Holistic Evaluation of Decarbonisation Pathways of Energy-intensive Industries Based on Exergy Analysis

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ABSTRACT

The decarbonisation of the industrial sector plays a crucial role for a successful energy transition. The transformation associated with the decarbonisation is very costly and complex and many of the production processes and process routes currently in use will have to be partially or entirely replaced in order to be able to reduce their CO_2 emissions. This raises the questions of how the significant reduction of CO_2 emissions resulting from the decarbonisation will affect the general use of resources to produce a certain product, and how this decarbonised production process will perform in terms of energy consumption and emissions. In this work, these questions will be addressed by applying the exergetic analysis for current state of the art and future decarbonised production processes. The resource use is evaluated with the help of the thermodynamic quantity exergy, in which both energetic and material components of the input materials used in industrial production processes are taken into account. To evaluate the resources used, the exergetic analysis is applied to industrial production processes by balancing the incoming and outgoing energy and material flows. Subsequently, the exergy flows are used to evaluate the thermodynamic efficiency of the energy and material conversion and thus of the resources used by determining the exergetic efficiency. By modelling a thermodynamically idealized reference process for the manufacture of a product, the minimum exergy requirement for its production can be determined. Based on the calculated resource efficiency, different production processes can be compared and conclusions about material and process changes due to the decarbonisation can be derived, including their theoretical potential for improvement.

Introduction

An energy transition towards a CO_2 neutral society is currently taking place. To reach the reduction targets as agreed in the Paris agreement the global CO_2 emissions from all sectors must be reduced significantly. The energy sector, the transport and industrial sectors play a decisive role. In Germany, industry in 2019 had a final energy consumption of approximately 700 TWh, corresponding to a share of 28% of total final energy consumption (AG Energiebilanzen e.V. 2020). Thus, the decarbonisation of the industrial sector has a crucial role to play in a successful energy transition.

The decarbonisation of industrial sectors is connected with major challenges. On the one hand, energy and material infrastructures have been built for their operation, and on the other hand, billions have been invested in existing production sites and plants, some of which also operate in cooperation with neighbouring sites. The decarbonisation of existing production processes and entire production sites through the conversion of current conventional processes to CO_2 neutral, the so-called "green" production processes, is usually linked to major certainties and high investments in new equipment.

In most cases, decarbonisation of industrial processes leads to a significant reduction of the direct CO_2 emissions. However, the alternative CO_2-neutral process does not necessarily have a better environmental performance, and the consumption of resources used could even increase as a result and would thus be worse than the conventional process from an environmental point of view.

To evaluate production processes holistically and from an environmental point of view, not only their CO_2 emissions but also the resources used in the process must be identified. Subsequently, the green or decarbonised processes can be compared with the conventional ones in order to be able to make a statement about their resource efficiency. These resource savings can then be related to the avoided CO_2 emissions in order to be able to compare and evaluate them across processes and sectors.

Thermodynamic fundamentals

The industrial sector is characterized by a large number of different production sites where products are manufactured for businesses and end consumers, such as steel, paper or glass. Raw materials and energy of all kinds are used to manufacture these products. The production processes cause energy and process related CO_2 emissions, which are released into the atmosphere and thus have an impact on our environment.

For the technical evaluation of production processes and to determine CO_2 emissions, the balance of energy and mass flows are calculated. The most important and significant indicator is usually energy intensity, in which the energy used per production quantity is calculated.

Another aspect is material efficiency, which is an indicator for the conversion of the raw materials used to the required product and reflects the ratio of the manufactured quantity of the product to the amount of raw materials used.

The calculation of energy intensity or energy efficiency is made possible by using the first law of thermodynamics, which describes the balancing of energy in a system or its conservation.

Another thermodynamic parameter for the technical evaluation of systems is the exergy. The exergy consists of the part of the energy that can be converted into work. Thus, it reflects the valuable and usable part of the energy and is an indicator for the quality or the grade of the energy. Exergy combines the first and second laws of thermodynamics. The latter describes the irreversibility of a real energy conversion, in which it is only partially convertible into other forms of energy. (Lucas 2008)

The concept of exergy is mainly used in energy conversion and power generation to describe the work capability or the maximum gain able work that can be obtained from a substance or energy carrier as a result of a reversible process. The exergy corresponds to the theoretically obtainable work when a material flow is reversibly brought into equilibrium with the environment. (Radgen 1996)

In contrast to energy, exergy is not bound by any law of conservation. This means that exergy can be destroyed. In the so-called exergy destruction, exergy is converted into anergy. Anergy describes the part of the energy that can not be used further or converted into work. Anergy is created as a result of irreversible processes such as heat transfer at different temperatures, friction and chemical reactions. The greater the difference or driving force of the process, the more exergy is destroyed. The exergy destruction is an indicator of the quality of a conversion process and quantifies its inefficiencies and irreversibility. (Meyer und Schiffner 1986)

Figure 1 shows the breakdown of energy and exergy graphically. Energy is divided into the two components exergy and anergy. There are forms of energy that consist of pure exergy and can thus be completely converted into work. These include, for example, electrical or mechanical energy. Exergy is further subdivided into a thermomechanical and a chemical component. (Radgen 1996)

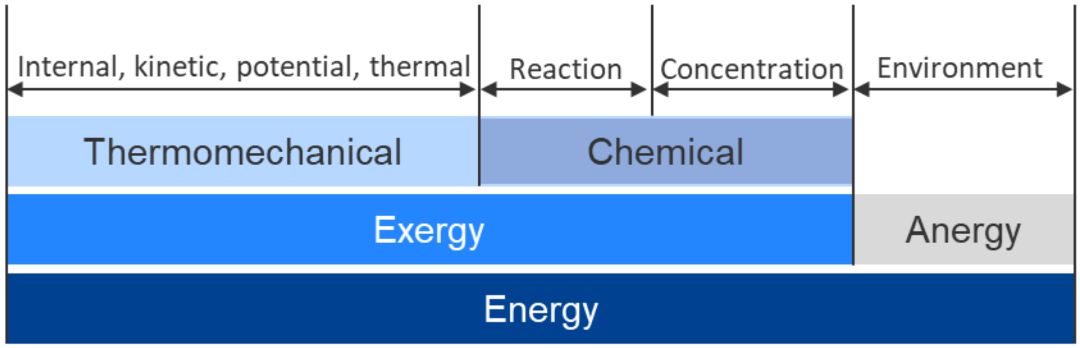

Figure 1: Composition of exergy (Own figure)

Thermochemical Exergy

As presented in formula (1), the thermomechanical exergy consists of the internal, thermal, kinetic and potential exergy. The kinetic and potential exergy can be neglected in most cases in the scope of industrial production processes. Thus, the thermomechanical exergy is mainly determined by the first two terms, which represent the internal and thermal exergy. This means that the thermomechanical exergy, neglecting the kinetic and potential exergy, depends directly on the enthalpy and entropy, which in turn are dependent on pressure and temperature.

$$ex_{thermochem} = \underbrace{(h - h_u) - T_u(s - s_u)}_{ex_{internal} + ex_{thermal}} + \underbrace{\frac{1}{2}\,(c_2^2 - c_1^2)}_{ex_{kinetic}} + \underbrace{g * (z_2 - z_1)}_{ex_{potential}} \qquad (1)$$

Chemical Exergy

The chemical exergy of a substance describes the minimum work required to produce a component through reversible reactions from substances in the environment. This parameter can be used to take into account the upstream chains of the considered systems and processes by balancing the theoretical work required to produce the substances used and thus the resources used (Szargut et al. 1988; Radgen 1996).The chemical exergy is constituted by the two parts of the reaction exergy and the concentration exergy, as presented in formula 2. (Rivero and Garfias 2006)

$$ex_{chemical} = ex_{chem,reaction} + ex_{chem,concentration} \qquad (2)$$

The reaction exergy results from the chemical reactions that must take place in order to produce the desired component from the reference substances in the environment. Thus, the reaction exergy of a compound consists of the individual chemical exergies of the components and the reaction exergy or Gibbs exergy ΔG_f released during the reaction.

$$ex_{chem,reaction} = \sum_{el} n_{el} * ex_{el} + \Delta G_f \tag{3}$$

The concentration exergy of a substance is a function of its occurrence in the environment and corresponds to the exergy that theoretically has to be applied in order to extract the requested component from the compound present in the environment with an ideal process. The concentration exergy is determined according to a rarity criterion, so that the rarer the occurrence of the substance in the environment, i.e. in the atmosphere, the sea or the earth's crust, the higher the exergy for substances and elements.

$$ex_{chem,concentration} = -R * T * \ln\left(\frac{x_{el}}{x_{ges}}\right) \tag{4}$$

In Szargut et al. 1988 the chemical exergies of almost all substances on earth were calculated and listed. In Meester et al. 2006 and Rivero und Garfias 2006 this list was extended so that the chemical exergy has been determined and listed for almost every element and compound on earth.

Method

The assessment of resource use in industrial production processes is based on exergetic analysis. The exergetic analysis is usually used to assess the efficiency of energy conversions, e.g., for the conversion of chemically bound energy into electrical energy. The efficiency of the conversion is determined by the losses that occur during this energy conversion, or by the resulting exergy destruction.

Another field of application of exergetic analysis is the balancing or assessment of production processes. Here, similar to the assessment of an energy conversion, a production process for the manufacture of a certain product can be thermodynamically assessed. The applicability of the exergetic analysis for industrial production processes has already been demonstrated many times, examples for exergetic analysis of energy-intensive production processes can be found in Luis und van der Bruggen 2014.

Application of exergetic analysis to production processes

For the exergetic analysis of a production process, the first required step is to define the system boundary of the process to be analysed. For this purpose, the selection of the entire production site is suitable in order to capture and assess the production process holistically. In addition, the sub-system boundaries can also be set around certain production steps or individual processes in order to analyze them specifically and to obtain results regarding their efficiency.

For the exergetic analysis, all mass and energy flows entering and leaving the defined system boundary are taken into account. (Gonzalez Hernandez et al. 2018, Volta 2014). For these flows, their exergetic value is calculated on the basis of the thermodynamic principles presented in the section "Thermodynamic fundamentals" of this paper.

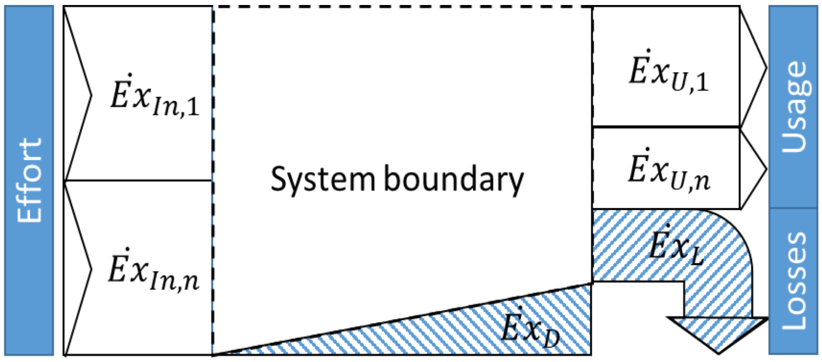

Figure 2: Balance of the exergy flows within a defined system boundary (Own figure)

The incoming exergy flows $\dot{E}x_{In}$ are defined as effort. This includes all material and energy flows that are used to manufacture the desired product. These can be, for example, the raw materials and energy carriers, but also the construction materials of the equipment and machines used in the production process.

The usage of industrial production processes $\dot{E}x_U$ is defined by the manufactured product. In addition, by-products and waste products can be defined as usage if they can be reused within the site or across sites as raw materials or energy carriers.

Produced substances and waste products that have no further use are defined as exergy loss $\dot{E}x_L$. This includes all materials that have to be removed or cannot be used further, such as the exhaust air or waste and exhaust gas streams that leaves the production after the last heat recovery or filtering.

The exergy that is destroyed within the conversion steps due to irreversible processes is defined as exergy destruction $\dot{E}x_D$. It can be calculated either by the entropy generated during a process or by balancing the incoming and outgoing exergy flows, as shown in the following formula:

$$\dot{E}x_D = \sum_n \dot{E}x_{In,n} - \sum_n \dot{E}x_{U,n} - \sum_n \dot{E}x_{L,n} \tag{5}$$

<u>Exergetic efficiency as an indicator of energy and material efficiency</u>

The efficiency of a manufacturing process can be quantified by determining the efficiency. In this work, a ratio of the sum of all usable exergy flows $\dot{E}x_{useful}$ and the sum of all incoming exergy flows $\dot{E}x_{in}$ is used to calculate the exergetic efficiency, see formula (6).

$$\eta_{ex} = \frac{\sum \dot{E}x_{useful}}{\sum \dot{E}x_{in}} \tag{6}$$

Typically, the usage of the final product consists of its chemical exergy since it is usually available at the end of the production process and leaving the system boundary of the site at ambient conditions ($T = 298.15$ K, $p = 1$ bar) and thus has no thermomechanical exergy embedded. Therefore, the exergy of the final product consists of the chemically bound reaction exergy and the extraction exergy of the contained raw materials, as illustrated in formula (2). If by-products, energy carriers or waste heat are produced in addition to the main product, these can be defined as additional benefits if they are further used at other sites. This would lead to an increase in usable exergy and thus have a positive effect on the exergetic efficiency of a site.

Resource efficiency

Gonzalez Hernandez et al. 2018 defined exergetic efficiency was also as resource efficiency. They describe how the value of exergy can be used to describe energy efficiency and material efficiency by one single metric. In Hernandez und Cullen 2019, different metrics for assessing resource efficiency were analyzed and evaluated. As a result, they identified exergy-based resource efficiency as the most relevant and robust metric. By balancing the raw materials and energy sources used by their exergetic value, the resources used can be put in relation to the product manufactured and thus a thermodynamic statement can be made about the "degree of quality" or efficiency of the considered production process. By balancing the material and energy flows via the exergetic analysis, both energy and material efficiency are taken into consideration.

In order to analyse an industrial production process, the system mass, energy and exergy balanced must be derived. For this purpose, the individual core processes occurring in the manufacture of the product are identified and the incoming and outgoing material and energy flows are listed, see Figure 3.

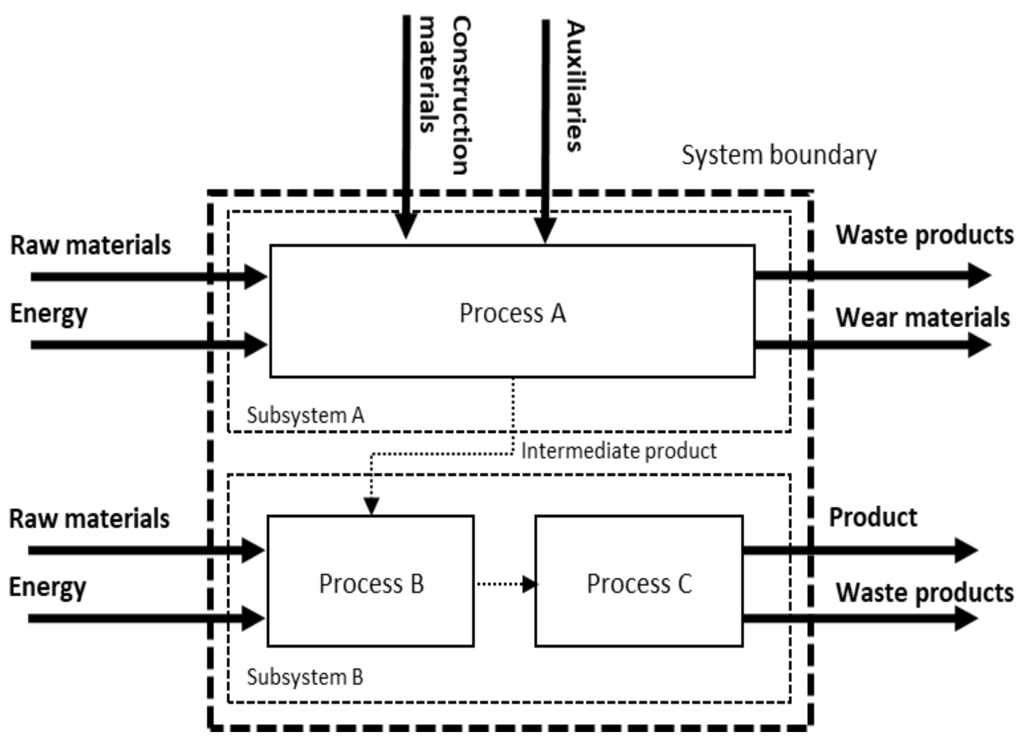

Figure 3: Modelling of an industrial production site (Own figure)

For this purpose, all raw materials and energy carriers used to manufacture the product under investigation are first recorded. The amount of input materials, such as raw materials, energy carriers, construction materials and auxiliary materials, reflects the resources used. This includes, for example, recycled materials such as steel or glass, which would otherwise only be reflected in the energy balance by the savings in energy carriers used. In this way, the chemical exergy of the materials used also balances the exergy required from upstream chains, e.g. exergy for the production of recycled materials such as steel scrap and cullets. However, only the theoretical demand for the production of the intermediate products is taken into account, as presented in the chapter Thermodynamic fundamentals. This does not include, for example, the exergy required for recovery, separation and transport to the production sites.

By taking into account the construction materials used in a production plant under investigation, the resources used to manufacture a product can be modelled holistically and different production routes can be better compared with each other. For this purpose, the materials used are related to the production quantity manufactured during the lifetime of the plant and added to the specific exergetic efforts. In this way, both high-value or rare resources, but also the quantities of building materials such as cement and steel for the construction of the systems, which are not listed in the usual energetic analyses, are also assessed.

In order to decarbonise the industrial sector, existing production sites and processes, which are still mostly designed for the use of fossil energy carriers, must be completely restructured in some cases. The transformation to be carried out can affect the energy supply required or the entire production process used. The decarbonisation of the energy supply systems could be achieved, for example, by substituting fossil energy carriers such as natural gas or oil with green hydrogen, synthetically produced methane or biogas.

In order to assess the decarbonisation of individual industrial sectors, it is first necessary to identify the production processes currently used as well as the possible decarbonised production processes of the future. For the identified production routes, an exergetic analysis can then be realized for a modelled location. This allows the exergetic efficiency of the production process to be calculated in order to draw conclusions about its efficiency and resource use. Finally, the determined exergetic efficiencies of the analyzed current and future decarbonised production processes can be compared in order to assess the change in efficiency in regard to the resources used.

Thermodynamically idealized production process as reference value

To assess the resource use of different production routes, the exergetic efficiencies are determined, taking into account all raw materials and energy carriers used as well as all usable products.

A thermodynamically idealized reference process is designed for the relative classification of the results and to show the possible potential for improvement in terms of resource use. This is intended to represent the optimal production process, which requires the minimum exergy necessary to manufacture a product under optimal and reversible conditions. In addition, this ideal production process only uses process steps that are absolutely necessary for manufacturing the product. For each of these production steps, the thermodynamically minimum chemical and thermomechanical exergy input required within this production process is calculated.

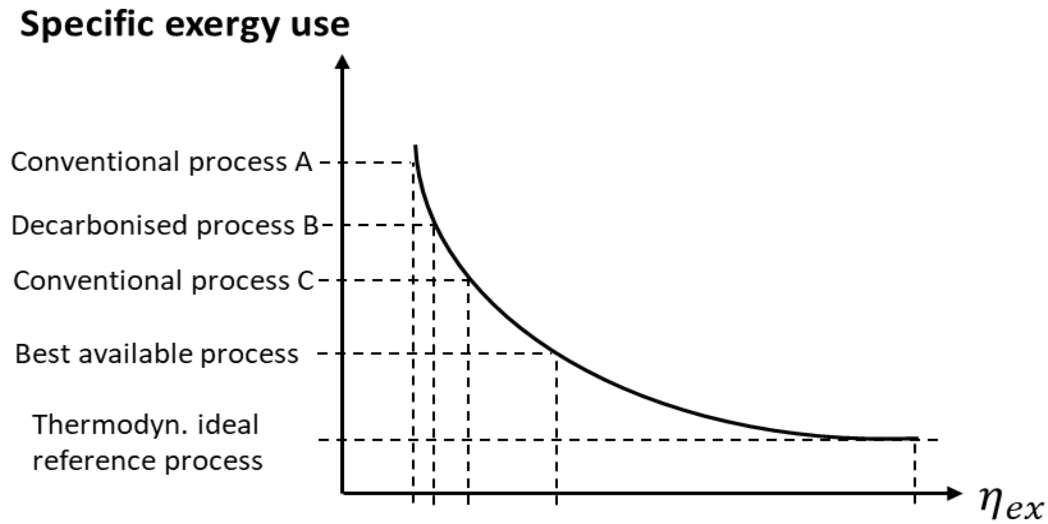

Figure 4: Exergetic efficiencies of different production routes (Own figure)

<u>Thermodynamically minimal exergy demand</u>

The thermodynamically ideal reference process consists of the essential production steps that take place under optimal thermodynamic conditions. Within this reference process, the reaction steps required for the conversion of the raw materials used and further conversion steps that are necessary for the manufacture of the product and its intermediate products are taken into account.

The modelling of the ideal reference processes is based on methodological principles from Radgen 1996 and Volta 2014. In Radgen 1996, for example, an ideal reference process for the production of ammonia is defined, in which the minimum energy requirement for the essential reaction steps in the production of ammonia is calculated. In Volta 2014 the determination of thermodynamic lower limits with regard to the energy demand of industrial production processes are described.

To determine the thermodynamically minimum exergy demand, a reference process is defined based on the two methods of Radgen 1996 and Volta 2014, in which the essential chemical reactions and production steps for manufacturing the required product are modelled. By applying the exergetic analysis to the defined production steps and chemical conversions, both the energy input and the chemical exergy values of the raw materials used are taken into account. These fictitious, idealized reference processes are theoretical in nature, and thus cannot be realized in practice and are used to determine the thermodynamic upper limit of efficiency that could be achieved under ideal conditions. The following general conditions are assumed for these processes:

- No heat loss due to ideal heat recovery
- No entropy generation
    - Heat transfer without temperature gradients
    - No friction
    - Ideal mixing
- Isentropic efficiency of 100% for all machines and systems used
- No production of material waste

Discussion and conclusions

Through the exergetic analysis of industrial production processes, their exergetic efficiencies and the quality of the conversion process can be determined. By applying the exergetic analysis to the current and possible future decarbonised manufacturing processes for product, they can be compared in regards to their resource efficiency.

In addition, the exergetic analysis of a modelled ideal reference process can show the theoretical thermodynamic improvement potential. The exergetic efficiency determined in this way represents the upper efficiency limit for the manufacture of a product with regard to the resources used and is independent of the production routes or technologies used.

Figure 5 shows the result of an exergetic analysis for an industrial production site in the form of a Sankey diagram. As described in the previous section of this paper, all incoming and outgoing energy and material flows are first balanced and their exergetic value are calculated. The incoming exergetic flows represent all required raw materials, energy carriers and auxiliary materials and are summarized as exergetic effort. Subsequently, the substances produced are defined either as usages or losses. The determined exergy flows consist of a thermomechanical and a chemical component.

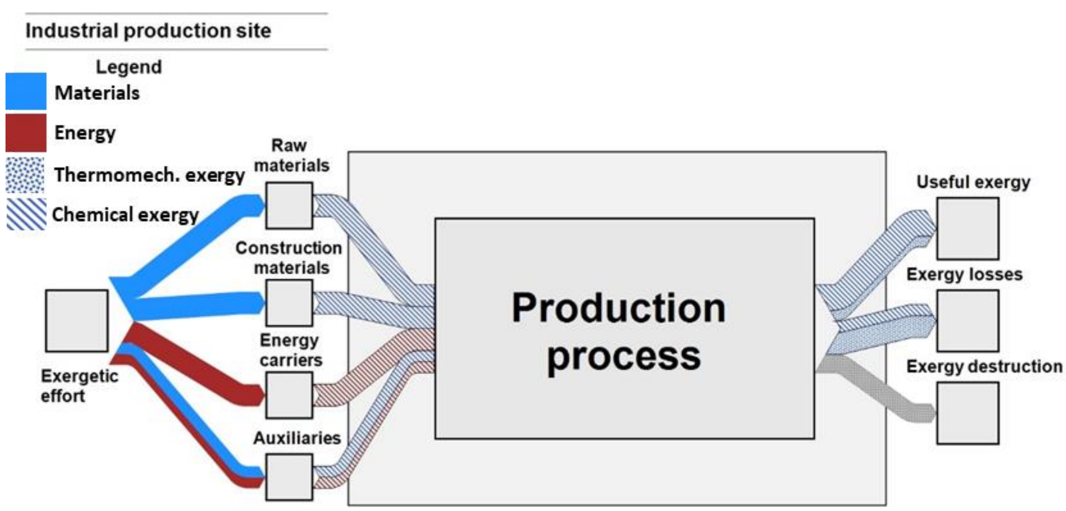

Figure 5: Sankey diagram of an exergetic analysis of an industrial production site (Own figure)

By determining the exergetic efficiency on the basis of the ratio of benefit to effort with regard to the incoming and outgoing exergetic flows, the examined production processes can be assessed thermodynamically. In addition, the quality of the process is quantified by the balanced exergy losses and exergy destruction.

The application of the exergetic analysis to current and possible decarbonised production processes shows their use of resources for the production of a certain product by comparing the determined exergetic efficiencies. In addition, the change in the resources used can be linked to the amount of CO_2 saved by decarbonising the production process. This allows a decision to be made whether the change in the production process associated with decarbonisation has a positive or negative impact on the resources used.

Additional value of exergetic analysis

The application of exergetic analysis to industrial production processes has a number of positive aspects, which generate an added value. At the same time, it is associated with some challenges and obstacles, which are addressed in the following section.

Advantages of exergetic analysis for industrial production processes

The main added value of exergetic analysis is achieved by adding another level to the previously one-dimensional assessment of industrial production processes by simultaneously assessing energy and material input and thus the total resources used. The efficiency of the energy and material input can be expressed dimensionless by a single parameter, the exergetic efficiency. In this way, production processes can be assessed holistically, whereby, for example, the change in the resources used as a result of decarbonisation of the production process can be shown. This makes it possible to assess thermodynamically whether the reduction of CO_2 emissions also has a positive effect on the use of resources. In addition, the dimensionless assessment of the resources used, makes it possible to compare production processes across sectors, which could lead to a prioritization with regard to limited goods such as biogas or rare raw materials.

Another significant advantage of the exergetic analysis is the consideration of the energy or exergy used to produce the raw materials and products used in the production process through their chemical exergy. This means that upstream chains are taken into account before the actual considered process, which makes the assessment of resource use more holistic.

Based on the thermodynamic assessment of the quality of the conversion process, the efficiency of the process can be obtained. At the same time, the overall theoretical potential for improvements can be quantified on the basis of exergy destruction and exergy losses. By modelling the thermodynamically idealised production process, the theoretical minimum exergy and resource input can be determined for a product, independent of the selected production process. This makes it possible to calculate the theoretical improvement potential of the current and future decarbonised production process with regard to the resources used. In addition, thermodynamic inefficiencies and the irreversibility of the production process under consideration or individual sub-processes can be identified through the exergetic analysis.

Disadvantages of exergetic analysis for industrial production processes

A clear obstacle to the use of exergetic analysis is its complexity and the number of parameters and data needed for its application. On the one hand, technical and thermodynamic knowledge must be available. On the other hand, the quantity, temperature and pressure and composition of all incoming and outgoing material flows must be known. This makes the application of exergetic analysis time-consuming and complex.

In addition, exergy is a theoretical thermodynamic parameter with which many engineers and technicians are unfamiliar. The exergetic analysis is a complex topic that must be dealt with intensively and is difficult to interpret. In addition, in order to model the thermodynamically idealised production process, one needs to have an extensive understanding of the processes and chemical reactions that take place. Hernandez and Cullen 2019 described that although exergy can be a useful and appropriate means of assessing the resources used, there has been little to no acceptance of it in industry to date.

Another aspect that raises concerns against exergetic analysis for industrial production processes is the assessment of the resource usage by the thermodynamic parameter exergy. The exergy describes the theoretical work ability that can be gained from a material flow when it is brought reversibly into equilibrium with the substances in the environment. Thus, this type of analysis has so far mainly been used in the conversion of energy carriers, for example in electricity generation, and is used to determine the possible work that can be extracted.

Conclusions

In conclusion, it can be said that the exergetic analysis for assessing the resources used in industrial production processes is meaningful and purposeful, since the totality of the energy carriers and substances used to produce a product are taken into account. In addition, the thermodynamic parameter exergy takes into account both the exergy requirement for the production of a resource used and its occurrence on earth through the rarity criterion in the chemical exergy. This makes it possible to determine the change in the resources used as a result of decarbonisation of a production process and thus to generate conclusions about how the efficiency of the resources used changes as a result of the transformation of the production process to reduce CO_2 emissions.

Nomenclature

Latin and greek symbols

Ex (ex)	(Specific) exergy [kJ/kg]
h	Specific enthalpy [kJ/kg]
T	Temperature [K]
s	Specific entropy [kJ/kg*K]
c	Specific velocity [kJ/kg]
g	Superficial mass velocity of reactants [kg/s*m²]
z	Specific potential energy [kg/s*m]
n	Amount of substance [mol]
ΔG_f	Specific Gibbs exergy of reaction difference [kJ/kg]
R	Ideal gas constant [kJ/kmol*K]
x	Species mol fraction
η	Exergetic efficiency

Subscript

Thermochem	Thermochemical
u	Ambient conditions [T = 298.15 K, p = 1 bar]
Chem	Chemical
el	Elements
ges	Whole amount
U	Usage
L	Loss
D	Destruction

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