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

TERMODYNAMIKA ABSORPČNÍ/DESORPČNÍ CO₂ SEKCE INTEGROVANÉHO
ZPLYŇOVACÍHO OBĚHU – I. MODELOVÁNÍ

Abstract

The carbon dioxide absorption/desorption unit of the Integrated Gasifying Combined Cycle has been detailed described to formulate appropriate model equations for the processes, suitable for further thermodynamic analyzes. There are two principal technologies of the CO₂-removing section, namely the absorption with the following expanding desorption process, and the absorption with the following classical plates (or packing) desorption one. The physics of thermodynamic properties of the water/carbon dioxide solution have been presented thoroughly using hitherto literature data. The Henry's Law has been emphasized as the base for further thermodynamic analyzes. The numerical results of appropriate absorption/desorption units have been compiled presuming fundamental relations, which are also presented. They should be the base for their thermodynamic analyzes.

Abstrakt

Ve článku je detailně popsána absorpční a desorpční jednotka pro oxid uhličitý integrovaného zplyňovacího kombinovaného oběhu tak, aby se mohl definovat přiměřený matematický model procesu vhodný pro další termodynamickou analýzu. Existují dvě principiální technologie pro extrakci CO₂ jmenovitě absorpce s následným expanzním desorpčním procesem a absorpce s následným klasickým desorpčním procesem. Fyzika termodynamických vlastností roztoku voda/oxid uhličitý je prezentována zatím na základě dat z literatury. Je zde zdůrazněn Henryho zákon jako základ pro další termodynamické analýzy. Numerické výsledky vhodných absorpčních / desorpčních jednotek byly určeny na základě předpokládaných základních vztahů, které jsou také prezentovány. Tyto tvoří základ pro jejich termodynamické analýzy.

1 INTRODUCTION

The so-called Integrated Gasifying Combined Cycle (IGCC) is one of the three discussed systems of the Carbon Capture and Storage technologies. It consists of the coal gasifying process followed by the CO₂-absorption/desorption section, and further the proper hydrogen combustion one. Thus, the turbine is almost driven by the hydrogen with exhaust gases consisting of water steam. The carbon dioxide is led to the appropriate storage system. The CO₂-wash is the absorption/desorption section. In traditional CO₂-wash the water is used as a solvent. In modern technologies newly

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developed CO₂-sorbents can be used that allow reasonable size reduction of the installations (columns).

2 CARBON DIOXIDE SOLUBILITY IN WATER

The carbon dioxide can be absorbed and desorbed by water, as the exceptional low-cost sorption agent. Temperature dependence of the Henry's constant (in fact the coefficient) for CO₂ in water is compiled in the following table (experimental data):

Tab. 1 Henry's constant (coefficient) for CO₂ solution in water — experimental data.

t [°C]	10	15	20	25	30	35	40
H_A [MPa]	106	124	144	165	188	212	236

However, according to [1] a form of Henry's law can be used for modeling the solubility of carbon dioxide in water for pressures up to about 100 MPa, as can be seen in Fig. 1. They conclude that the Krichevsky–Kasarnovsky Equation, which can be derived from Henry's Law, can be used to calculate the system CO₂/H₂O at temperatures below 100 °C.

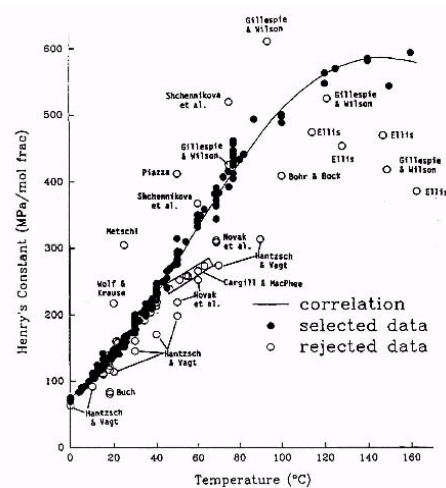


Fig. 1 Henry's constant for carbon dioxide in water, [1].

Because solubility of gases decreases with increasing temperature, the partial pressure a given gas concentration has in liquid must increase. While heating water (saturated with nitrogen) from 25 °C to 95 °C the solubility will decrease to about 43% of its initial value. Partial pressure of CO₂ in seawater doubles with every 16 K increase in temperature.

If only the temperature of a system changes the Henry's constant will also change. This is why some people prefer to name it Henry's coefficient. There are multiple equations assessing the effect of temperature on the constant. This form of the van't Hoff's equation is one example:

$$H_A(T) = H_A(T_{ref}) \cdot e^{\left[-C \left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right]}$$

where H_A for a given temperature is the Henry's Law constant (T is in kelvins, T_{ref} refers to the standard temperature of 298 K). The above equation is an approximation only and should be used only when no better experimentally derived formula for a given gas exists. The following table lists some values for constant C (dimension of kelvins) in the equation above:

Tab. 2 Parameter C for chosen gases water solutions in the Henry's constant temperature dependence.

gas	O ₂	H ₂	CO ₂	N ₂	He	Ne	Ar	CO
$C=$	1700	500	2400	1300	230	490	1300	1300

Henry's constants (or better to say: coefficients) can be approximated as temperature dependent. Some such relations are given in [2], i.e.

$$\text{Eqn. 3: } H_A = -470417 + 26.57845T - 0.0376298T^2 + 9.63891 \cdot 10^{-6} \cdot T^3 \quad [\text{MPa}]$$

$$\text{Eqn. 4: } H_A = -503299 + 30.74113T - 0.052667T^2 + 2.630218 \cdot 10^{-5} \cdot T^3 \quad [\text{MPa}]$$

$$\text{Eqn. 7: } H_A = 507629 + 31.9877T - 0.057691T^2 + 3.18012 \cdot 10^{-5} \cdot T^3 \quad [\text{MPa}]$$

Appropriate graphical tracings are presented in Fig. 2.

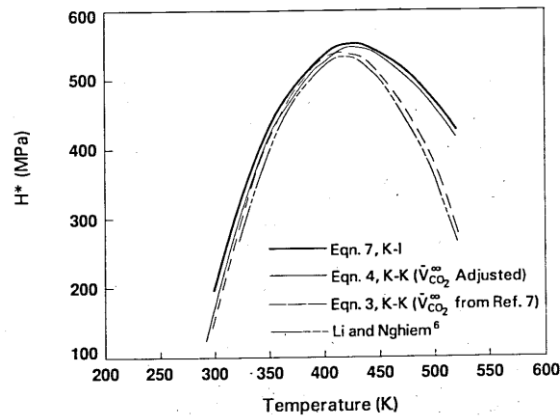


Fig. 2 Henry's constant in CO₂/H₂O system (for different approximations) — the curve according to Eqn. 4 and Eqn. 3 are formulated and recommended by authors, [2]: ($H^* \equiv H_A$).

A solution is a mixture of materials, one of which is usually a fluid. A fluid is a material that flows, such as a liquid or a gas. The fluid of a solution is usually the solvent. The material other than the solvent is the solute. It can be said that the solute is dissolved into the solvent.

The equilibrium conditions (the so-called equilibrium line) using Henry's constants (or coefficients) are expressed by the relation $Y^* = f_Y(X)$ or $X^* = f_X(Y)$ in form of

$$Y^* = \frac{1}{\frac{p}{H_A X} + \frac{p}{H_A} - 1} \quad \text{or} \quad X^* = \frac{1}{\frac{H_A}{pY} + \frac{H_A}{p} - 1}$$

where p is the pressure in the same units as the Henry's coefficient. X and Y are the mole loads (or mole ratios), i.e. moles per „inert” moles amount, first in liquid and for the second in gas phase. The last quantities can be converted into the habitual mole fractions using following relations:

$$X = \frac{x}{1-x} \quad Y = \frac{y}{1-y} \quad \text{and} \quad x = \frac{X}{1+X} \quad y = \frac{Y}{1+Y}$$

Using these mole loads the balance (or operation) line in Y, X -diagram for absorption/desorption processes is a straight line, which makes graphical interpretation and calculations of the processes much easier, if not possible at all.

More effective CO₂ solvents are nowadays searched, e.g. [3]. Alas, appropriate thermo-physical data have not been published yet.

2.1 The Henry's vs. Raoult' Laws

There is very often not distinguished between the two important laws concerning dilute solutions. It is important to make it properly because of the further thermodynamic analysis of processes in gas solutions.

In the case of dilute solution the concentration of the solute is proportional to its mole fraction x , and the Henry's Law gives a relation

$$p = H_A \cdot x$$

whereas the Raoult's Law states once the components in the solution have reached equilibrium, when the total vapor pressure p of the solution is

$$p = p^* \cdot x$$

where p^* is the vapor pressure of the pure component. The two equations seem to be the same, if only $H_A = p^*$. But this is true hardly ever, namely for pairs of closely related substances. The general case is that Laws are limit laws, i.e. they are limits of functions, and they apply at opposite ends of the composition range. The vapor pressure of the component in large excess, such as the solvent for a dilute solution, is proportional to its mole fraction, and the constant of proportionality is the vapor pressure of the pure substance (Raoult's Law). The vapor pressure of the solute is also proportional to the solute's mole fraction, but the constant of proportionality is different and must be determined experimentally (Henry's Law). It yields

$$\text{Raoult's Law} \quad \text{---} \quad \lim_{x \rightarrow 1} \left(\frac{p}{x} \right) = p^*$$

$$\text{Henry's Law} \quad \text{---} \quad \lim_{x \rightarrow 0} \left(\frac{p}{x} \right) = H_A$$

Raoult's Law can also be related to non-gas solutes, but the Henry's Law cannot.

3 TECHNOLOGICAL ABSORPTION AND DESORPTION PROCESSES

The technological substance exchange process can be presented similarly to the heat exchange one. The usual display of the last process is made in $T-A$ coordinates, the absorption process display, however, in concentration-phases contact largeness axes, Fig. 3.

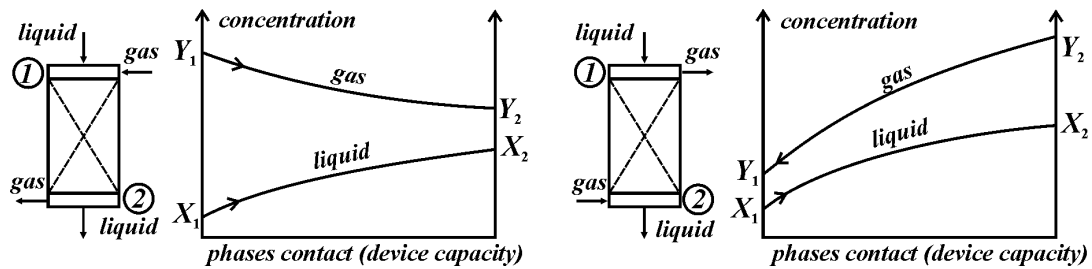


Fig. 3 Concurrent and counter-current absorption process.

In fact, this graphical interpretation of the technological substance exchange processes is not used. Commonly it is showed in $Y-X$ coordinates, where two lines are of conclusive importance: the equilibrium line and the balance (operation) straight line, Fig. 4 for absorption and Fig. 5 for desorption process (both counter-current). The shape of the equilibrium line is not always that regular, but in the case of practical CO_2 -water solutions almost excluded is that the two lines cross between the start and final points X^* and Y^* . It would make the modeling procedure more complicated. Sometimes it is useful to replace the non-linear equilibrium line relation by the straight one, certainly in appropriate narrow limits.

Using the two diagrams, Fig. 4 and Fig. 5, intensity parameters for the two technological substance exchange processes can be formulated, namely

$$t_{\text{abs}} = \frac{Y_{\text{CO}_2,2} - Y_{\text{CO}_2,1}}{Y_{\text{CO}_2,2} - Y_{\text{CO}_2,1}^*} \quad \text{where} \quad Y_{\text{CO}_2,1}^* \parallel X_{\text{CO}_2,1}$$

for the absorption, and

$$t_{\text{des}} = \frac{X_{\text{CO}_2,2} - X_{\text{CO}_2,1}}{X_{\text{CO}_2,2} - X_{\text{CO}_2,1}^*} \quad \text{where} \quad X_{\text{CO}_2,1}^* \parallel Y_{\text{CO}_2,1}$$

for the desorption.

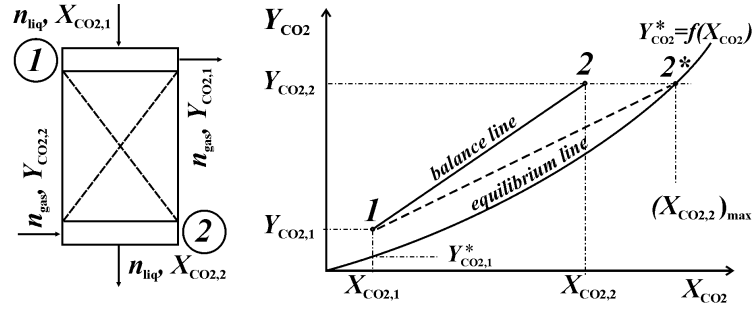


Fig. 4 Concurrent and counter-current absorption process (dashed line corresponds to the minimum reflux ratio $R_{abs,min}$).

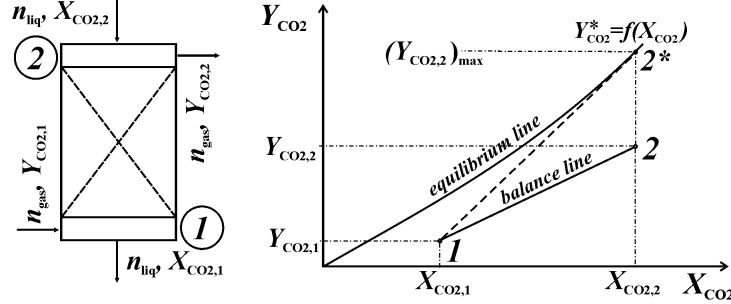


Fig. 5 Concurrent and counter-current desorption process (dashed line corresponds to the minimum reflux ratio $R_{des,min}$).

The two processes discussed are characterized by the so-called reflux ratios R_{abs} or R_{des} , which are the ratios of the gas and liquid phase flows (or inversely), expressed in moles (kilo moles):

$$R_{abs} = k_{abs} R_{abs,min} = k_{abs} \left(\frac{\dot{n}_{liq}^{abs}}{\dot{n}_{gas}^{abs}} \right)_{min} = k_{abs} \frac{Y_{CO2,2} - Y_{CO2,1}}{(X_{CO2,2})_{max} - X_{CO2,1}} \quad \text{with} \quad (X_{CO2,2})_{max} \equiv X_{CO2,2}^* \parallel Y_{CO2,2}$$

$$R_{des} = k_{des} R_{des,min} = k_{des} \left(\frac{\dot{n}_{gas}^{des}}{\dot{n}_{liq}^{des}} \right)_{min} = k_{des} \frac{X_{CO2,2} - X_{CO2,1}}{(Y_{CO2,2})_{max} - Y_{CO2,1}} \quad \text{with} \quad (Y_{CO2,2})_{max} \equiv Y_{CO2,2}^* \parallel X_{CO2,2}$$

The maximum loads $(X_{CO2,2})_{max}$ and $(Y_{CO2,2})_{max}$ have been introduced in above expressions. They are identical with the equilibrium values if only intersections of equilibrium and balance lines between the process begin and the process end do not exist. Correcting coefficients k_{abs} and k_{des} are equal to 1.3–1.6 (according to [4]) or 1.2–2.0 according to [5]–[6].

In the basic calculation method, the so-called method of absorption/desorption coefficients, the balance line and the equilibrium line will be referred to the straight ones, [5], but also [4]. The absorption coefficient is defined as

$$C_{abs} = \frac{1}{m_{YX,abs}^{eq-linear}} \left(\frac{\dot{n}_{liq}^{abs}}{\dot{n}_{gas}^{abs}} \right) = \frac{R_{abs}}{m_{YX,abs}^{eq-linear}}$$

and the desorption one

$$C_{des} = m_{YX,des}^{eq-linear} \left(\frac{\dot{n}_{gas}^{des}}{\dot{n}_{liq}^{des}} \right) = m_{YX,des}^{eq-linear} R_{des}$$

where $m_{YX,abs}^{eq-linear}$ (or $m_{YX,des}^{eq-linear}$) is the substitute mean slope of the equilibrium line (as a straight one), i.e.

$$m_{YX}^{\text{eq-linear}} = \frac{dY_{\text{CO}_2}^*}{dX_{\text{CO}_2}} \approx \frac{\Delta Y_{\text{CO}_2}^*}{\Delta X_{\text{CO}_2}}$$

Using coefficients C_{abs} and C_{des} the theoretical plates number can be determined, [5]. For the absorption unit it will be

$$N_{\text{abs}}^{\text{theoret}} = \frac{\ln\left(\frac{C_{\text{abs}} - t_{\text{abs}}}{1 - t_{\text{abs}}}\right)}{\ln C_{\text{abs}}} \quad \text{for} \quad C_{\text{abs}} \neq 1$$

$$N_{\text{abs}}^{\text{theoret}} = \frac{C_{\text{abs}}}{C_{\text{abs}} - t_{\text{abs}}} \quad \text{for} \quad C_{\text{abs}} = 1$$

and for the desorption one

$$N_{\text{des}}^{\text{theoret}} = \frac{\ln\left(\frac{t_{\text{des}} - C_{\text{des}}}{t_{\text{des}} - 1}\right)}{\ln C_{\text{des}}} \quad \text{for} \quad C_{\text{des}} \neq 1$$

$$N_{\text{des}}^{\text{theoret}} = \frac{C_{\text{des}}}{C_{\text{des}} - t_{\text{des}}} \quad \text{for} \quad C_{\text{des}} = 1$$

The process intensity $t \rightarrow 1$ requires the infinite number of theoretical plates, i.e.

$$\lim_{t_{\text{abs}} \rightarrow 1} N_{\text{abs}}^{\text{theoret}} = \infty \quad \text{and} \quad \lim_{t_{\text{des}} \rightarrow 1} N_{\text{des}}^{\text{theoret}} = \infty$$

Thus, using process intensities as modeling parameters the appropriate apparatus can be approximately dimensioned. Operating in the section, where another processes are of prevailing importance, the particular intensity factor will be adjusted.

4 CO₂-ABSORPTION WITH AN EXPANDING DESORPTION UNIT

The CO₂-absorption/desorption system is presented in Fig. 6. The absorption process runs at the process pressure of p_{abs} , the desorption one (called also the regeneration), however, at p_{des} , whereas $p_{\text{abs}} > p_{\text{des}}$. It means, the sorbent expands in a turbine from p_{abs} to p_{des} , and after leaving the desorption column it should be pumped from p_{des} to p_{abs} (or a little bit higher to compensate eventual pressure losses). The CO₂ enriched synthesis gas leaves a certain amount of the carbon dioxide in an absorption process, and to remove it from the sorption agent (water) the process pressure will be dropped in a desorption process, whereby the CO₂ will be set free. In fact there is no need to use a special desorption unit, but it helps the captured released carbon dioxide to transfer into the storage place (the so-called *CCS* technology which means *Carbon Capture and Storage*). The absorption pressure is p_{abs} and is significantly higher than the desorption one p_{des} . Usually $p_{\text{des}} = p_0$, i.e. it corresponds to the atmospheric pressure. The whole absorption/desorption section operates at the same temperature, usually a little bit higher than the natural environment one, i.e. $t_{\text{abs}} = t_{\text{des}}$. In fact, such a process is easy but it is necessary to design a reliable CO₂ capture method in an expanding desorption vessel.

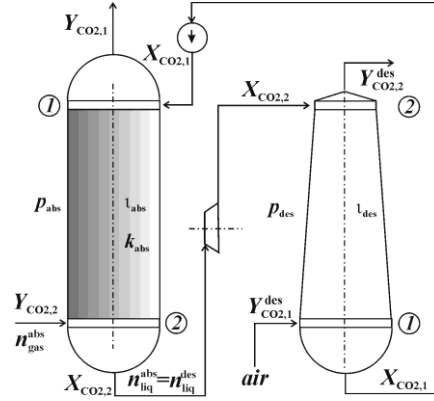


Fig. 6 Absorption process with the following expanding desorption.

To follow the modeling procedure an example will be adopted from [7], pp. 205–215. The synthesis gas (from the gasifying process) consists of: $y_{\text{CO}_2}=0.297$, $y_{\text{CO}}=0.035$, $y_{\text{H}_2}=0.5$, $y_{\text{N}_2}=0.162$, $y_{\text{CH}_4}=0.004$, $y_{\text{Ar}}=0.002$ (mole fractions, symbolic y for gas phase, and x for liquid, only for the substance exchange purposes: usually x is commonly used in both cases). The carbon dioxide should be removed in the absorption/desorption section.

Absorption/desorption section with an expanding CO_2 -desorption unit should operate assuming following input data (Fig. 6):

$$Y_{\text{CO}_2,2} = 0.422 \quad \dot{n}_{\text{gas}}^{\text{abs}} = 141.3 \text{ kmol/h}$$

$$Y_{\text{CO}_2,1}^{\text{des}} = Y_{\text{CO}_2}^{\text{air}} = 0.0003 \quad (y_{\text{CO}_2}^{\text{air}} = 0.0003) \quad Y_{\text{CO}_2}^{\text{air}} = \frac{y_{\text{CO}_2}^{\text{air}}}{1 - y_{\text{CO}_2}^{\text{air}}}$$

$$p_{\text{abs}} = 2.65 \text{ MPa} \quad p_{\text{des}} = 0.1 \text{ MPa} \quad t_{\text{abs}} = t_{\text{des}} = 25 \text{ }^\circ\text{C} \quad \text{for which } H_A = 165 \text{ MPa}$$

$$t_{\text{abs}} = 0.98 \quad k_{\text{abs}} = 1.25$$

Calculation formulas (in the procedure sequence) are

$$Y_{\text{CO}_2,1}^* = \frac{1}{\frac{p_{\text{abs}}}{H_A X_{\text{CO}_2,1}} + \frac{p_{\text{abs}}}{H_A} - 1}} = \frac{1}{\frac{2.65}{165 \cdot X_{\text{CO}_2,1}} + \frac{2.65}{165} - 1}} \quad (Y_{\text{CO}_2,1}^* \| X_{\text{CO}_2,1})$$

$$t_{\text{abs}} = \frac{Y_{\text{CO}_2,2} - Y_{\text{CO}_2,1}}{Y_{\text{CO}_2,2} - Y_{\text{CO}_2,1}^*}$$

where from

$$Y_{\text{CO}_2,1} = Y_{\text{CO}_2,2} - t_{\text{abs}}(Y_{\text{CO}_2,2} - Y_{\text{CO}_2,1}^*)$$

$$X_{\text{CO}_2,2}^* = \frac{1}{\frac{H_A}{p_{\text{abs}} Y_{\text{CO}_2,2}} + \frac{H_A}{p_{\text{abs}}} - 1}} = \frac{1}{\frac{165}{2.65 \cdot Y_{\text{CO}_2,2}} + \frac{165}{2.65} - 1}} \quad (X_{\text{CO}_2,2}^* \| Y_{\text{CO}_2,2})$$

$$R_{\text{abs}} = k_{\text{abs}} R_{\text{abs}}^{\text{min}} = k_{\text{abs}} \frac{Y_{\text{CO}_2,2} - Y_{\text{CO}_2,1}}{X_{\text{CO}_2,2}^* - X_{\text{CO}_2,1}}$$

and hence

$$\dot{n}_{\text{liq}}^{\text{abs}} = R_{\text{abs}} \dot{n}_{\text{gas}}^{\text{abs}} \quad (= \dot{n}_{\text{liq}}^{\text{des}})$$

$$X_{\text{CO}_2,2} = X_{\text{CO}_2,1} + \frac{1}{R_{\text{abs}}}(Y_{\text{CO}_2,2} - Y_{\text{CO}_2,1})$$

The desorption process in the expanding vessel will be restricted only by the location of the balance (operating) and equilibrium lines in the Y, X -diagram, Fig. 5. In the whole range of X change,

i.e. from $X_{CO_2,2}$ to $X_{CO_2,1} < X_{CO_2,2}$ the operation line cannot be tangential to the equilibrium one. If there is any common point, the natural desorption process would stop there. The appropriate proof is commonly made using graphical method, but it can be also accomplished in an analytical way, Fig. 7

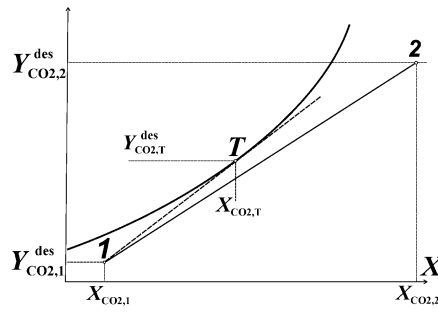


Fig. 7 Analytical proof of the desorption process: 1–T: balance line at minimum reflux ratio (the process stops in T–point), 1–2: balance line at enlarged reflux ratio, symbols correspond to Fig. 5.

Tab. 3 Results for 25 °C ($H_A=165$ MPa) isothermal conditions.

INPUT DATA		RESULTS	
		<i>absorption unit</i>	
$Y_{CO_2,2}$	0.422	$Y_{CO_2,1}^*$	0.004824
$y_{CO_2,2}$	0.2968	$Y_{CO_2,1}$	0.01317
\dot{n}_{gas}^{abs} [kmol/h]	141.3	$y_{CO_2,1}$	0.01210
$Y_{CO_2,1}^{des} = Y_{CO_2,1}^{air}$	0.0003	$X_{CO_2,2}^*$	0.004789
$t_{abs} = t_{des}$ [°C]	25	R_{abs}	108.4564
p_{abs} [MPa]	2.65	$\dot{n}_{liq}^{abs} = \dot{n}_{liq}^{des}$ [kmol/h]	15324.897
p_{des} [MPa]	0.1	$X_{CO_2,2}$	0.003847
k_{abs}	1.25	$x_{CO_2,2}$	0.003704
k_{des}	2	$X_{CO_2,1}^{*,abs} (X_{CO_2,1}^* Y_{CO_2,1}^{des})$	0.0000001818
t_{abs}	0.98	$X_{CO_2,1}$	0.00007711
		$x_{CO_2,1}$	0.00007105
		<i>expanding desorption unit</i>	
		$X_{CO_2,T}$	0.0002162
		$Y_{CO_2,T}^{des}$	0.5544
		$R_{des,min}$	0.0002509
		$R_{des} = k_{des} R_{des,min}$	0.0005019
		\dot{n}_{gas}^{des} [kmol/h]	7.6916
		$Y_{CO_2,2}^{des}$	7.5117
		$y_{CO_2,2}^{des}$	0.8825

The $X_{CO_2,1}$ value difference is the condition for the proper absorption calculation procedure (the $X_{CO_2,1}$ value has been also used as a start one): if the $X_{CO_2,1}$ -start value matches with the calculated one, the solution is assumed to be correct (e.g. the start value of $X_{CO_2,1} = 0.00001024$ has been used).

The point T, at which the desorption process would stop, results from the simultaneous solution of the two equations: the balance (operation) straight line and the equilibrium line. The last one can be written down as

$$Y = \frac{1}{\frac{p_{\text{des}}}{H_A X} + \frac{p_{\text{des}}}{H_A} - 1} \quad \text{or} \quad Y = \frac{X}{a + bX}$$

with

$$a = \frac{p_{\text{des}}}{H_A} \quad \text{and} \quad b = \frac{p_{\text{des}}}{H_A} - 1$$

The first derivation equals to

$$Y' = \frac{a}{(a + bX)^2}$$

and hence the balance line at minimum reflux ratio

$$Y_{\text{CO}_2,1}^{\text{des}} - Y_{\text{CO}_2,T}^{\text{des}} = Y'(X_{\text{CO}_2,1} - X_{\text{CO}_2,T})$$

or

$$Y_{\text{CO}_2,1}^{\text{des}} - \frac{X_{\text{CO}_2,T}}{a + bX_{\text{CO}_2,T}} = \frac{a}{(a + bX_{\text{CO}_2,T})^2} (X_{\text{CO}_2,1} - X_{\text{CO}_2,T})$$

because $Y_{\text{CO}_2,T}^{\text{des}} \parallel X_{\text{CO}_2,T}$. The solution is not that exact, which justifies the graphical procedure. Thus, the minimum reflux ratio, at which the process would stop (Fig. 7), can be determined, i.e.

$$R_{\text{des,min}} = \frac{(a + bX_{\text{CO}_2,T})^2}{a} = \frac{X_{\text{CO}_2,T} - X_{\text{CO}_2,1}}{Y_{\text{CO}_2,T}^{\text{des}} - Y_{\text{CO}_2,1}^{\text{des}}} = \frac{\dot{n}_{\text{gas}}^{\text{des}}}{\dot{n}_{\text{liq}}^{\text{des}}}$$

This equation is valid for $X_{\text{CO}_2,T} < X_{\text{CO}_2,2}$. If the condition would not be fulfilled, e.g. if $X_{\text{CO}_2,T} > X_{\text{CO}_2,2}$, the minimum reflux ratio should be determined from

$$R_{\text{des,min}} = \frac{X_{\text{CO}_2,2} - X_{\text{CO}_2,1}}{Y_{\text{CO}_2,2}^{\text{des,*}} - Y_{\text{CO}_2,1}^{\text{des}}} \quad \text{with} \quad Y_{\text{CO}_2,2}^{\text{des,*}} \parallel X_{\text{CO}_2,2}$$

i.e.

$$Y_{\text{CO}_2,2}^{\text{des,*}} = \frac{1}{\frac{p_{\text{des}}}{H_A X_{\text{CO}_2,2}} + \frac{p_{\text{des}}}{H_A} - 1} = \frac{1}{\frac{0.1}{165 \cdot X_{\text{CO}_2,1}} + \frac{0.1}{165} - 1}$$

With the presumed k_{des} factor, it will be

$$R_{\text{des}} = k_{\text{des}} R_{\text{des,min}} \quad \text{or} \quad \dot{n}_{\text{gas}}^{\text{des}} = R_{\text{des}} \dot{n}_{\text{liq}}^{\text{des}} = R_{\text{des}} \dot{n}_{\text{liq}}^{\text{abs}}$$

because of the previous assumptions. Finally

$$Y_{\text{CO}_2,2}^{\text{des}} = Y_{\text{CO}_2,1}^{\text{des}} + \frac{1}{R_{\text{des}}} (X_{\text{CO}_2,2} - X_{\text{CO}_2,1}) = Y_{\text{CO}_2}^{\text{air}} + \frac{\dot{n}_{\text{liq}}^{\text{des}}}{\dot{n}_{\text{gas}}^{\text{des}}} (X_{\text{CO}_2,2} - X_{\text{CO}_2,1})$$

Determination of the number of theoretical absorption plates will be proceeded as follows

$$m_{YX,\text{abs}}^{\text{eq-linear}} = \frac{Y_{\text{CO}_2,2} - Y_{\text{CO}_2,1}^*}{(X_{\text{CO}_2,2})_{\text{max}} - X_{\text{CO}_2,1}} = \frac{Y_{\text{CO}_2,2} - Y_{\text{CO}_2,1}^*}{X_{\text{CO}_2,2}^* - X_{\text{CO}_2,1}} = \frac{0.422 - 0.004824}{0.004789 - 0.00007711} = 88.5359$$

and

$$C_{\text{abs}} = \frac{1}{m_{YX,\text{abs}}^{\text{eq-linear}}} \left(\frac{\dot{n}_{\text{liq}}^{\text{abs}}}{\dot{n}_{\text{gas}}^{\text{abs}}} \right) = \frac{R_{\text{abs}}}{m_{YX,\text{abs}}^{\text{eq-linear}}} = \frac{108.2644}{88.3791} = 1.2250$$

$$N_{\text{abs}}^{\text{theoret}} = \frac{\ln\left(\frac{C_{\text{abs}} - t_{\text{abs}}}{1 - t_{\text{abs}}}\right)}{\ln C_{\text{abs}}} = \frac{\ln\left(\frac{1.2250 - 0.98}{1 - 0.98}\right)}{\ln 1.2250} = 12.3461 \quad (\text{i.e. 13 plates})$$

Because of the assumed simplification, the result should be enlarged by at least ca. 50%, [5]. Thus, for the absorption column yields 20 theoretical plates (or equivalent height). It is assumed that the expanding desorption column does not contain any plates.

5 CO₂-ABSORPTION WITH A CLASSICAL PLATE DESORPTION UNIT

The section presented here is common for all sorption agents other than water. Water is the cheapest one, it can be replaced, but more expensive, sophisticated agents need to work in a closed absorption-desorption scheme.

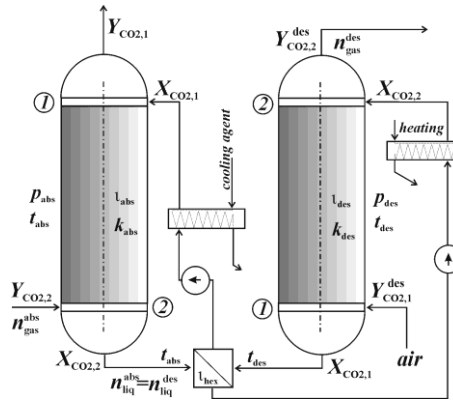


Fig. 8 Absorption process with the following desorption unit.

Results obtained for the absorption unit are the same as determined in Chapter 4. The difference is only in the case of the desorption unit. The appropriate procedure (excluding the absorption one presented in previous Chapter) sequence follows. The T -point, in which the process ultimately stops will be determined in the same way, as in the previous Chapter, but for $H_A=307.75$ MPa (which is the Henry constant's value for 50 °C) and for the process pressure of $p_{des}=2.65$ MPa. The process would stop after the T -point is attained, but the appropriate reflux ratio, greater than the minimum one, will be chosen to avoid such a coincidence.

Because the molar loads of the liquid $X_{CO_2,1}$ and $X_{CO_2,2}$ are determined by the conjugated absorption process, the needed desorption intensity can be calculated, namely

$$t_{des} = \frac{X_{CO_2,2} - X_{CO_2,1}}{X_{CO_2,2} - X_{CO_2,1}^*} \quad X_{CO_2,1}^* \parallel Y_{CO_2,1}^{des}$$

Thus,

$$X_{CO_2,1}^* = \frac{1}{\frac{H_A}{p_{des} Y_{CO_2,1}^{des}} + \frac{H_A}{p_{des}} - 1}$$

and finally $t_{des}=0.9944$.

Tab. 4 Results for 25 °C (absorption, $H_A=165$ MPa) and 50 °C (desorption, $H_A=307.75$ MPa)

INPUT DATA		RESULTS	
		absorption unit	
$Y_{CO_2,2}$	0.422	$Y_{CO_2,1}^*$	0.001490
$y_{CO_2,2}$	0.2968	$Y_{CO_2,1}$	0.00990
\dot{n}_{gas}^{abs} [kmol/h]	141.3	$y_{CO_2,1}$	0.009803
$Y_{CO_2,1}^{des} = Y_{CO_2,1}^{air}$	0.0003009	$X_{CO_2,2}^*$	0.0003598
t_{abs} [°C]	25	$R_{abs,min}$	1150.9834
t_{des} [°C]	50	R_{abs}	1438.7293
$p_{abs} = p_{des}$ [MPa]	0.2	$\dot{n}_{liq}^{abs} = \dot{n}_{liq}^{des}$ [kmol/h]	203292.447
k_{abs}	1.25	$X_{CO_2,2}$	0.0002881

k_{des}	1.25	$x_{CO_2,2}$	0.0002881
t_{abs}	0.98	$X_{CO_2,1}^{*,abs} (X_{CO_2,1}^* Y_{CO_2,1}^{des})$ at t_{abs}	0.0000003636
		$X_{CO_2,1}$	0.000001803
		$x_{CO_2,1}$	0.000001803
<i>classical plate desorption unit</i>			
		$X_{CO_2,T}$	0.00003429
		$Y_{CO_2,T}^{des}$	0.05568
		$R_{des,min}$	0.0005864
		$R_{des}=k_{des}R_{des,min}$	0.0007330
		\dot{n}_{gas}^{des} [kmol/h]	149.0135
		$Y_{CO_2,2}^{des}$	0.391073
		$y_{CO_2,2}^{des}$	0.281131
		t_{des}	0.9944
		$X_{CO_2,1}^{*,des} (X_{CO_2,1}^* Y_{CO_2,1}^{des})$ at t_{des}	0.0000001950
		$Y_{CO_2,2}^{*,des} (Y_{CO_2,2}^{des} X_{CO_2,2})$	0.7966

The $X_{CO_2,1}$ value difference is the condition for the proper absorption calculation procedure (the $X_{CO_2,1}$ value has been also used as a start one): if the $X_{CO_2,1}$ -start value matches with the calculated one, the solution is assumed to be correct (e.g. the start value of $X_{CO_2,1} = 0.00001024$ has been used).

Determination of the number of theoretical absorption plates will be proceeded just like in the previous case, i.e. as follows:

$$m_{YX,abs}^{eq-linear} = \frac{Y_{CO_2,2} - Y_{CO_2,1}^*}{(X_{CO_2,2})_{max} - X_{CO_2,1}} = \frac{Y_{CO_2,2} - Y_{CO_2,1}^*}{X_{CO_2,2}^* - X_{CO_2,1}} = \frac{0.422 - 0.001490}{0.0003598 - 0.000001803} = 11744884$$

and

$$C_{abs} = \frac{1}{m_{YX,abs}^{eq-linear}} \left(\frac{\dot{n}_{liq}^{abs}}{\dot{n}_{gas}^{abs}} \right) = \frac{R_{abs}}{m_{YX,abs}^{eq-linear}} = \frac{14387293}{11744884} = 1.2250$$

$$N_{abs}^{theoret} = \frac{\ln\left(\frac{C_{abs} - t_{abs}}{1 - t_{abs}}\right)}{\ln C_{abs}} = \frac{\ln\left(\frac{1.2250 - 0.98}{1 - 0.98}\right)}{\ln 1.2250} = 12.3461 \quad (\text{i.e. 13 plates})$$

The number of theoretical plates for the absorption unit will be almost the same (the same input data and comparable results), i.e. 20 plates (or equivalent height). For the classical desorption unit for yields

$$m_{YX,des}^{eq-linear} = \frac{Y_{CO_2,2}^{*,des} - Y_{CO_2,1}^{des}}{X_{CO_2,2} - X_{CO_2,1}^{*,des}} = \frac{0.7966 - 0.00030009}{0.0002882 - 0.0000001950} = 27642926$$

$$C_{des} = m_{YX,des}^{eq-linear} \left(\frac{\dot{n}_{gas}^{des}}{\dot{n}_{liq}^{des}} \right) = m_{YX,des}^{eq-linear} R_{des} = 27642926 \cdot 0.0007330 = 2.0264$$

and finally

$$N_{des}^{theoret} = \frac{\ln\left(\frac{t_{des} - C_{des}}{t_{des} - 1}\right)}{\ln C_{des}} = \frac{\ln\left(\frac{0.9944 - 2.0264}{0.9944 - 1}\right)}{\ln 2.0264} = 7.3815 \quad (\text{i.e. 8 plates})$$

Enlarging the result according to literature recommendations it means again ca. 12 theoretical plates. The same calculations but for $k_{des}=2$, which is somehow the limit value for classical plates columns, give results put into Tab. 5.

Tab. 5 Same as Tab. 4, but for $k_{des}=2$.

<i>RESULTS</i>	
<i>classical plate desorption unit</i>	
$X_{CO_2,T}$	0.00003429
$Y_{CO_2,T}^{des}$	0.05569
$R_{des,min}$	0.0005864
$R_{des}=k_{des}R_{des,min}$	0.001173
\dot{n}_{gas}^{des} [kmol/h]	238.4216
$Y_{CO_2,2}^{des}$	0.2445
$y_{CO_2,2}^{des}$	0.1964
t_{des}	0.9944
$X_{CO_2,1}^{*,des}$ ($X_{CO_2,1}^* Y_{CO_2,1}^{des}$) at t_{des}	0.0000001950
$Y_{CO_2,2}^{*,des}$ ($Y_{CO_2,2}^{*,des} X_{CO_2,2}$)	0.7962

It yields

$$m_{YX,des}^{eq-linear} = \frac{Y_{CO_2,2}^{*,des} - Y_{CO_2,1}^{des}}{X_{CO_2,2} - X_{CO_2,1}^{*,des}} = \frac{0.7962 - 0.00030009}{0.0002881 - 0.0000001950} = 27639056$$

$$C_{des} = m_{YX,des}^{eq-linear} \left(\frac{\dot{n}_{gas}^{des}}{\dot{n}_{liq}^{des}} \right) = m_{YX,des}^{eq-linear} R_{des} = 27639056 \cdot 0.001173 = 3.2415$$

$$N_{des}^{theoret} = \frac{\ln \left(\frac{t_{des} - C_{des}}{t_{des} - 1} \right)}{\ln C_{des}} = \frac{\ln \left(\frac{0.9944 - 3.2415}{0.9944 - 1} \right)}{\ln 3.2415} = 5.0973 \quad (\text{i.e. 6 plates})$$

Enlarging the result according to literature recommendations it means ca. 9 theoretical plates.

6 CONCLUSIONS

The presented above absorption/desorption processes are their simplest possible realizations. In real conditions additional flux loops are applied to improve the economy. They are detailed described e.g. in [8]–[9] — the two valuable monographs deal with thermodynamic analyzes of substance exchange processes in general. They do not refer appropriate modeling (calculation) procedures, but they do focus on the 2. *Law Analysis*, especially the exergy method. In fact, chemical engineering text–books do not give such a uniform method, which can be applied to the thermodynamic modeling of absorption/desorption units. Thermodynamic modeling procedures of complex technological systems do need usually simplifications, which allow proper conclusions — it should be distinguished between the system analysis and the particular process thermodynamic analysis. The last one is the next step after appropriate system analysis has been made.

Remark: all intermediate numerical results are showed with four (or six) meaning numbers, although more numbers have been used in calculation, as it is usually made in chemical engineering.

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