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Energy and materials conversion with the help of regeneration and energy transformation ☆

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Abstract — The comprehension of the unity of materials and energy conversion is the basis for energetic effective design of materials conversion processes. Besides regenerative heat utilisation energy transformation can open up further possibilities of energy saving. The principal procedure for the design of energetic effective regenerative heat transfer systems and the effects which are within reach with regeneration are shown through the instance of a brewery — a typical multilevel heat consumer. Brewery process offers possibilities for heat transformation both in open and closed cycles. For the purpose of an equally good description of heat fluxes and material fluxes in open heat transformation processes, a concept for exergetic evaluation of material fluxes is necessary. Normalised exergy and corresponding generalised temperature are developed as evaluation characteristics and illustrated with help of an energy–entropy diagram. Heat transformation in the sense of open cycles appears also in single processes or unit operations. Aspects of energy transformation in connection with materials conversion are discussed through the examples of absorption and dehumidification. The regard of chemical reactions from the view of heat transformation opens interesting aspects for the evaluation of the conversion potential of fuels and other chemical compounds. This is discussed for some thermochemical cycles, reversible combustion and fuel cell. © 2001 Éditions scientifiques et médicales Elsevier SAS

energy transformation / heat transformation / materials conversion / regeneration / dehumidification / thermochemical cycles

Nomenclature

$E,\ e$	exergy, specific exergy	$\mathrm{J},\ \mathrm{J\cdot kg^{-1}}$
e^*	normalised exergy $\Delta e/\Delta h$	
ΔE_{V}	exergy loss	J
g	specific free enthalpy	$\mathrm{J\cdot kg^{-1}}$
$\bar{g}$	molar free enthalpy	$\mathrm{J\cdot mol^{-1}}$
$H,\ h$	enthalpy, specific enthalpy	$\mathrm{J},\ \mathrm{J\cdot kg^{-1}}$
$\bar{h}$	molar enthalpy	$\mathrm{J\cdot mol^{-1}}$
K_p	equilibrium constant	
Q	heat	J
s	specific entropy	$\mathrm{J\cdot kg^{-1}\cdot K^{-1}}$
T	temperature	K
T^*	generalised temperature	K
W	work	J
x	absolute humidity	$\mathrm{kg\cdot kg^{-1}}$
$\Delta_{\mathrm{R}}\bar{z}_{(0)}$	molar standard reaction properties for $\bar{z}=\bar{h},\bar{s},\bar{g}$	

Greek symbols

φ	relative humidity
ξ	mass fraction

Subscripts

ab	rejected from
i	component
sat	saturation
tot	total
U	environment
zu	transferred to

1. SIMPLE ENERGY CONVERSION AND ENERGY TRANSFORMATION

The unity of materials and energy conversion is a well-known and accepted view to materials conversion processes from the thermodynamic viewpoint. In this

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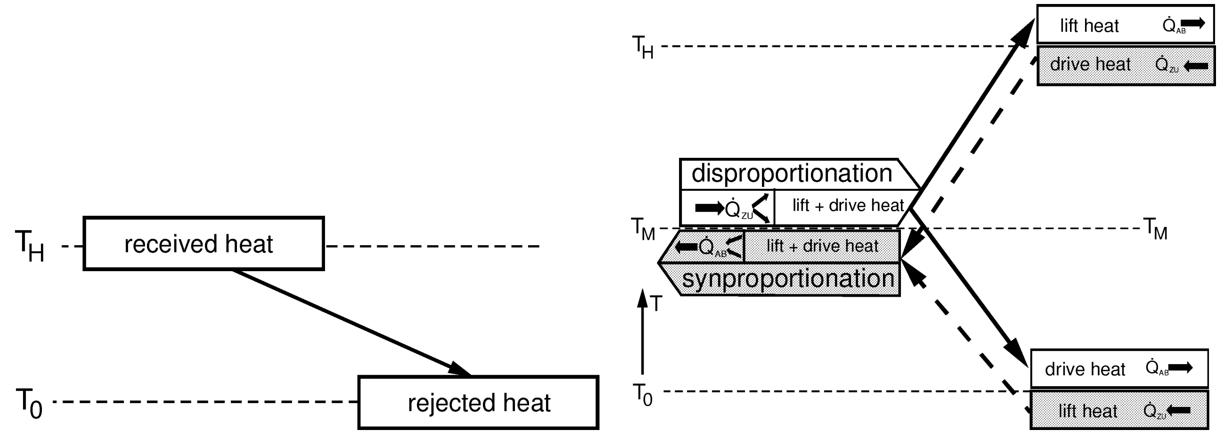


(a) (b)

Figure 1. (a) Simple energy conversion and (b) energy transformation.

paper the unity of energy transformation and materials conversion will be discussed.

Thermodynamics distinguishes by means of the second law and the resulting property entropy between three different kinds of processes: reversible processes as theoretical process model, impossible processes which are not feasible, and irreversible processes — the only class of real processes. In this sense thermodynamics knows at present no classification of processes.

In nature a main direction of energy flow exists. Heat flows from warmer body to the colder one, but also for all other energy forms is valid that energy flows from the higher to lower potential. Those processes, only devaluing energy, can be defined as simple energy conversion processes. But both in nature and in technology processes exist, with which the energy is transported contrary to the main direction. Processes which increase the value of a part of energy contrary to the main direction are called energy transformation processes. Simple energy conversion processes only devalue one or more potentials whereas energy transformation processes build up a potential. In accordance with the message of the second law this is only possible if another potential is devalued. So energy transformation processes require always at least three temperature levels for the interaction with the environment. In dependence of the temperature level of the upvalued part of heat, all energy transformation processes can be classified into two groups (*figure 1*). If the increase of value takes place from the lowest to the middle temperature level the process is called synproportionation process, if it takes place from middle to highest level it is called disproportionation [1].

The classification into simple energy conversion and energy transformation processes is not a valuation of quality, but it leads to a definition of the thermodynamic essence of the processes. Of course, in practice both simple energy conversion processes and energy transformation processes go irreversible and can be realised with more or less losses. An energy transformation process usually has to exchange the upvalued heat several times, connected with thermodynamic losses of heat transfer. On certain conditions an energy transformation process so can have a lower efficiency than a simple energy conversion. For effective process design of materials conversion are used both simply energy conversion and energy transformation but the rule in practice is: first all advantage should be taken from regeneration, only then transformation is to be used.

2. REGENERATION AND TRANSFORMATION IN A TECHNOLOGICAL PROCESS

The use of simple energy conversion is called regeneration and it means the devaluation of heat from one temperature level to that of the next process. The multiple use of the energy is called energy cascade. In a technological process the energy cascade is the more effective, the more frequently energy is used on its path from high temperature level to ambient temperature. An advantageous and widespread method for optimisation of heat exchanger systems is the pinch point method [2]. In this

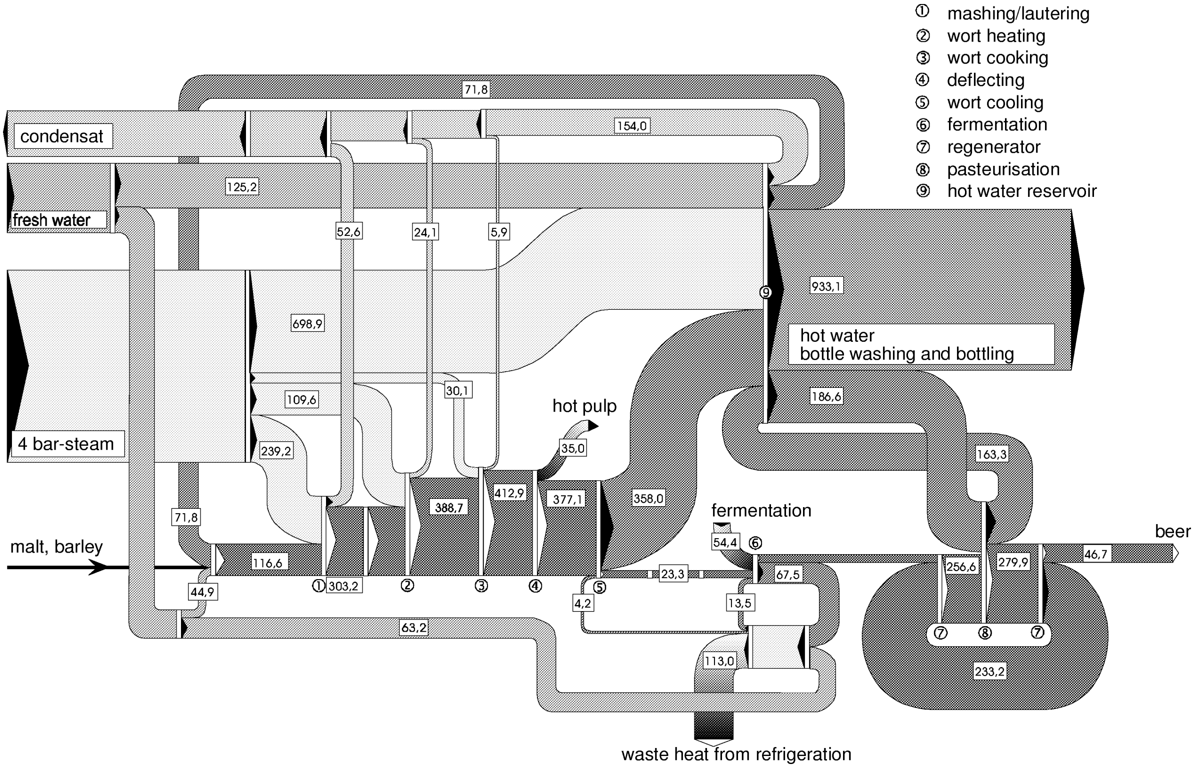
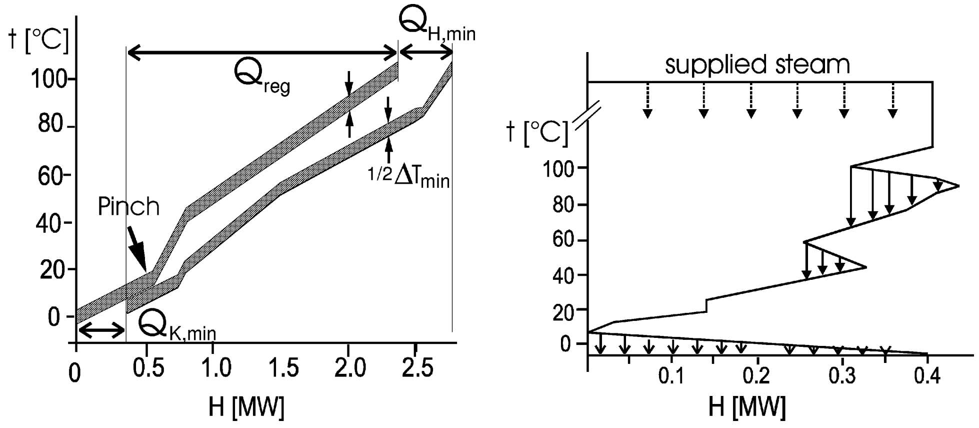


Figure 2. Energy flow sheet of brewery.

passage we will show briefly the organisation of an optimal energy cascade with help of pinch technology. This will be shown through the example of a brewery, because the brewery process is characterised by a multiplicity of heating and cooling processes and so it is a typical example for a multilevel heat consumer. Main needs of heat occur from heating and cooking the wort and from washing and pasteurising the bottles. Main refrigeration requirements are from fermentation and wort cooling. *Figure 2* shows an energy flow sheet for a brewery with a capacity of 234 thousand hectolitres per year and heat supply with mean pressure steam [3].

Pinch method combines all hot streams in terms of their heat content to a composite hot profile and all cold streams to a respective cold profile. The resulting composite curves are shown in *figure 3(a)* for the example brewery process. The composite curves are moved exactly so that the closest approach is the minimum allowable temperature difference for heat transfer $\Delta T_{\min}$. The point at which this closest approach occurs is termed the pinch. The optimal temperature difference must be chosen in consideration of capital cost and can be optimised later by pinch method. *Figure 3(a)* shows that the optimal temperature difference can be assigned to the hot and the cold composites, to each a half of it.

This temperature difference is caused by the driving force of the process and leads to corresponding thermodynamic losses. Temperature differences between the fluxes going beyond the driving-force-caused losses follow from system design of heat exchangers. Those losses are called system-caused losses. The overshoots of the composite curves determine the minimal demand for heating and cooling which results from process data. The aim of the pinch method is to achieve this minimum utility consumption of heating and cooling in the system. That is achieved by the regenerative heat recovery in the area of overlapping of the composite curves. The grand composite curve — a profile of the horizontal separation of the composite curves — reveals where heat is to be transferred between utilities and process and where the process can satisfy its own heat demand. Moreover, the grand composite curve shows all temperature differences going beyond the driving-force-caused temperature difference. Those temperature differences can be used as driving force for transformation processes with which the system-caused losses can be reduced. *Figure 3(b)* shows the grand composite curve for the brewery process. In



(a) (b)

Figure 3. (a) Composite and (b) grand composite curve for brewery process.

the example the heat utility is only mean pressure steam from district heating, so the highest temperature differences occur from utility to process temperature. If different utilities at different temperature levels are available the external losses can be reduced by minimising temperature differences between process temperatures and temperature levels of utilities. Otherwise the system-caused thermodynamic losses are avoidable by the use of heat transformation processes. In contrast to this the thermodynamic losses inside the technology are comparatively small, shown by the temperature differences in the area of overlapping of the grand composite curve. Nevertheless, in principle transformation processes also here can be used for a near-reversible devaluation of the heat with simultaneous upvaluation of a part of the heat.

Below the pinch point a surplus of waste heat exists. Only a part of waste heat is usable regeneratively. This part is not visible in the grand composite curve because of the identical rises of hot and cold composites. The rest of heat must be rejected into the environment. In the example process the heat must be rejected below ambient temperature and so this must be done with a refrigeration process.

The most important waste heat source in brewery is the exhaust steam of wort-cooking process, especially in breweries supplied by a district heating hot water net. Here the exhaust steam cannot be used regeneratively but it is usable as heat source for heat transformation processes. *Figure 4* shows three possible applications for heat transformation:

1. Synproportionation by mechanical vapour compression, the whole vapour can be used for wort kettle heating.
2. Disproportionation with absorption heat transformer. The exhaust vapour here serves for heating of desorber and evaporator and about 50 % of the heat can be upgraded to the temperature level for wort kettle heating.
3. The waste heat can be used as driving heat for absorption chiller or for a combined absorption heating and cooling device because of the relative high refrigeration requirements of breweries. The delivered heat of condensation and absorption can be used for preheating of rinse water.

3. ENERGY TRANSFORMATION IN CYCLES AND IN UNIT OPERATIONS

The whole of transformation processes with their interactions to the environment can be clearly represented in an energy–entropy diagram (*figure 5*). In this diagram the energy balance is represented at the ordinate

$$\sum Q_{\mathrm{zu}} + \sum Q_{\mathrm{ab}} + W_{\mathrm{KP}} = 0$$

and the — with T_{U} multiplied — entropy balance is shown on the abscissa

$$\sum T_{\mathrm{U}} \frac{Q_{\mathrm{zu}}}{T} + \sum T_{\mathrm{U}} \frac{Q_{\mathrm{ab}}}{T} + \sum T_{\mathrm{U}} \Delta S_{\mathrm{V}} = 0$$
$$\text{with } T_{\mathrm{U}} \Delta S_{\mathrm{V}} = \Delta E_{\mathrm{V}}$$

Entropy balance shows that the exergetic losses result from the difference between transferred and rejected exergy. The energy–entropy diagram contains also an indication of the respective temperature of the participated

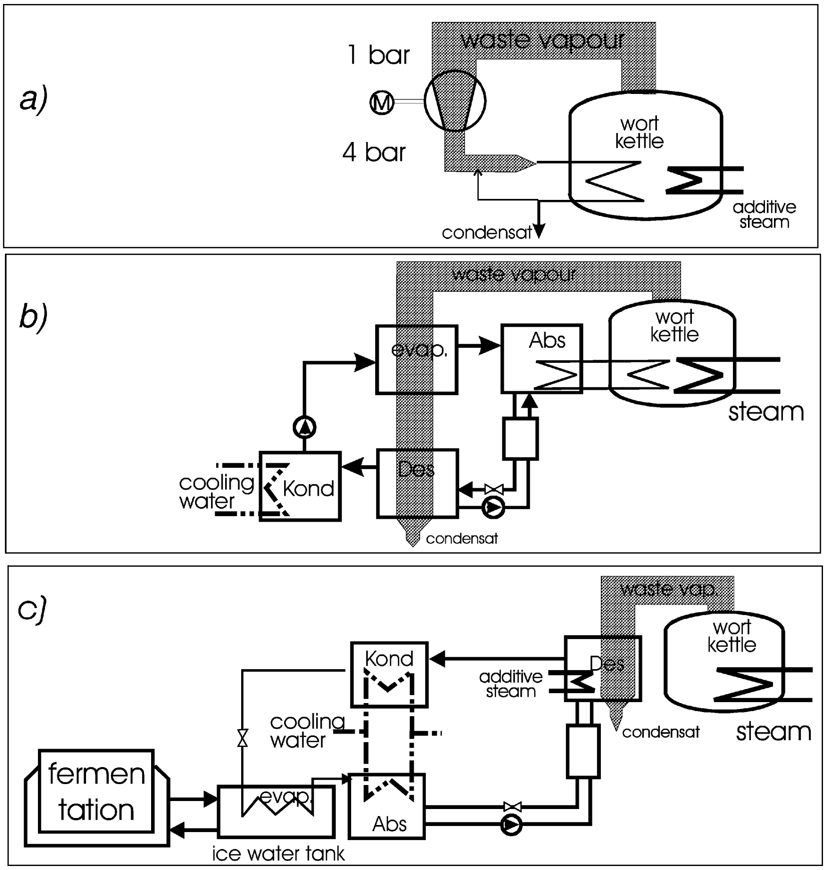


Figure 4. Heat transformation in the brewery: (a) vapour compression, (b) absorption heat transformer, (c) absorption heating and cooling combination.

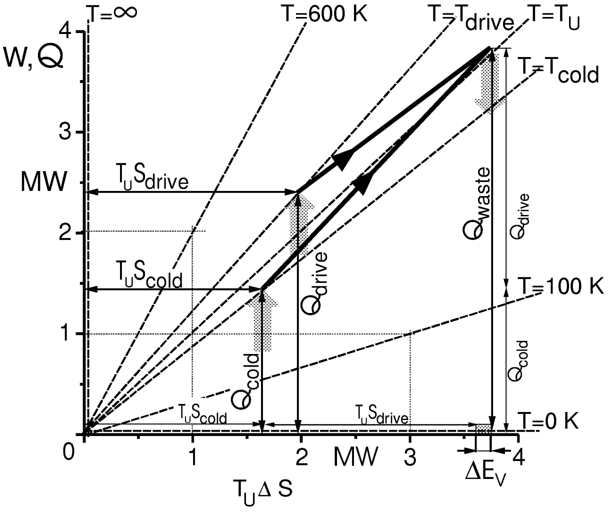


Figure 5. Energy–entropy diagram with combined absorption heating and cooling process.

heat fluxes. The temperature of a heat is shown through lines with constant rise, following from the entropy definition of a heat $S = Q/T$ and the chosen axis by the quotient

$$\frac{\Delta y}{\Delta x} = \frac{Q}{T_{\mathrm{U}} S} = \frac{Q}{T_{\mathrm{U}} Q/T} = \frac{T}{T_{\mathrm{U}}}$$

So the 45° line describes the ambient temperature, the abscissa means $T = 0$ K, and the ordinate describes heat of infinitely high temperature or entropy-free energy like work.

Figure 5 shows the appearance of transformation processes in the energy–entropy diagram by means of an absorption chiller (synproportionation process). For closed cycles the entropy of all transferred heat fluxes can be determined by the mean temperature of this heat. Starting points of the process graph are driving heat and supplied cold. The graph ends near ambient temperature and at the sum of both energies. The balance of the amounts on the abscissa is fulfilled only including exergy loss. In comparison to a reversible process with the same temperature of heat rejection the amount of needed driving heat for the real process is higher, resulting in a lower efficiency of the process.

Heat transformation occurs not only in closed cycles but it can be realised also with open processes like the vapour compression heat pump in *figure 4(a)*. In open processes not only heat fluxes but also material fluxes cross the control surface and must be evaluated adequately.

It is advantageous to characterise material fluxes with their exergy–energy ratio which can be developed from their energy–entropy ratio. If the exergy $\Delta e = \Delta h - T_{\mathrm{U}}\Delta s$ is related to the energy Δh a dimensionless property follows which is called standardised exergy e^* in the following:

$$\frac{\Delta e}{\Delta h} = e^* = 1 - T_{\mathrm{U}}\frac{\Delta s_{\mathrm{tot}}}{\Delta h_{\mathrm{tot}}}$$

Analogous to the definition of thermodynamic middle temperature of an isobaric process a generalised temperature $T^* = \Delta h_{\mathrm{tot}}/\Delta s_{\mathrm{tot}}$ can be defined. For standardised exergy it yields

$$e^* = \frac{\Delta e}{\Delta h} = 1 - \frac{T_{\mathrm{U}}}{T^*} = \frac{T^* - T_{\mathrm{U}}}{T^*}$$

what corresponds to a Carnot factor and makes possible a uniform treatment of materials and heat fluxes in transformation processes.

Both energy and entropy changes can result not only from thermal parts but they include also contributions from pressure and concentration changes as well as excess parts. Later it will be shown that also chemical potentials and the entropy of reaction which is important in this connection can be included in the concept of generalised temperatures. So, the generalised temperature T^* is not a measurable temperature but it is an evaluation property that describes the relation between energy and entropy change.

From the definitions of T^* and e^* follows that both properties embody the rise in the energy–entropy diagram. The drawn lines of constant temperatures are also lines of a respective constant standardised exergy. The diagram makes possible an informal description of normalised exergy $e^* > 1$, like it is found for fossil fuels which have an larger exergy then energy. These lines $e^* > 1$ are placed in the upper left quarter of the diagram, and lead to negative values for generalised temperature. Below the line $T_{\mathrm{U}} = \mathrm{const}$ the standardised exergy becomes negative and expresses that energy is needed to bring an mass flux into environmental conditions.

From the energy–entropy diagram it is possible to read not only the temperatures of heat fluxes exchanged with the environment but also the normalised exergy or generalised temperature of substance fluxes in open cycles. *Figure 6* shows the complete diagram with the three example transformation processes from brewery.

The two closed absorption processes can use about 2 400 kW waste heat from exhaust steam under consideration of the necessary temperature difference for heat transfer. The combined heat and refrigeration process corresponds to this one in *figure 5*. With the absorption heat transformer 1 100 kW are upvalued to the usable heat temperature, the rest is rejected at ambient temperature to the environment.

The vapour compression (synproportionation) processes demands 400 kW electrical energy in order to supply 2 800 kW usable heat. Both the production of exhaust steam and the use of produced vapour can be characterised by the respective thermodynamic middle temperature for the vapour. The received work is marked on the y-axis as an entropy-free value. The exergy loss follows from entropy difference of received and rejected heat only.

Not only a cycle but also a single process or a unit operation can be understood as heat transformation processes and be shown in the energy–entropy diagram. For instance, condensation or partial condensation are simple energy conversion processes characterised by the generalised temperature of phase change and the temperature of the heat sink. The process is a horizontal line in the diagram in accordance to the first law and the length of the process graph characterises the exergy losses caused by temperature differences (*figure 7(a)*). The character of the process is changed fundamentally if the simple condensation is replaced by the absorption in a hygroscopic solution.

During the absorption of the vapour in the solution the release of energy takes place at a significantly higher temperature level than through condensation. The increasing temperature of energy release is caused by the solution. The exergy needed for temperature raise of the vapour is supplied by the solution which has a high exergy because of its mixing energy and entropy. High exergy content of solution is shown in *figure 7(b)* by its position in the energy–entropy diagram with a normalised exergy over one. A comparison between reversible and irreversible absorption can be easily accomplished if the losses are

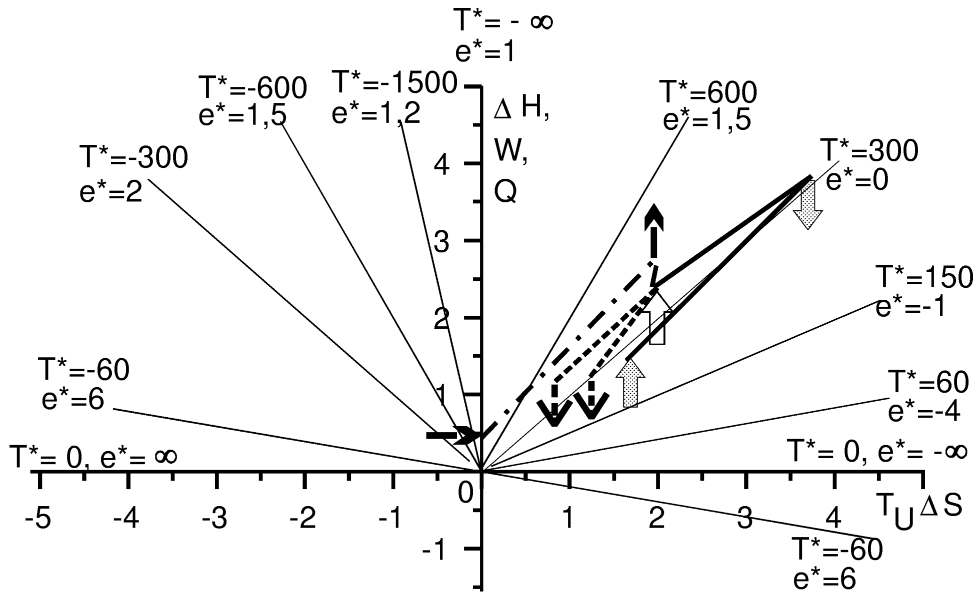
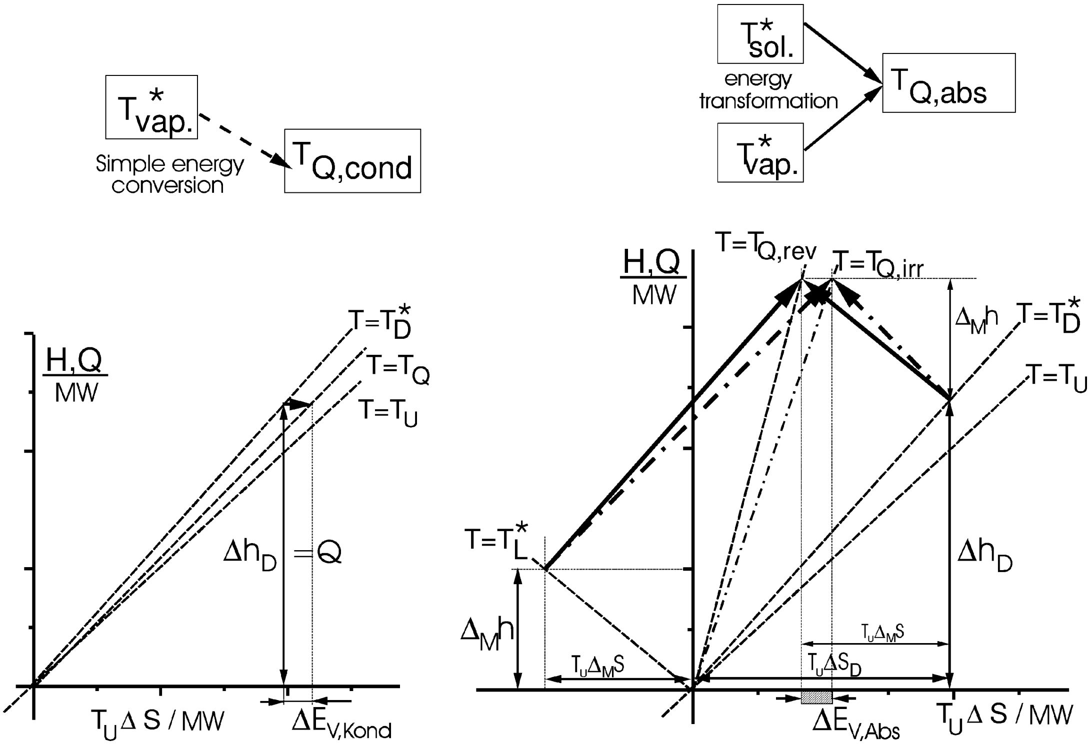


Figure 6. Energy–entropy diagram with lines of constant generalised temperature and open and closed heat transformation processes in the brewery.



(a)

(b)

Figure 7. (a) Condensation and (b) reversible and irreversible absorption in the energy–entropy diagram.

expressed by a decreasing temperature of the energy release.

In a similar manner many other unit operations can be characterised as simple energy conversion and energy transformation processes. The concept should be explained in the following by the example of dehumidification of a gas flux. The dehumidification has importance in energy technology in the sense of energetic use of the condensation heat of water vapour but also in materials conversion in the sense of cleaning or drying a gas.

4. ENERGY TRANSFORMATION AND DEHUMIDIFICATION

The nowadays most used method of latent heat recovery from flue gases is the gross calorific value use which cools the flue gas below its dew point. The use of heat here is possible only in form of simple heat transfer below dew temperature. The application of condensing boiler technology is limited to low temperature heating systems. Higher temperatures for gross calorific value use can be reached with open absorption cycles [4]. The flue gas humidity here is absorbed by a hygroscopic solution at a higher temperature than the water dew point. The lg p–$(1/T)$ diagram (*figure 8*) shows like the temperature level of usable heat is upvalued from dew point of flue gas — determined by partial pressure of water vapour in the gas — to the absorption temperature. For later on considerations it is useful to draw also lines of constant relative humidity into the diagram which are parallels to the saturation line of water due to $p_{i,\mathrm{H_2O}} = \varphi p_{\mathrm{sat}}(t)$.

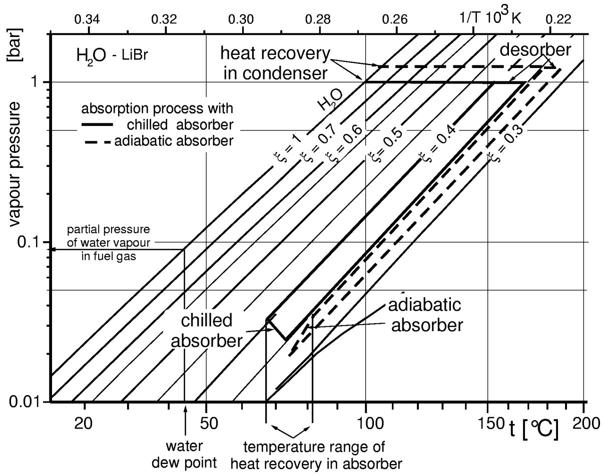


Figure 8. Open absorption processes with cooled and adiabatic absorber in vapour pressure diagram.

In the diagram two processes are shown: one with a chilled absorber and the other one with an adiabatic absorber. Both absorbers are counter-current absorbers where the dilute solution is in contact with the humid flue gas at the bottom of the apparatus. With adiabatic absorbers it is possible to use simple absorber constructions like washing tower with packing or spray nozzles. However, high solution fluxes are necessary because the absorber heat is accumulated as sensible heat in the solution flux. The heat exchanger following the absorber can work with high heat transfer coefficients because the heat transfer is separated from mass transfer. It is visible from diagram that adiabatic absorption goes with increasing temperature and both maximum and mean temperature of heat recovery are higher in the adiabatic absorber than in the chilled absorber. The end temperature of absorption equals the maximum temperature of heat recovery. The absorbed humidity must be removed from the solution again in the desorber. For that, high temperature heat is needed which is reused in the condenser and is delivered to the heating like in closed absorption heat pumps. High temperature condensing value technology so represents a synproportionation process which uses high temperature heat to upvalue the condensation heat of humidity in a flue gas. *Figure 9* shows a technological scheme of an open absorption heat pump with chilled absorption.

Contrary to the condensing boiler technology nearly no notice is taken of the energetic effect of dehumidification if drying of a gas flux is a technological necessity. If a humidity content less than saturation humidity at ambient temperature is to be achieved the use of transformation processes is inevitable. Often a low temperature dehumidification is used with help of an external refrigerant process. In this case, for the only purpose to condense the very low rate of humidity, the whole gas flux must be cooled down to the low temperature. For

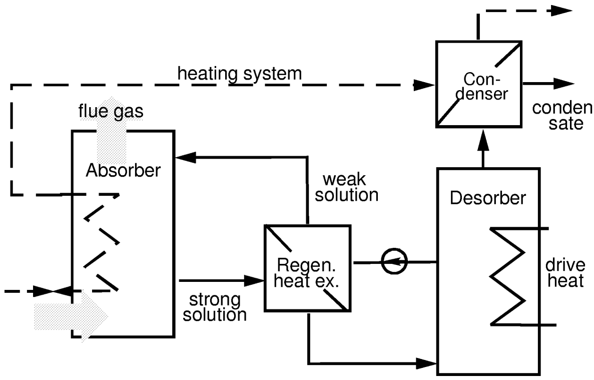


Figure 9. Gross calorific value use at high temperature with the help of an open absorption process.

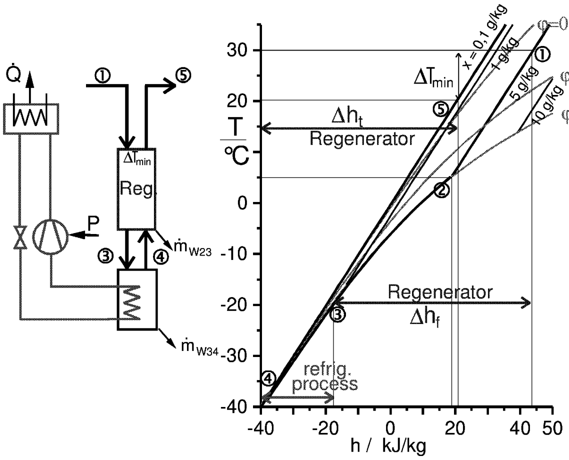


Figure 10. Dehumidification with use of an external refrigeration process.

instance, in the case of dehumidification of vinyl chloride the 10 000-fold mass flux — related to the water which is condensed — is cooled down to −40 °C. The process is shown in *figure 10* in a T–h diagram. This diagram resembles the T–Q diagram for pinch method and in this sense permits more fundamental statements as the usual Mollier h–x diagram for humid air. The lines of constant relative humidity show in the T–h diagram a similar course like in the h–x diagram, the isenthalpes follow as verticals and the lines of constant absolute humidity as oblique lines. Regenerative cooling of humid warm gas (① → ②) by the dehumidificated cold gas (④ → ⑤) reduces the need of refrigeration, however, then the cold must be supplied on the lowest temperature level. If the minimal temperature difference in the heat exchanger is fixed the final state of regenerative cooling can easily be found out by transferring the corresponding enthalpy difference. The remaining enthalpy of the humid gas flux must be removed by the external refrigeration process which transforms the cold to ambient temperature with help of work and rejects it to environment. So refrigeration dehumidification is a process with use of an external synproportionation process.

To condense water out of the gas flux by going beyond the saturation humidity is possible also by an increase of system pressure with proportional increase of the partial pressure of water vapour. If the T–h diagram is extended to different total pressures, different saturation lines appear only, absolute humidity and enthalpy are assumed to be not influenced by pressure. The best conceivable compression process is the isothermal compression at ambient temperature because of the lowest need of work.

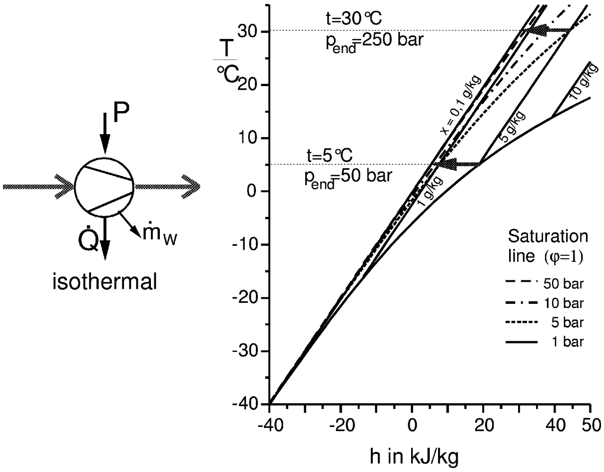


Figure 11. Compression dehumidification.

The above-mentioned demanded humidity (saturation humidity at normal pressure and −40 °C) is attainable with the shown isothermal compression only with total pressure about 50 bar, even if the compression is done at normal pressures dew temperature. It is remarkable that the shown enthalpy change is only the amount of enthalpy reduction due to dehumidification. The needed compression work of more than 300 $\text{kJ}\cdot\text{kg}^{-1}$ must be removed as heat from the system and so does not appear in the diagram. Because of the high expenditure of electrical energy and the requirements at materials and apparatus such a method should only be used if the compression of the gas is moreover a technological necessity. Nevertheless, compression dehumidification is a synproportionation process too, consuming work.

Besides dehumidification by undercooling below dew temperature or compressing beyond the saturation pressure, the partial pressure can also be reduced by absorption–dehumidification. Similar to the gross calorific value use, the gas contacts a concentrated hygroscopic solution. The vapour pressure over solution is much lower than the partial pressure of water vapour in the gas, therefore, the solution absorbs the water and the gas is dried. The solution can be concentrated again after the transport into an inert gas-free desorber. The steam is rejected to environment if it is possible with use of condensation heat. *Figure 12* shows the absorption dehumidification in the vapour pressure diagram but it can be shown also in the T–h diagram. The lines of constant LiBr concentration are similar to the lines of constant relative humidity respective to the course in the $\lg p$–$(1/T)$ diagram. It is visible that the existence of solubility curve of LiBr solution permits a dehumidification to the demanded final humidity only at low temperatures too. So

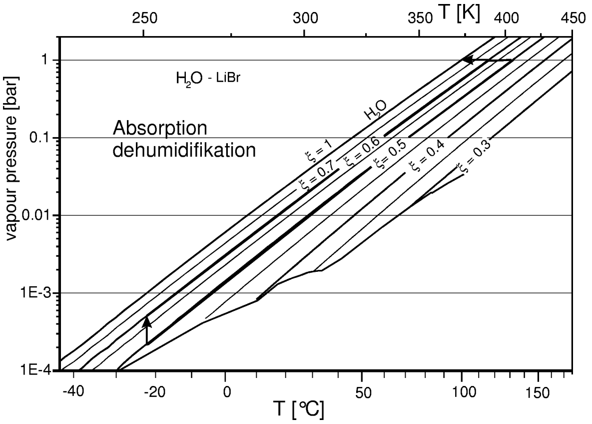


Figure 12. Absorption dehumidification.

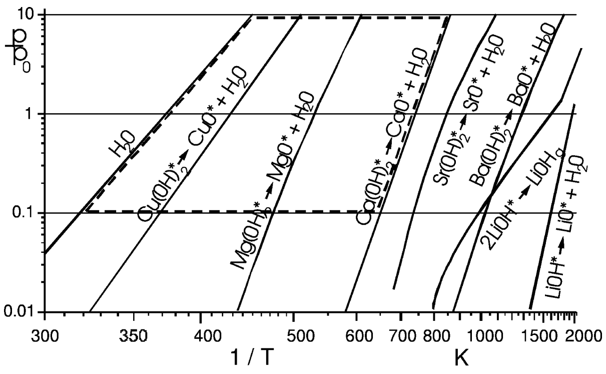


Figure 13. Reaction system for adding and splitting water.

an external synproportionation process which supplies cold will be necessary, however, in smaller scale than for pure refrigeration dehumidification. If a working substance with a wider working area is used, e.g., silica gel or activated carbon, a process is conceivable which allows a comparable dehumidification also at a temperature over 0 °C.

Such very wide "solution" fields are also found for chemical compounds which are able to add and to split water (*figure 13*). The occurring reaction enthalpies are — corresponding to the higher bound energy — usually much larger than the caloric effects of absorption and desorption. The much wider temperature range which is usable with such reactive systems is even more essential. The addition reaction with the wished dehumidification can take place at a temperature of 200 °C and so could deliver useable heat [5]. In contrast, the same absorption dehumidification needs a refrigeration capacity. Of course, also high temperatures for regeneration of the reaction system are necessary, according to the course of equilibrium lines in the $\lg p$–$(1/T)$ diagram (*figure 13*).

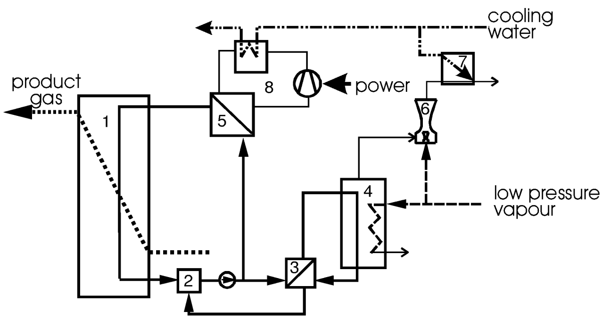


Figure 14. Technological scheme for vinyl chloride drying with external cooling, absorption dehumidification and compression of absorbed vapour stream.

A dehumidification process in such a temperature range can be driven nearly exclusively by heat.

For practical dehumidification it will be advantageous to use a combination of different possibilities. In *figure 14* is shown such a combination for the instance of the vinyl chloride dehumidification. The product gas is dried by a 42 % potassium hydroxide solution which is precooled by an external compression refrigeration machine to −10 °C. The absorbed humidity is rejected from a partial stream of the solution in a vacuum desorber. The swiped out vapour is compressed with help of low pressure steam (0.3 MPa) in a steam-jet apparatus to atmospheric pressure and condensed with cooling water.

5. CHEMICAL REACTIONS

Not only processes to add and split water are interesting from standpoint of heat transformation. Also chemical reactions can be understood as heat transformation processes. For the discussion of concerned chemical reactions it is helpful to define a generalised reaction temperature. Such a temperature can be found with the help of the relation between equilibrium constant and free reaction enthalpy $\Delta_R g_{(0)}$:

$$\ln K_p = -\frac{\Delta_R \bar{g}_{(0)}}{RT} = \frac{\Delta_R \bar{h}_{(0)} - T \Delta_R \bar{s}_{(0)}}{RT}$$

For any reaction system a generalised temperature can be defined in dependence of equilibrium constant

$$T_m = \frac{\Delta_R \bar{h}_{(0)}}{\Delta_R \bar{s}_{(0)} - R \ln K_p}$$

The influence of $\ln K_p$ is not so strong. In a gas-phase reaction $K_p = 1$ can be assumed for simplicity, i.e. all

TABLE I
Generalised temperatures and normalised exergies for different reactions.

Reaction system	$\Delta_R\bar{h}_0$ kJ·mol^{-1}	$\Delta_R\bar{s}_0$ J·mol^{-1}·K^{-1}	T^* K	$e^* = \Delta e/\Delta h$
Combustion				
$C + O_2 \rightarrow CO_2$	−393.1	2.8	−140 000	1.002
$CO + 1/2\,O_2 \rightarrow CO_2$	−284.2	−86.5	3 300	0.908
$H_2 + 1/2\,O_2 \rightarrow H_2O_{fl}$	−285.5	−163.0	1 750	0.829
$H_2 + 1/2\,O_2 \rightarrow H_2O_g$	−241.6	−44.7	5 400	0.945
$CH_4 + 2\,O_2 \rightarrow CO_2 + 2\,H_2O_g$	−802.6	−5.4	147 700	0.998
$CH_3OH_{fl} + 3/2\,O_2 \rightarrow CO_2 + 2\,H_2O_g$	−637.9	156.5	−4 075	1.074
$C_{12}H_{22}O_{11} + 12\,O_2 \rightarrow 12\,CO_2 + 11\,H_2O_g$	−5 181.9	1 861.9	−2 833	1.106
Gasification				
$CH_4 + 1/2\,O_2 \rightarrow CO + 2\,H_2$	−35.5	169.7	−210	2.431
$CH_3OH \rightarrow CO + 2\,H_2$	90.1	218.8	412	0.271
$C_{12}H_{22}O_{11} + 1/2\,O_2 \rightarrow 12\,CO + 11\,H_2$	899.0	3 342.2	269	−0.115
$CH_4 + H_2O \rightarrow CO + 3\,H_2$	206.0	214.1	962	0.688
$C_{12}H_{22}O_{11} + H_2O \rightarrow 12\,CO + 12\,H_2$	1140.6	3 386.4	337	0.109
Pyrolisis				
$CH_4 \rightarrow C_f + 2\,H_2$	74.8	80.7	930	0.681
$C_2H_2 \rightarrow 2\,C_f + H_2$	−226.6	−58.5	3 870	0.923
$C_6H_{6fl} \rightarrow 6\,C_f + 3\,H_2$	−49.0	250.8	−195	2.542
$C_{12}H_{22}O_{11} \rightarrow C_f + 11\,CO + 11\,H_2$	857.6	2 802.7	306	0.020
Splitting				
$CaCO_3 \rightarrow CaO + CO_2$	183.1	161.4	1 134	0.737
$Ca(OH)_2 \rightarrow CaO + H_2O$	113.9	145	783	0.619
$2NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O_g$	92.3	174.5	529	0.436
$MgCl_2 + H_2O \rightarrow MgO + 2HCl$	96.9	126.0	770	0.613

components have concentrations in the same range, then $\ln K_p = 0$ follows and

$$T_m = \frac{\Delta_R\bar{h}_{(0)}}{\Delta_R\bar{s}_{(0)}}$$

A reaction can proceed theoretically reversibly if the concentration of all components deviates minimally from equilibrium concentration and if it is possible to exchange the heat with the surroundings at the calculated generalised reaction temperature. From the generalised temperature the normalised exergy can be derived with the help of Carnot factor. The generalised temperature is also a scale of normalised exergy of the selected conversion reaction. The combustion reaction converts the reactant into products which are structural components of the environment. Thus, the normalised reaction exergy is identical with the normalised exergy of the reactant or for instance of a fuel.

The reaction properties of the desorption of water from $Ca(OH)_2$ deliver a generalised reaction temperature of about 780 K which is in good agreement with the shown vapour pressure curve at normal pressure in *figure 13*. *Table I* shows generalised temperatures for different reaction systems. There are reactions interesting in view of supply with customer energy, e.g., cumbustion, gasification and pyrolisis reactions of carbon-containing substances and of hydrogen, as well as there are reactions with relevance in materials conversion industry.

Several combustion reactions and the gasification reactions with oxygen are especially remarkable because they have different signs of reaction enthalpy and reaction entropy. This leads to negative generalised reaction temperatures and it shows that those reactions never can go reversible. Heat cannot be exchanged at the generalised reaction temperature and so the reacting components cannot be found near equilibrium concentration. On the other hand, negative generalised reaction temperatures indicate that the normalised exergy of the reactant is higher than 1. This means that the reactant contains more exergy than energy. In order to gain the full amount of availability of the reactant, i.e. to achieve a reversible transformation, it is necessary to supply heat to the reaction system. In the

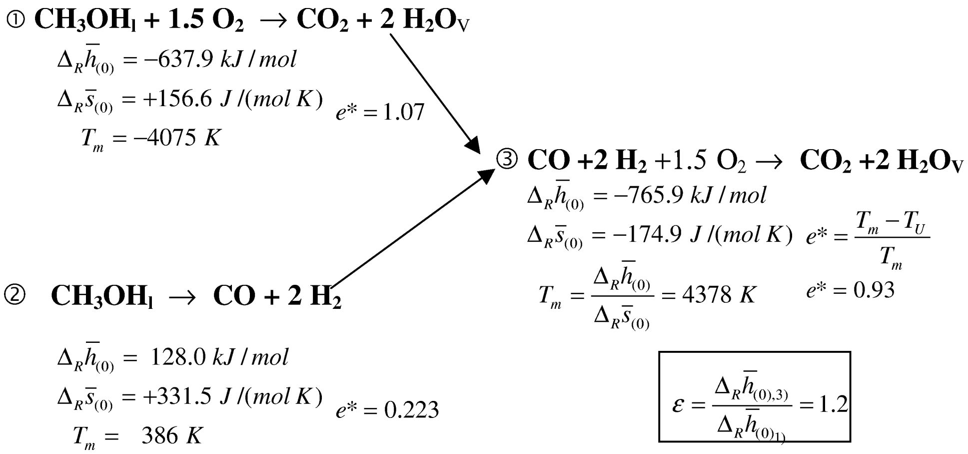


Figure 15. Open chemical cycle for methanol conversion.

case of reversibility a work generation is possible over the measure of the energy contained in the initial product. In the sense of heat transformation every reaction describes heat exchange on a defined temperature level. Combinations of reactions make possible energetic interactions between several temperature levels and so make possible heat transformation with so-called thermochemical cycles.

Figure 15 shows it through the instance of methanol conversion. The direct combustion reaction, i.e. the conversion of the reactant to CO_2 and water, is replaced by a two-step reaction system. First it is possible to transfer low temperature heat to the system with help of an endothermic gasification with water vapour. Second reaction is the combustion of the gasification reaction products. This reaction goes at positive generalised temperature and so it is theoretically possible to use the normalised exergy of combustion reaction in full range by using a higher amount of heat at lower temperature. In the sense of heat transformation the reaction system describes an open cycle in which the normalised exergy of the reactant in the combustion reaction represents the highest energy level. Low temperature heat is supplied to the system with gasification. Both amounts of energy are rejected at middle temperature level as the reaction enthalpy from the combustion of gasification products. The relation between this reaction enthalpy and the calorific value of the reactant can be defined as COP. It shows that through gasification and a following combustion can be delivered 20 % more heat than from simple combustion.

Normalised exergy larger than 1 means that a reversible conversion of the exergy of the fuel is possible only with help of a heat transformation process which receives additional heat from surroundings. On the other hand, the positive sign of normalised exergy shows that an exothermal reaction ($\Delta h < 0$) is connected with a release of exergy ($\Delta e < 0$) from the system, i.e. the release of heat or generation of work. Corresponding an endothermic reaction with positive normalised exergy demands an exergy transfer to the system. However, reactions exist whose generalised (reversible) reaction temperature is lower than ambient temperature, e.g., the gasification reaction of sucrose with water vapour in *table I*. If it concerns an endothermic reaction the transfer of thermal energy to the reaction is connected with a cold production, i.e. an exergy generation. The originating temperature difference can be used, for instance, to carry out a cycle generating work. Heat supply so is connected with exergy production and this is the reason for the negative sign of normalised exergy.

Fuel cells realise a direct conversion of chemical energy of the fuel into current or respectively work. If the fuel is hydrogen with a normalised exergy $e^* < 1$ this is a disproportionation process which has to upvalue a part of energy to the higher level (work with $e^* = 1$). The remaining energy is to be rejected as heat. The lower temperature of heat release is the higher could be the theoretical amount of work production. If the hydrogen is gained first from an internal or external reaction system without production of work than this first conversion step is a simple energy conversion with energy devaluation only. Other for the direct methanol fuel cell. Here a fuel with a normalised exergy $e^* > 1$ is used. In this case the only conversion into heat and work represents a simple energy conversion. For a reversible transformation an increase of energy (in relation to calorific value) through heat supply from the surroundings would be necessary. Such a process would be a synproportionation process. However, the normalised exergy is only a little larger than 1 and in consideration of the losses of a real process which are higher than 7 %, there will be no possibility of heat supply from surroundings.

6. CONCLUSION

In contrary to the main stream of energy flow in simple energy conversions the energy transformation is able to upvalue the quality of a part of energy, for instance, the temperature level of a heat flux. Many materials conversion technologies are connected with high energy consumption and can be improved by the use of regeneration and transformation. Materials conversion processes themselves are connected with building up and reduction of potentials and so can be characterised as simple energy conversion or energy transformation processes. For this purpose generalised temperature and normalised exergy are developed as characteristics for exergetic evaluation of material fluxes. Through the instance of dehumidification it is shown that there exists a great variety of transformation processes to reach a certain technological aim. The efficiency of the possible solutions must be examined in dependence on the available sources of energy and the process specific boundary conditions. The regard of chemical reactions as heat transformation processes opens further possibilities in view of reduction of thermodynamic losses, improvement of energetic efficiency and waste heat recovery.

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