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EXERGY IN TECHNOLOGICAL SEPARATION PROCESSES

EXERGIE V TECHNOLOGICKÝCH SEPARAČNÍCH PROCESECH

Abstract

The exergy concept applied to technological separation processes has been presented and discussed in detail. Especially the building of thermodynamic effectivity quotients has been emphasized. Two main separation processes have been analyzed in detail. They are the rectification process and the extraction. The last one is not that important for the power engineering, but while analyzing it a special behavior of the exergy can be discussed. It depends not only on one parameter (temperature, pressure or concentration), but on two parameters (amount of the substance and its concentration). Thus, the special procedure of partition exergy changes into vanishing and created exergies (i.e. thermodynamic expenditures and advantages in a process) could be presented. Two numerical examples for the rectification have been calculated and one such an example for the one-stage and two-stage extraction process.

Abstrakt

Exergetický koncept byl použit na technologické separační procesy a byl detailně prodiskutován. Zejména je zdůrazněno využití koeficientů termodynamické efektivity. Dva hlavní separační procesy, byly analyzovány detailně. Jsou to procesy rektifikace a extrakce. Posledním z nich není tak důležitý pro energetiku, ale pro své speciální chování exergie byl prodiskutován. Nezáleží zde pouze na jednom z parametrů (teploty, tlaku nebo koncentrace), ale záleží významně na dvou parametrech (množství látky a její koncentrace). Tak, speciální postup změn v rozdělení exergie mizí a vytváří se postup určující termodynamický výdej energie a jejich výhody v technologickém procesu. Dva početní příklady pro rektifikaci byly vypočteny a jeden takový příklad pro jedno a dvoustupňový proces extrakce.

1 INTRODUCTION

It has been previously stated a special behavior of substance (or chemical) exergy changing its concentration, [1]. There exists a certain extreme-point, in which the exergy change while altering the concentration starts to continue in an opposite direction. E.g. in a process of nitrogen N_2 concentration change in a mixture from 0 to 1 its so-called concentration exergy first diminishes (negative numerical values) until the nitrogen mole fraction reaches the exergy change algebraic sign inversion point ($x_{N_2,extr}=0.28728$), and from this point up, it rises (negative numerical values) until the concentration exergy reaches the value of 0 again at $x_{N_2,0}=0.7809$, which is the mole (volume) concentration of nitrogen in an atmospheric air (the natural environment). Thereafter it rises in the positive numerical values range till the concentration reaches 1, i.e. until the pure nitrogen has been produced. The end numerical value at $x_{N_2}=1$ and at the natural environment temperature T_0 is the so-called nitrogen zero exergy, e.g. [2].

In the following general separation processes will be discussed, and especially how they can be balanced, analyzed and rated using exergy concept. The special concept of the thermodynamic

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transition and thermodynamic effectivity will be used to make the presented processes comparable with others, which have been analyzed and rated with the exergy concept, either.

2 SEPARATION PROCESSES IN GENERAL

Any separation of a mixture into unless two components (streams) of different composition needs a certain energy supply. The driving energy (or an additional energy flow) can be supplied as the mechanical, chemical, electric or thermal one. There are many different technologies of components separation, with many special cases. E.g. the atmospheric air separation from the thermodynamics point of view can be presented as symmetrical to a heat pump or a compressor (e.g. [3]–[7]), Figure 1, the air separation is an oxygen production, the symbolic for particular power devices is used according to the proposal discussed e.g. in [6].

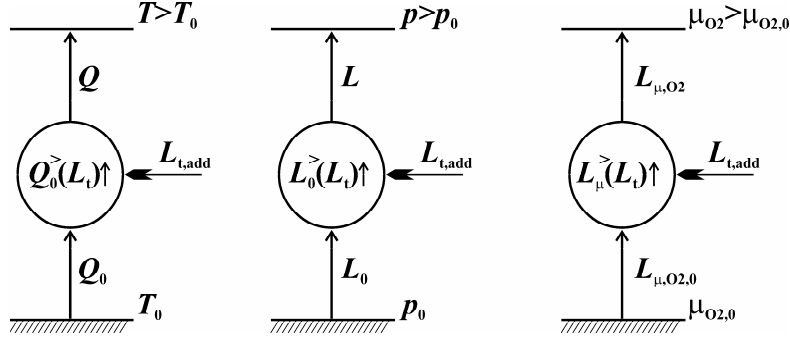


Fig. 1 Symmetry of heat pump, compressor and air separation device (oxygen generator)

In the first case, the heat pump, the minimal useful (i.e. shaft or technical) work needed for the temperature change from T_0 to $T > T_0$ to produce the heat Q (from Q_0) is

$$(L_{t,add})_{\min} = Q - Q_0 = T\Delta S - T_0\Delta S = (T - T_0)\Delta S = (T - T_0)\frac{Q}{T} = \left(1 - \frac{T_0}{T}\right)Q$$

The same procedure can be applied to the symmetric mechanical device, the compressor, which rises the volume work from the environment pressure p_0 to $p > p_0$, i.e. it produces the volume work L from L_0 :

$$(L_{t,add})_{\min} = L - L_0 = p\Delta V - p_0\Delta V = (p - p_0)\Delta V = (p - p_0)\frac{L}{p} = \left(1 - \frac{p_0}{p}\right)L$$

In the third case, the chemical device rising the chemical potential of oxygen from the value in the natural environment $\mu_{O2,0}$ to $\mu_{O2} > \mu_{O2,0}$ the minimal useful work is needed, which equals to the appropriate chemical work rising 1 mol (or 1 kmol) oxygen from $\mu_{O2,0}$ to a certain value μ_{O2} . The last value can be in particular the chemical potential of the pure oxygen ($x_{O2}=1$). Hence,

$$(L_{t,add})_{\min} = L_{\mu,O2} - L_{\mu,O2,0} = (\mu_{O2} - \mu_{O2,0})n_{O2} = (\mu_{O2} - \mu_{O2,0})\frac{L_{\mu,O2}}{\mu_{O2}} = \left(1 - \frac{\mu_{O2,0}}{\mu_{O2}}\right)L_{\mu,O2}$$

All the above equations mean the exergy of heat, volume work and chemical work, respectively. As applied to the pure oxygen generation in a device shown in Figure 1 (to the right) for $n_{O2}=1$ kmol (or 1 mol) and the temperature of the natural environment T_0 it yields

$$(L_{t,add})_{\min} = (\mu_{O2}^0 + \bar{R}T_0 \ln x_{O2} - \mu_{O2}^0 - \bar{R}T_0 \ln x_{O2,0})n_{O2} = -\bar{R}T_0 \ln x_{O2,0} \equiv \Delta \bar{e}_{\mu,O2}^0$$

which is the so-called oxygen zero exergy (e.g. $x_{O_2,0}=0.21$). The natural environment pressure p_0 in the above formula results from the DALTON's Law, i.e. from the equation $p_{O_2,0}=x_{O_2}p_0$.

In the case of a total separation process from a certain specie i concentration $x_{i,m}$ in a mixture into the pure species with $x_i=1$ the appropriate minimal useful work needed obviously equals to

$$(L_{t,add})_{\min} = -\bar{R}T \sum_i x_{i,mix} \ln x_{i,mix} = \bar{R}T \sum_i x_{i,mix} \ln \frac{1}{x_{i,mix}}$$

whereby the process temperature T has been assumed (and additionally $dp=0$). In the practice the mixture containing a certain number of species i is separated into two or more streams, in which the species are present with different concentrations. Assuming the number of those streams as equal to k and concentrations of species i in them as $x_{i,k}$, the minimal useful work needed to accomplish the separation process yields

$$(L_{t,add})_{\min} = -\bar{R}T \sum_i x_{i,mix} \ln x_{i,mix} + \sum_k \frac{n_k}{n} \bar{R}T \sum_i x_{i,k} \ln x_{i,k}$$

For the isobar-isothermal separation process of the two-species mixture (A and B) into two streams with $x_{i,k} \neq 1$ it becomes

$$(L_{t,add})_{\min} = -\bar{R}Tx_{A,mix} \ln x_{A,mix} - \bar{R}Tx_{B,mix} \ln x_{B,mix} + \\ + v_1 \bar{R}Tx_{A,1} \ln x_{A,1} + v_1 \bar{R}Tx_{B,1} \ln x_{B,1} + v_2 \bar{R}Tx_{A,2} \ln x_{A,2} + v_2 \bar{R}Tx_{B,2} \ln x_{B,2}$$

where

$$v_1 = \frac{n_1}{n_1 + n_2} \quad \text{and} \quad v_2 = \frac{n_2}{n_1 + n_2}$$

Solving the linear equation system

$$v_1 x_{A,1} + v_2 x_{A,2} = x_{A,mix} \quad \text{and} \quad v_1 x_{B,1} + v_2 x_{B,2} = x_{B,mix}$$

with $v_1 + v_2 = 1$, $x_{A,1} + x_{B,1} = 1$ and $x_{A,2} + x_{B,2} = 1$ it yields

$$v_1 = \frac{x_{A,mix} - x_{A,2}}{x_{A,1} - x_{A,2}} \quad \text{and} \quad v_2 = \frac{x_{A,1} - x_{A,mix}}{x_{A,1} - x_{A,2}}$$

After rearranging the final result is

$$(L_{t,add})_{\min} = -\frac{\bar{R}T}{x_{A,1} - x_{A,2}} \left\{ \begin{aligned} & (x_{A,mix} - x_{A,2}) \left[x_{A,1} \ln \frac{x_{A,mix}}{x_{A,1}} + (1 - x_{A,1}) \ln \frac{1 - x_{A,mix}}{1 - x_{A,1}} \right] - \\ & - (x_{A,mix} - x_{A,1}) \left[x_{A,2} \ln \frac{x_{A,mix}}{x_{A,2}} + (1 - x_{A,2}) \ln \frac{1 - x_{A,mix}}{1 - x_{A,2}} \right] \end{aligned} \right\}$$

If the analyzed separation process runs at the natural environment temperature T_0 and the natural environment pressure p_0 , the above minimal separation work is the exergy of separation. In general, to the technological separation process the heat supply is needed, or — usually in the same time — the heat should be carried away from the balance region. This general case is presented schematically in Figure 2 for the separation of two component mixture into two products in a isothermal-isobaric process.

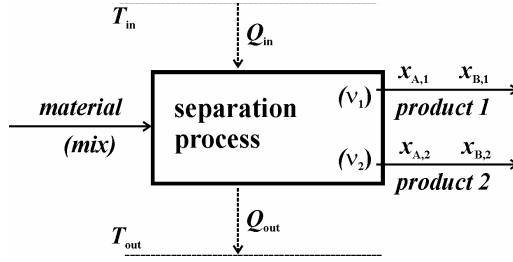


Fig. 2 Symmetry of heat pump, compressor and air separation device (oxygen generator)

3 RECTIFICATION

Rectification is a multiple distillation process with reflux, [8]. The analysis of large industrial rectification columns for air separation shows that energy supply needed for producing a technical oxygen in a gaseous phase are 6.5 to 7.2. times greater than the theoretical minimal work. Hence, energy efficiency of such processes is usually less than 0.17 (17%), [9] (the losses in condenser and reboiler have been taken into account).

To realize a reversible mixture separation in a rectification column, the phase equilibrium saturated liquid and saturated vapor, isobaric condition and infinitely small temperature differences should be secured in its every intersection. It is possible only in the case of infinite number of stages. In a reversible rectifier the heat should be supplied to all stages below the feed stage intersection (the stripping section) and carried away above it (the enriching section). The practical operation of a such fractionating unit is not possible and there are observed exergy losses due to temperature and concentration changes.

For separation processes rectifier are used, in which the heat is supplied to the higher temperature zone (reboiler) and carried away from the lower temperature zone. Hence, the whole unit is assumed to be adiabatic one, in which equilibrium is not observed, even in the case of infinite stage number, i.e. at minimal reflux ratio.

In the column reboiler (bottom) the provided heat Q_{REB} at T_{REB} is taken over by the boiling liquid and the heat Q_{CON} at T_{CON} is carried away from the boiling distillate (top). The appropriate energy balance (under adiabatic conditions) is to

$$Q_{REB} - Q_{CON} = n_{CON} \bar{i}_{CON} + n_{REB} \bar{i}_{REB} - (n_{CON} + n_{REB}) \bar{i}_{FED}$$

and the exergy balance

$$E_{Q,REB} - E_{Q,CON} = n_{CON} \bar{e}_{CON} + n_{REB} \bar{e}_{REB} - (n_{CON} + n_{REB}) \bar{e}_{FED} + T_0 \Delta S_{irr}$$

whereby it can be assumed, that the condensate, reboiler liquid and feed molar enthalpies and exergies are known. Appropriate heat exergies are

$$E_{Q,REB} = \left(1 - \frac{T_0}{T_{REB}}\right) Q_{REB} \quad \text{and} \quad E_{Q,CON} = \left(1 - \frac{T_0}{T_{CON}}\right) Q_{CON}$$

They should be parted into exergies in particular ranges below (superscript <) and above (subscript >) the natural environment temperature T_0 , i.e.

$$E_{Q,REB} - E_{Q,CON} = |E_{Q,REB}^>| - |E_{Q,REB}^<| - |E_{Q,CON}^>| + |E_{Q,CON}^<|$$

so that for the exergy balance yields

$$|E_{Q,REB}^>| + |E_{Q,CON}^<| = |E_{Q,REB}^<| + |E_{Q,CON}^>| + n_{CON} \bar{e}_{CON} + n_{REB} \bar{e}_{REB} - (n_{CON} + n_{REB}) \bar{e}_{FED} + T_0 \Delta S_{irr}$$

or

$$\left|E_{Q,REB}^>\right| + \left|E_{Q,CON}^<\right| = \left|E_{Q,REB}^<\right| + \left|E_{Q,CON}^>\right| + n_{CON}\Delta\bar{e}_{CON} + n_{REB}\Delta\bar{e}_{REB} + T_0\Delta S_{irr}$$

The molar exergy changes $\Delta\bar{e}_{CON}$ and $\Delta\bar{e}_{REB}$ do consist from the thermal and chemical concentration parts (chemical reactions are excluded)

$$\Delta\bar{e} = \Delta\bar{e}_T + \Delta\bar{e}_\mu^x$$

The molar chemical concentration exergy changes of a particular specie i can be written down as

$$\Delta\bar{e}_{\mu,i,CON}^x = \bar{R}T_0(x_{i,CON} \ln x_{i,CON} - x_{i,FED} \ln x_{i,FED})$$

and

$$\Delta\bar{e}_{\mu,i,REB}^x = \bar{R}T_0(x_{i,REB} \ln x_{i,REB} - x_{i,FED} \ln x_{i,FED})$$

according to earlier derived dependencies. After adding the two exergy changes the total minimal separation work of the specie i at T_0 will be obtained, [10]. Taking into account the substance balance, it yields

$$\Delta E_{\mu,i}^x = \bar{R}T_0(n_{CON}x_{i,CON} \ln x_{i,CON} + n_{REB}x_{i,REB} \ln x_{i,REB} - n_{FED}x_{i,FED} \ln x_{i,FED})$$

or for all the i species

$$\Delta E_\mu^x = \sum_i \Delta E_{\mu,i}^x$$

To determine vanishing and created exergies in a process, above equations can be rewritten as

$$\Delta E_{\mu,i,CON}^x = n_{CON}\bar{R}T_0(x_{i,CON} \ln x_{i,CON} - x_{i,FED} \ln x_{i,FED})$$

$$\Delta E_{\mu,i,REB}^x = n_{REB}\bar{R}T_0(x_{i,REB} \ln x_{i,REB} - x_{i,FED} \ln x_{i,FED})$$

or in the case of species represented in the natural environment with the appropriate concentration $x_{j,0}$

$$\Delta E_{\mu,j,CON}^x = n_{CON}\bar{R}T_0\left(x_{j,CON} \ln \frac{x_{j,CON}}{x_{j,0}} - x_{j,FED} \ln \frac{x_{j,FED}}{x_{j,0}}\right)$$

$$\Delta E_{\mu,j,REB}^x = n_{REB}\bar{R}T_0\left(x_{j,REB} \ln \frac{x_{j,REB}}{x_{j,0}} - x_{j,FED} \ln \frac{x_{j,FED}}{x_{j,0}}\right)$$

The two last equation can be divided into parts according to the criterion presented in earlier contributions, e.g. [1] and [11]. Finally the thermodynamic effectivity quotient can be determined and its numerator and denominator used for general rating procedure of complex systems.

Thermal exergy changes of the particular substance fluxes depend on the thermodynamic state of the feed product flow, distilled (at the top) and an enriched (at the bottom) products. The distillate is usually carried away as a saturated vapor (i.e. at the boiling point). Hence, its temperature is lower than the feed product temperature T_{FED} . It means the thermal exergy change: below T_0 its diminishing ($dE_T < 0$, „thermodynamic expenditures”) and above T_0 its creating ($dE_T > 0$, „thermodynamic advantages”). The feed product is supplied usually at the boiling point in condensed phase as a saturated liquid. The thermal exergy of condensing components at condensation temperature $T_{cond} > T_0$ is less than the thermal exergy of these components in gaseous phase (vapor). Hence, the vaporization process means the appropriate exergy rise („thermodynamic advantages”).

Below the environment temperature at $T_{\text{cond}} < T_0$ it is, however, greater than the thermal exergy of components in the gaseous phase, so the exergy change is a „thermodynamic expenditures” (negative numerical value). If r is a phase change heat, the appropriate exergy change yields (e.g. [12])

$$\Delta e_r = \left(1 - \frac{T_0}{T_{\text{cond}}}\right) r$$

whereas the thermal exergy change due to the temperature difference without any phase change

$$\Delta e_T = c_p (T - T_{\text{FED}}) - c_p T_0 \ln \frac{T}{T_{\text{FED}}}$$

Because of the relative poor accuracy of material thermo–physical data no good numerical results are to be expected. There have been worked out „enough accurate” computation methods of entropy or exergy changes, but they are mostly graphical–analytical ones and refer to special cases. Besides, they are very efforts–consuming methods, disproportionate to their practical usefulness, e.g. [10], [13], but also [14].

To simplify analyzes in the practice very often there is assumed the isothermic process. The accuracy will be worse, but the tests have showed that it is not that much worse than using labor–consuming calculation methods. As a mean separation temperature following thermodynamic mean temperature can be assumed ([15])

$$T_{\text{mean}} = \frac{T_{\text{CON}} - T_{\text{REB}}}{\ln \frac{T_{\text{CON}}}{T_{\text{REB}}}}$$

The appropriate procedure does not take into account thermal exergy changes, which makes the expected accuracy lower, but it makes it possible to determine the rectification thermodynamic effectivity at all.

If for example the feed substance is supplied as a saturated vapor at the vaporizing temperature (i.e. the condensing one) and at the same state the bottom and top product are carried away from the fractioning column, from the energy balance equation follows $Q_{\text{REB}} = Q_{\text{CON}}$ (the latent heat as relatively low for all mixing and separation processes can be neglected). Exergy changes are only caused by concentration changes of particular components and the appropriate thermodynamic effectivity quotient becomes to

$$\varepsilon = \frac{|E_{Q,\text{REB}}^<| + |E_{Q,\text{CON}}^>| + \sum |\Delta E_{\mu,i}^x|}{|E_{Q,\text{REB}}^>| + |E_{Q,\text{CON}}^<| + \sum |\nabla E_{\mu,i}^x|}$$

If, however, thermodynamic states of all the bottom (reboiler) and to (condenser) products differ from the state of the feeding substance, then the phase change heat is a difference $Q = Q_{\text{REB}} - Q_{\text{CON}}$, which follows directly from the energy balance. Exergy changes determination for particular flows can be passed round by taking into account the additional exergy change in the form of

$$E_{Q,\text{mean}} = \left(1 - \frac{T_0}{T_{\text{mean}}}\right) (Q_{\text{REB}} - Q_{\text{CON}})$$

The algebraic sign of the result obtained will determine the position of its absolute value in the thermodynamic effectivity quotient, and finally

$$\varepsilon = \frac{|E_{Q,\text{REB}}^<| + |E_{Q,\text{CON}}^>| + \sum |\Delta E_{\mu,i}^x| + |E_{Q,\text{mean}}^>|}{|E_{Q,\text{REB}}^>| + |E_{Q,\text{CON}}^<| + \sum |\nabla E_{\mu,i}^x| + |E_{Q,\text{mean}}^<|} \quad (1)$$

where the superscript >0 means the positive numerical value and <0 the negative one.

The calculated values should be treated as approximate ones because of assumptions made, especially the isotherm conditions. Irreversibilities in reboiler and condenser have not been taken into account (appropriate brief discussion e.g. in [14]).

3.1 Numerical example I

In the rectifier 8.45 t/h the methanol(1) – water(2) mixture should be separated. There are in total 4.30 t/h of methanol(1) in this mixture. The supply and condensate flows are saturated liquids. The methanol purity of 0.995 should be produced, and the water obtained can contain less than 0.2 mole-% of methanol. Data and process calculation results are presented below.

	FED	CON	REB
n	365.4 kilo-moles	134.6 kilo-moles	230.8 kilo-moles
x_1	0.368	0.995	0.2
x_2	0.632	0.005	0.8
Q	—	$9.22 \cdot 10^6$ kJ	$9.50 \cdot 10^6$ kJ
T	76.0 °C	64.7 °C	100.0 °C

The mole concentration, at which the algebraic sign inversion of the exergy change occurs, equals to $1/e$, i.e. $x_{1,\text{extr}}=1/e=0.368$, [1], [11]. Total concentration changes in the enriching or concentration column (above feed inlet) FED–CON and in the stripping column or stripper (below feed inlet) FED–REB are:

	FED–CON	FED–REB
methanol(1)	0.368 → 0.995	0.368 → 0.2
water(2)	0.632 → $1/e$ → 0.005	0.632 → 0.8

Appropriate chemical concentration exergy changes are:

$$\Delta E_{1,\text{FED-CON}}^{x,>} = n_{\text{CON}} \bar{R} T_0 (x_{1,\text{CON}} \ln x_{1,\text{CON}} - x_{1,\text{FED}} \ln x_{1,\text{FED}}) = 117\,780 \text{ kJ}$$

$$\Delta E_{1,\text{FED-REB}}^{x,<} = n_{\text{REB}} \bar{R} T_0 (x_{1,\text{REB}} \ln x_{1,\text{REB}} - x_{1,\text{FED}} \ln x_{1,\text{FED}}) = 25\,595 \text{ kJ}$$

$$\nabla E_{2,\text{FED-CON}}^{x,>} = n_{\text{CON}} \bar{R} T_0 \left(\frac{1}{e} \ln \frac{1}{e} - x_{2,\text{FED}} \ln x_{2,\text{FED}} \right) = -25\,275 \text{ kJ}$$

$$\Delta E_{2,\text{FED-CON}}^{x,<} = n_{\text{CON}} \bar{R} T_0 \left(x_{2,\text{FED}} \ln x_{2,\text{FED}} - \frac{1}{e} \ln \frac{1}{e} \right) = 110\,800 \text{ kJ}$$

$$\Delta E_{2,\text{FED-REB}}^{x,>} = n_{\text{REB}} \bar{R} T_0 (x_{2,\text{REB}} \ln x_{2,\text{REB}} - x_{2,\text{FED}} \ln x_{2,\text{FED}}) = 62\,046 \text{ kJ}$$

The exergies of heat carried away from condenser (top or head) and of heat supplied into reboiler (bottom) are

$$|E_{Q,\text{REB}}^{>}| = \left(1 - \frac{T_0}{T_{\text{REB}}} \right) Q_{\text{REB}} = 2\,116\,911 \text{ kJ}$$

$$|E_{Q,\text{CON}}^{>}| = \left(1 - \frac{T_0}{T_{\text{CON}}} \right) Q_{\text{CON}} = 1\,305\,838 \text{ kJ}$$

The mean thermodynamic temperature is $T_{\text{mean}}=355.2$ K. Thus, the exergy of the „phase conversion heat exergy” yields

$$E_{Q,\text{mean}}^{>0} = \left(1 - \frac{T_0}{T_{\text{mean}}}\right) (Q_{\text{REB}} - Q_{\text{CON}}) = 51\,401 \text{ kJ}$$

Hence, the process thermodynamic effectivity — according to Eq.(1) — equals to

$$\varepsilon = \frac{|E_{Q,\text{CON}}^{>}| + |\Delta E_{1,\text{FED-CON}}^{x,>}| + |\Delta E_{1,\text{FED-REB}}^{x,<}| + |\Delta E_{2,\text{FED-CON}}^{x,<}| + |\Delta E_{2,\text{FED-REB}}^{x,>}| + |E_{Q,\text{mean}}^{>0}|}{|E_{Q,\text{REB}}^{>}| + |\nabla E_{2,\text{FED-CON}}^{x,>}|}$$

or

$$\varepsilon = \frac{1\,305\,838 + 117\,780 + 25\,595 + 110\,800 + 62\,046 + 51\,401}{2\,116\,911 + 25\,275} = \frac{1\,673\,460}{2\,142\,186} = 0.7812$$

3.2 Numerical example II

In the simple rectification process the atmospheric air ($x_{\text{O}_2,0}=0.21$ and $x_{\text{N}_2,0}=0.79$) is to separate. Further parameters are:

	FED	CON	REB
n	1 kilo-mole	0.93315 kilo-mole	0.06685 kilo-mole
x_{O_2}	0.21	0.1615	0.8871
x_{N_2}	0.79	0.8385	0.1129
Q	—	—	4 747.37 kJ
T	T_{cond}	71.269 K	88.731 K

The mole concentrations, at which the exergy change algebraic sign inverses, are $x_{\text{O}_2,\text{extr}}=0.21/e=0.0772547$ and $x_{\text{N}_2,\text{extr}}=0.79/e=0.290625$. Total concentration changes in the enriching or concentration column (above feed inlet) FED-CON and in the stripping column or stripper (below feed inlet) FED-REB are:

	FED-CON	FED-REB
O_2	0.21 → 0.1615	0.21 → 0.8871
N_2	0.79 → 0.8385	0.79 → 0.79/e → 0.1129

Appropriate chemical concentration exergy changes are:

$$\nabla E_{\text{O}_2,\text{FED-CON}}^{x,>} = n_{\text{CON}} \bar{R} T_0 \left(x_{\text{O}_2,\text{CON}} \ln \frac{x_{\text{O}_2,\text{CON}}}{0.21} - x_{\text{O}_2,\text{FED}} \ln \frac{x_{\text{O}_2,\text{FED}}}{0.21} \right) = -95.42 \text{ kJ}$$

$$\Delta E_{\text{O}_2,\text{FED-REB}}^{x,>} = n_{\text{REB}} \bar{R} T_0 \left(x_{\text{O}_2,\text{REB}} \ln \frac{x_{\text{O}_2,\text{REB}}}{0.21} - x_{\text{O}_2,\text{FED}} \ln \frac{x_{\text{O}_2,\text{FED}}}{0.21} \right) = 206.03 \text{ kJ}$$

$$\Delta E_{\text{N}_2,\text{FED-CON}}^{x,>} = n_{\text{CON}} \bar{R} T_0 \left(x_{\text{N}_2,\text{CON}} \ln \frac{x_{\text{N}_2,\text{CON}}}{0.79} - x_{\text{N}_2,\text{FED}} \ln \frac{x_{\text{N}_2,\text{FED}}}{0.79} \right) = 112.41 \text{ kJ}$$

$$\nabla E_{\text{N}_2,\text{FED-REB}}^{x,>} = n_{\text{REB}} \bar{R} T_0 \left(\frac{0.79}{e} \ln \frac{0.79}{e} - x_{\text{N}_2,\text{FED}} \ln \frac{x_{\text{N}_2,\text{FED}}}{0.79} \right) = -57.89 \text{ kJ}$$

$$\Delta E_{\text{N}_2,\text{FED-REB}}^{x,<} = n_{\text{REB}} \bar{R} T_0 \left(x_{\text{N}_2,\text{REB}} \ln \frac{x_{\text{N}_2,\text{CON}}}{0.79} - \frac{0.79}{e} \ln \frac{0.79}{e} \right) = 22.48 \text{ kJ}$$

The exergy of heat supplied into reboiler equals to

$$|E_{Q,REB}^{<}| = \left(1 - \frac{T_0}{T_{REB}}\right) Q_{REB} = 10\,768.39 \text{ kJ}$$

The process thermodynamic mean temperature is $T_{mean}=79.68 \text{ K}$ and the „phase conversion heat exergy” becomes

$$E_{Q,mean}^{<0} = \left(1 - \frac{T_0}{T_{mean}}\right) (Q_{REB} - Q_{CON}) = -12\,530.96 \text{ kJ}$$

Hence, the thermodynamic effectivity quotient according to Eq.(1) yields

$$\varepsilon = \frac{|E_{Q,REB}^{<}| + |\Delta E_{O_2,FED-REB}^{x,>}| + |\Delta E_{N_2,FED-CON}^{x,>}| + |\Delta E_{N_2,FED-REB}^{x,<}|}{|E_{Q,mean}^{<0}| + |\nabla E_{O_2,FED-CON}^{x,>}| + |\Delta E_{N_2,FED-REB}^{x,>}|}$$

or

$$\varepsilon = \frac{10\,768.39 + 206.03 + 112.41 + 22.48}{12\,530.96 + 95.42 + 57.89} = \frac{11\,109.31}{12\,684.27} = 0.8758$$

4 EXTRACTION

The extraction process can be in fact treated as one of substance exchange processes. Because of its rarity in power engineering systems it will be presented below, as one of the most important processes of chemical engineering. That’s why the following discussion has been drafted independently from the previous Chapters of the contribution.

The extraction is a thermal separation process of a liquid mixture (the material AB), from which the additional liquid, the extractant C , takes up one or more particular components B in a selective way — schematically it can be described by the symbolic formula $AB+C \rightarrow CB+A$, where A is the so-called extract, [8]. In general the extractive separation is less economically effective than the distillative one (the appropriate comparison e.g. in [16]). With some simplifying assumptions:

- $dq=dT=dp=0$, and
- chemical reactions excluded.

the exergy balance of a generalized (heat, mass i.e. substance) exchange process can be written as

$$E_{1,in} - E_{1,out} + E_{2,in} - E_{2,out} = T_0 \Delta S_{irr} \quad \text{or} \quad -\Delta E_1 - \Delta E_2 = T_0 \Delta S_{irr}$$

and with the assumptions mentioned above ($dp=dT=0$)

$$-\Delta E_{\mu,1}^x - \Delta E_{\mu,2}^x = T_0 \Delta S_{irr}$$

where the indices μ (subscript) or x (superscript) point out the concentration part of the chemical exergy of the flux 1 and 2, respectively. In the analyzed substance exchange process not only concentrations will change (like in a mixing process), but also the substance exchanging fluxes 1 and 2. Hence, the appropriate exergy balance will be to

$$\bar{R} T_0 \sum_{k=1}^2 \sum_j \left(n_{k,in} x_{j,k,in} \ln \frac{x_{j,k,in}}{x_{j,0}} - n_{k,out} x_{j,k,out} \ln \frac{x_{j,k,out}}{x_{j,0}} \right) = T_0 \Delta S_{irr}$$

whereby the process temperature $T=T_0$ and process pressure $p=p_0$ is assumed.

The total chemical (concentration) exergy of a one of the two the mass (substance) exchanging fluxes equals in any moment to

The first derivative is in general equal to

$$\frac{1}{RT_0} \frac{dE_{\mu,j}^x}{dx_j} = f'(x_j) x_j \ln \frac{x_j}{x_{j,0}} + f(x_j) \ln \frac{x_j}{x_{j,0}} (= 0)$$

The simplest (and the most probable) case is the linear dependence $n=f(x_j)$:

$$n_l = a_{j,k} x_{j,k} + b_{j,k}$$

where

$$a_{j,k} = \frac{n_{k,in} - n_{k,out}}{x_{j,k,in} - x_{j,k,out}} \quad \text{and} \quad b_{j,k} = n_{k,in} - a_{j,k} x_{j,k,in}$$

Inserting the last function into Equation (2), yields

$$\frac{E_{\mu,j}^x}{RT_0} = a_{j,k} x_{j,k}^2 \ln x_{j,k} + b_{j,k} x_{j,k} \ln x_{j,k} - a_{j,k} x_{j,k}^2 \ln x_{j,0} - b_{j,k} x_{j,k} \ln x_{j,0}$$

and the first derivative is herewith equal to

$$\frac{1}{RT_0} \frac{dE_{\mu,j}^x}{dx_{k,j}} = 2a_{j,k} x_{j,k} \ln x_{j,k} + a_{j,k} x_{j,k} + b_{j,k} \ln x_{j,k} + b_{j,k} - 2a_{j,k} x_{j,k} \ln x_{j,0} - b_{j,k} \ln x_{j,0} \quad (= 0)$$

From this equation the $x_{j,K}$ and further the n_K can be calculated, as the coordinates of the concentration exergy change inversion point \mathbf{K} , Figure 3. The linear function $n=f(x_j)$ points out, that the driving force of the process is assumed to be constant. Such a characteristics is to expect, if only the process runs in a continuous device.

The elementary concentration exergy changes for each specie between the points

$$(n_{k,in}; x_{j,k,in}) \quad \text{and} \quad (n_{k,out}; x_{j,k,out})$$

are

$$n_{k,in} x_{j,k,in} \ln \frac{x_{j,k,in}}{x_{j,0}} - n_{k,out} x_{j,k,out} \ln \frac{x_{j,k,out}}{x_{j,0}}$$

or should be divided into two parts (arising and vanishing in a process) if the point \mathbf{K} exists between the two states: *inlet* and *outlet*. The last means, that the concentration exergy change inversion point is crossed. It will be then enough data to state, if the point \mathbf{K} exists (the flux quantity change dn alone doesn't lead to an exergy change inversion point!).

4.1 Numerical example III

From 10 moles mixture of 62% methanol and 38% trichlorethylene by 20 °C the methanol should be extracted with water. There will be applied 6 moles water. The equilibrium solutions, calculated in [18] are contented in the statement. It is the appropriate process thermodynamic effectivity quotient to determine. The species (j) are: \mathbf{A} — methanol, \mathbf{B} — water and \mathbf{C} — trichlorethylene.

One stage extraction statement:

material/raffinate (\mathbf{R}):

$x_{A,R,in} = 0.62$	$x_{A,R,out} = 0.073$	
$x_{B,R,in} = 0.00$	$x_{B,R,out} = 0.006$	$n_{R,in} = 10.00 \text{ mol}$
$x_{C,R,in} = 0.38$	$x_{C,R,out} = 0.921$	$n_{R,out} = 3.95 \text{ mol}$

extractant/extract (E):

$$x_{A,E,in} = 0.00$$

$$x_{B,E,in} = 1.00$$

$$x_{C,E,in} = 0.00$$

$$x_{A,E,out} = 0.488$$

$$x_{B,E,out} = 0.492$$

$$x_{C,E,out} = 0.020$$

$$n_{E,in} = 6.00 \text{ mol}$$

$$n_{E,out} = 12.05 \text{ mol}$$

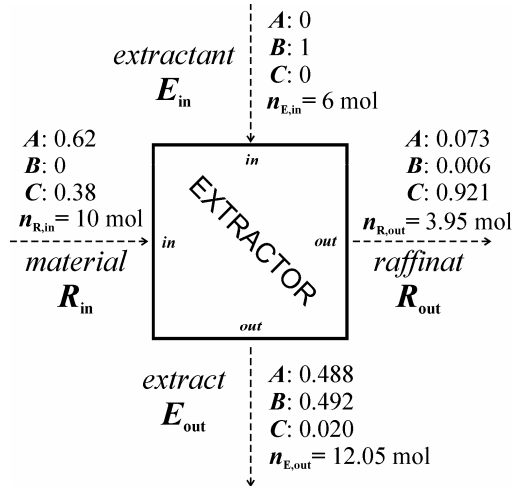


Fig. 4 One stage batch extraction process — to the numerical example III

The procedure for the raffinate will be showed below. Considering the constant driving force in a process and the conditions $dp=dT=dq=0$, yields $n_k = a_{j,k}x_{j,k} + b_{j,k}$. The coefficients $a_{j,k}$ and $b_{j,k}$ for the methanol (specie A) in raffinate (flux R) are equal to

$$a_{A,R} = \frac{10 - 3.95}{0.62 - 0.073} = 11.060329 \quad \text{and} \quad b_{A,R} = 10 - 11.060329 \cdot 0.62 = 3.142596$$

Hence, the coordinates of the exergy change inversion point K can be calculated by solving the nonlinear equation

$$2a_{A,R}x_{A,R,K} \ln x_{A,R,K} + a_{A,R}x_{A,R,K} + b_{A,R} \ln x_{A,R,K} + b_{A,R} = 0$$

and

$$n_{A,R,K} = a_{A,R}x_{A,R,K} + b_{A,R}$$

Using a standard programmable electronic calculator (or the *MS Excel*) to solve the nonlinear equation, there is

$$x_{A,R,K} = 0.547124 \quad \text{and} \quad n_{A,R,K} = 9.193974$$

For the methanol (specie A) it was considered $x_{A,0}=1$. Because the above values lie between the appropriate values of $n_{R,in}$ and $n_{R,out}$ or $x_{A,R,in}$ and $x_{A,R,out}$, respectively, in the given extraction process the concentration exergy change inverts in the calculated point K . It does mean, that the whole exergy change will be parted into increasing (arising) and decreasing (vanishing) exergy changes:

$$(0.62 ; 10.00) \rightarrow (0.5471 ; 9.1940) \quad \text{and} \quad (0.5471 ; 9.1939) \rightarrow (0.073 ; 3.95)$$

These concentration exergy changes are then equal to:

$$\frac{\nabla E_{A,R}^>}{RT_0} = (n_{A,R,K}x_{A,R,K} \ln x_{A,R,K} - n_{R,in}x_{A,R,in} \ln x_{A,R,in}) = -0.069814$$

The concentration of the methanol (specie A) in the raffinate (flux R) diminishes (symbol ∇) and it takes place in the concentration values above the inverse point (zero-point) of the exergy change (superscript $>$). That's why the above exergy change is the „decreasing” part. After the coordinates of

the inversion point K will be crossed, the appropriate exergy increases (symbol Δ and superscript $<$ for $x_{A,R}$ values less than $x_{A,R,K}$):

$$\frac{\Delta E_{A,R}^<}{RT_0} = (n_{R,out} x_{A,R,out} \ln x_{A,R,out} - n_{A,R,K} x_{A,R,K} \ln x_{A,R,K}) = 2.278939$$

The algebraic signs should be inverted because of the convention „end minus start” (above there is calculated for „start minus end”)

In the same way the appropriate values for water (specie B , $x_{B,0}=1$) and for trichlorethylene (specie C , $x_{C,0}=1$) are calculated:

$$a_{B,R} = \frac{10-3.95}{0.00-0.006} = -1008.3(3) \quad \text{and} \quad b_{B,R} = 10+1008.3(3) \cdot 0.00 = 10.00$$

Hence,

$$x_{B,R,K} = 0.609025 \quad \text{and} \quad n_{B,R,K} = -604.100312$$

which means, that there is no any zero-point of the exergy change for water concentration change between 0 and 0.006. The exergy change is then equal to

$$\frac{\nabla E_{B,R}^<}{RT_0} = (n_{B,R,out} x_{B,R,out} \ln x_{B,R,out} - n_{R,in} x_{B,R,in} \ln x_{B,R,in}) = -0.121249$$

For trichlorethylene the coordinates of the K -point are:

$$a_{C,R} = \frac{10-3.95}{0.38-0.921} = -11.182994 \quad \text{and} \quad b_{C,R} = 10+11.182994 \cdot 0.38 = 14.249538$$

Hence,

$$x_{C,R,K} = 0.260385 \quad \text{and} \quad n_{C,R,K} = 11.337650$$

The appropriate inversion point K is not crossed during the process, so

$$\frac{\Delta E_{C,R}^>}{RT_0} = (n_{C,R,out} x_{C,R,out} \ln x_{C,R,out} - n_{R,in} x_{C,R,in} \ln x_{C,R,in}) = 3.377433$$

The algebraic sign indicates the vanishing (minus) and arising (plus) exergy parts.

Results matrix:

	material (raffinate)			extractant (extract)		
$n_{k,in}$	10.00			6.00		
$n_{k,out}$	3.95			12.05		
specie	methanol	water	tri-	methanol	water	tri-
$x_{i,k,in}$	0.62	0.00	0.38	0.00	1.00	0.00
$x_{i,k,out}$	0.073	0.006	0.921	0.488	0.492	0.020
$a_{i,k}$	11.0603	-1008.3(3)	-11.1830	12.3975	-11.9094	302.50
$b_{i,k}$	3.1426	10.00	14.2495	6.00	17.9094	6.00
$x_{i,k,K}$	0.547124	0.609025	0.260385	0.517173	0.275504	0.601634
$n_{k,K}$	9.193974	-604.1003	11.337650	12.411679	14.628347	187.994199
$K?$	yes	no	no	no	no	no
$\frac{ \Delta E_{j,k}^< }{RT_0}$	2.278939	-	-	-	-	-
$\frac{ \Delta E_{j,k}^> }{RT_0}$	-	-	3.377433	-	-	-
$\frac{ \nabla E_{j,k}^< }{RT_0}$	-	0.121249	-	4.218833	-	0.942797
$\frac{ \nabla E_{j,k}^> }{RT_0}$	0.069814	-	-	-	4.205017	-

Thermodynamic effectivity of the extraction process equals to

$$\varepsilon = \frac{\sum \left(\sum |\Delta E_{j,k}| \right)}{\sum \left(\sum |\nabla E_{j,k}| \right)} = \frac{5.656372}{9.557711} = \underline{0.5918}$$

The numerical example in [18] is widened: the same batch extraction process is presented as a two stage one, in which the extractant (water *B*) is led at the amount of 3 moles into each stage. Appropriate numerical data are presented in the statement below.

Two stage extraction statement — the first stage (stage I):

material/raffinate (**R**):

$x_{A,R,in} = 0.62$	$x_{A,R,out} = 0.180$	
$x_{B,R,in} = 0.00$	$x_{B,R,out} = 0.022$	$n_{R,in} = 10.00 \text{ mol}$
$x_{C,R,in} = 0.38$	$x_{C,R,out} = 0.798$	$n_{R,out} = 3.80 \text{ mol}$

extractant/extract (**E**):

$x_{A,E,in} = 0.00$	$x_{A,E,out} = 0.600$	
$x_{B,E,in} = 1.00$	$x_{B,E,out} = 0.314$	$n_{E,in} = 3.00 \text{ mol}$
$x_{C,E,in} = 0.00$	$x_{C,E,out} = 0.086$	$n_{E,out} = 9.20 \text{ mol}$

Two stage extraction statement — the second stage (stage II):

material/raffinate (**R**):

$x_{A,R,in} = 0.180$	$x_{A,R,out} = 0.013$	
$x_{B,R,in} = 0.022$	$x_{B,R,out} = 0.001$	$n_{R,in} = 3.80 \text{ mol}$
$x_{C,R,in} = 0.798$	$x_{C,R,out} = 0.986$	$n_{R,out} = 3.04 \text{ mol}$

extractant/extract (**E**):

$x_{A,E,in} = 0.00$	$x_{A,E,out} = 0.176$	
$x_{B,E,in} = 1.00$	$x_{B,E,out} = 0.823$	$n_{E,in} = 3.00 \text{ mol}$
$x_{C,E,in} = 0.00$	$x_{C,E,out} = 0.001$	$n_{E,out} = 3.76 \text{ mol}$

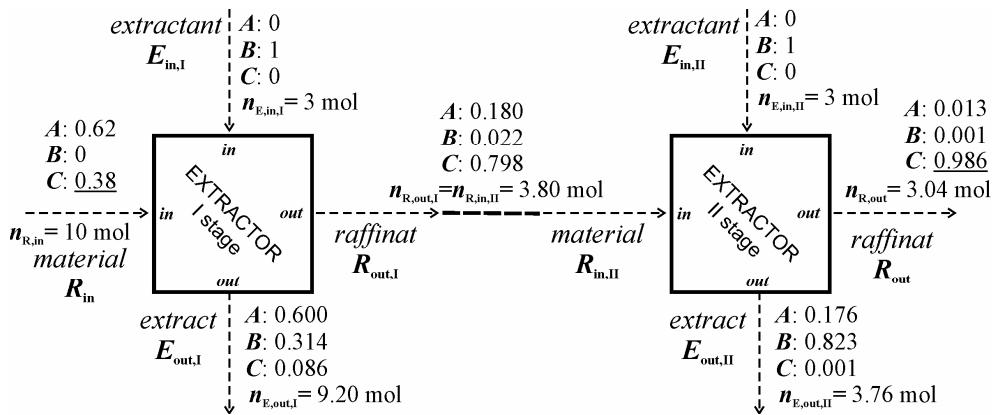


Fig. 5 Two stage batch extraction process — to the numerical example III

Results matrix for stage I of the two stage batch extraction:

stage I	<i>material (raffinate)</i>			<i>extractant (extract)</i>		
$n_{k,in}$	10.00			3.00		
$n_{k,out}$	3.80			9.20		
<i>specie</i>	<i>methanol</i>	<i>water</i>	<i>tri-</i>	<i>methanol</i>	<i>water</i>	<i>tri-</i>
$x_{j,k,in}$	0.62	0.00	0.38	0.00	1.00	0.00
$x_{j,k,out}$	0.180	0.022	0.798	0.600	0.314	0.086
$a_{j,k}$	14.09(09)	-281.81(81)	-14.8325	10.33(33)	-9.0379	72.0930
$b_{j,k}$	1.2636	10.00	15.6364	3.00	12.03791	3.00
$x_{j,k,K}$	0.585333	0.615597	1.027275	0.546097	0.264585	0.596395
$n_{k,K}$	9.511505	-604.1003	0.39926	8.643001	9.646606	45.995921
K?	<i>yes</i>	<i>no</i>	<i>no</i>	<i>yes</i>	<i>no</i>	<i>no</i>
$\frac{ \Delta E_{j,k}^< }{RT_0}$	1.808835	-	2.992568	-	-	-
$\frac{ \Delta E_{j,k}^> }{RT_0}$	-	-	-	0.035598	-	-
$\frac{ \nabla E_{j,k}^< }{RT_0}$	-	0.319077	-	2.855355	-	1.941136
$\frac{ \nabla E_{j,k}^> }{RT_0}$	0.017935	-	-	-	3.346277	-

Thermodynamic effectivity of the extraction process equals to

$$\varepsilon_1 = \frac{\sum \left(\sum |\Delta E_{j,k}| \right)}{\sum \left(\sum |\nabla E_{j,k}| \right)} = \frac{5.156078}{8.160704} = \underline{0.6318}$$

Results matrix for stage II of the two stage batch extraction:

stage II	<i>material (raffinate)</i>			<i>extractant (extract)</i>		
$n_{k,in}$	3.80			3.00		
$n_{k,out}$	3.04			3.76		
<i>specie</i>	<i>methanol</i>	<i>water</i>	<i>tri-</i>	<i>methanol</i>	<i>water</i>	<i>tri-</i>
$x_{i,k,in}$	0.180	0.022	0.798	0.00	1.00	0.00
$x_{i,k,out}$	0.013	0.001	0.986	0.176	0.823	0.001
$a_{i,k}$	4.5509	36.1905	-4.0425	4.3188	-4.2938	760.00
$b_{i,k}$	2.9808	3.0038	7.0259	3.00	7.2938	3.00
$x_{i,k,K}$	0.497322	0.586827	0.287367	0.493323	0.285568	0.605547
$n_{k,K}$	5.244101	24.241375	5.864259	5.130258	6.067617	463.215561
K?	<i>no</i>	<i>no</i>	<i>no</i>	<i>no</i>	<i>no</i>	<i>no</i>
$\frac{ \Delta E_{j,k}^< }{RT_0}$	1.0012945	0.298078	-	-	-	-
$\frac{ \Delta E_{j,k}^> }{RT_0}$	-	-	0.641990	-	-	-
$\frac{ \nabla E_{j,k}^< }{RT_0}$	-	-	-	1.149657	-	0.025973
$\frac{ \nabla E_{j,k}^> }{RT_0}$	-	-	-	-	0.602802	-

Thermodynamic effectivity of the extraction process equals to

$$\varepsilon_{II} = \frac{\sum(\sum|\Delta E_{j,k}|)}{\sum(\sum|\nabla E_{j,k}|)} = \frac{1.299372}{1.778432} = \underline{0.7306}$$

The total two stage batch extraction process can be rated using the thermodynamic effectivity quotient (with the appropriate procedure) and it becomes

$$\varepsilon_{total} = \frac{5.156078 + 1.299372}{8.160704 + 1.778432} = \underline{0.6495}$$

which means, any partition of a process into stages makes the thermodynamic conversion processes more effective. Like it has been determined above, the thermodynamic effectivity of the one-stage process equals to 0.5918. The general derivation of such an behavior has been already presented in [19]. Appropriate mathematical weight coefficients can be calculated, namely

$$\gamma_I = \frac{8.160704}{8.160704 + 1.778432} = 0.821068 \quad \text{and} \quad \gamma_{II} = \frac{1.778432}{8.160704 + 1.778432} = 0.178932$$

It means, the first stage thermodynamic effectivity is mostly decisive for the total process thermodynamic effectivity (for the presented energy conversion process in a two-stage batch extraction). The total thermodynamic effectivity quotient for the above Example yields

$$\varepsilon_{total} = \gamma_I \cdot \varepsilon_I + \gamma_{II} \cdot \varepsilon_{II} = 0.821068 \cdot 0.631818 + 0.178932 \cdot 0.730628 = \underline{0.6495}$$

which is the same numerical result as obtained above.

In fact, in [18] balance equations are not exactly solved. E.g. for the case of the one stage batch process presented above, the correct numerical $x_{j,k,out}$ -values for the raffinate components (at given extract composition) should be equal to

specie	material (raffinate)			extractant (extract)		
	methanol	water	tri-	methanol	water	tri-
$x_{j,k,in}$	0.62	0.00	0.38	0.00	1.00	0.00
$x_{j,k,out}$	<u>0.0809</u> instead of 0.073	<u>0.0181</u> instead of 0.006	<u>0.9010</u> instead of 0.921	0.488	0.492	0.020

Alas, graphically obtained values could not be verified. Nevertheless, the Example has been taken from [18] because it shows that the presented method of exergy analysis and rating is correct and enough flexible — the appropriate thermodynamic effectivity quotient for the corrected numerical values of $x_{j,k,out}$ yields

$$\varepsilon' = \frac{2.226271 + 3.305799}{0.065983 + 0.286827 + 4.218834 + 4.205017 + 0.942797} = \frac{5.532070}{9.719458} = \underline{0.5692}$$

instead of determined above numerical value of 0.5918.

5 CONCLUSIONS

The up-to-date formulated exergy efficiency quotients for technological separation processes by rectification, e.g. [20]–[21], contain in the denominator (expenditures) the so-called „exergy load” ($E_{Q,REB} - E_{Q,CON}$), but in fact they can be applied in a very limited scale. The variety of possible realizations of these processes needs almost in every case special calculation procedures, but also special thermodynamic analyzes, e.g. [22]. All existing calculation methods should be treated as approximate ones and the results obtained as „enough accurate”. This inaccuracy is mostly due to inexact material thermo-physical data.

In technological separation processes change not only mole concentrations of particular species, but also flow quantities, temperatures and states of aggregation. All these changes are sources of irreversibilities or exergy losses, which cannot be determined in a satisfactory way, e.g. [13].

In fact, thermodynamic analyzes can base only on parameters of the product supply (feed), products on the top and in the column bottom. Thus, the flows inside the apparatus (reflux) are beside analyzes. A certain time ago some exergy analyzes of technological separation processes have been presented, e.g. [23]–[26]. Calculation procedure of these methods was extreme labor-consuming, which required many simplifying assumptions. The in [23] presented exergy efficiency refers in general to the thermodynamic effectivity quotient determined above in this Chapter, however, there were not discussed any possible cases, e.g. if thermodynamic states of particular flows are different. Additionally, exergy changes have not been parted into rising (or created: „thermodynamic advantages”) and diminishing („thermodynamic expenditures”) components. The total chemical concentration exergy change has been treated as process thermodynamic advantages. Similar analyzes have been presented in [14].

The extraction process has been analyzed, although its application in modern power systems is not that interesting. It shows, however, the usability of the exergy approach with the thermodynamic effectivity quotient and is important for such analyzes and ratings of chemical reactions of combustion and gasification, which are of the first rank in the power engineering (e.g. [27]). Especially the Figure 3 is important, because reactants change their amounts and molar fractions in the reaction mixture. Besides, the numerical example does illustrate the behavior of processes while parting them into stages: the appropriate exergy efficiency is higher [19]. For the first time this opportunity has been reported by J.H. KEENAN in the year 1932 on the occasion of analyzing the multi-stage steam turbine [28].

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