Review

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Exergy analysis of energy-intensive production processes: advancing towards a sustainable chemical industry

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Abstract

Exergy analysis is becoming a very powerful strategy to evaluate the real efficiency of a process. Its application in the chemical industry is still at an early stage but many interesting remarks can be obtained from the recent research in the most energy intensive processes of the chemical industry: the production of chemicals, the cement industry, the paper industry and, the iron and steel industry. The present review analyzes the opportunities and challenges in those sectors by considering exergy analyses as the first required step (although not sufficient) to advance towards a more sustainable chemical industry. Social, environmental and economic factors play a role in the critical evaluation of a process and exergy could be considered as the property that joins together those three cores of sustainability.

Keywords: exergy efficiency; chemicals production; cement industry; paper industry; iron and steel industry; carbon dioxide emissions

INTRODUCTION

Production processes require a large amount of raw materials, which are utilized as feedstock for numerous products and as an energy source to drive the process itself. However, due to the limited availability of natural resources and the need for closed cycles in the ecosphere, the sustainability of the process industry is questioned.[1] A system can be evaluated in terms of energy efficiency, indicating the differences between the ideal thermodynamic situation and the current process. The first law of thermodynamics (conservation of energy) provides no information on the energy efficiency of a process since it allows a knowledge of the inputs and outputs of energy in the process but it is not possible to determine the lost work nor the quality of the energy involved in the system.[2] On the other hand, entropy, obtained from the second law of thermodynamics as a measure of the amount of molecular disorder within a system, can help to explain the natural direction of energy transfers and conversions. Quality of energy can also be determined since energy sources with low entropy such as work and kinetic and gravitational potential energy are the most useful (high quality energy) while heat, a high-entropy form of energy, is less useful (low quality energy). However, the units of entropy (energy/temperature) make its application very unpractical in the evaluation of process efficiencies.[2,3] It is in this point in which the combination of the first and second laws of thermodynamics is of great interest to work with another thermodynamic property with units of energy/time (power): Exergy.

Exergy is defined as the maximum theoretical useful work obtained if a system S is brought into thermodynamic equilibrium with the environment by means of processes in which S interacts only with this environment. The mathematical definition of exergy can be found in Luis *et al.*[2] An exergy analysis requires the precise definition of the environment that functions as a reference state for the analysis, the temperature, the pressure and, the mixture of substances (commonly found in abundance in nature) must be defined and given a zero exergy value, this being the starting point of an exergy analysis.[4,5]

Exergy analyses are commonly represented in Grassmann diagrams in which the work potential of natural resources (resources used as feedstock or resources applied as fuel) are represented as the inputs and the work potential of the desired product(s) and of recovered useful heat are represented as the outputs.[1] Figure 1 represents a generic Grassmann diagram for a process in which material and energy conversions take place. Note that the work potential that enters the system is higher than that leaving the system. This is due to the losses caused by process inefficiencies or material or heat release to the environment. Exergy is only conserved when all processes occurring in a system and the environment are reversible and it is destroyed whenever an irreversible process occurs. Thus, the thermodynamic imperfections can be quantified as exergy destructions, which represent losses in energy quality or usefulness (see decreasing lines in Fig. 1). This means that when energy loses its quality, exergy is destroyed.[6] Since reversible processes do not exist, exergy is always destroyed, partially or totally, according to the second law of thermodynamics.[7] Thus, evaluating how the exergy and exergy destruction is distributed over the process will tell us how to allocate engineering effort and resources.[7]

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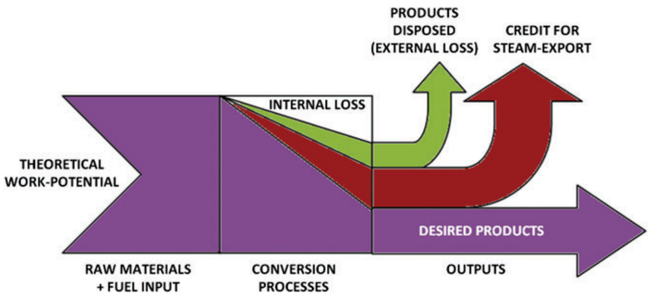

Figure 1. Generic Grassmann diagram for a material and energy conversion process.[1]

The use of energy is the main part of the production costs for most chemical processes, hence, the energy cost should be minimized, and exergy analyses can be used to optimize the process from this perspective.[5] Exergy analyses can also be applied to reduce the use of natural resources since the thermodynamic imperfections of the process can be detected and quantitatively assessed.[8] However, in terms of sustainability, exergy analyses are not sufficient to determine if a process is sustainable or not since a sustainable use of resources must also consider their renewable character (e.g. solar energy, biomass). A process can be energetically very efficient but using non-renewable natural resources, which indicates a lack of sustainability. Indeed, as indicated by Hinderink *et al.*,[1] a chemical conversion process can be 100% efficient when all non-renewable exergy ends up in the desired product(s). However, real processes present exergy losses, hence, more exergy enters the process than leaves it. This excess of exergy entering the process to make it proceed has to originate from renewable sources (e.g. solar exergy) in order to contribute to sustainability. When more renewable exergy is used, the process becomes more sustainable. If all the starting materials are renewable, such as carbon dioxide and water, the driving force is solar energy, and all the outputs become inputs, a complete sustainable process is obtained. Thus, the degree of sustainability is based on these three parameters:[1] (i) the thermodynamic efficiency (exergy efficiency); (ii) the use of renewable resources (at least to produce the fraction of exergy that will be destroyed during the production process); and (iii) the extent to which circles (reuse, recycling) have been closed. The cost of renewable energy is rapidly becoming competitive with other sources of energy, and with additional engagement of the scientific, financial, and public-policy communities, as well as the general public, the transition to affordable, accessible and sustainable energy that will power economic growth, increase energy security and mitigate the risks of climate change is possible.[9] Remarkable is the study performed by Taibi *et al.*[10] of the long-term potential for renewable energy in industrial applications, which suggests that up to 21% of all final energy use and feedstock in manufacturing industry in 2050 can be of renewable origin. In addition, their work stresses that renewable energy in industry has not yet received the same attention as in power generation and buildings. However, it is technically possible to substitute half of the industrial fossil energy and feedstock use with renewable, with biomass dominating (around 75%) and, solar heating as a second key category. It is evident that the role of decision makers is critical to pay more attention to the potential for renewable energy in industry.

Increasing exergy efficiency in the industry has as a consequence the conservation of energy resources, cheaper production processes and higher competitiveness. The optimization of processes to obtain the maximum production per unit of consumed energy while keeping the maximum quality of energy during the production process should be considered as a critical strategy not only by industry but also by the decision makers in government. There are also very strong social implications since fossil fuel dependence creates insecurity for fossil fuel importing countries.[11] Decisions from the level of production of goods to the level of political negotiations will have a very direct impact on economic, social, cultural and, environmental aspects. Thus, performing exergy analyses in the chemical industry becomes an essential measure to ensure the responsible use of global resources. In addition, carbon dioxide (CO_2) emissions are directly related to energy utilization. The industry accounts for one-third of all the energy used globally and for almost 40% of worldwide CO_2 emissions, where the iron and steel, cement and chemicals industry are the main sources of CO_2: 30, 26 and 17% of the total industrial emission, respectively.[12–14]

Thus, exergy analyses are necessary (although as said, not sufficient) to ensure the sustainability of processes.[15,16] However, its popularity has been mainly focused on energy systems where heat is converted to power or electricity, but there is a lack of studies in the chemical process industry, maybe due to its greater complexity[1] or to the fact that the recent pioneers of exergy analyses share a common interest in mechanical engineering. In a previous work,[2] the lack of exergy studies in the field of chemical engineering was highlighted (as shown in Fig. 2, less than 15% of the publications included exergy analyses in chemical engineering), which may appear inconceivable since chemical processes are a main target in which exergy destruction can be significantly reduced. This lack of sufficient data and data reliability has already been observed to be a barrier to compare the energy consumption and efficiency by sector and country (e.g. fossil power generation, steel and cement sectors, reviewed by Oda *et al.*[11]). Thus, it is necessary to evaluate and optimize specific processes case by case to obtain the maximum exergetic efficiency and minimize the process irreversibilities, and to continue developing breakthrough technologies that improve and update the current best available technologies.[17]

The present review tries to evaluate the application and usefulness of exergy analyses in the chemical industry, showing the path to follow to advance towards a more sustainable industry. Exergy analyses have recently been applied in the most energy intensive processes in chemical engineering, which form the structure of the present review: production of chemicals, cement industry, paper industry and, iron and steel industry.

EXERGY ANALYSIS FOR OPTIMIZATION OF ENERGY-INTENSIVE PRODUCTION PROCESSES

Energy is the bottleneck of many production processes due to increasing operating costs associated with the variable price of mineral resources (i.e. coal, oil, etc.). Thus, the use of intense energy-saving technologies is directly related to the final price of the manufactured product, which promotes the research and application of novel technology that efficiently uses the resources, minimizing energy consumption. The final aim is to use a minimal amount of resources (energy and materials) per unit amount of a manufactured product. Achieving this objective involves the evaluation and optimization of each production step, analyzing each operating unit and even beyond, reaching the molecular level inside the unit to know how microscopic changes can affect

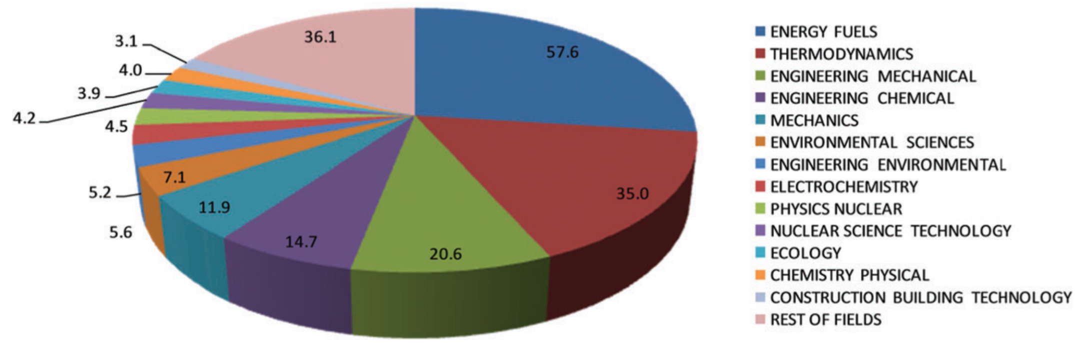

Figure 2. Percentage of publications on exergy per field of research in the period 1980–2013 (total: 5446 items). Published with permission from Luis.[2]

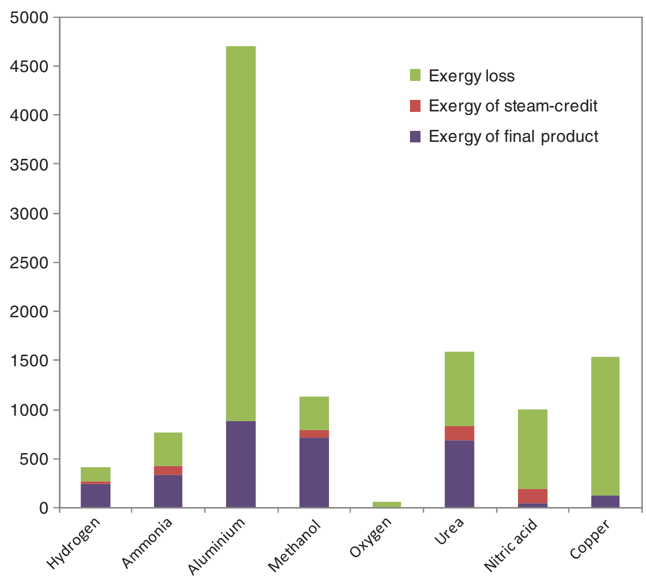

Figure 3. Exergy analysis for some production processes.[1]

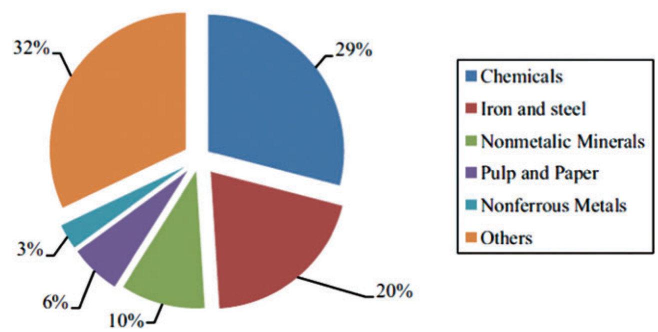

Figure 4. World industrial sector energy consumption by major energy-intensive industry shares in 2006. Published with permission from Abdelaziz *et al.*[21]

the overall efficiency (e.g. reaction, thermodynamics, transfer of mass, heat and, momentum). Thus, by knowing the consumption of resources or the exergy value at each step of the process in the ideal system, it is possible to detect the least efficient units of the production system and the points to which energy-saving measures must be applied.[18]

According to Hinderink *et al.*,[1] the thermodynamic efficiencies based on exergy analysis do not exceed 70% when starting from primary resources. In addition, the production of organic products is found at the higher side of the efficiency range, while inorganic and metallurgical processes are at the lower side of the efficiency range. Some absolute figures for the process industries are shown in Fig. 3. This figure is a clear indication of which processes are being operated efficiently and which ones present a considerable exergy loss that should be avoided. However, it is important to highlight once more that this is not an indication of the sustainability of a process since no information about the use of renewable resources is given.

In addition to the economic and social implications that exergy losses (and exergy destruction) produce, there are also direct environmental effects enhanced by a bad management of resources and imperfections from an exergy point of view. Such a case is the emission of carbon dioxide in industrial processes. These emissions are not only produced by combustion systems for energy production (e.g. combustion of fossil fuels) but also as a consequence of having reactions that chemically transform raw materials to waste gases, including CO_2. These processes include iron, steel and metallurgical coke production, cement manufacturing process, ammonia production, lime production, limestone and dolomite use (e.g. flux stone, flue gas desulfurization, and glass manufacturing), soda ash production and consumption, titanium dioxide production, phosphoric acid production, ferroalloy production, silicon carbide production and consumption, aluminum production, petrochemical production, nitric acid production, lead and zinc production.[19] In this case, process optimization from an energy and exergy point of view is even more crucial to avoid CO_2 emissions due to exergy losses or exergy destruction.

The most energy intensive sectors in industry have been found to be chemicals, iron and steel, nonmetallic minerals, pulp and paper, and nonferrous metals.[20,21] Figure 4 shows the global energy consumption by sector. A recent review by Boroumand Jazi *et al.*[22] obtained conclusions from the evaluation of those sectors in different countries. Mainly: (i) there are significant differences between the energy and exergy efficiency of different industries and it determines the importance of second law analysis in performance optimizing of the industrial sector; (ii) heating processes, steam generation and the extent of electricity dependence are the main factors that contribute to the differences between the first and second law efficiencies; and (iii) comparing the energy efficiency analysis and exergetic efficiency of a system, it can be indicated that the exergy analysis provides a more realistic picture considering the irreversibilities and potential optimization of the process.

In this context, the optimal use of resources is critical, and exergy analyses are applied to optimize production processes. Examples are found in chemicals production (e.g. acetylene, sulfuric acid, phosphorous, olefins, sodium hydroxide and, methanol), cement industry, paper manufacture and, iron and steel industry. In the following sections, a deeper analysis of these sectors is performed.

Production of chemicals

Chemical processes can be considered as a transfer of chemical energy from the starting material into the products. Already in 1974, Riekert[23] evaluated the efficiency of energy utilization in the large-scale manufacture of ammonia and of nitric acid as examples to demonstrate the potential of exergy analyses. A chemical reaction changes the capacity of matter to yield useful work, whereas it cannot change the overall elemental composition; it is essentially a conversion of energy.[24] Furthermore, for most chemical production, the use of energy constitutes the main part of the cost value of the production in addition to the serious issues from energy resources deficiency and environmental pollution.[25] Thus, energy reduction is a target in the progress of chemical technology and new generation energy systems with higher efficiency and less environmental impact are required. On this basis, exergy becomes a meaningful property to study the transformations of energy in the system that interacts with the environment, keeping in mind that the available energy will always depend on the properties of the environment (and the environment being a source or sink of materials in exactly the same sense as it is a source or sink of heat), and to measure the efficiency of a chemical process.[5]

Recently, the application of exergy analyses in chemical manufacture has shown the path towards an effective method to gather information on the inefficiencies and weak points of processes. Table 1 shows the latest research work and the main conclusions obtained from the application of exergy analysis in the production of chemicals. Polygeneration systems refer to the integration of high efficiency systems to produce simultaneously electricity, chemical products and/or clean synthetic fuels.[25,26] From these studies, it can be inferred that reducing the thermodynamic irreversibility of chemical reactions is critical to reduce exergy losses since 65–90% of the exergy losses are due to the thermodynamic irreversibility of chemical reactions, and only 10–20% of the exergy losses arise in the separation stages. Thus, from the results of exergy analyses, it is possible to determine which components and sub-processes of chemical plants should be subject to major efforts to improve efficiency and sustainability.[2] As reference, Leites *et al.*[35] proposed to avoid reactions running to completion in order to reduce exergy losses and find the optimal conversion, which corresponds to the minimal exergy losses per unit of useful reaction product. The chemical reaction step largely determines the overall thermodynamic efficiency[1,36] and chemical reactions are a notorious source of lost work. Since all processes are irreversible, the exergy loss can be decreased when decreasing the reaction rate since the departure from equilibrium decreases[37] and, as a consequence, the exergy efficiency would be enhanced.[22] Similarly to heat exchangers, in which the driving force (i.e. temperature gradient) determines the rate of transfer and the degree of devaluation of work-potential, chemical reactions are driven by a gradient from high to low chemical affinity, leading to releases of heat and losses of work-potential (the relation between the Gibbs free energy of reaction and lost work is linear).[1] A significant improvement in energy efficiency and process economics can be achieved if attention is paid to the chemical reactor.[38,39] Hence, the development of new chemical processes should focus on exergy-neutral reactions.[1] These kinds of study establish a thermodynamic compromise between energy consumption and conversion rate.

Cement industry

Cement production is a highly energy intensive process consisting basically of three production units: raw material preparation, clinker production (pyro-processing), and clinker grinding and blending, in which the pyro-processing unit takes around 90% of the total energy required for cement production.[19] Figure 5 shows the main stages involved in the process. In the pyro-processing unit, most of the thermal heat losses occur due to the temperature variations of the feed solid stream from 50 °C to 1450 °C and then from 1450 °C to 100 °C, caused by chemical reactions as well as heat exchange with hot flue gases in the heating section followed by ambient air streams in the cooling section.[19,40] In general heat losses in pyro-processing units can lead to wasting up to 20% of initial energy,[41] resulting in the release of 8% extra CO_2 from a cement plant, which cannot be ignored due to environmental, societal and economic reasons. Indeed, cement manufacturing is considered one of the highest CO_2 emitting industries on a global scale as result of the emissions caused by the combustion of fossil fuels in pyro-processing unit (40% of total emissions) in addition to the CO_2 emitted during the decomposition of $CaCO_3$ and $MgCO_3$ to produce CaO and MgO, raw materials transportation and generation of electricity.[19] The process emits around 900 kg of CO_2 per ton of cement produced,[42] which accounts for 5–7% of the global anthropogenic CO_2 emissions.[43] Thus, avoiding exergy losses and minimization of CO_2 emissions in the cement industry is essential. Table 2 shows a summary of the last publications on cement production analyzed from an exergy point of view.

It is estimated that about 25% of the total energy used in a typical cement production plant is electricity and 75% is thermal energy.[44] However, the process presents significant heat losses mainly by the flue gases and the ambient air stream used for cooling the clinker (together about 35–40% of the process heat loss).[45] Thus, recent publications evaluate the efficiency of different heat recovery systems (e.g. waste heat recovery) from an energy and exergy point of view while contributing to emissions decrease.[44,46,47] The recent number of publications focused on the cement industry is an example of the importance of the optimization of this sector.[42,48–53]

Exergy analysis allows the calculation of exergy losses and thus those systems in which the highest losses are produced can be identified and optimization measures can be taken to minimize those losses. Madlool *et al.*[8] presented an overview of the application of exergy analysis in the cement industry. The exergy efficiency for cement production units was observed to range from 18 to 49% and the exergy losses due to the irreversibility in the kiln are higher than other units in a cement production plant. Figure 6 shows the irreversibilities for the main systems involved in the production of cement. The exergy analysis, exergy balance and exergy efficiency allowed interesting conclusions to be obtained that are not possible with a simple energy balance: (i) exergy analyses can improve the performance of the system and reduce energy costs; (ii) the units with the lowest exergy efficiency (i.e. the trass mill) can be identified as well as the main sources of irreversibility (i.e. the rotary kiln); and (iii) the exergy efficiency can be evaluated under different operating conditions (e.g. the exergy efficiency is inversely proportional to dead-state temperatures). Furthermore, in an attempt to evaluate the cement industry in Greece, Koroneos *et al.*[54] observed via an exergy analysis that 50% of exergy losses take place at various stages of the system, with the biggest losses

Table 1. Recent results of exergy analysis in the production of chemicals

Author	Production process	Specific objective	Main conclusions
Guo *et al.* (2012)[27]	Acetylene production	To evaluate thermodynamically a low-rank-coal-based oxygen-thermal acetylene manufacturing process in which process middle coke refined from low-rank coal is used as the coke feeding.	The calcium carbide production unit has the maximum exergy loss, which accounts for 57.52% of the internal exergy loss, large carbon consumption, and large energy discharge of off-gas. Reducing carbon consumption in the carbide furnace and reusing the off-gas will do better to improve the energy consumption of the whole system. The exergy loss of the calcium carbide production unit results from irreversibility of the carbon combustion reaction in the energy donor.
Wang *et al.* (2007)[26]	Acetylene production	To evaluate a novel polygeneration system that integrates the acetylene process and the use of fuel cells.	The power generation efficiency was 26.8% and the exergy efficiency was 43.4% (20.2% higher than the traditional acetylene production process in which the useful output exergy converted to C_2H_2 accounts for 23.2% of the total inlet exergy).
Wang *et al.* (2009)[28]	Acetylene production	To apply the flowrate-exergy diagram for thermodynamic analysis and energy integration in an acetylene production process and a H_2/O_2 cycle system.	Comparing the novel system with the original processes, C_2H_2 production process and H_2/O_2 cycle, the natural gas consumption was decreased by 37.5% and the internal exergy loss was reduced by 35.2 MW, which was almost 20.3% less than the original processes.
Panchenko (2004)[18]	Phosphorus production	To evaluate the energy efficiency of phosphorus production.	The heat and exergy utilization factors in the system can be increased to 0.76 and 0.26, respectively. Since the cost of energy resources constitutes 34–43% of the phosphorus cost, a 6% decrease in the cost of energy resources causes a 2–3% decrease in the cost.
Qian *et al.* (2009)[29]	Olefin production	To increase the overall efficiency by a novel natural gas-based poly-generation system for olefin and power production.	The exergy destruction occurs mainly in the gasification process and the power plant, which account for 36.4% and 42.1% of the whole exergy loss of the system, respectively. Physical exergy destruction in heat transfer and chemical exergy destruction in the combustion process are the main reasons for the exergy loss of the poly-generation system.
Gao *et al.* (2004)[25]	Methanol production	To evaluate one coal-based polygeneration system for power and methanol production, and compared it with its original individual processes.	Through the combination of a power system with a chemical process, the polygeneration system results in 3.9% energy saving, and synthesis on the basis of thermal energy cascade utilization is the main contribution to the performance increment in this kind of polygeneration system.
Duan *et al.* (2002)[30]	Methanol production	To analyze a polygeneration system based on coal gasification using the exergy method in order to calculate the system thermal efficiency.	The exergy cost in the gasification and cleanup sections which change the dirty coal fuel to clean syngas is unavoidable; all the syngas can be used in a once-through process to synthesize methanol after high-efficiency cleaning of the gas to produce a highly integrated system; changing the H2/C0 ratio using the water gas shift reaction will change the methanol output and the electrical output in the combined cycle, which varies with fuel gas composition; optimization of the heat utilization can improve system exergy efficiency because the temperatures in the polygeneration system range from 100 to 1800 K.
Rihko-Struckmann *et al.* (2010)[31]	Methanol production	To evaluate the thermodynamic and operational boundaries to store electrical energy chemically. Methanol is considered for chemical energy storage.	Energetic analysis reveals that exergy losses are most severe in the parts of the system when electrical energy is converted to chemical (electrolysis) and when chemical energy is converted to electrical (power generation). The energy storage system with hydrogen as storage medium shows higher exergetic efficiency than the methanol route. However, the storage of hydrogen is clearly more complex and cost-intensive.

Table 1. continued

Author	Production process	Specific objective	Main conclusions
Guang-jian *et al.* (2010)[32]	Methanol production	To evaluate a methanol/electricity co-production system.	The total exergy efficiency is 47%, which is in between that of IGCC (integrated gasification combined cycle) system (39%) and stand-alone methanol production system (54%). The biggest energy-saving factor is associated with heat exchange processes, accounting for 35% of the total coal exergy savings; the next is the energy-saving factor of combustion process, accounting for 22% of the total coal exergy saving.
Zhou et al. (2008)[33]	Dimethyl- ether (DME) production	To evaluate a co-feed and coproduction system (Co–Co) based on syngas, using coal and natural gas as feedstock and co-producing electricity, heat and DME.	The Co–Co system has higher exergy efficiency when producing the same electricity and chemical product. It has higher economic benefit (mainly when the scale is as big as over 25×10^4 t/year). The Co–Co system is environmentally friendly releasing the least CO_2 when CO_2 removed and CO_2 in tail gas are all considered.
Shablovskii (2013)[5]	Reactions with solid phases	To analyze the chemical and thermal components of exergy of solid-phase reaction systems.	When there is a crystal component in the reaction mixture, the chemical exergy depends not only on the temperature and composition of this mixture, but also on the structural modification of the component. The temperature dependence of the chemical exergy of the exothermic reaction mixture has a maximum and the temperature dependence of the chemical exergy of the endothermic reaction mixture has a minimum.
Richards *et al.* (2009)[34]	NaOH production	To perform a preliminary evaluation to select the best alternative for producing sodium hydroxide on a Kraft pulp mill site.	The two best options for increasing the production of sodium hydroxide for internal use in a mill are the conventional lime cycle process or direct causticization with titanates. A higher energy requirement and lower exergy efficiency is observed in the titanate process without heat integration.

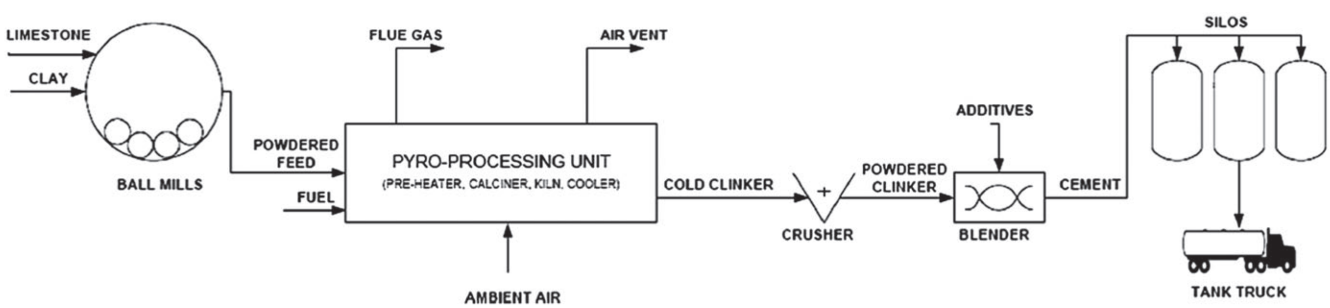

Figure 5. Block diagram of cement production process. Published with permission from Benhelal *et al.*[19]

(30.9%) due to the irreversibilities in the preheating of feed and the cooling of the product, while 15.1% of the exergy losses were caused due to the exhaust gases from the combustion of fuel. In addition, due to the features that the cement industry shares with other sectors such as the production of lime, very similar results have been also obtained, with the most irreversible process being the kiln and obtaining more than 10% of efficiency loss due to the exergy lost with the exhaust gases.[55]

However, in addition to the pre-heating and rotary kiln unit, the coal-preparation unit consumes a large amount of energy and should be included in an exergy analysis. This unit consists of a dryer and a ball grinder. Sögüt *et al.*[47] observed that the energy efficiency of this unit was around 74% and the exergy efficiencies varied between 11.7 and 30.7%, depending on the ambient temperature, with exergy destruction between 69.2 and 88.3%. The low exergy efficiency leads to CO_2 emissions that could very often be avoided. Thus, it is evident that each stage in the production of cement can be improved to operate under more sustainable conditions.

Burning wastes in the cement industry is under research since the cement industry is characterized by high energy thermal consumption due to the high temperatures necessary to produce the clinker (around 1450 °C).[56,57] The use of alternative fuels in the cement industry can change the temperature profile of the kiln, the sintering temperature, the length of the sintering zone and the cooling conditions, which can modify the final characteristics of the clinker. Nevertheless, provided excellent control of operating conditions is ensured, technical viability can be obtained for several hazardous waste materials.[56] The use of wastes in the cement industry can be achieved by their mineralization, incorporating the waste (e.g. waste from aluminium industry evaluated by Renó *et al.*)[57] in small proportions while improving

Table 2. Recent results of exergy analysis in the cement industry

Author	Specific objective	Main conclusions
Camdali *et al.* (2004) [a 60]	To examine the applications of energy and exergy analyses for a dry system rotary burner with pre-calcinations in a cement plant in Turkey.	Heat losses by conduction, convection and radiation from the dry system rotary burner are about 3% of the initial input energy. It was also found that the energy and exergy efficiencies were about 97% and 64.4%.
Utlu *et al.* (2006) [a 61]	To analyze energy and exergy of a raw mill (RM) and raw materials preparation unit in a cement plant in Turkey using the actual operational data.	Energy and exergy efficiencies of the raw mill were determined to be 84.3% and 25.2%.
Wang et al. (2009) [a 62]	To find the most efficient case among different cogeneration systems including single flash steam cycle, dual-pressure steam cycle, organic Rankine cycle and the Kalina cycle aimed to reuse waste heat from the exhaust gas and air vent streams in cement plant.	Thermal heat losses in turbine, condenser, and heat recovery vapor generator are relatively large and optimization strategy indicated that the Kalina cycle could achieve the best performance in cement plant.
Sögüt et al. (2010) [a 63]	To assess the possibility of using heat losses to supply thermal energy for dwellings in the vicinity.	51% of the initial energy of the process is lost. By using these losses instead of coal and natural gas it was possible to decrease domestic coal and natural gas consumption by 51.55% and 62.62% and also to reduce CO_2 emissions by 5901.94 kg h^{-1} and 1816.90 kg h^{-1}.
Karellas *et al.* (2013)[64]	To examine and compare energetically and exergetically, two different waste heat recovery methods: a water-steam Rankine cycle, and an organic Rankine cycle.	Waste heat recovery is feasible for a cement industry and it can offer about 6 MW of electric power for a typical cement plant. The energy and exergy analysis proved that the water steam-cycle has better performance with a system efficiency of 23.58% compared with 17.56% of the organic Rankine cycle.
Madlool *et al.* (2012)[8]	Review of exergy analysis, exergy balance, and exergetic efficiencies for cement industry.	The exergy efficiency for cement production units ranges from 18% to 49% as well as the exergy losses due to the irreversibility from kiln are higher than other units in cement production plant. The main irreversibility source in the cement industry is the rotary kiln, whereas the raw feed pre-heating causes the lowest irreversibility within the cement plant.
Koroneos *et al.* (2005)[54]	Evaluation of cement production in Greece by using the exergy analysis methodology.	50% of the exergy is being lost even though a large amount of waste heat is being recovered. The greatest loss of exergy, 30% is due to irreversibilities in the following stages: preheating of raw feed, cooling of clinker and combustion of pet coke. A large portion of exergy loss is due to exhaust gases from the combustion of Pet-Coke (15%).
Sögüt *et al.* (2012)[47]	To conduct the energy and exergy analyses of a coal-preparation unit in a cement plant and investigate the effects of varying ambient temperatures on exergy efficiency.	The energy efficiency of the coal-preparation unit was 74.03%. The exergy efficiency varies between 11.70% and 30.73% depending on the ambient temperature. Exergy destruction for the coal-preparation unit ranged from 69.27% to 88.3%. On average, 78.64% of the input exergy was destroyed depending on the system working conditions and the ambient temperature.
Renó *et al.* (2013)[57]	To confirm the advantages of the application of waste SPL (spent pot lining) as a mineralizer in clinker production from an exergetic viewpoint.	The main irreversibility source in the cement industry is the rotary kiln and calciner process where the clinkerization process occurs. Therefore the use of mineralizers and alternative fuels is important, especially for reducing the fossil fuel consumption (in this study the reduction was 17.32 t day^{-1} of fossil fuel) and waste management problems.
Kolip and Savas (2010)[64]	To analyse the energy and exergy of the four cyclone parallel flow cement production system.	Total exergy loss of the system was found to be about 72%.
Ari (2011)[51]	To determine and analyze energy- exergy utilization, heat balance, exergy balance and their irreversibility in cement plant and two types of recovery systems.	The exergy efficiency of the existing system was 28.9%. The waste energy recovery systems must also be incorporated in the design of new industries to minimize energy consumption, manufacturing costs and to improve the product quality.
Ashrafizadeh *et al.* (2012)[46]	To study the effect of a second burner on the temperature profile and combustion factors of the system, and evaluate the exergy and greenhouse gases emissions.	The temperature gradient distribution by installation of a secondary burner has positive effects on both exergy and environmental functions of cement production process. The higher the production capacity of the kiln, the higher the decrease in both exergy losses and greenhouse gas emissions.
Sagastume Gutiérrez *et al.* (2013)[b 55]	To identify the main factors affecting the thermal efficiency of a vertical shaft kiln for lime production and their influence on the fuel consumption.	The most irreversible processes taking place in the kiln are the exergy destruction due to fuel combustion and the exergy destruction due to internal heat and momentum transfer both accounting for about 40% of the efficiency loss. The exergy loss with the exhaust gases contributes with more than 10% of the efficiency loss.
Sagastume Gutiérrez and Vandecasteele (2011) [b 65]	To evaluate the exergy efficiency of limekilns and to assess the effectiveness of the exergy consumption of the dissociation reaction by two new exergy-based Indicators.	The indicators permit to identify the origin of the exergy loss and different actions to reduce fuel consumption and CO_2 emissions can be derived.

[a] Adapted from Benhelal (2013); [b] CaO production

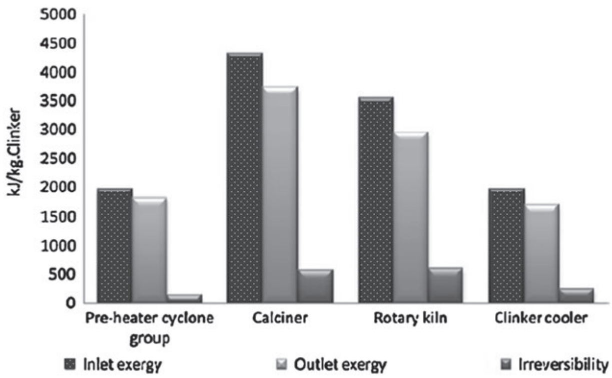

Figure 6. Inlet exergy, outlet exergy and irreversibility for each unit within a cement plant. Published with permission from Madlood *et al.*[8]

the clinkering conditions and decreasing the maximum clinkering temperature without altering the final properties of the product.[57] These strategies can be a possible solution to reduce fossil fuel consumption and waste management problems in the cement industry when applied together with energy saving measures,[45] which would reduce CO_2 emissions and improve the energy efficiency.[58,59] A significant improvement in exergy savings has also been demonstrated.[57] However, challenges associated with the use of wastes such as keeping the quality of the final product and ensuring good environmental management and social communication must be overcome, leading to a rich area of research and development.

Paper industry

The pulp and paper industry is the fourth largest consumer of primary conventional energy in the industrial sector worldwide (the share of industrial energy consumption is about 4%[66–69]) with almost half of the energy being used for operating a paper mill.[70] This sector has a demand for energy that is higher for example than that for cement and steel production. Paper manufacture can be performed in industries with an integrated pulp and paper mill, normally located close to their main raw material input (wood), or with a mill only, where paper is produced from imported pulp. In this case, the non-integrated mills may be located closer to the market. The energy consumption is hardly affected by whether the paper mill is integrated or not but by the type of energy carrier (e.g. wood chips or natural gas) and the method of energy generation (e.g. black liquor recovery boiler or cogeneration plant).[71]

The processes in a conventional non-integrated paper mill consists of three main steps: (1) stock preparation: pulp and waste paper are screened, de-inked and mixed with water, then, additives are added, forming a mixture called stock; (2) paper machine: forming (dispersing the stock over a wire screen to form a sheet and subsequently removing most of the water by gravity and suction), pressing (passing the sheet through three or four pairs of press cylinders) and drying (the sheet is passed over 40–50 steam-heated cylinders) takes place during this stage; and (3) finishing operations: smoothing the paper surface, winding on wheels, cutting, etc.[71] Figure 7 shows the main operations involved in paper manufacture. In an integrated mill, there is the pulp mill, divided into a series of sub-operations such as cooking, pulp washing, bleaching, washing and sheet forming, and the paper mill, which performs the stages described above.[72]

The main reason for the paper industry being a very energy intensive industry is due to the removal of the water that is initially added to the fibers, leading to an overall consumption of 3–9 GJ heat per tonne of paper and 1.3–2.9 GJ electricity per tonne.[71] Heat is mainly required in the form of low-pressure steam, from which 90% is consumed during paper drying (i.e. process to remove excess water from the paper sheet by evaporation and in which the evaporated water is carried away by a large volume of fresh supply air). The paper drying stage consumes around 70% of the total energy required in coated papermaking, and almost all the thermal energy used in the process can be found in the exhaust air, giving the opportunity for interesting research to recover this heat.[73] Regarding the electricity demand, it is more evenly distributed over the various unit operations, mainly to drive pumps and fans and, the paper machine.[71] Thus, in such an intensive industry, the heat needed in the processes is often produced in a combined heat and power plant (CHP) in which heat and power are produced simultaneously in the same power plant process.[74]

Many studies have detected the potential for performing energy-saving measures to minimize the plant energy cost by implementing numerous designs and processes to increase the energy and exergy efficiencies.[71,75–80] For instance, the exergy loss in the paper machine is about 35% of the total exergy loss (9.6 GJ per tonne) with about one third of this loss caused by lost fibers.[71] Table 3 shows recent conclusions on the application of exergy analyses in the pulp and paper industry.

Figure 8 shows the energy and exergy efficiency of the sub-processes that are involved in the pulp and paper industry.[83] As observed in this figure, the recovery boilers and the digester are the least efficient conversion process and the debarking shows the least energy loss. Differences between energy and exergy losses are also clearly appreciated. The largest internal exergy loss occurs in the CHP unit (see Fig. 7) and it is caused by the conversion of a high-quality fuel (e.g. natural gas) to low-quality steam. In addition, it is important to highlight that fossil fuels and electricity are still the major non-renewable energy inputs,[72,86] which indicates that there is much room for improvement in the pulp and paper industry to enhance the degree of sustainability. Minimizing exergy losses may also lead to an increase in CHP production without a reduction in fuel consumption.[77] Furthermore, the paper industry is responsible for a considerable amount of greenhouse gas emissions, mainly due to its intensive energy profile,[87] and although the CHP plants provide benefits to the pulp and paper industry such as reliable power supply, emissions related to their operation should be analyzed to consider emission reducing measures[81] or the substitution of fossil fuels for renewable energy resources.

The environmental impact has been evaluated via a life cycle exergy analysis (LCEA), which can be considered as a next step in an exergy analysis.[83] This analysis was proposed by Gong[83] for the pulp and paper industry showing that the exergy output amounts to over 3 times the spent exergy as non-sustainable resources. By replacing the present use of non-sustainable resources, mostly fuel oil, the mill could move towards a truly sustainable process. In addition, Gong[83] also concluded that the heating processes are highly exergy inefficient due to the fact that the thermal exergy of a system is often much lower than the thermal energy, particularly at temperatures close to ambient temperature. Also, waste water at a few degrees above ambient temperature has no practical amount of exergy but could be a problem for the environment due to its exergy content.[83] Thus, a combination of exergy and environmental analysis allows a broad perspective on

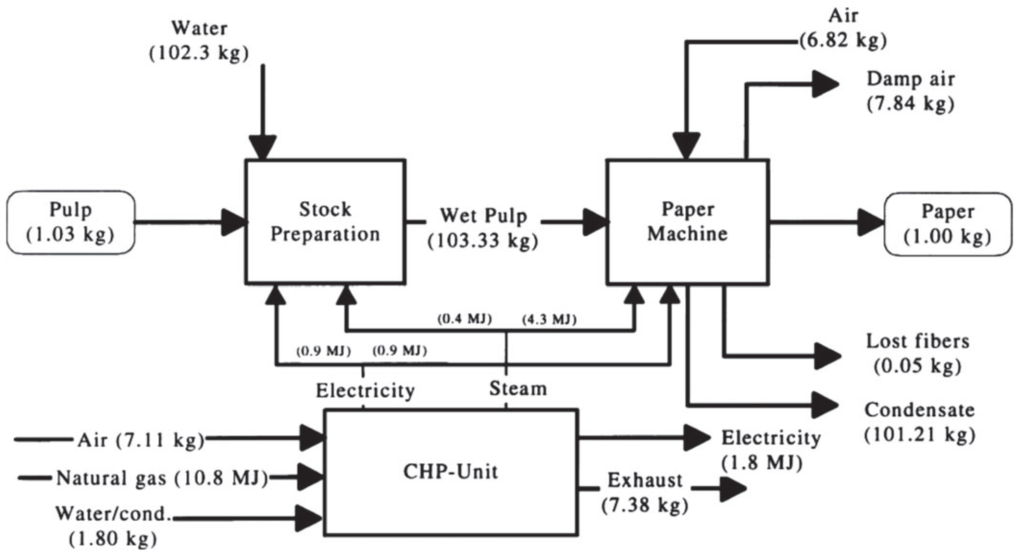

Figure 7. Unit operations involved in paper manufacturing. Published with permission from De Beer *et al.*[71] CHP-Unit: combined heat and power unit.

the sustainability of the pulp and paper industry and the degree of optimization that can realistically be achieved.

Iron and steel industry

The iron and steel industry is energetically very intensive with a worldwide average specific energy consumption of 24 GJ per tonne.[88] In addition, it is estimated that at the current level of production the world's identified iron ore reserves containing 230 billion tons of iron would last for nearly 50 years.[89] Thus, the optimization of exergy-source utilization is essential in the integrated iron and steel industry.[90]

Steel production can be carried out at an integrated facility from iron ore or at a secondary facility, producing steel mainly from recycled steel scrap. An integrated facility usually includes coke production blast furnaces, and basic oxygen steelmaking furnaces (BOFs), or in some cases open hearth furnaces (OHFs), although most OHFs world-wide were closed by the early 1990s because of their fuel inefficiency and resource intensity and are being replaced by BOFs.[89] Raw steel is produced using a basic oxygen furnace from pig iron produced by the blast furnace and then processed into finished steel products. Secondary steelmaking most often occurs in electric arc furnaces (EAFs). A brief description of the steel manufacturing technologies is presented by Yellishetty *et al.*[89] Figure 9 shows the steel production routes and energy intensities for the furnaces mentioned. The iron-making system not only consumes energy but also provides fuel to the downstream processes, such as steel making, re-heating, forming, power plant, etc.[91]

Seven specific smelting reduction processes and four groups of near-net-shape casting techniques (techniques that can attain the final shape with fewer operations, or even in one step, reducing or eliminating the reheating demand in the shaping of products) were described and evaluated by De Beer *et al.*,[88] including an exergy analysis that led to a clear conclusion: long-term energy-efficiency improvement should be directed toward reducing exergy losses by: (a) avoiding intermediate heating and cooling steps; (b) reducing the temperature required at various process steps; and (c) recovering and applying heat at high temperatures to possible routes for energy-efficiency improvement. These conclusions come from the fact that exergy losses are due mainly to the application of high temperatures and the need for several cooling and reheating steps, with radiation and convection losses (the largest source of external losses), physical exergy lost with gaseous streams, losses resulting from the conversion of chemical energy to gases with a high temperature, irreversibilities in heat transfer, and even irreversibilities in some undesired chemical reactions that occur only at higher temperatures contributing to these exergy losses. Using scrap instead of 'new' steel has been proved to be an effective method to reduce energy consumption as well as thermal energy recovery in semi-finished products and by-products, the utilization of other forms of valuable energy to obtain work and self-production of electric power with recovery fuels and steam in cogeneration and with combined cycles.[90,92]

The selection of fuel has been observed to be an important factor in the evaluation of exergy losses. Bisio[90] indicated that when combustion is considered (the main source of internal losses) two kinds of irreversibilities (always present and in different amounts for the various fuels) take place, and the chemical exergy is not suitable to quantify the technical value of a fuel. In addition, the work differs according to the fuel. On this basis, Bisio[90] defined the concept of 'usable exergy', defined as the exergy value following an adiabatic combustion with a given air excess minus the exergy loss resulting from the irreversible mixing of the combustion gases with the atmosphere, after having reached its pressure and temperature. Using this concept, the technical value (and in general also the economic value) of the various fuels can be determined, considering that they will be utilized in combustion without work transfer and that the waste gases will be mixed with the environmental atmosphere without useful work. Nevertheless, studying the chemical exergy potential of the process gives essential information to evaluate where exergy destruction takes place and thus, focus the efforts on the right process step to minimize the overall exergy losses.[93]

The iron and steel-making industry is also a concern from the point of view of CO_2 emissions. Global CO_2 emissions from steel production from the different manufacturing routes are estimated to be 3169 Mt from approximately 1781 Mt of steel production by 2020.[89] Figure 10 shows the main processes in which greenhouse gases are produced in a typical conventional blast furnace

Table 3. Recent results of exergy analysis in the paper industry

Author	Specific objective	Main conclusions
De Beer *et al.* (1998)[71]	To assess the potential for energy-efficiency improvement in the long term and selection and characterization of technologies that might reduce exergy losses.	A combination of new pressing and drying techniques, latent heat recovery systems, and a number of minor improvements can reduce the specific heat demand by 75–90%.
Utlu *et al.* (2013)[72]	To analyze a pulp and paper mill in Turkey by examining possibilities for making the entire operation thermodynamically efficient and analysing all mechanical and physical sub-processes for energy and exergy losses.	The energy efficiencies for each of the mechanical and physical steps in the pulp and paper vary between 34% and 97.4%, whereas the exergy efficiencies vary between 30.2% and 94.2%.
Aldrich *et al.* (2011)[81]	To evaluate different published allocation methods and applies them to a real case of a combined heat and power plant integrated in a paper mill and to propose a new allocation method.	All existing methods allocate emissions into power and steam outputs. Inefficiencies concerning those intrinsic to the system and the operational ones should be weighted with an allocation method.
Brown *et al.* (2005)[77]	To develop a new method based on pinch analysis techniques and optimization to identify and evaluate the opportunities for reducing energy costs by improving the energy conversion in the process.	Minimizing the exergy losses related to the studied paper drying conditions would increase the CHP production by 2.9 MWe (12%) with no significant reduction of the fuel consumption.
Cortes and Rivera (2010)[82]	To perform exergy, exergoeconomics, thermoeconomics and pinch analysis to improve the overall utilization of energy in a pulp and paper industry.	High irreversibility in the evaporator line, this, a new line of evaporators was proposed.
Gong (2005)[83]	To evaluate the exergy of the sub-process in the mill, and to indicate the largest exergy losses and possibilities to improve them.	The largest exergy losses appear in the boilers. Heating processes are highly exergy inefficient. A limited Life Cycle Exergy Analysis (LCEA) shows that the exergy output amounts to over 3 times the spent exergy as non-sustainable resources.
Goortani *et al.* (2011)[79]	To propose an efficient and practical system to recover heat from stack gases as part of an overall energy efficiency improvement of a Kraft process.	10.8 MW of heat from stack gases (7% of the process energy demand) can be reused to heat process streams such as the deaerator water, hot water, drying filtrates, and black liquor.
Holmberg *et al.* (2012)[74]	To compare three methods (energy, exergy and market based methods) to allocate fuel costs and CO_2-emissions to heat and electricity in a CHP plant in an integrated pulp and paper mill.	The best allocating method depends on the perspective (the CHP plant or the mill). From the mill perspective, the exergy method seems to be the best method to allocate both fuel costs and CO_2-emissions in most cases.
Hong *et al.* (2011)[84]	To apply the energy flow model to the Taiwanese pulp and paper industry and to analyze the energy-saving opportunities and potential.	The main energy losses were from distribution, boilers and electricity generation and equipment inefficiencies. The greatest energy-saving potential lies with improving energy distribution and equipment efficiency, and potentially comprises 86.8% in total energy conservation.
Kong *et al.* (2011)[73]	To study the possibility of improving energy efficiency by using a thermodynamic analysis in an operating coating paper machine.	A waste heat integration scheme is proposed, in which the exhaust heat from the post-drying section is recovered to heat the supply air for the pre-drying section through conventional heat recovery units installed before the steam heaters. The results show an energy efficiency improvement of 7.3% and a specific energy consumption reduction of 4.6% with profitable investments.
Mateos-Espejel *et al.* (2011)[85]	To assess the current energy performance of a Kraft pulping mill in order to identify areas of inefficiencies and to establish enhancement targets.	The utilization of the exergy analysis strengthens the grasp of existing energy inefficiencies of the process. The quantification of the exergy destroyed in the production and distribution of the utilities is a straightforward method to monitor the energy degradation in the process.

iron-making system, which consists of a coke oven, sintering machine, rotary kiln, hot stove and blast furnace.[94]

Due to the main use of coal as the primary reducing agent, the energy consumption in this industry is proportional to CO_2 emission. Measures such as the use of metallic iron as the charged material and natural gas as the auxiliary reducing agent have been observed to effectively reduce the CO_2 emissions,[91] although the injection of natural gas increases the energy and exergy consumption compared with traditional iron-making.[95] Also, using pulverized coal decreases the emission of CO_2.[96] Petela *et al.*[95] showed that oxygen enrichment has an insignificant effect on the performance in terms of energy, exergy or CO_2 emissions; and, the injection of geologically older solid natural fuels (e.g. high, medium, or low volatile coals) reduces CO_2 emission, with a

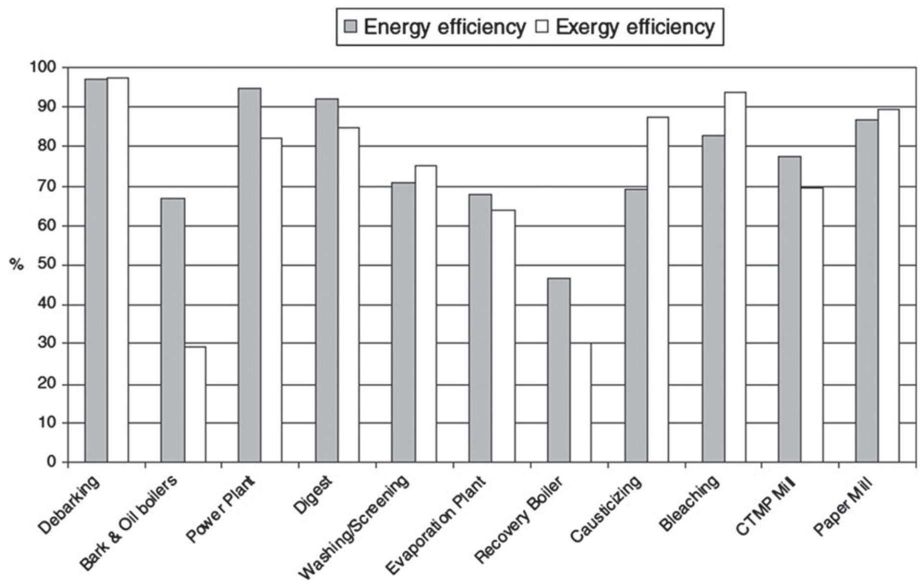

Figure 8. Energy and exergy efficiency of sub-processes in pulp and paper industry. Published with permission from Gong.[83]

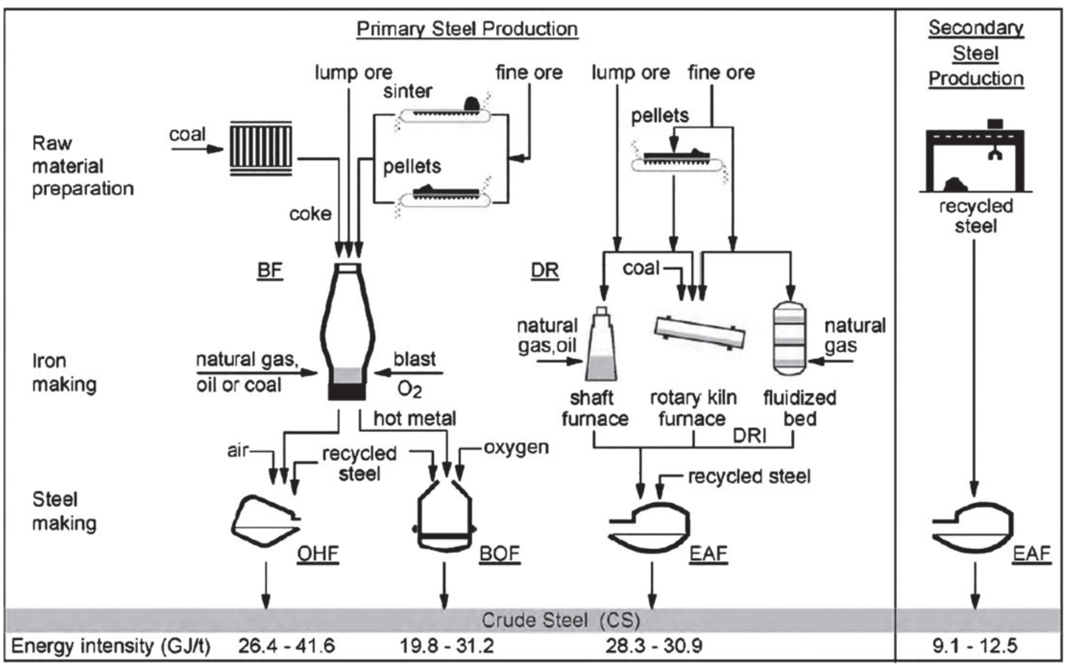

Figure 9. Steel production routes and energy intensities for basic oxygen steelmaking furnaces (BOFs), opens hearth furnaces (OHFs) and electric arc furnaces (EAFs). Published with permission from Yellishetty *et al.*[89]

simultaneous reduction in energy and exergy consumption. From this study, the importance of fuel selection is clearly observed, which may suggest a trade-off between energy and exergy efficiencies and CO_2 emission that are associated with the use of the fuel.

The emissions related to the sea transport of iron ore and steel have also to be considered in the overall analysis since the major iron ore producing countries are not the major steel producing countries and vice versa, contributing an additional 10–15% of total CO_2 emissions to steel production.[89] Thus, until the time the steel industry achieves any process technological breakthroughs (smelt reduction, strip casting, alternative fuels and carbon sequestration), it could focus attention on streamlining the world flows of materials connected with it in order to contribute towards sustainable development.

Table 4 shows a summary of recent research that aims at improving the iron and steel industry efficiency using exergy analyses. The main findings are focused on the evaluation of different processes to produce iron and steel, the variation in operating conditions in the process to minimize exergy losses, including heat recovery and the use of alternative fuels to coal, and the concerns over the high emissions of CO_2 related to this industry. In addition, process integration appears an option to improve the efficiency of the total site,[101] to overall decrease CO_2 emissions and to decrease energy and exergy inefficiencies as well as consumption of raw materials. Some examples are the integration of steel industry's

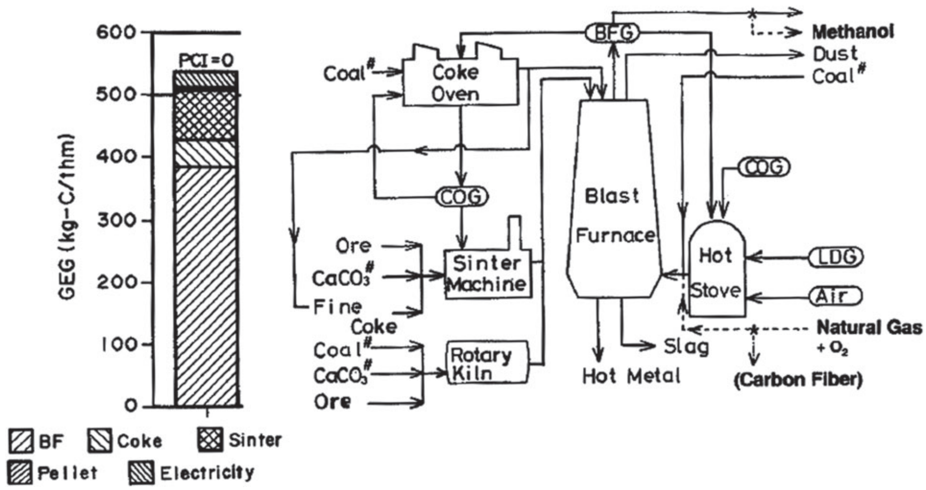

Figure 10. Greenhouse effect gas (GEG) emission in a blast furnace ironmaking system. Published with permission from Akiyama *et al.*[94] # indicates the original source of GEG.

Table 4. Recent results of exergy analysis in the iron and steel industry

Author	Specific objective	Main conclusions
Nogami *et al.* (2006)[91]	To analyze material and energy balances of iron-making system that consists of hot stove, coke oven, coke dry quenching, sintering and blast furnace.	The metallic charging to blast furnace decreases both energy input and CO_2 emission. The natural gas injection operation decreases the CO_2 emission from the iron-making system while the decrease in the energy input is small. The top gas recycling operation increases the CO_2 emission due to the scrubbed CO_2 from the recycled top gas.
Çamdali and Tunç (2005)[93]	To calculate the chemical exergy potential in an electric arc furnace depending on production materials, emphasizing the chemical exergy concept.	The chemical exergy destruction during the process occurred due to chemical reactions and combustions.
Mert *et al.* (2012)[97]	To perform an exergoeconomic analysis of a cogeneration plant in an iron and steel factory in Turkey.	Due to the results of exergy analysis, the most efficient component was the gas turbine (93.66%) while the heat recovery steam generator (HRSG) was the most inefficient (76.33%) among components of the cogeneration plant. The efficiency of the combustion chamber (77.38%) was higher than the efficiency of the HRSG (76.33%). The highest amount of exergy destruction and improvement potentials occurred in the combustion chamber and the lowest values occurred in the gas turbine.
Petela *et al.* (2002)[95]	To analyze the energy and exergy consumption and CO_2 emissions in an iron-making process	The injection of natural gas reduced the CO_2 emission, however the energy or exergy consumption increased. The coal injection effect depends on the type and rate of injected coal. The injection of the low volatile coal at the oxygen enriched blast is recommended as the best of the considered technologies. However, from the viewpoint of blast furnace operation, the injection of medium- and high-volatile coals are recommended.
Romão *et al.* (2012)[98]	To evaluate CO_2 fixation using magnesium silicate minerals by studying the energy efficiency and the integration with iron-and steelmaking.	The integration of mineral carbonation with the steel industry permits a considerable reduction of raw materials inputs and a net CO_2 reduction superior to the initial CO_2 fixed, despite the faster rate of the carbonation reactor. Further optimization is needed to make it energy-neutral.
Shigaki *et al.* (2002)[99]	To develop a methodology for evaluating the degree of optimization in the system including material recycling.	The recovery of sensible heat is effective for the improvement of overall energy efficiency in the steelmaking process.
Zhang *et al.* (2013)[92]	To analyze the thermal efficiency, exergy efficiency and power generation of three generation systems to utilize flue gas emissions from 200 to 450 °C.	An organic Rankine cycle achieves higher thermal efficiency, exergy efficiency, and power generation than when the heat source temperature varies from 200 to 375 °C, but show lower values when the heat source temperature is above 350 °C.
Yetisken *et al.* (2013)[100]	To optimize the charging materials for steelmaking.	The physical and chemical properties of the scrap and the auxiliary materials affect the chemical properties of the liquid steel and the energy and time needed to make it, either in an electric-arc furnace or a ladle furnace.

Table 4. continued

Author	Specific objective	Main conclusions
Grip *et al.* (2013)[101]	To describe the application and experience with different process integration tools at the SSAB site in Luleå, including in-house simulation models, mathematical programming, exergy analysis and Pinch analysis.	Exergy is a suitable tool for problems involving different types of energy and transformations between them. In some cases the lack of good reference data is a serious impediment.
Wang *et al.* (2012)[102]	To perform an exergy analysis of Organic Rankine Cycle (ORC) units driven by low-temperature exhaust gas waste heat and charged with dry and isentropic fluid.	The performance of the ORC unit is mainly affected by the thermodynamic property of working fluid, the waste heat temperature, the pinch point temperature of the evaporator, the specific heat capacity of the heat carrier and the turbine inlet temperature under a given environment temperature.
Nduagu *et al.* (2012)[103]	To investigate the contribution of iron to the energy requirements of a process for producing magnesium hydroxide from alkaline-earth Mg–silicate rock that contains iron.	Exergy analysis shows that at the experimental optimal temperature of 400 °C, the energy penalties of having iron oxide (FeO), hematite (Fe_2O_3) and magnetite (Fe_3O_4) as dominant iron compounds results are (for 10 wt% Fe in the rock) an increase of 0.3 GJ/t CO_2 (7%), 0.7 GJ/t CO_2 (20%) and 2.2 GJ/t CO_2 (60%), respectively, when compared with an iron-free base case.
Kadrolkar *et al.* (2012)[104]	To identify the causes, locations, and magnitudes of process inefficiencies for the COREX process, which is a smelting reduction process to produce hot metal by using noncoking fuel as a reductant. In the COREX process, reduction of iron-ore and later its melting takes place in two separate reactors, the reduction shaft and the smelter gasifier, respectively.	Operating the COREX process is theoretically feasible at lower coal rates with higher exergy efficiencies when less export gas is generated. Exergy loss (4500 to 7015 MJ/THM) varies linearly with the coal rate.
Sun *et al.* (2010)[105]	To analyze the theoretical minimum specific energy consumption and the actual one of a typical steel manufacturing process.	Several byproducts, like blast furnace gas, coke oven gas and lintz donawiz gas are essential to the internal exergy efficiency of the steelwork plant; whereas other byproducts, like benzol, tar, ammonia and slags can be used in economic activities. Thus, it is reasonably assumed that products and byproducts are both useful outputs and deducts the exergy embodied in wastes.
Ziebik and Stanek (2006)[106]	To evaluate the influence of increased thermal parameters on the thermodynamic perfection of the process and the blast-furnace plant.	The internal exergy losses in the blast furnace are comparable with the exergy losses in the processes of compressing and preheating of the blast. The best results are achieved when pulverized coal is applied. The preheating of the blast and enrichment with oxygen effects an improvement of the main energy and exergy characteristics of the blast-furnace plant.
Costa *et al.* (2001)[107]	To calculate and compare exergy losses and efficiencies for distinct steel production processes (conventional integrated, semi-integrated and new integrated with smelt reduction).	Exergy losses are the lowest for the semi-integrated plants. Life cycle inventory exergy analysis can address some trade-offs (for energy and materials flows) arising from diverse technological options for steelworks and the complete production route.
Camdali *et al.* (2001)[108]	To perform a thermodynamic analysis of a steel production step carried out in a ladle furnace (LF) in Turkey.	Exergy efficiency is found to be 50%. The actual work, the reversible work and the irreversibility increase as the temperature of the liquid steel outgoing from the LF increases but they show small changes with the temperature of the stack gas of the LF. The reversible work and the irreversibility also change with the production times in the LF. Irreversibilities occurring in the LF stem from chemical reactions and heat transfer to the surroundings.
Camdali *et al.* (2003)[109]	To perform an exergy analysis in an electric arc furnace at a steel producing company.	The second law efficiency of the system can be increased by using a pre-heating system. In this way, some of the heat lost with the stack gas to the surroundings can be recovered. The actual work, reversible work and irreversibility increase with increase in cooling water temperature. However, the exergy efficiency decreases with cooling water temperature because the increase in actual work is more than that in the reversible work.

CO_2 emissions with mineralization in which CO_2 is mineralized using magnesium silicates, leading to a significant amount of iron by-product from the mineral in the form of FeOOH that can be used as a secondary raw material stream for the iron- and steel-making industry[98] and the integration of the blast furnace iron-making system with methanol synthesis, as indicated by dotted lines in Fig. 10.[94] Nevertheless, it can be observed that in spite of the efforts to improve exergy efficiency and minimize CO_2 emissions, great difficulties are found in an industry that is energetically so extremely demanding.

CONCLUSIONS

Exergy analyses lead to a new way of thinking of how to evaluate the real efficiency of a process and they are a required but not sufficient step to evaluate the sustainability of the process. In general terms, some statements could be established: (i) the lost work should be evaluated for each production step, analyzing each operating unit and even beyond, reaching the molecular level inside the unit to know how microscopic changes can affect the overall efficiency (e.g. reaction, thermodynamics, transfer of mass, heat and momentum); (ii) the quality of energy should always be kept as high as possible; and (iii) high exergy efficiency should be the aim but keeping in mind that the best source of exergy is a renewable resource to increase the sustainability of the process.

Specifically, the following points could be highlighted for the sectors studied:

Production of chemicals:

A thermodynamic compromise between energy consumption and conversion rate is required. Since chemical reactions are a notorious source of lost work and irreversibility is unavoidable, reactions should not be run to completion and the reaction rate should be decreased in order to increase the exergy efficiency of the process.

Cement industry:

Recent publications on exergy analyses in the cement industry evaluate the efficiency of different heat recovery systems (e.g. waste heat recovery) from an energy and exergy point of view while contributing to emissions decrease since significant heat losses are incurred by the flue gases and the ambient air stream used for cooling down the clinker (about 35–40% of the process heat loss). In addition, burning wastes in the cement industry is also a hot topic in the recent research since the cement industry is characterized by high temperatures necessary to produce the clinker (around 1450 °C).

Paper industry:

The paper industry is a very energy intensive industry due to the removal of the water that is initially added to the fibers. Most of the required energy is supplied as fossil fuels and also electricity, i.e. non-renewable energy inputs. Furthermore, the paper industry is responsible for a considerable amount of greenhouse gases emissions. Thus, by replacing the present use of non-sustainable resources, the process could move towards a truly sustainable process. There is still much room for improvement in the pulp and paper industry to enhance the degree of sustainability.

Iron and steel industry:

Research on iron and steel production shows that the main internal losses of exergy occur during the combustion process and other reactions involved in iron and steel production. External exergy losses can be decreased by avoiding intermediate heating and cooling steps, reducing the temperature required in various process steps, and recovering and applying heat at high temperatures to possible routes for energy-efficiency improvement. Using scrap instead of 'new' steel has been proved to be an effective method to reduce energy consumption. The emissions related to the sea transport of iron ore and steel have also to be considered in the overall evaluation of the iron and steel production as well as the selection of the fuel since it may involve a trade-off between energy and exergy efficiencies and CO_2 emission associated with the use of the fuel.

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