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THERMODYNAMIC ANALYSIS AND RATING OF MODERN POWER SYSTEMS

TERMODYNAMICKÁ ANALÝZA A HODNOCENÍ MODERNÍCH ENERGETICKÝCH SYSTÉMŮ

Abstract

The special approach to thermodynamic analysis and modeling oriented onto thermodynamic analyzes has been presented. The modern power engineering systems differ mainly by goals of optimization from the process & chemical engineering ones. That is why they should be analyzed in a slightly another way. The needed features are the simplicity; conformability with real processes ran in real devices and independence on the system inner structure. Obviously the exergy method of thermodynamic analysis should be used. It is possible after some problems of its applications have been overcome. The discussion bases on the technological scheme of the so–called clean coal combustion system.

Abstrakt

Speciální přístup k termodynamické analýze a modelování je prezentován. Moderní energetické systémy se odlišují cíly optimalizace oproti systémům chemického a procesního inženýrství. Proto musí být analyzovány jinými metodami. Hlavními vlastnostmi je zjednodušení přispůsobivosti s reálnými procesy v energetických zařízeních a jejich nezávislost na vnitřní struktuře systému. Obvykle je využívána exergetická metoda termodynamické analýzy. Počáteční problémy s její aplikaci byly úspěšně vyřešeny. Diskuze je založena na technologických schématech čistých uhelných spalovacích systémů.

1. INTRODUCTION

Modern power engineering systems (PESs) become more and more complex. They do not only contain processes typical for the mechanical (power) engineering like compression, expansion in a turbine or heat exchange. They have to take into account processes typical for process & chemical engineering systems (PChESs) like chemical reactions, substance separation and so on. The chemical reactions that are to analyze in modern PESs are not only complex processes of fuel combustion, but also gasifying processes. There is often needed to foreseen emissions and to reduce some of flue gases components, e.g. the sulfur oxides SO_x. The NO_x emissions can be reduced by the appropriate run of the combustion process (regarding its thermodynamics and fluid mechanics), and the CO_2 emissions by the fundamental new system structure and use of new processes, which are typical for PChESs, in particular the absorption (the so–called CO_2–wash).

It can be stated that the analysis of PESs becomes similar to the analysis of PChESs. The statement, however, is a very apparent one. The existing, very sophisticated modeling and analysis methods and appropriate tools for PChESs can not be directly applied that easy for modern PESs. In the first case the substance as a product is the goal, in the second one, however, the energy. Although

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some requirements to standards should be fulfilled, e.g. that of emissions, the most important characteristics and demand is the power (energy) output. In the case of PChESs there are practically an infinite number of structures (or... cycles). E.g. a very small amount of a particular substance should be obtained for pharmaceutical or cosmetics branches and the appropriate huge and complex PChES should be built and operated. Hence, very flexible methods for its analysis have to be applied. In fact, the economy is not the most important factor. In opposite to them PESs are usually very typical structures (the very good known thermodynamic cycles of heat engines), even systems of modern power technologies. They can differ only by a special fuel application (e.g. biomass) or by emissions reduction utilities of particular components. In Fig. 1 the example of a simple PES (the clean coal combustion system, the so–called *Integrated Gasification Combined Cycle*, but without the CO–shift, i.e. the CO conversion process: $CO+H_2O \rightarrow CO_2+H_2$). The main goal of the system first is to achieve maximum energy output with an optimized CO_2 emission. Will be the system treated as the PChES then the goal of its operation is to produce carbon dioxide CO_2 with appropriate energy supply and recovery. The main goal of such a system, however, is to achieve maximum substance output with optimized energy consumption, Fig. 2.
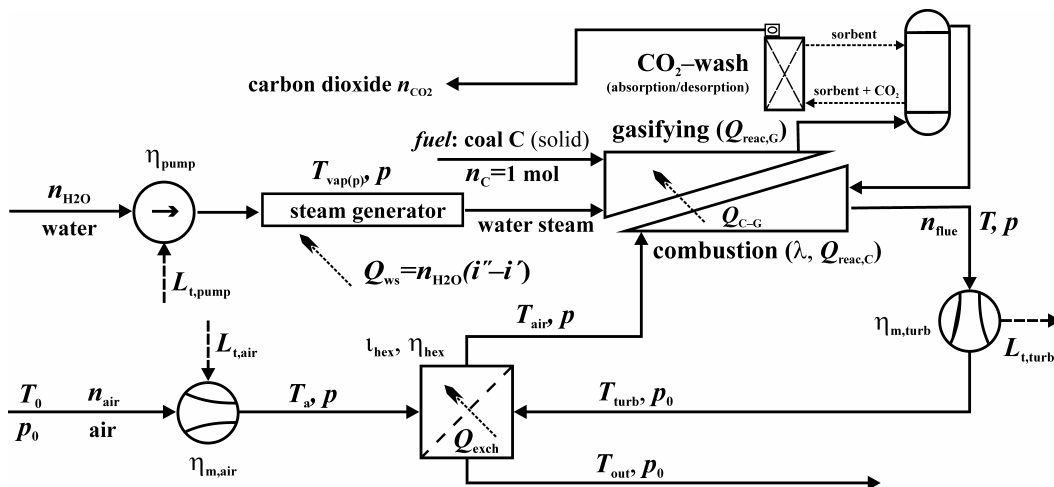

Fig. 1 The clean coal combustion system (simplified IGCC)

In Fig. 1 has been presented one of the modern power systems (simplified), which should fulfill the special requirements due to CO_2 emissions. There are three possible ways to build such CO_2 free (or CO_2 poor) power systems. One of them is the presented one, the so–called *Integrated Gasification Combined Cycle*, [1]. Besides, clean coal combustion can be achieved using the so–called *Post Combustion Cycle* where the carbon dioxide will be separated after the fundamental power processes have been done, i.e. at the end of the fuel–flue gases track. The third group of clean coal combustion is the so–called *OxyFuel Method*, in which the oxygen from the air separation device will be supplied to the combustion chamber, and after the fundamental power processes have been occurred, the water steam will be condensed and the pure CO_2 stream obtained.
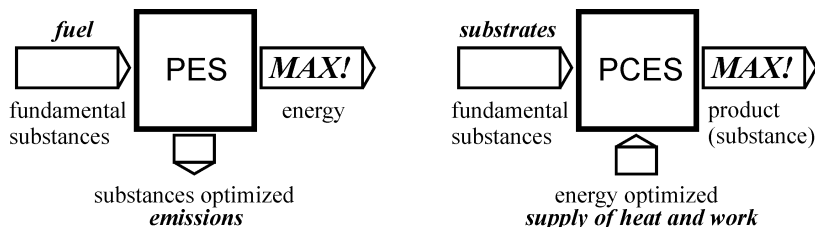

Fig. 2 Power Engineering System (PES) vs. Process & Chemical Engineering System (PChES)

There are two main ways of CO_2 utilization: either it is pumped into the underground caverns or used in the so–called CO_2–chemistry (instead of coal, oil and natural gas).

2. THERMODYNAMIC APPROACH

For usability analysis and optimization of PChESs there have been worked out some special methods, which are not strictly thermodynamic ones. E.g. the so–called *process integration* is widely used for chemical engineering systems analysis because of the very practical existing software. In fact it is applied for energy supply optimization, especially the heat recovery in particular processes of a complex system. It can be stated that is has been developed to avoid problems in advanced thermodynamic analysis in the early seventies of the last century. The problems arose by taking into account the exergy method. Appropriate approaches for typical chemical processes like chemical reactions or technological mass transfer processes (rectification, absorption, and so on) were not ready at that time, and the need for special optimization methods was very essential.

The founder of the most advanced existing optimization method for PChESs has pointed out that in fact they are thermodynamic approaches and the appropriate thermodynamic quantity is exergy, [2]. Moreover, other researchers point out the importance of the exergy analysis for improving system's operation. E.g. „Increasingly environmental issues are coming more to the fore. An approach to considering environmental issues has been to consider exergy utilization. The tools of process integration also utilize this concept. It is a widely held belief that greater integration contributes to greater control difficulties particularly because of the energy recycles causing greater interactions". And „Exergy is the useful energy that can be used in a process. It can easily be wasted by inefficient use of heat and mass transfer fluxes. The optimal thermodynamic operation of a heat exchanger for example is achieved by a small temperature difference between hot and cold streams. It was shown that major reductions in exergy loss could be achieved by optimizing the heat transfer conditions", [3]. The statement of the author of the contribution cited was that the exergy analysis is essential and indispensable. The very interesting trials to optimize the power output (and not the useful work output) using the so–called *Finite Time Thermodynamics* did not bring any useful results, e.g. [5].

Because of the major importance of the energy in the PESs (maximum output power!), the exergy analysis for these systems is a natural way of analysis and optimization. The exergy is the thermodynamic property, which is every day used by a power engineer (according to [6] or [7]: *Der Energiebegriff des Energietechnikers und Energiewirtschaftlers deckt sich nicht mit dem Energiebegriff des Physikers, sondern weitgehend stimmt mit dem Exergiebegriff überein*).

There are some misunderstandings to the exergy concept. The most popular and probably the only logical way of defining exergy is making it symmetrical to the free inner energy (Helmholtz potential or function) or to the free enthalpy (Gibbs potential or function). The energy consists of two parts: the first is the convertible one (exergy) and the second one is the inconvertible on (anergy). This statement formulated by Zoran Rant is the so–called exergy impression of the 1. Law of Thermodynamics, e.g. [8]. Thus, the exergy is the maximal part of energy (i.e. system energy or energy interaction), which in the presence of natural environment can be converted into any other form of energy (i.e. system energy or energy interaction), especially into the useful work. In addition to it, the term "maximal part" is a requisite for the reversible energy conversion.

In the subject literature there is another definition promoted very strongly, which is a very original (or personal) one and in fact does not fulfill expected aims (the discussion in [9]). Because of its rarity it can not be applied in the praxis of thermodynamic analyzes, although it marks some new problems.

The unsolved subjects in applying the energy method for analyzing complex technological systems were:
–   the lack of the universal rating quotient that would express the obvious advantages of the energy concept (irreversibility's and the natural environment), and which would be in the only logical range between zero and 1;

- no method of investigation of the influence of the particular constituent process thermodynamic efficiency onto the in the same way defined thermodynamic efficiency of the whole systems;
- the variable natural environment intensities, especially the temperature and pressure, which have to be held constant during the analysis.

These three problems have found their solutions, which do emphasize the exergy concept advantages. The third problem mentioned above is in fact not an obstacle because it allows a very important influence analysis of the variable natural environment onto the energy conversions in a system (the early discussions in [10]–[11]. The very good known experience is the operation of the automobile engine by different environmental temperatures, pressures and air humidity. The same is valid for every technological system, especially for a complex one. The first problem has been solved by taking into account the very special property of the exergy concept in processes crossing the natural environment intensities. It has been stated, that the whole exergy changes in such processes do consist of two parts: the created and the disappearing one. E.g. while supplying heat started from temperatures below the environment temperature T_0 the system exergy gets lower (disappears) and after crossing the value of T_0, it gets higher (will be created). Thus, the total system exergy change in the process consists of two parts or it is an algebraic sum of the disappearing and created one. The same refers to the heat exergy supplied. The problem solution of the process exergy rating using the universal exergy rating quotient, the so–called thermodynamic effectivity, has been worked out in the research team of professor Wolfgang Fratzscher, one of the most important founders of the exergy method of thermodynamic analysis, [12] presented later on in its matured form e.g. in [9]. The thermodynamic effectivity rating quotient allows also a solution of the second problem mentioned above.

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The exergy balance of a particular constituent process of a complex system is thus divided into created and disappearing exergy parts (or „exergies") whereby the thermal, mechanical and chemical terms are do be distinguished. E.g. during gas compression the technical (shift or useful) work is supplied; the gas pressure and temperature increase. The supplied work is exergy (its anergy equals to zero), and the increased gas exergy consists of the thermal (temperature change) and the mechanical (pressure change) parts. Hence, the useful work supplied will be the exergy disappearing in the process, and the gas thermal and mechanical exergy change the exergy created. Thus, he last ones will placed in the numerator of the appropriate process rating quotient, the thermodynamic effectivity, and the work into its denominator. If the heat exchange is present, i.e. the compression is not an adiabatic one; the exergy of heat carried away in the process will be an advantage and will be placed into the numerator. Cooling in a gas compression means a better thermodynamic efficiency, which is expressed by the thermodynamic effectivity quotient. And this is a very logical — one can say an obvious — conclusion, very good known in thermodynamics.

The process effectivity is in general

$$\varepsilon = \frac{\sum E_j^+}{\sum E_i^-}$$

whereby it results from the exergy balance in a form

$$\sum E_i^- \rightarrow \sum E_j^+ + T_0 \Delta S_{irr}$$

This equation shows that in an analyzed process exist i disappearing (superscript −) and j created (superscript +) exergies. It does not mean, however, the equality sign should be placed instead of a pointer: every term of the classical exergy balance can consist both, of the disappearing and created exergies, e.g. [8]–[9]. Joining all the disappearing and created exergies, which occur in complex systems of an unrestricted structure consisting of m constituent processes,

$$\sum \left(\sum E_i^- \right)_m \rightarrow \sum \left(\sum E_j^+ \right)_m + T_0 \Delta S_{irr}$$

the thermodynamic effectivity of this complex technological system is

$$\varepsilon_\Sigma = \frac{\sum\left(\sum E_j^+\right)_m}{\sum\left(\sum E_i^-\right)_m}$$

or

$$\varepsilon_\Sigma = \sum_m \frac{\left(\sum E_j^+\right)_m}{\sum\left(\sum E_i^-\right)_m} = \sum_m \left(\frac{\left(\sum E_j^+\right)_m}{\sum\left(\sum E_i^-\right)_m} \cdot \frac{\left(\sum E_i^-\right)_m}{\left(\sum E_i^-\right)_m}\right) = \sum_m \left(\frac{\left(\sum E_i^-\right)_m}{\sum\left(\sum E_i^-\right)_m} \cdot \frac{\left(\sum E_j^+\right)_m}{\left(\sum E_i^-\right)_m}\right) = \sum_m \gamma_m \varepsilon_m$$

whereby

$$\gamma_m = \frac{\left(\sum E_i^-\right)_m}{\sum\left(\sum E_i^-\right)_m}$$

is a mathematical weight coefficient of the in m–th process disappearing exergies.

The main disadvantage of the presented method is that the thermodynamic effectivity quotient approaches the value one, if it contains a very large number of constituent processes. E.g. for infinite process number yields

$$\lim_{m \to \infty} \varepsilon_\Sigma = 1$$

independently of the Second Law irreversibilities. Thus

$$\gamma_m \to 0$$

On a contrary, for a system consisting of only one process it will be

$$\lim_{m \to 1} \varepsilon_\Sigma = \varepsilon_m \qquad \text{or} \qquad \gamma_m \to 1$$

respectively. It is obvious that this circumstance confirms the correctness of the presented method. In [9] the way of overcoming these difficulties has been discussed. Nevertheless, the decisive advantage of the method presented above is the possibility of the complex system sensitivity investigations using the mathematical weight coefficients γ_m. Moreover, the last analysis can be made for different values of natural environment intensities, especially the temperature T_0. Computations of simplified power systems containing chemical reactions of combustion and gasifying have confirmed this statement and pointed out the correctness and usefulness of such analyses.

3. MODELING APPROACH

The modeling approach should be strictly oriented onto thermodynamic analyzes. The basics of such a method have been worked out in the research team of professor Wolfgang Fratzscher, [12]–[13], and later on developed and tested many times, e.g. [14]–[17]. The most powerful modeling approach uses dimensionless parameters of numerical values between 0 and 1 that can univocally determine the process in the praxis.

The processes that are parts of complex technological systems, especially the power engineering ones, can be divided into:

– working (or pressure changing) processes;
– equilibrium approaching processes;
– supporting (or coupling) processes.

The working processes are the most popular pressure changing processes in compressors and turbines with or without heat exchange with surroundings (cooling by compression, heating up by expansion). The equilibrium approaching processes are all heat and substance exchange processes in heat exchangers and absorbers (desorbers) and chemical reactions. To the last group belong such processes like simple water vaporization to obtain water steam (e.g. for chemical reactions), throttling, etc.

After detailed analyzes have been made there could be stated that for univocal determining of pressure changing processes in compressors and turbines the obviously known polytropic efficiency is very useful. With its help the main thermodynamic parameters of the most important working processes can be calculated: the useful (i.e. technical or shift) work, heat exchanged and

irreversibilities. There are known polytropic efficiency experimental values for the typical pressure changing processes, e.g. [13]. For compression processes it is defined as

$$\eta_{m,com} = \frac{l_{t,m}}{l_{t,+}} = \frac{\int vdp}{\int vdp + q_{irr}} = \frac{m}{m-1} \frac{k-1}{k}$$

and for expansion ones (in a turbine, detander, which is an expansion machine working in temperatures $T<T_0$, and so on) as

$$\eta_{m,exp} = \frac{l_{t,-}}{l_{t,m}} = \frac{\int vdp + q_{irr}}{\int vdp} = \frac{m-1}{m} \frac{k}{k-1}$$

Numeric values of these quotients lie always between zero (no process) and one (a perfect, reversible adiabatic process). Irreversible heat losses q_{irr} due to the irreversible entropy production according to the Second Law ($q_{irr}=T·\Delta s_{irr}$) are not heat losses because of the non–adiabatic apparatus characteristics; they are the so–called friction (or throttling) losses, [18]–[19]. The above dimensionless parameter can be also applied to the water–cooled compressor units, while the water/gas heat exchange will be assumed to occur in a separate cooling device (heat exchanger). In a case of cylinder cooling, the appropriate polytropic efficiency is also applicable to get the exponent m, thus the heat exchanged with surroundings (more details in [12]).

It should be mentioned here that the problem of polytropic efficiency is very rarely discussed in the conventional thermodynamics monographs. One of the positive exceptions is the text–book by the late professor Tadeusz Haupt, where the problem is very carefully explained, [20]. The appropriate thermodynamics research were also led at the AGH – University of Science and Technology by the late professor Roman Woźniacki. Very interesting and complete analysis of the polytropic efficiency for compression processes has been presented in the monograph [21].

Knowing the η_m value the polytropic exponent m can be determined. The adiabatic exponent is κ (or as a mean value: k), thus

$$m = \frac{1}{1 - \frac{k-1}{k} \cdot \eta_{m,com}} \qquad \text{and} \qquad m = \frac{1}{1 - \frac{k-1}{k} \cdot \frac{1}{\eta_{m,exp}}}$$

for a compression and expansion process, respectively. In the special case of adiabatic ones, which are also called the pseudo–polytropic processes, the appropriate useful (technical) work can be determined as

$$l_{t,com} = \frac{\Delta i}{\eta_{m,com}} \qquad \text{and} \qquad l_{t,exp} = \eta_{m,exp}\Delta i$$

The transfer processes will be detailed presented for the case of heat exchange (subscript *hex*) one. The characteristic dimensionless coefficient here, suitable for modeling purposes, is the so–called process intensity ι, [12]. It takes into account how does the real process differ from the perfect process, in which the equilibrium could be reached. Another words, it gives an information about the process kinetics in an indirect manner.

The intensity dimensionless coefficient for heat transfer (exchange) processes is defined as

$$\iota_{hex} = \frac{Q}{Q^*} \qquad \qquad \text{or} \qquad \qquad \iota_{hex} = \frac{Q}{Q_\infty} \qquad\qquad (01)$$

where Q is the heat transferred (exchanged), Q^* the heat transferred (exchanged) until the equilibrium has been reached, and Q_∞ is the same as Q^*, but written down as the heat exchanged on the infinitely large apparatus. It can be generally distiguished between cocurrent and counter–current. The last one is the usually applied media guidance, Fig. 3.

Additionaly one more dimensionsless coefficient can be formulated that takes into account heat losses to the surroundings. Basicaly they are very law, but they can be expressed by the energy (or thermal) efficiency, just like the quotient

$$\eta_{\text{hex}} = \frac{Q_{\text{abs}}}{Q_{\text{des}}} = \frac{Q_C}{Q_H}$$

is, where Q_{abs} is the heat supplied from the hot (subscript H) medium, and Q_{des} the heat absorbed by the cold (subscript C) one. Usually the temperatures (or in general the parameters) at the start of a process are known, depending on system analyzed.
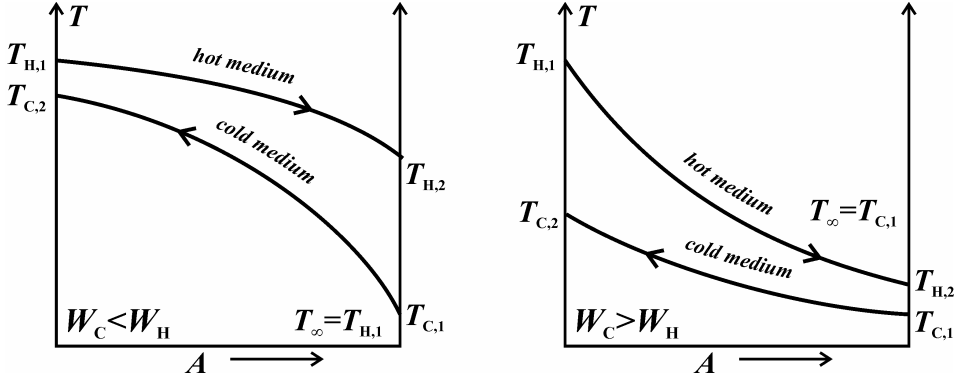

Fig 3 Heat exchange in a counter–current flow: characteristic cases $W_C < W_H$ and $W_C > W_H$

In Fig. 3 the equilibrium temperatures T_∞ have been shown for the both cases. With the given process intensity the heat supplied from the hot medium Q_H will be determined. For the water value W_C (German: *Wasserwert*), which is the product of the medium quantity (mass M or substance n) and the specific heat c_p (or $\bar{c}_p$, respectively) greater than W_H of the hot medium (Fig. 3, left), the process intensity, Equation (01) will be to

$$t_{\text{hex}} = \frac{c_{p,C}\left(T_{C,2}^{\text{adiabat}} - T_{C,1}\right)}{c_{p,C}\left(T_\infty - T_{C,1}\right)} = \frac{T_{C,2}^{\text{adiabat}} - T_{C,1}}{T_{H,1} - T_{C,1}} \tag{02}$$

where from

$$T_{C,2}^{\text{adiabat}} = T_{C,1} + \left(T_{H,1} - T_{C,1}\right) \cdot t_{\text{hex}}$$

But from the energy balance for the lack of heat losses (in the sense of the First Law),

$$n_C \cdot \bar{c}_{p,C}\left(T_{C,2}^{\text{adiabat}} - T_{C,1}\right) = n_H \cdot \bar{c}_{p,H}\left(T_{H,1} - T_{H,2}\right)$$

yields

$$T_{H,2} = T_{H,1} - \frac{n_C \cdot \bar{c}_{p,C}}{n_H \cdot \bar{c}_{p,C}}\left(T_{C,2}^{\text{adiabat}} - T_{C,1}\right) \tag{03}$$

and the heat carried away from the hot medium is

$$Q_{\text{des}} = n_H \cdot \bar{c}_{p,H}\left(T_{H,1} - T_{H,2}\right)$$

Taking the thermal efficiency into account the heat absorbed byu the cold medium equals to

$$Q_C = \eta_{\text{hex}}Q_H = n_C \cdot \bar{c}_{p,C}\left(T_{C,2} - T_{C,1}\right)$$

where from the end temperature of the cold medium can be expressed by the formula

$$T_{C,2} = T_{C,1} + \eta_{\text{hex}} \frac{n_H \cdot \bar{c}_{p,H}}{n_C \cdot \bar{c}_{p,C}}\left(T_{H,1} - T_{H,2}\right) \tag{04}$$

or using Equation (03)

$$T_{C,2} = T_{C,1} + \eta_{\text{hex}}\left(T_{C,2}^{\text{adiabat}} - T_{C,1}\right) \tag{05}$$

and with Equation (02)

$$T_{C,2} = T_{C,1} + \eta_{\text{hex}}\left(T_{H,1} - T_{C,1}\right) \cdot t_{\text{hex}}$$

Applying Equations (04)–(05) it becomes

$$T_{H,2} = T_{H,1} - \frac{n_C \cdot \bar{c}_{p,C}}{n_H \cdot \bar{c}_{p,H}}\left(T_{H,1} - T_{C,1}\right) \cdot t_{\text{hex}}$$

The equation obtained is the same, as Equation (03), if only no heat losses to the surroundings exist, i.e. $\eta_{hex}=1$. The case $W_C < W_H$ has been already analyzed in a simple gas turbine model for the heat regeneration process, e.g. [22]–[25]. For the another case, i.e. for $\underline{W_C > W_H}$ (Fig. 3, right), is the process intensity coefficient

$$t_{hex} = \frac{T_{H,1} - T_{H,2}}{T_{H,1} - T_\infty} = \frac{T_{H,1} - T_{H,2}}{T_{H,1} - T_{C,1}}$$

Furthermore, for the adiabatic (no heat losses to the surroundings: $\eta_{hex}=1$) follows

$$T_{H,2} = T_{H,1} - \left(T_{H,2} - T_{C,1}\right) \cdot t_{hex}$$

$$n_C \cdot \bar{c}_{p,C}\left(T_{C,2}^{adiabat} - T_{C,1}\right) = n_H \cdot \bar{c}_{p,H}\left(T_{H,1} - T_{H,2}\right)$$

$$T_{C,2}^{adiabat} = T_{C,1} + \frac{n_H \cdot \bar{c}_{p,H}}{n_C \cdot \bar{c}_{p,C}}\left(T_{H,1} - T_{H,2}\right) \tag{06}$$

and taking into account heat losses ($\eta_{hex} \neq 1$), it will be

$$Q_{abs} = Q_C = \eta_{hex}Q_H = n_C \cdot \bar{c}_{p,C}\left(T_{C,2} - T_{C,1}\right) = \eta_{hex} n_C \cdot \bar{c}_{p,C}\left(T_{C,2}^{adiabat} - T_{C,1}\right)$$

$$n_C \cdot \bar{c}_{p,C}\left(T_{C,2} - T_{C,1}\right) = \eta_{hex} n_H \cdot \bar{c}_{p,H}\left(T_{H,1} - T_{C,1}\right)$$

$$T_{C,2} = T_{C,1} + \eta_{hex}\left(T_{C,2}^{adiabat} - T_{C,1}\right) = T_{C,1} + \eta_{hex}\frac{n_H \cdot \bar{c}_{p,H}}{n_C \cdot \bar{c}_{p,C}}\left(T_{H,1} - T_{H,2}\right)$$

$$T_{C,2} = T_{C,1} + \eta_{hex}\frac{n_H \cdot \bar{c}_{p,H}}{n_C \cdot \bar{c}_{p,C}}\left(T_{H,1} - T_{C,1}\right) \cdot t_{hex}$$

The last equation is the same, as Equation (06), if only heat losses does not exist ($\eta_{hex}=1$). The exergy analysis of such a heat exchange has been presented e.g. in [26] and [27].

The very similiar approach can be applied to the mass transfer (exchange) porcesses, although certain simplifications are needed.

Finally, the combustion process will be determined by the reaction intensity parameter, which can be calculated as a quotient

$$t_{reac} = \frac{\xi}{\xi^*} \tag{07}$$

whereby ξ is an extent of a chemical reaction (according to [29], or *reactions coordinate* according to [30]; in Polish: *liczba postępu reakcji*, [28]). The superscript asterisk means the state of equilibrium. Numerical values of ξ vary from zero (no reaction) to $\xi=\xi*$ (equilibrium). Józef Szarawara, who also defined such a parameter ([28], page 405) calls it the thermodynamic (theoretical) yield (Polish: *termodynamiczna teoretyczna wydajność reakcji*) and marks it symbolically by the Greek letter η. The extent of a chemical reaction in a differential form is defined by

$$d\xi = \frac{dn_A}{|\nu_A|} = \frac{dn_B}{|\nu_B|} = \frac{dn_C}{|\nu_C|} = \dots$$

and it can be written down in an integral form as

$$\xi = \frac{\Delta n_A}{|\nu_A|} = \frac{\Delta n_B}{|\nu_B|} = \frac{\Delta n_C}{|\nu_C|} = \dots$$

or

$$n_{substrate} = n_{substrate,start} - |\nu_{substrate}| \cdot \xi = n_{substrate,0} - |\nu_{substrate}| \cdot \xi \tag{08}$$

for parent substances (substrates), and

$$n_{product} = n_{product,start} + |\nu_{product}| \cdot \xi = n_{product,0} + |\nu_{product}| \cdot \xi \tag{09}$$

or

$$n_{product} = |\nu_{product}| \cdot \xi$$

for products obtained from a given chemical reaction. The last relation is valid, if no reacting substance that has been earlier marked as a reaction product does occur in the reaction mixture at the start of a process.

By presence of non–reactive substances in a process, the inerts, additionally yields

$$n_{inert} = n_{inert,start} = n_{inert,0}$$

Is then the reaction intensity parameter ι_{reac} equal to zero, there is no process. Is it, however, equal to one, the equilibrium state will be reached. Equations (08)–(09) can be written down according to the definition equation (07) as follows

$$n_{substrate} = n_{substrate,start} - \left| \nu_{substrate} \right| \cdot \iota_{reac} \cdot \xi^* = n_{substrate,0} - \left| \nu_{substrate} \right| \cdot \iota_{reac} \cdot \xi^*$$

and

$$n_{product} = n_{product,start} + \left| \nu_{product} \right| \cdot \iota_{reac} \cdot \xi^* = n_{product,0} + \left| \nu_{product} \right| \cdot \iota_{reac} \cdot \xi^*$$

After computing the value of ξ^* in an equilibrium state, the "real" extent of reaction can be determines and the appropriate quantities of reactants in a resulting reacting mixture.

3.1. An Overall Computing Example for the Reaction Intensity Parameter

It will be analyzed the so–called water–gas–shift reaction

$$CO + H_2O = CO_2 + H_2$$
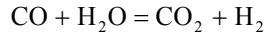
that occurs at the temperature 1100 K. The intensity parameter value will be chosen to be $\iota_{reac}=0.9$, which is up to the process kinetics. The composition of the reacting mixture at the end of the process should be determined (Example 15.6 from [29]).

For the temperature 1100 K the reaction equilibrium constant equals to $K=1$, and there is

$$K = \frac{x_{H2}^* \cdot x_{CO2}^*}{x_{CO}^* \cdot x_{H2O}^*}$$

Are there at the start of the process 1 kmol H_2O and 1 kmol CO (the stoichiometric mixture), then the amounts of reactants in equilibrium can be determined with help of the extent of reaction, i.e.

$$n_{CO} = n_{CO,start} - \xi = 1 - \xi \qquad n_{H2O} = n_{H2O,start} - \xi = 1 - \xi \qquad n_{H2} = n_{H2,start} + \xi = \xi \qquad n_{CO} = n_{CO,start} + \xi = \xi$$

and

$$n = \sum n_i = n_{CO} + n_{H2O} + n_{H2} + n_{CO2} = \sum n_{i,start} + \xi \sum \nu_i = 1 - \xi + 1 - \xi + \xi + \xi = 2$$

where from

$$x_{CO} = \frac{n_{CO}}{n} = \frac{1 - \xi}{2} \qquad\qquad\qquad x_{H2O} = \frac{n_{H2O}}{n} = \frac{1 - \xi}{2} \qquad\qquad (10)$$

$$x_{H2} = \frac{n_{H2}}{n} = \frac{\xi}{2} \qquad\qquad\qquad x_{CO2} = \frac{n_{CO2}}{n} = \frac{\xi}{2} \qquad\qquad (11)$$

It is obvious, that in the equilibrium state yields $\xi = \xi^*$. It follows then

$$K = \frac{x_{H2}^* \cdot x_{CO2}^*}{x_{CO}^* \cdot x_{H2O}^*} = \frac{\left(\xi^* \right)^2}{\left(1 - \xi^* \right)^2} = 1 \qquad\qquad (12)$$

and as a result

$$\xi^* = 0.5$$

But according to equation (07) there is

$$\xi = \iota_{reac} \cdot \xi^* = 0.9 \cdot 0.5 = 0.45$$

and the mole fractions of reactants in the „real" reacting mixture at the end state of the process are up to the given value of the reaction intensity parameter ι_{reac}, taking into account process kinetics. With equations (10)–(11) they equal to

$$x_{CO} = \frac{n_{CO}}{n} = \frac{1 - \xi}{2} = \frac{1 - 0.45}{2} = 0.275 \qquad x_{H2O} = \frac{n_{H2O}}{n} = \frac{1 - \xi}{2} = \frac{1 - 0.45}{2} = 0.275$$

$$x_{H2} = \frac{n_{H2}}{n} = \frac{\xi}{2} = \frac{0.45}{2} = 0.225 \qquad\qquad x_{CO2} = \frac{n_{CO2}}{n} = \frac{\xi}{2} = \frac{0.45}{2} = 0.225$$

In the equilibrium state these fractions were equal to

$$x_{CO}^{*} = \frac{n_{CO}^{*}}{n^{*}} = \frac{1-\xi^{*}}{2} = \frac{1-0.5}{2} = 0.250 \qquad\qquad x_{H2O}^{*} = \frac{n_{H2O}^{*}}{n^{*}} = \frac{1-\xi^{*}}{2} = \frac{1-0.5}{2} = 0.250$$

$$x_{H2}^{*} = \frac{n_{H2}^{*}}{n^{*}} = \frac{\xi^{*}}{2} = \frac{0.5}{2} = 0.250 \qquad\qquad x_{CO2}^{*} = \frac{n_{CO2}^{*}}{n^{*}} = \frac{\xi^{*}}{2} = \frac{0.5}{2} = 0.250$$

The above water–gas–shift reaction, as an equimolar one ($n=n^{*}$), gives the same already computed values for an arbitrary chosen process pressure. At the temperature e.g. $T=1650$ K, the molar fractions, however, are different. The appropriate equilibrium constant equals to $K=0.316$, and according to the equation (12) the extent of the reaction at equilibrium will be $\xi^{*}=0.36$. Hence, in the equilibrium state there is

$$x_{CO}^{*} = 0.320 \qquad\qquad x_{H2O}^{*} = 0.320 \qquad\qquad x_{H2}^{*} = 0.180 \qquad\qquad x_{CO2}^{*} = 0.180$$

and in the given „real" process, where $\xi = t_{reac}\cdot\xi^{*} = 0.9\cdot0.36 = 0.324$ yields:

$$x_{CO} = 0.338 \qquad\qquad x_{H2O} = 0.338 \qquad\qquad x_{H2} = 0.162 \qquad\qquad x_{CO2} = 0.162$$

The method allows taking into account the special behavior of processes that do not reach their equilibrium state because of their kinetics. Are there inert substances in the reacting mixture, just like nitrogen (from the air), the amount of the last substance equals to 2 kmol for the stoichiometric water–gas–shift reaction, the equation (12) will be solved in the same manner and the resulting value of the extent of the reaction will be either equal to $\xi^{*}=0.5$ (resp. $\xi^{*}=0.36$). The nitrogen molar fraction will be the same at the start of a process and at its end (equimolarity). The computed values of molar fractions will be then by assumed amount of 2 kmol nitrogen N_2 (and 1 kmol CO or/and 1 kmol H_2O) two times less.

In the case, the reacting mixture at the start is not a stoichiometric one; the computing procedure should be made in a little bit different way. Are there the 1 kmol H_2O and 2 kmol CO, i.e.

$$n_{H2O,start} = 1\,\text{kmol} \qquad\qquad \text{and} \qquad\qquad n_{CO,start} = 2\,\text{kmol}$$

taken to the reaction process, there are then in total 3 kmol at the start, equations (09)–(10) will be to

$$x_{CO} = \frac{n_{CO}}{n} = \frac{1-\xi}{3} \quad x_{H2O} = \frac{n_{H2O}}{n} = \frac{2-\xi}{3} \qquad x_{H2} = \frac{n_{H2}}{n} = \frac{\xi}{3} \qquad x_{CO2} = \frac{n_{CO2}}{n} = \frac{\xi}{3} \qquad (13)$$

and the equation (12) for $T=1100$ K will be to

$$K = \frac{x_{H2}^{*}\cdot x_{CO2}^{*}}{x_{CO}^{*}\cdot x_{H2O}^{*}} = \frac{\left(\xi^{*}\right)^2}{\left(1-\xi^{*}\right)\left(2-\xi^{*}\right)} = 1$$

The solution for the process temperature $T=1100$ K gives $\xi^{*}=0{,}667$. Taking into account the process intensity it follows $\xi = t_{reac}\cdot\xi^{*} = 0.9\cdot0.667 = 0.6003$, and with equations (13)

$$x_{CO} = 0.1332 \qquad\qquad x_{H2O} = 0.4666 \qquad\qquad x_{H2} = 0.2001 \qquad\qquad x_{CO2} = 0.2001$$

whereby

$$x_{CO}^{*} = 0.1110 \qquad\qquad x_{H2O}^{*} = 0.4443 \qquad\qquad x_{H2}^{*} = 0.2223 \qquad\qquad x_{CO2}^{*} = 0.2223$$

Very similar should be proceeded in the case, in which there are some reaction products in the reacting mixture at the start of the process. Are there for example 1 kmol H_2O, 1 kmol CO and 1 kmol CO_2 at the start, then in an every moment of the process there will be also

$$x_{CO} = \frac{n_{CO}}{n} = \frac{1-\xi}{3} \quad x_{H2O} = \frac{n_{H2O}}{n} = \frac{1-\xi}{3} \qquad x_{H2} = \frac{n_{H2}}{n} = \frac{\xi}{3} \qquad x_{CO2} = \frac{n_{CO2}}{n} = \frac{1+\xi}{3}$$

and the equation (12) will be to

$$K = \frac{x_{H2}^{*}\cdot x_{CO2}^{*}}{x_{CO}^{*}\cdot x_{H2O}^{*}} = \frac{\left(1-\xi^{*}\right)\cdot\xi^{*}}{\left(1-\xi^{*}\right)\cdot\left(2-\xi^{*}\right)} = 1$$

The solution gives the value of $\xi^{*}=0.333$, and hence $\xi = 0.9\cdot0.333 = 0.2997$. Using this result there will be at the end

$$x_{CO} = 0.2334 \qquad x_{H2O} = 0.2334 \qquad x_{H2} = 0.0999 \qquad x_{CO2} = 0.4332$$

or in the case of full equilibrium

$$x_{CO}^* = 0.2223 \qquad x_{H2O}^* = 0.2223 \qquad x_{H2}^* = 0.1110 \qquad x_{CO2}^* = 0.4443$$

Herewith all the typical cases of simple chemical reactions could be discussed. Another dimensionless parameter for the chemical reaction determining in a model is the appropriate thermal efficiency, which can be formulated in the same manner, just like it was by the heat exchanging processes. This thermal efficiency refers to the heat absorbed or created in a given chemical process.

4. CONCLUSIONS

The modern power technologies become similar to the complex process & chemical engineering systems. The goal of their operation, however, is somehow different. Thus, optimization procedures developed for the PChESs can not be applied directly. They need to be adopted, or a definitely different approach should be worked out. In the present paper a modeling oriented onto pure thermodynamic analyzes has been introduced. Many tests have proved its advantages. Thermodynamic analyzes of complex power systems, but also of process & chemical ones, can be made in a very convenient way. Using dimensionless parameters determining each process appropriate thermodynamic statements can be made. The parameters refer very strong to realized processes. Not only working (pressure changing) and equilibrium approaching processes can be univocally described by them. The supporting processes can be also determined by dimensionless parameters, e.g. the water vaporization can be characterized by the parameter equal to 1, if there are no heat losses to the surroundings. The same can be made with all coupling processes, i.e. for cases where between two main unit processes (operations) the energy or substance will be transferred. The value 1 will refer two the losses free couplings.

There are two tasks to make the presented modeling method mature for practical thermodynamic analyzes. The first one is an exact analysis of the dimensionless parameters for the important processes that can be here treated as the unit operation as they are known from the process & chemical engineering. As a result general indications for their use should be formulated. The second task, however, is the practical use of the whole method of modeling and thermodynamic analysis. It means an appropriate programming language and the overall model building. It can be made just like the known good programming tools for optimizing process & chemical engineering systems, which allows on the base of the given system flow chart appropriate model creation. The task, however, is more aimed for modeling specialists.

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