \rightarrow \Sigma|E_i^+| + T_0\Delta S_{\text{irr}} \quad \text{and hence} \quad \varepsilon = \frac{\Sigma|E_i^+|}{\Sigma|E_j^-|} < 1$$

because according to the *Second Law of Thermodynamics* there is always $\Delta S_{\text{irr}} > 0$.

Appropriate concentration chemical exergy changes have been determined using the above equation for $\Delta \dot{E}_{\text{CO}_2,\text{liq}}^x$ and $\Delta \dot{E}_{\text{CO}_2,\text{liq}}^x$. Their numerical values did not differ significantly one from another. Moreover, thermodynamic effectivity quotients calculated in previous Chapters did not change appreciably. Because the approach presented above is a new one, it needs a proper number of tests and additional discussion to be applicable without any doubts.

6 CONCLUSIONS

There have been carried out thermodynamic analyzes of the absorption/desorption section of the so-called Integrated Combustion and Gasifying Cycle technology. These processes are somehow embarrassing for any discussion because of the lack in the subject literature appropriate generalizations that allow their clear calculating (modeling) procedure. Even worse situation is in hitherto thermodynamic analyzes worked out applying the Second Law, especially the exergy concept. The only contributions are the cited monographs [3]–[4] and separate articles of their co-authors. Alas, they cannot convincingly explain strange results obtained, e.g. [4].

The presented modeling and thermodynamic analysis approach is a trial to apply the exergy method. The worked out „thermodynamic transition” and „thermodynamic effectivity” concepts have been used, but two special difficulties are to emphasize: the problem of coupled processes, such as an absorption/desorption or better to say absorption with further regeneration unit, and the problem of exergy changes in diluted solutions, like the CO₂ solution in water. The two main problems are to be further discussed and solved fulfilling general conditions.

Worked out within the research project:

ENET (Power Units for Utilization of non Traditional Energy Sources),
CZ.1.05/2.1.00/03.0069

REFERENCES

- [1] KOZACZKA, J. & KOLAT, P. *Exergy and Its Applications*. (Monographs on Science and Education). Tarnów: TANT Publishers, 2010. ISBN 978–83–928990–1–3
- [2] KOZACZKA, J. *Thermodynamic Analysis of Energy Conversion Processes*. (Problems of Mechanical Engineering and Robotics Nr 8), Kraków: Wydział Inżynierii Mechanicznej i Robotyki AGH, 2002. ISBN 83–913400–0–7
- [3] LEITES, I.L. & SOSNA, M.Kh. & SEMENOV, V.P. (ЛЕЙТЕС, И.Л. & СОСНА, М.Х. & СЕМЕНОВ, В.П.). *Теория и практика химической энерготехнологии*. Москва: Изд. «Химия», 1988
- [4] FRATZSCHER, W. & PICT, H.–P. & SZOLCSÁNYI, P. & FONYÓ, Z. & FÖLDES, P. *Energetische Analyse von Stoffübertragungsprozessen*. Leipzig: Deutscher Verlag für Grundstoffindustrie. 1980 — Czech Edition: *Energetická analýza destilace, sorpce a extrakce*. Praha: SNTL – Nakladatelství technické literatury. 1987
- [5] KARPOVA, Yu.G. & LEITES, I.L. (КАРПОВА, Ю.Г. & ЛЕЙТЕС, И.Л.). Эксергетический к.п.д. процессов очистки газов от двуокиси углерода. *Газовая промышленность*. 1971 (10), 16. pp.33–36
- [6] LEITES, I.L. & DYMOV, V.E. & KARPOVA, Yu.G. (ЛЕЙТЕС, И.Л. & ДЫМОВ, В.Е. & КАРПОВА, Ю.Г.). Влияние внешних и внутренних параметров на термодинамическую эффективность абсорбционных процессов разделения газов. *Теоретические Основы Химической Технологии (ТОХТ)* 1976(5), 10. pp.678–690
- [7] LEITES, I.L. & KARPOVA, Yu.G. & BRODYANSKII, V.M. (ЛЕЙТЕС, И.Л. & КАРПОВА, Ю.Г. & БРОДЯНСКИЙ, В.М.). Эксергетический к.п.д. абсорбционных процессов разделения газовых смесей. *Теоретические Основы Химической Технологии (ТОХТ)* 1973(1), 7 pp.24–29
- [8] KOCH, R. & KOZIOŁ, A. *Dyfuzyjno–cieplny rozdział substancji*. (Inżynieria Chemiczna). Warszawa: Wydawnictwa Naukowo–Techniczne, 1994 (ISBN 83–204–1784–8)
- [9] FRATZSCHER, W. & PICT, H.–P. *Stoffdaten und Kennwerte der Verfahrenstechnik* (Verfahrenstechnik — Ein Lehrwerk für Universitäten und Hochschulen). Leipzig: VEB Deutscher Verlag für Grundstoffindustrie, 1979