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Multicriteria cost–benefit assessment of tannery production: The need for breakthrough process alternatives beyond conventional technology optimization

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ABSTRACT

The worldwide use of chromium-based processes in tanneries generates increased concerns about their related environmental burdens. Cleaner production alternatives for leather production are being proposed, based on the optimization of specific aspects or criteria, for instance, reducing demand for specific materials and energy, or reducing local toxicological emissions. While improvement on individual characteristics of the process is certainly to be favored, a more comprehensive evaluation of alternatives is also needed to prevent the risk of shifting the burden to increase global load while addressing one specific critical factor of production. This work aims to discuss the importance of a multicriteria, multiscale approach to address cleaner production strategy costs and benefits. For this, materials balance, an economic approach, and emergy (with an "m") accounting methods are applied to selected unhairing/liming, pickling/tanning and wastewater treatment steps in a tannery process, which was chosen as a case study. Results show that the assessed recycling cleaner production strategies assessed allow the manufacturer to reduce by one half the amount of water used and the demand for chemicals up to 4% with respect to the business-as-usual process, at the expense of increasing electricity demand by 10%. Economic cost-to-benefit ratio was 25$ benefits per 1$ invested, as well as an emergy-based cost-to-benefit of 33Em$ per 1Em$ invested, of course these improvements were limited to the three investigated process steps. The improvement in cost/benefit ratios indicates that converting scenario #0 into #1 is favorable under economic and emergy views. However, when the two scenarios are investigated from the point of view of the imbalance in local and renewable resource use versus imported and nonrenewable use, the emergy method shows a small overall increase in renewability (from 3.51% to 3.85%), a low, but expected, emergy yield ratio equal to 1, and a high environmental loading ratio (24.95 and 27.47). While the environmental cost–benefit ratio shows that recycling is a favorable option, the emergy performance indicators highlight that the efficiency of recycling is still insufficient and improvements in the tanning processes are needed to ensure renewability and sustainability. A number of process chemicals were involved in the investigated tannery operations, which required emergy evaluations. As a side result of this study, the Unit Emergy Values (UEVs) of SO_2, H_2SO_4 Na_2SO_4, HCL, Na_2S, NaOH, CaO, $Ca(OH)_2$, Cr_2O_3, $MnSO_4$, and $Al(OH)_3$, were also calculated thus adding to the emergy database about chemicals.

1. Introduction

Evidence of rawhide use as human vestments comes from 100,000 B.C., allowing the human to spread to cold regions, in which processes to obtain good quality hides moved from a simple smog process to the currently most commonly used chromium-based tanning. According to FAO (2003), the world bovine hide production was 6.5 million tons in 2011, denoting the socio-economical importance of hide production and the increasing environmental related concerns. The potential environmental impacts of tanning processes are significant, because this industry produces toxic gases (for instance, hydrogen sulfide and solvent vapors), putrefied solid waste, and copious volumes of wastewater containing high concentrations of inorganic salts, heavy metals, and organic substances in solution or suspension (UNEP-IE, 1996).

End-of-pipe actions, as frequently used during the last century, are no longer enough to guarantee decreased load on the environment. In this sense, the International Union of Leather Technologies and Chemists Societies (IULTCS, 2008) recommends the following cleaner strategies for tannery operations: reduce salt use in pickling floats;

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degreasing operations; wet-white pre-tanning; direct recycling of chromium tanning floats; recovery after precipitation; high exhaustion tanning process; and chromium-free tanning. A wide range of technological routes exists for waste minimization and treatment of tannery final liquid effluents. Due to their significant socio-environmental impacts, cleaner production strategies in tannery industries are mainly focusing on unhairing/liming and pickling/tanning processes; some studies propose new tanning methods (Li et al., 2010; Manfred et al., 2012; Sundar et al., 2002), while others suggest technological processes of recycling chromium after the tanning stage (Kanagaraj et al., 2008; Rivela et al., 2004; Sundar et al., 2002). New process for unhairing/liming, which demands less water and chemicals compared to conventional processes also have been proposed (Dettmer et al., 2013; Raghava Rao et al., 2003; Thanikaivelan et al., 2003), as well as general recommendations related to specific cases (Giannetti et al., 2008; Hu et al., 2011; IULTCS, 2008). All of them aim at producing high quality products while reducing the demand for resources, reducing costs, and generating lower environmental impacts. However, most of these studies focus mainly on the local or direct impacts, such as the reduction of chemicals and water usage, and the toxic content of effluents, disregarding supply-chain aspects that can be revealed only from a global scale perspective.

Direct indicators at the local scale are recognized as important aspects for decision making focusing on economic benefits and cleaner production strategies, because they drive direct reduction of materials and energy inputs. However, these indicators are not able to address sustainability issues of production systems (Gasparatos et al., 2008). In accordance with Schnitzer and Ulgiati (2007), there are cases in which “less bad is not good enough”. For instance, Manfred et al. (2012) found that using supercritical fluids for tanning processes saves large amounts of water and chromium; however, new equipment (i.e., steel and other materials) is demanded as well as increased use of electric energy. Obviously, electricity and steel do not have the same socio-environmental toxicological impact as high chromium wastewater, but their use stresses the environment in such a way by demanding environmental investments in providing material and energy resources at larger scales than the tannery process scale. The present work evaluates the proposals by Class and Maia (1994), as well as by Ludvík and Buljan (2000) for recycling of water, sodium sulfide, calcium hydroxide, and chromium (III) oxide after the unhairing/liming and pickling/tanning processes in tanneries. These proposals were adopted by São Paulo's State agency for environmental sanitation technology (Pacheco, 2005). Such cleaner production strategies are suggested as good alternatives for all chromium-based tannery plants in Brazil. However, this recommendation is directed to the reduction of chemicals and water, and at the same time of the total amount of wastewater generated. On the other hand, the demand for other direct and indirect materials and energy needed to allow the functioning of recycling processes is disregarded. In this sense, can a decision be made for cleaner production strategies based exclusively on the local reduction of specific materials? Are there any further hidden costs of using this kind of cleaner production strategy?

These questions were partially answered by means of methodologies characterized by broader evaluation windows, such as the Life Cycle Assessment (LCA), which is already being used in the study of tanneries (Kiliç et al., 2011; Joseph and Nithya, 2009; Nazer et al., 2006; Canals et al., 2002; Rivela et al., 2004; among others). However, most of the LCA studies focus on the environmental consequences of input and output material flows (from cradle to grave) and do not include the renewable sources that broadly support production processes (e.g. pollutant dispersal by wind) nor the time scale involved in the generation of resources by biosphere work nor they do include the environmental support to labor and services supplied within the larger country's economic dynamics. LCA's impact categories are recognized as fundamental for environmental assessments, but they do not fully capture a system's sustainability within the larger scale of the biosphere. The emergy accounting (spelled with an “m”; Odum, 1996) is used in this study as a complementary scientific tool to generate sustainability assessment indicators, in order to provide additional criteria for decision-making. Emergy accounting is a donor-side approach, i.e. it accounts for the environmental work for resource generation and provision to natural and human-made processes. Emergy based indicators are specially designed for decisions regarding sustainability: its supply-side “quality” concept includes time, evolution and resources convergence into an environmental cost calculation framework, thus providing a complementary added value to traditional economic, energy and material flow accounting.

By recognizing the importance of a multiscale, multicriteria analysis to identify the hidden costs and benefits of production systems, this study assesses the cleaner production strategies for the optimization of water and chemicals used and recycling in tanneries, through the use of (i) material and energy balances, (ii) economic analysis, and (iii) emergy accounting methods.

2. Materials and methods

2.1. System description

In tannery processes, animal hides and skins are treated to remove non-structured proteins and fat, and an essentially pure collagen matrix is preserved by tanning. This involves the impregnation of the skins with mineral, synthetic or vegetable tanning agents. Basically, the processes involved in tannery plants (from rawhides to leather) are the following: (i) soaking; (ii) green fleshing; (iii) unhairing/liming; (iv) lime fleshing; (v) deliming/bathing; (vi) degreasing (sheep/pig skins); (vii) pickling/tanning; (viii) chrome splitting; (ix) shaving; (x) retanning/dyeing/fat liquoring; (xi) drying; (xii) batting/trimming (see UNEP-IE, 1996, for a detailed processes explanation). All these processes release wastewater, airborne pollutants, and solid waste. Due to their high environmental impact (i.e. high amount of waste, high treatment cost, and high toxicological effects; Joseph and Nithya, 2009; Canals et al., 2002) compared to the other steps, the unhairing/liming and pickling/tanning processes are the focus of the present study (Fig. 1).

As far as cleaner production strategies are concerned, alternative technological routes have been suggested, aiming at the reduction of materials and energy demand in tannery processes, as well as at the reduction of generated waste (Sundar et al., 2002; Thanikaivelan et al., 2003; Kanagaraj et al., 2008; Rivela et al., 2004; among others). Tannery companies already know alternative technological solutions that would allow cleaner production practices (for instance, the counter-current methods described by Raghava Rao et al., 2003), but in practical terms, Pacheco (2005) argues that these technologies are restricted by market conditions, systemic failures, and also cultural barriers.

Fig. 2 describes the alternative proposed by Class and Maia (1994) for the Brazilian tannery plants aiming at profit increase by reducing materials demand (water and chemicals), and at the same time, at reduction of toxicological effects thanks to wastewater decrease. Although published twenty years ago, Class and Maia's recommendations can be considered innovative for the Brazilian case because the majority of tanneries still use the traditional hide production processes represented by Fig. 1.

The general characteristics of the case study tannery are described in Table 1, including implementation and operation phases.

The unhairing/liming recycling process consists in the separation of the thickest solid particles by sieves, and the sedimentation process for the dissolved particles in the aqueous environment. For these solid–liquid separation processes, electric energy is the only additional input in the operation phase, needed to power pumps and blenders. Materials are demanded during the implementation phase for infrastructure and equipment. No chemical inputs are necessary for recycling; the separated aqueous solution containing Na_2S and $Ca(OH)_2$ is recycled

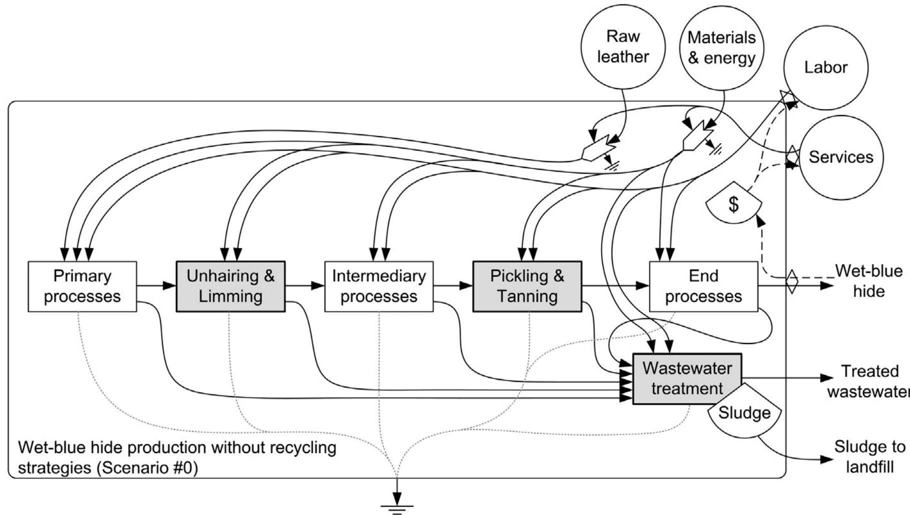

Fig. 1. Diagram representing the scenario #0: the wastewater plant treatment without any recycling processes within tannery plant. Gray rectangles indicate the assessed processes.

several times. Class and Maia (1994) report cases in which the aqueous solution was recycled for two years without interfering with the quality of the leather final product. The amounts of Na_2S and $Ca(OH)_2$ consumed during the first unhairing/liming cycle and/or lost during the recycling process are replaced in the next cycle, and the ideal concentration is maintained. According to Class and Maia (1994), the local and clearly identified recycle benefits in the unhairing/liming process are: reduction of the amount of chemicals and water inputs used; reduction of the wastewater volume to be released; reduction of H_2S released resulting in lower corrosion of infrastructure and equipment, bad odors, and toxicity; reduction of biological and chemical oxygen demand for wastewater treatment; and reduction of nitrogen concentration and sludge generation in the wastewater treatment plant.

The pickling/tanning recycling process occurs by adding NaOH into the aqueous solution to precipitate the residual chromium as trivalent chromium hydroxide. The precipitate flows through a press-filter for water extraction; finally, chromium hydroxide in the solid state is dissolved by the addition of H_2SO_4 resulting in Cr_2O_3, which is used again in the pickling/tanning process. According to Pacheco (2005), the advantages of chromium recycling are: reduction of chromium input into the process; reduction of wastewater with consequent reduction of treatment costs; and decrease of potential environmental disasters due to the chromium released.

From a larger perspective, it can be seen that even if scenario #0 (Fig. 1) does not consider recycling strategies, it demands goods and services for wastewater treatment to reach the minimum concentration levels for some discharged elements as established by the Brazilian regulations. In a like manner, scenario #1 (Fig. 2) shows that, while recycling strategies are able to reduce the demand for some materials, they also demand other kinds of materials and energy to enable the recycling process. Thus, there is a trade-off that establishes the need for a multicriteria multiscale assessment to verify which system is more aligned to sustainability concepts.

2.2. Environmental performance biophysical indicators at local scale

Usually, the environmental burden can be assessed under two spatial perspectives: local and global. Both ways, despite their importance, represent different viewpoints. While the local scale (or

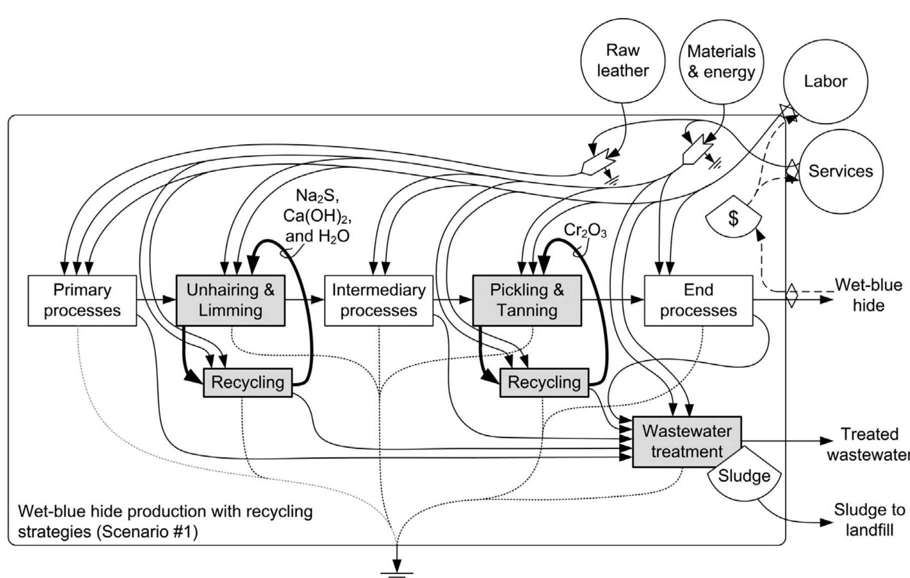

Fig. 2. Diagram representing the scenario #1: two recycling processes were added to the tannery plant, before the wastewater treatment. Gray rectangles indicate the assessed processes.

Table 1
Main characteristics[a] of the wet blue hide[b] tannery.

Description	Amount	Unit
Tannery capacity	6,500,000	$kg_{rawhide}$/yr
Plant's work time	260	day/yr
Water demand on unhairing/liming	300	% on rawhide weight
Sodium sulfide demand on unhairing/liming	3	% on rawhide weight
Water demand on pickling/tanning	100	% on rawhide weight
Chromium demand on pickling/tanning	8	% on rawhide weight
Wastewater flow (without recycling)	750	m^3/day
Wastewater flow (with recycling)[c]	675	m^3/day
Plant's lifetime (structure and equipments)	25	Yr

[a] Adapted from Class and Maia (1994).
[b] Wet blue hide is a chrome leather in a humid state before finishing processes.
[c] Scenario #1 in this study, i.e. recycling in unhairing/liming and tanning/pickling processes.

direct approach) is mainly concerned with the outputs and looks at the environmental consequences of the emissions, the global scale (or indirect approach) is mainly concerned with the system's inputs and focuses on the depletion of environmental resources. Locally, the environmental loads are mainly related to measurements of gaseous, liquid and solid emissions. On the other hand, the global scale represents the so-called "hidden" environmental burdens, in that they are most often disregarded in policy and planning (Ulgiati et al., 2006). Both scales are important for sustainability assessments, but the reductionist perspective should be used with care (Gasparatos et al., 2008) not to risk shifting the burden from the local to the global scale.

This work considers the following local environmental indicators for a comparative assessment of scenarios #0 and #1: (i) acid level and concentration of some elements in the wastewater before the wastewater treatment (i.e., pH, settleable solids, chemical and biochemical oxygen demand, chromium and sulfide concentration); (ii) material and energy demand (including water, chemicals, and electricity) to produce 1 ton of wet-blue hide.

2.3. Environmental performance biophysical indicators at the global scale: emergy accounting

As a complement of the performance indicators considered on the local scale, global scale indicators cumulatively account for all the hidden process costs required to produce and make available all the goods and services used locally (Agostinho and Siche, 2014). For this task, several assessment methods are available, each one using different criteria, such as energy, mass, land use, and so on. For example, emissions can be assessed under a life cycle approach (Jensen et al., 1997), energy under an embodied energy analysis (Slesser, 1974), mass under a material intensity analysis (Wuppertal Institute, 2014), and land area under an ecological footprint framework (Wackernagel et al., 2005). Most of these approaches are gradually being taken into account within the most advanced LCA studies and software (e.g. CML 2000, CED—Cumulative Energy Demand and RECIPE, all within the Ecoinvent database; Ecoinvent, 2013). However, the systemic design of the emergy accounting approach (Odum, 1996), aligned to the capacity of accounting also for economic and free environmental resources (i.e., considered provided for free by the environment or simply not considered by other methodologies), as well as of recognizing the supply-side "quality" of energy, confers to this method higher eligibility and robustness than other available tools (Agostinho and Pereira, 2013; Giannetti et al., 2013a), when sustainability comes into play.

Emergy is "the available energy of one kind previously used up, directly and indirectly, to make a service or product" (Odum, 1996 p.7). In accordance to the second law of thermodynamics, each transformation process degrades the available energy (exergy) of the input flows, but the "quality" of the output flow is increased within the thermodynamic hierarchy of the system/process. Emergy can be considered a scientific measure of environmental support in terms of "resources" virtually embodied in goods and services provided to a system or a process. Further information about the emergy methodology, rules, and meanings, can be found mainly in Odum (1996) and Brown and Ulgiati (2004).

Emergy has been used in several different case studies, from the assessment of natural (Ulgiati et al., 2011a), agricultural (Agostinho et al., 2008; Bonilla et al., 2010; Giannetti et al., 2011), and industrial systems (Giannetti et al., 2008) to also assessing buildings and cities (Ascione et al., 2009; Conte and Monno, 2012; Mori and Christodoulou, 2012; Zucaro et al., 2014), and information (Abel, 2013). To perform an emergy evaluation, first the system under study must be represented by a detailed energy diagram using the energy system symbols proposed by Odum (1996). All flows in the diagram are characterized in accordance to the supply quality of its source (Fig. 3). An emergy table is then generated in which all quantitative values of the identified energy and mass inflows are multiplied by their respective Unit Emergy Values (UEV, measures of emergy intensity of a resource; Appendix A), resulting in flows with the same unit of solar emjoules (seJ). Finally, these flows are combined for the calculation of total emergy "U" and emergy indices (Fig. 3), which help to draw conclusions about system's performance — at this point, the ternary diagram as proposed by Giannetti et al. (2006) and later described in detail by Almeida et al. (2007) could be helpful for a graphical interpretation of the assessed systems.

All UEVs used in this work do not include Labor and Services and are based on the global emergy budget of 15.2 E24 seJ/yr (Brown and Ulgiati, 2010). Prior to 2011, the annual emergy driving the geobiosphere was estimated as 15.83 E24 seJ/yr (Odum, 2000) and 9.44 E24 seJ/yr (Odum, 1996). UEVs calculated according to Odum (1996) need to be updated to the most recent baseline, by multiplying by 1.61 (= 15.2 / 9.44). Values calculated according to Odum (2000) generally should be multiplied by 0.96 to fit the Brown and Ulgiati (2010) baseline. However, the changes would be very small and would fall within the uncertainty range of the calculated baselines. As a consequence, we do not update the Odum (2000) values to Brown and Ulgiati's baseline.

A brief description of emergy indices used in this work is given below:

(a) Unit Emergy Value (UEV) is the general label for all emergy intensities, i.e. it is defined as the solar emergy required to make one unit of system's product output (be output measured in energy, mass, as well as any other kind of units). It is calculated by the ratio of total emergy (U) that was used in a process to the product amount (UEV = U/Product). When using Joules as unit

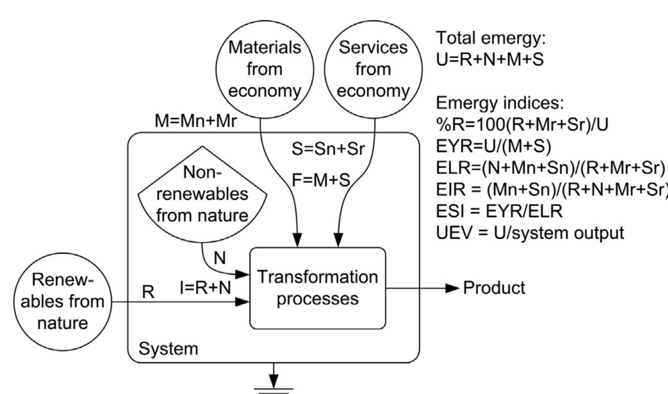

Fig. 3. General diagram representing all energy sources involved in the transformation process. Symbols from Odum (1996). Suffixes "n" and "r" means non-renewable and renewable respectively, referring to the renewable and nonrenewable component of material and energy flows. Emergy indices are explained in the main text.

of the product, the UEV is named Transformity, considered as a fundamental intensive variable in emergy accounting. UEV is an expression of efficiency and supply-side quality of the output itself, for the higher the UEV, the more emergy is required to make the product flow. If the process is not discontinued in the long run, this means that the product proves to be useful to the system's performance compared to others and therefore its quality is recognized.

(b) Renewability (%R = 100 ∗ (R + Mr + Sr)/U) is the ratio of renewable emergy to total emergy use. It ranges from 0 to 100%, where higher values mean better rating. In this work, the partial renewabilities of each input are considered for %R calculation, as suggested by Ulgiati et al. (2005) and recently discussed by Ulgiati and Brown (2014). The inclusion of partial renewabilities is an attempt to include the renewability of each system input by expanding the boundary of their generation and supply process; this approach is particularly appropriate when the system uses materials and labor from the local or regional economy, which could be renewable or, at least, partially renewable. The assumed partial renewability values for some inputs as done in this work were based on the authors' experience and from published scientific works. The following values were used: 50% for water, 68% for electricity, and 15.2% for labor and services in Brazil; for all other items, partial renewability was considered negligible (see Appendix B for details).

(c) The Emergy Yield Ratio, EYR = U/(M + S), is the ratio of the total emergy driving a process to the emergy imported. It is a measure of the system's ability to exploit the local natural resources by means of an external resource investment from the outside economic system, and reflects the potential contribution of the process to the main economy (Brown and Ulgiati, 2004). A pure conversion process has EYR = 1, while higher EYR values mean that each unit of investment from outside is amplified and returns higher amounts of emergy to the larger economic system.

(d) The Environmental Loading Ratio, ELR = (N + Mn + Sn)/(R + Mr + Sr), is the ratio of non-renewable and imported emergy use to renewable emergy use. It indicates the pressure on the environment produced by the system and can be considered as a measure of ecosystem stress (i.e., distance from a system state supported by renewable sources only). According to Brown and Ulgiati (2004), ELR values lower than 2 indicate low load on local environment; values between 2 and 10 mean moderate pressure; and values higher than 10 mean large pressure and impact. As well as for emergy renewability index, partial renewabilities of flows are considered for ELR calculation in this study.

(e) The Emergy to Money Ratio, EMR = U/GDP, is the ratio of the total emergy supporting a national economy (its Gross Domestic Product) in one year, expressed as seJ per currency unit. In general, countries with developed financial systems have large monetary circulation, which translates into lower EMRs than for developing countries. Inflation contributes to increase the GDP faster than available resources (U) used within the country boundaries, which most often causes EMRs to decrease over time.

Other emergy indices were not considered in the present work because of the particular boundary of the systems assessed in this study. In fact, the investigated systems only represent a small and specific step of a more complete leather production chain. Thus, using other emergy indices might be less telling and hard to adapt to the specific boundary.

2.4. Economic performance under traditional and emergy views

For economical purposes, the Cost–Benefit Analysis (CBA) is most useful when analyzing a single alternative or proposed system to verify whether the system's benefits exceed the costs, or when comparing systems to verify which achieves the greatest net benefits. CBA is frequently used for economic analysis, however, the main difficulty with CBA is related to establishing dollar values for all environmental costs and benefits under a donor-side view therefore, this work considers the CBA estimation using traditional economic and also emergy perspectives.

Emergy accounting is based on a different conceptual framework compared to traditional economic theory. While the economic theory assigns value under a user-side point of view (i.e., the willingness to pay for a good or service), emergy accounting considers a donor-side perspective, i.e. it accounts for all energy invested by the biosphere (through nature and the economy) to make available a good or a service. To this purpose, an emergy-related economic indicator is used, namely the ECE (Emergy Currency Equivalent; Dong et al., 2014), sometimes named Emdollar value (Em$), defined as the amount of gross economic product ($ or other currency) potentially supported by a given flow of emergy (obtained by dividing the emergy of the flow by the appropriate emergy-to-money ratio of the country). The ECE expresses the fraction of a country's economic product (fraction of GDP) virtually supported by a given emergy inflow to the economic process. The ECE indicates the direct and indirect contribution of each emergy flow or component to the economic process. It also helps understand the "economic equivalence" (value to the economy) of processes and flows that are not market commodities (e.g., ecosystem services, such as water cycling, CO_2 uptake, nitrogen fixation, biodiversity, etc). The ECE value of a good or service has also been referred to as "macroeconomic value", to indicate the wealth driven by resource availability, measured in emergy terms. Being a ratio of emergy to EMR, not only does it incorporate the environmental support embodied in the resource flow, but also it takes into account a country's performance, i.e. its conversion efficiency of resources into wealth. According to Odum (1996), the ECE is an appropriate measure when discussing large-scale considerations of an economy and comparing it with real monetary circulation. Making decisions to maximize the ECE is the same as maximizing emergy use, resulting in a sustainable and competitive economy.

The Cost–Benefit Ratio (CBR) in this work is calculated as the ratio of Costs to Benefits. This index may be an important tool for appropriate discussion of recycling issues, because it indicates if the cleaner production practices are economically justified. It can be interpreted as the costs of obtaining one unit of benefit. This ratio is usually calculated in money terms, however since money disregards aspects of environmental sustainability, we suggest that the same ratio might be defined in emergy terms (seJ) or in emergy currency equivalents (Em$ or other currency). The money-based cost-to-benefit ratio can be calculated as the ratio of the economic value of the product to the money invested in the process. This cannot be done in our case study, because we are not investigating the entire process but only selected improved steps and therefore we are not comparing costs and benefits for the process as a whole. The same limitation applies to an emergy-based cost-to-benefit ratio. Therefore, we define our indicators as the ratio of the money or emergy invested for the alternative scenario (scenario #1) to occur to the money or emergy saved thanks to the implemented innovation, relative to the "business as usual scenario" (scenario #0). The following performance indices are therefore used in this work: (i) investment costs in $ and Em$; (ii) benefits in $ and Em$ for scenario #1 with respect to scenario #0; (iii) Cost-to-Benefit Ratio based on the economic ($CBR_{\$}$) and emergy accounting ($CBR_{Em\$}$) frameworks. All data refer to 1 ton of produced "wet-blue" hide. An emergy-to-money ratio (EMR, emergy use per unit of gross domestic product) for Brazil of 4.24 E12 seJ/$ in 2013 (Appendix A) was used to convert emergy units into equivalent currency, i.e. to convert from "seJ" to "Em$".

2.5. Methodological approach for results analysis

This paper assesses the performance of tannery process scenarios using a multicriteria multiscale approach, by means of indicators

Table 2
Improvement of wastewater quality parameters due to recycling strategies in unhairing/liming and pickling/tanning processes.

Parameter	Scenario #0 (without recycling)[a]	Scenario #1 (with recycling)[a]	Quality improvement in %	Maximum levels allowed[b]
pH	8.6	7.5	12.8	6.0–9.0
Settleable solids (mg/L)	90	21	76.7	500
COD (mgO_2/L)[c]	7250	4000	44.8	–
BOD_5 (mgO_2/L)[d]	2350	1800	23.4	3
Chromium, Cr^{+3} (mg/L)	94	15	84.0	0.05
Sulfite, S^{2-} (mg/L)	26	10	61.5	0.002

Source: Class and Maia (1994).
[a] Values correspond to water quality parameters before it goes to wastewater treatment plant.
[b] Maximum values allowed before disposing wastewater in rivers (CONAMA, 2005).
[c] Chemical oxygen demand.
[d] Biochemical oxygen demand.

based on different dimensions as well as space and time scales. The analysis of results is based on the assumption that all indicators are given the same weight and importance during the decision-making process. Two approaches were considered: (a) a simple index-by-index comparison for both scenarios; (b) an integrated view supported by a radar diagram. In option (b), to draw the diagram, all the indicators obtained for scenario #0 (without recycling) were considered as reference parameters and their values were set equal to “1”. Then, each individual indicator of scenario #1 (with recycling) was divided by its equivalent indicator of scenario #0 and the ratios diagrammed. The graphical reading shows how much the new design scenario's indicator has better or worse performance compared to the same indicator in the reference scenario and which scenario has the best overall performance looking at all indicators as a whole. Under the procedure adopted, a smaller area would be interpreted as having a better performance.

3. Results

3.1. Environmental performance biophysical indicators at the local scale

Brazilian regulations establish a national classification of water resources, according to their physical, chemical, and biological characteristics, their intended use, as well as quality parameters for wastewater before its discharge into water bodies (CONAMA, 2005). Regarding tannery activities, the main wastewater quality parameters are presented in Table 2. The values obtained for scenario #1 indicate an improvement for all parameters when compared to those of scenario #0, in which the concentration of chromium and sulfite – considered important due to their potential toxicities – shows a reduction of 84% and 61% respectively. However, it must be highlighted that although the recycling scenario presents better water quality parameters, they are still higher than the thresholds for wastewater quality established by the Environmental Brazilian Legislation before its disposal into water bodies. Thus, even with recycling processes, scenario #1 still needs to be coupled to a wastewater treatment plant; in general, the latter is implemented in almost all Brazilian tanneries. This important aspect was also pointed out by Freitas and Melnikov (2006) when investigating the performance of two tanneries in the central region of Brazil.

For any production system, recycling strategies are suggested as a good alternative when the purpose is to attain more efficient resource use. However, recycling also demands additional materials and energy, for implementation of infrastructure and equipment, as well as for the operational phase. Thus, the key point is to understand whether recycling operations demand more or less resources than traditional processes, or put in other words, if saved resources are more than invested resources so that results are worth the effort. The improvement of wastewater quality parameters of scenario #1, resulting from unhairing/liming and pickling/tanning recycling strategies, translates into lower demand of water, sodium sulfide, calcium hydroxide, chromium (III) oxide, manganese (II) sulfate, and aluminum sulfate (Table 3). On the other hand, there is an increase in the use of the electricity, sodium hydroxide, and sulfuric acid, raising doubts about the real effectiveness of scenario #1. Does this trade-off translate into a better environmental performance of scenario #1? This question cannot be answered by considering solely the biophysical local scale

Table 3
Biophysical indicators at local scale for the assessed scenarios.

Item	Scenario #0 (without recycling)	Scenario #1 (with recycling)	Gross recycling benefit[a]	Gross recycling cost[a]
Operational phase of unhairing/liming process				
Water (kg/ton_{hide})	3000	1021	1979	–
Electricity (kWh/ton_{hide})	8	25	–	−17
Sodium sulfide, Na_2S (kg/ton_{hide})	30	15	15	–
Calcium hydroxide, $Ca(OH)_2$ (kg/ton_{hide})	30	21	9	–
Operational phase of pickling/tanning process				
Water (kg/ton_{hide})	1000	1000	–	–
Electricity (kWh/ton_{hide})	3	9	–	−6
Chromium (III) oxide, Cr_2O_3 (kg/ton_{hide})	80	61	19	–
Sodium hydroxide, NaOH (kg/ton_{hide})	0	4	–	−4
Sulfuric acid, H_2SO_4 (kg/ton_{hide})	0	3	–	−3
Operational phase of wastewater plant				
Electricity (kWh/ton_{hide})	208	208	–	–
Manganese (II) sulfate, $MnSO_4$ (kg/ton_{hide})	1	<1	<1	–
Aluminum sulfate, $Al(OH)_3$ (kg/ton_{hide})	6	5	<1	–
Polyelectrolyte(kg/ton_{hide})	<1	<1	<1	–

Adapted from Class and Maia (1994).
[a] Gross recycling benefit = (scenario #0) − (scenario #1). Negative numbers indicate an increase in energy or material demand, thus a recycling cost.

Table 4
Emergy evaluation of scenario #0 (without recycling).

Item	Description and category	Renewability fraction[(a)]	Amount [(b)]	$Unit/ton_{hide}$	UEV (seJ/Unit)[(c)]	Renewable emergy (seJ/ton_{hide})[(d)]	Nonrenewable emergy (seJ/ton_{hide})[(e)]	Emergy (seJ/ton_{hide})[(f)]	Emergy (%)	Emergy ($Em\$/ton_{hide}$)[(g)]
Implementation phase										
1	Concrete (M)	0.0	8.18E + 00	g	2.42E + 09	0.00E + 00	1.98E + 10	1.98E + 10	0.0	0.00
2	Steel (M)	0.0	2.92E + 01	g	7.81E + 09	0.00E + 00	2.28E + 11	2.28E + 11	0.0	0.05
3	Copper (M)	0.0	2.95E − 01	g	9.80E + 10	0.00E + 00	2.89E + 10	2.89E + 10	0.0	0.00
4	Plastic (M)	0.0	1.23E + 00	g	5.51E + 09	0.00E + 00	6.78E + 09	6.78E + 09	0.0	0.00
5	Diesel (M)	0.0	6.96E + 04	J	1.81E + 05	0.00E + 00	1.26E + 10	1.26E + 10	0.0	0.00
6	Labor (S)	15.2	1.11E − 01	$	4.24E + 12	7.15E + 10	3.99E + 11	4.71E + 11	0.0	0.11
7	Services (S)	15.2	5.72E + 00	$	4.24E + 12	3.69E + 12	2.06E + 13	2.43E + 13	0.3	5.72
Operational phase										
8	Electricity (M)	68.0	8.31E + 08	J	1.47E + 05	8.30E + 13	3.91E + 13	1.22E + 14	1.3	28.80
9	Labor (S)	15.2	1.02E + 01	$	4.24E + 12	6.54E + 12	3.65E + 13	4.30E + 13	0.4	10.15
10	Water (M)	50.0	4.00E + 06	g	3.27E + 05	6.54E + 11	6.54E + 11	1.31E + 12	0.0	0.31
11	Na_2S (M)	0.0	3.00E + 04	g	2.71E + 10	0.00E + 00	8.13E + 14	8.13E + 14	8.4	191.75
12	$Ca(OH)_2$ (M)	0.0	3.00E + 04	g	3.18E + 09	0.00E + 00	9.54E + 13	9.54E + 13	1.0	22.50
13	Cr_2O_3 (M)	0.0	8.00E + 04	g	8.17E + 10	0.00E + 00	6.54E + 15	6.54E + 15	67.7	1541.51
14	$MnSO_4$ (M)	0.0	1.05E + 03	g	3.34E + 11	0.00E + 00	3.51E + 14	3.51E + 14	3.6	82.79
15	$Al(OH)_3$ (M)	0.0	6.00E + 03	g	7.56E + 09	0.00E + 00	4.54E + 13	4.54E + 13	0.5	10.70
16	Polyelectr. (M)	0.0	3.00E + 01	g	4.50E + 11	0.00E + 00	1.35E + 13	1.35E + 13	0.1	3.18
17	Rain (R)	100.0	9.54E + 05	J	3.05E + 04	2.91E + 10	0.00E + 00	2.91E + 10	0.0	0.01
18	Services (S)	15.2	3.81E + 02	$	4.24E + 12	2.45E + 14	1.37E + 15	1.61E + 15	16.7	380.66
	Total emergy accounting for Services (items 7 and 8):					3.39E + 14	9.32E + 15	9.66E + 15	100.0	2278.25
	Total emergy without account for Services (items 7 and 8):					9,03E + 13	7,93E + 15	8,02E + 15	–	1891,87

Locally natural renewable resources are not considered due to their inexpressive direct contribution to total emergy; (R) = renewable resources from nature; (M) = materials from economy; (S) = services from economy.

(a) From B.

(b) From Supplementary Material S.1.

(c) From A.

(d) Renewable emergy = (Amount) ∗ (UEV) ∗ (Renewability fraction).

(e) Non-renewable emergy = (Amount) ∗ (UEV) ∗ (100 − Renewability fraction).

(f) Emergy in seJ/ton_{hide} = (Amount) ∗ (UEV).

(g) Emergy in $Em\$/ton_{hide}$ = (Emergy in seJ/ton_{hide}) / (4.24 E12 seJ/$; Brazilian emergy per money ratio from A).

indicators, but requires a larger scope to be understood, especially if it deals with planning and environmental decision-making. Such broader scope can be provided by the emergy method, adopted in the present study in addition to traditional economic and resource accounting.

3.2. Environmental performance biophysical indicators at the global scale: emergy accounting

Table 3 shows that water is the input with the largest reduction in units of mass for the recycling scenario #1, reaching 1.98E + 06 g/ton$_{hide}$, followed by chromium III oxide, and sodium sulfide. The direct reduction of energy and materials within the recycling scenario is a good start to assess which process has higher direct net benefits. However, mass and heat content of flows, while easily converted to money value, do not capture the complexity of and the environmental support of resource generation within biosphere cycles. Flows used or saved in largest amounts may not be those for which the highest demand for biosphere work is required (and therefore subtracted from other uses). In fact, matter flow accounting and energy analysis disregard the donor-side quality of each flow, namely the time needed for resource generation and the ongoing natural selection over the different resource production pathways. Moreover, energy and material accounting disregard direct and indirect labor demand (i.e. resources supporting labor) as well as direct ecosystem services supporting the process (wind for dispersal of pollutants, biosphere water and heat cycling for atmospheric temperature control, among others). Tables 4 and 7 show the cost of both scenarios under a more comprehensive emergy evaluation, the results of which are essential in the calculation of more telling cost–benefit index. These tables, added to Tables 5 and 6, allow a much different assessment of benefits and costs.

Table 4 indicates that out of a total emergy demand of 9.66E + 15 seJ/ton$_{hide}$ in scenario #0, the input of chromium III oxide corresponds to 68% of the total, while sodium sulfide, the second most representative material, only accounts for 8%. Recognizing that chromium is a non-renewable resource, efforts for its reduction could lead to a more sustainable system. This strategy is considered in scenario #1 (Table 7), where out of a total emergy demand of 7.22E + 15 seJ/ton$_{hide}$, chromium still accounts for about 69% of this total, but its absolute amount decreased from 6.54 E15 to 4.97 E15 seJ/ton$_{hide}$. The reduced amount of total emergy demand of scenario #1 compared to #0 (about 25%) also translates into a higher efficiency of scenario 1 in converting resources into wet blue hides.

Table 6 shows that the item with the largest emergy reduction is chromium (III) oxide, reaching 370 Em$/ton$_{hide}$ followed by sodium sulfide (96 Em$/ton$_{hide}$), manganese II sulfate (9 Em$/ton$_{hide}$), and calcium hydroxide (7 Em$/ton$_{hide}$); the reduction of water demand, under an emergy perspective, can instead be considered negligible compared to other items (0.15 Em$/ton$_{hide}$). This goes against the biophysical local indicators which pointed out that water was the most significant in terms of total material reduction, however, the emergy approach considers the quality of the resource and thus water is considered to be negligible compared to other material reductions. There is a clear difference between the traditional economic approach ($) and the emergy approach (Em$), because while the first one points out 115 $/ton$_{hide}$ of benefits, the emergy approach shows benefits of 598 Em$/ton$_{hide}$, i.e. the amount saved is virtually able to generate an additional economic benefit if properly used in other processes.

Which numeraire (g, seJ, Em$, or $) should therefore be considered for decision-making? As pointed out by Ulgiati et al. (2006, 2011b), a multicriteria approach should always be adopted – to the largest possible extent – when dealing with sustainability issues of goods and services, within which emergy accounting plays a special role.

4. Discussion

4.1. Economic performance under traditional and emergy points of view

The biophysical local indicators presented in Table 3 are certainly useful in choosing the best system, but only when the target is limited to one or maybe two indicators. For instance, if there is a huge concern regarding the use of electricity due to scarcity arising from decreased availability of water resources or fossil fuels, then the most preferable system is the one

Table 5
Additional emergy demand (or cost) in converting scenario #0 into scenario #1.

Item	Description and category	Renewability fraction[(a)]	Amount[(b)]	Unit/ton$_{hide}$	UEV (seJ/Unit)[(c)]	Renewable emergy (seJ/ton$_{hide}$)[(d)]	Nonrenewable emergy (seJ/ton$_{hide}$)[(e)]	Emergy (seJ/ton$_{hide}$)[(f)]	Emergy (%)	Emergy (Em$/ton$_{hide}$)[(g)]
Implementation phase										
1	Concrete (M)	0.0	8.00E − 01	g	2.42E + 09	0.00E + 00	1.94E + 09	1.94E + 09	0.0	0.00
2	Steel (M)	0.0	1.86E + 01	g	7.81E + 09	0.00E + 00	1.45E + 11	1.45E + 11	0.2	0.03
3	Copper (M)	0.0	2.00E − 01	g	9.80E + 10	0.00E + 00	1.96E + 10	1.96E + 10	0.0	0.00
4	Plastic (M)	0.0	7.70E − 01	g	5.51E + 09	0.00E + 00	4.24E + 09	4.24E + 09	0.0	0.00
5	Diesel (M)	0.0	4.39E + 03	J	1.81E + 05	0.00E + 00	7.95E + 08	7.95E + 08	0.0	0.00
6	Glass fiber (M)	0.0	2.31E + 00	g	1.32E + 10	0.00E + 00	3.05E + 10	3.05E + 10	0.0	0.01
7	Labor (S)	15.2	4.94E − 02	$	4.24E + 12	3.18E + 10	1.78E + 11	2.09E + 11	0.2	0.05
8	Services (S)	15.2	9.10E − 01	$	4.24E + 12	5.86E + 11	3.27E + 12	3.86E + 12	4.4	0.91
Operational phase										
9	Electricity (M)	68.0	8.31E + 07	J	1.47E + 05	8.30E + 12	3.91E + 12	1.22E + 13	13.9	2.88
10	Labor (S)	15.2	3.38E + 00	$	4.24E + 12	2.18E + 12	1.22E + 13	1.43E + 13	16.3	3.38
11	NaOH (M)	0.0	4.00E + 03	g	4.21E + 09	0.00E + 00	1.68E + 13	1.68E + 13	19.1	3.97
12	H_2SO_4 (M)	0.0	3.00E + 03	g	8.63E + 09	0.00E + 00	2.59E + 13	2.59E + 13	29.4	6.11
13	Services (S)	15.2	3.41E + 00	$	4.24E + 12	2.20E + 12	1.23E + 13	1.45E + 13	16.4	3.41
	Total emergy accounting for Services (items 8 and 13):					1.33E + 13	7.47E + 13	8.80E + 13	100.0	20.75
	Total emergy without account for Services (items 8 and 13):					1.05E + 13	5.92E + 13	6.97E + 13	–	16.43

Locally natural renewable resources are not considered due to their inexpressive direct contribution to total emergy; (R) = renewable resources from nature; (M) = materials from economy; (S) = services from economy.
(a) From B.
(b) From Supplementary Material S.2.
(c) From A.
(d) Renewable emergy = (Amount) ∗ (UEV) ∗ (Renewability fraction).
(e) Non-renewable emergy = (Amount) ∗ (UEV) ∗ (100 − Renewability fraction).
(f) Emergy in seJ/ton$_{hide}$ = (Amount) ∗ (UEV).
(g) Emergy in Em$/ton$_{hide}$ = (Emergy in seJ/ton$_{hide}$) / (4.24 E12 seJ/$; Brazilian emergy per money ratio from A).

Table 6
Emergy saved (or benefits) in converting scenario #0 into scenario #1.

Item	Description and category	Renewability fraction[(a)]	Amount[(b)]	Unit/ton_{hide}	UEV (seJ/Unit)[(c)]	Renewable emergy (seJ/ton_{hide})[(d)]	Nonrenewable emergy (seJ/ton_{hide})[(e)]	Emergy (seJ/ton_{hide})[(f)]	Emergy (%)	Emergy (Em\$/ton_{hide})[(g)]
Operational phase										
1	Water (M)	50.0	1.98E + 06	g	3.27E + 05	3.24E + 11	3.24E + 11	6.47E + 11	0.0	0.15
2	Na_2S (M)	0.0	1.50E + 04	g	2.71E + 10	0.00E + 00	4.07E + 14	4.07E + 14	16.0	95.87
3	$Ca(OH)_2$ (M)	0.0	9.00E + 03	g	3.18E + 09	0.00E + 00	2.86E + 13	2.86E + 13	1.1	6.75
4	Cr_2O_3 (M)	0.0	1.92E + 04	g	8.17E + 10	0.00E + 00	1.57E + 15	1.57E + 15	61.9	369.96
5	$MnSO_4$ (M)	0.0	1.10E + 02	g	3.34E + 11	0.00E + 00	3.67E + 13	3.67E + 13	1.4	8.67
6	$Al(OH)_3$ (M)	0.0	6.00E + 02	g	7.56E + 09	0.00E + 00	4.54E + 12	4.54E + 12	0.2	1.07
7	Services (S)	15.2	1.15E + 02	\$	4.24E + 12	7.43E + 13	4.15E + 14	4.89E + 14	19.3	115.30
	Total emergy accounting for Services (item 7):					7.46E + 13	2.46E + 15	2.53E + 15	100.0	597.77
	Total emergy without account for Services (item 7):					3.24E + 11	2.05E + 15	2.05E + 15	–	482.47

Locally natural renewable resources are not considered due to their inexpressive direct contribution to total emergy; (R) = renewable resources from nature; (M) = materials from economy; (S) = services from economy.
[(a)] From B.
[(b)] Reference to Table 3; original values from Class and Maia (1994).
[(c)] From A.
[(d)] Renewable emergy = (Amount ∗ (UEV) ∗ (Renewability fraction).
[(e)] Non-renewable emergy = (Amount) ∗ (UEV) ∗ (100 − Renewability fraction).
[(f)] Emergy in seJ/ton_{hide} = (Amount) ∗ (UEV).
[(g)] Emergy in Em\$/ton_{hide} = (Emergy in seJ/ton_{hide}) / (4.24 E12 seJ/\$; Brazilian emergy per money ratio from A).

which demands less electricity. However, assuming that all indicators have the same or comparable importance, then it is difficult to make a decision about maximizing or optimizing flows characterized by different parameters (price, mass, scarcity, energy cost). What is preferable, a system which reduces its dependence on electricity or a system which reduces its demand for sodium sulfide? To answer this question, a traditional economic approach is often used, by considering monetary value as the most important aspect in the decision process. This is, however, a very questionable choice (due to ambiguity of the willingness to pay approach in evaluating resources and wealth) and it is rarely aligned to with sustainability concepts. In this sense, Emergy Accounting provides an important alternative because, in addition to converting all different

Table 7
Emergy evaluation of scenario #1 (with recycling).

Item	Description and category	Renewability fraction[(a)]	Amount[(b)]	Unit/ton_{hide}	UEV (seJ/Unit)[(c)]	Renewable emergy (seJ/ton_{hide})[(d)]	Nonrenewable emergy (seJ/ton_{hide})[(e)]	Emergy (seJ/ton_{hide})[(f)]	Emergy (%)	Emergy (Em\$/ton_{hide})[(g)]
Implementation phase										
1	Concrete (M)	0.0	9.98E + 00	g	2.42E + 09	0.00E + 00	2.42E + 10	2.42E + 10	0.0	0.01
2	Steel (M)	0.0	4.78E + 01	g	7.81E + 09	0.00E + 00	3.73E + 11	3.73E + 11	0.0	0.09
3	Copper (M)	0.0	4.95E − 01	g	8.80E + 10	0.00E + 00	4.85E + 10	4.85E + 10	0.0	0.00
4	Plastic (M)	0.0	2.00E + 00	g	5.51E + 09	0.00E + 00	1.10E + 10	1.10E + 10	0.0	0.00
5	Diesel (M)	0.0	7.40E + 04	J	1.81E + 05	0.00E + 00	1.34E + 10	1.34E + 10	0.0	0.00
6	Glass fiber (M)	0.0	2.31E + 00	g	1.32E + 10	0.00E + 00	3.05E + 10	3.05E + 10	0.0	0.01
7	Labor (S)	15.2	1.60E − 01	\$	4.24E + 12	1.03E + 11	5.77E + 11	6.80E + 11	0.0	0.16
8	Services (S)	15.2	6.63E + 00	\$	4.24E + 12	4.27E + 12	2.38E + 13	2.81E + 13	0.4	6.63
Operational phase										
9	Electricity (M)	68.0	9.14E + 08	J	1.47E + 05	9.13E + 13	4.30E + 13	1.34E + 14	1.9	31.68
10	Labor (S)	15.2	1.35E + 01	\$	4.24E + 12	8.72E + 12	4.86E + 13	5.74E + 13	0.8	13.53
11	Water (M)	50.0	2.02E + 06	g	3.27E + 05	3.30E + 11	3.30E + 11	6.61E + 11	0.0	0.16
12	Na_2S (M)	0.0	1.50E + 04	g	2.71E + 10	0.00E + 00	4.07E + 14	4.07E + 14	5.6	95.87
13	$Ca(OH)_2$ (M)	0.0	2.10E + 04	g	3.18E + 09	0.00E + 00	6.68E + 13	6.68E + 13	0.9	15.75
14	Cr_2O_3 (M)	0.0	6.08E + 04	g	8.17E + 10	0.00E + 00	4.97E + 15	4.97E + 15	68.8	1171.55
15	$MnSO_4$ (M)	0.0	9.50E + 02	g	3.34E + 11	0.00E + 00	3.17E + 14	3.17E + 14	4.4	74.83
16	$Al(OH)_3$ (M)	0.0	5.40E + 03	g	7.56E + 09	0.00E + 00	4.08E + 13	4.08E + 13	0.6	9.63
17	Polyelectr. (M)	0.0	2.71E + 01	g	4.50E + 11	0.00E + 00	1.22E + 13	1.22E + 13	0.2	2.88
18	Rain (R)	100.0	9.54E + 05	J	3.05E + 04	2.91E + 10	0.00E + 00	2.91E + 10	0.0	0.01
19	NaOH (M)	0.0	4.00E + 03	g	4.21E + 09	0.00E + 00	1.68E + 13	1.68E + 13	0.2	3.97
20	H_2SO_4 (M)	0.0	3.00E + 03	g	8.63E + 09	0.00E + 00	2.59E + 13	2.59E + 13	0.4	6.11
21	Services (S)	15.2	2.69E + 02	\$	4.24E + 12	1.73E + 14	9.67E + 14	1.14E + 15	15.8	268.84
	Total emergy accounting for Services (items 8 and 21):					2.78E + 14	6.94E + 15	7.22E + 15	100.0	1701.70
	Total emergy without account for Services (items 8 and 21):					1.01E + 14	5.95E + 15	6.05E + 15	–	1426.23

Locally natural renewable resources are not considered due to their inexpressive direct contribution to total emergy; (R) = renewable resources from nature; (M) = materials from economy; (S) = services from economy.
[(a)] From B.
[(b)] From Supplementary Material S.3.
[(c)] From A.
[(d)] Renewable emergy = (Amount) ∗ (UEV) ∗ (Renewability fraction).
[(e)] Non-renewable emergy = (Amount) ∗ (UEV) ∗ (100 − Renewability fraction).
[(f)] Emergy in seJ/ton_{hide} = (Amount) ∗ (UEV).
[(g)] Emergy in Em\$/ton_{hide} = (Emergy in seJ/ton_{hide}) / (4.24 E12 seJ/\$; Brazilian emergy per money ratio from A).

flows to the same unit (solar equivalent joule), it stems from a donor-side approach and accounts for aspects that are usually disregarded in other methods (e.g. ecosystem services, information and know-how, environmental cost of labor and services, among others).

Table 8 shows the calculated summary indicators of costs and benefits by converting scenario #0 (without recycling) into scenario #1 (with recycling). The benefit of scenario #1 is 115 $/ton$_{hide}$ when calculated in actual money units, while it is much higher, around 597 Em$/ton$_{hide}$ when calculated in emergy-based equivalents. Regarding costs, while the economic costs showed a value of $4.32 in converting scenario #0 into #1, the emergy cost reached Em$ 20.75. Although different, this difference did not affect the benefit–cost ratio, because both approaches obtained similar results: 0.04 for economic and 0.03 for emergy accounting. From another perspective, these results indicate that each unit of monetary cost ($) invested returns 25 units of $, while for the emergy approach, each unit of emergy invested (Em$) returns about 33 units of Em$. Both traditional economic and emergy approaches indicate that scenario #1 with recycling is a better alternative than scenario #0 without recycling, because more benefits than costs are obtained.

4.2. Emergy indicators

Previous results showing material and energy reduction at local or global scales (Table 3) as well as cost–benefit ratios (Table 8) help identify which system reaches higher net benefits. However, nothing has been pointed out yet about the origin of that emergy. Did it come from renewable resources? Does it provides a net contribution to society or simply divert resources from one use to allocate them to the tannery? What is the environmental load in providing that emergy? Emergy intensity indicators (emergy per unit of product) are important because they point out the efficiency of the process, but a complete evaluation also requires a set of differently designed indicators, so as not to rely only on a single indicator when trying to evaluate a complex system.

The renewability index presented in Table 9 shows that the recycling scenario #1 has slightly higher renewability than the scenario without recycling (3.85 vs. 3.51%), i.e. it uses more emergy from renewable sources than non-renewable ones; however, this difference can still be considered as negligible. Renewability values for industrial systems found in literature are 8% for the polyethylene industry (Mu et al., 2011), 3.16% for sulfuric acid production and 4.35% for titanium dioxide production (Zhang et al., 2011); for agricultural systems, Agostinho et al. (2010) report values from 19% to 50%, as Giannetti et al. (2011) who found 19% for coffee production. Systems with low renewability will not be able to perform their activities in a future with fossil resources becoming scarcer.

Renewability could be improved by replacing some of the materials used (mainly chemicals) by others with higher renewability, or using energy (electricity) produced from renewable sources. While the last one can be considered as an extremely hard target – because the electricity used in the Brazilian tanneries comes from the public grid – the first one could be reached by replacing the traditional tanning process with more "environmentally friendly" ones as suggested by Raghava Rao et al. (2003), Manfred et al. (2012), Li et al. (2010), Kanagaraj et al. (2008), among others, after double-checking their performance through the same methodological approach used in this work.

Focusing now on the emergy yield ratio (EYR) index, Table 9 shows that both scenarios are characterized by a value equal to 1. As expected, this indicates that, rather than exploiting new local resources and making them available to the user (as with agricultural processes or with solar photovoltaic modules), both tannery systems are exclusively converting the input emergy resources into the desired product, without any additional net emergy contribution. Both convert resources extracted or collected elsewhere (purchased from the market economy) rather than exploiting local resources. Since the EYR is an indicator showing the reliance on local resources, such a low performance points out that the process (in both its versions) is heavily dependent on outside emergy flows. Both scenarios are also responsible for wastewater generation, which requires additional resources to be treated in order to reduce the direct impacts on the local environment. In short, the EYR shows similar performance for both scenarios and it is much lower, for instance, than agricultural systems (EYR from 1.33 to 2.84; Agostinho et al., 2010).

A similar discussion applies to the ELR index [$=(N + F)/R$]. Both scenarios cause a large pressure (stress) on the local and surrounding environment because their ELRs are higher than 10 (27 for scenario #0 and 24 for scenario #0), considered as an alarming threshold by Brown and Ulgiati (2004). These values are much higher than for agricultural systems, in which ELR ranges from 0.98 to 4.33 (Agostinho et al., 2010). An ELR > 10 means that use of resources invested from outside and local nonrenewable resources is too high compared to the locally available renewable resources. The imbalance is evident and signals an

Table 8
Cost–benefit ratio in converting scenario #0 into #1.

Methodological approach and indicators	
Economic approach	
Economic investment cost ($/ton$_{hide}$)[(a)]	4.32
Recycling benefit ($/ton$_{hide}$)[(b)]	115.30
CBR$_{\$}$, Cost–benefit ratio[(c)]	0.04
Emergy approach	
Emergy-based investment cost (Em$/ton$_{hide}$)[(d)]	20.75
Recycling benefit (Em$/ton$_{hide}$)[(e)]	597.77
CBR$_{Em\$}$, Cost–benefit ratio[(c)]	0.03

[a] Total services from Table 5.
[b] Total services from Table 6.
[c] Cost-to-benefit ratio = (Investment cost) / (Saved benefit).
[d] From Table 5.
[e] From Table 6.

Table 9
Emergy indices for scenarios with and without recycling.

Emergy indices	Scenario #0 (without recycling)	Scenario #1 (with recycling)
%R	3.51	3.85
EYR	1.00	1.00
ELR	27.47	24.95

Numbers account for labor & services.

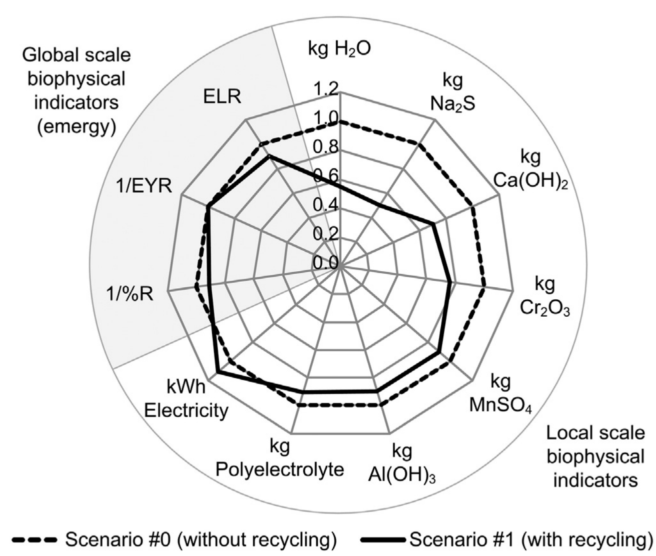

Fig. 4. Radar diagram showing the performance of scenarios #0 and #1. Economic and local scale indicators refer to a ton$_{hide}$ as functional unit. The amount of NaOH and H_2SO_4 were not diagramed because scenario #0 does not demand these materials and comparison in the diagram is impossible.

unsustainable pattern. Performances would improve if more renewable sources and materials were used all over the entire supply chain of energy, chemicals, and disposal services.

4.3. An integrated view

A unique indicator should not be considered sufficient for informed and sound decision making, while instead different assessment procedures and indicators should be jointly applied to support the decision making process. For example, a system can be considered strongly sustainable but with low productivity, not promoting the economic exchanges and harming the regional development. It is recognized that the aim of tannery plants is to produce high quality leather. However, these plants must operate with minimum local and global environmental impact. Recycling materials is one option related to industrial ecology and cleaner production practices that usually are labeled as environmentally friendly, but appropriate scientific methods are needed to provide quantitative indicators supporting this target. As discussed before, emergy accounting covers global impacts from a supply-side perspective instead of limiting to local ones assessed from a user-side point of view. On the other hand, local biophysical impacts and economic aspects have their importance for those who live in proximity of the production process. This is why an integrated approach is suggested in this study.

A summary of the two different points of view (user and donor side approach) is provided by Fig. 4. The diagram shows that scenario #1 (with recycling) demands 0.5 times the amount of H_2O and Na_2S than scenario #0 (without recycling), about 0.73 times $Ca(OH)_2$ and Cr_2O_3, 0.90 times $MnSO_4$, $Al(OH)_3$ and polyelectrolyte. On the other hand, scenario #1 uses NaOH e H_2SO_4 – not showed in the diagram of Fig. 4 because both inputs were not used in the scenario #0 – and also demands 1.1 times more electricity than scenario #0. In other words, scenario #1 demands fewer chemicals but more electricity than scenario #0. Similar renewability is expressed by both systems.

The EYR (defined in Fig. 3 as total emergy divided by emergy from economy) might be increased by replacing nonrenewable resources by means of renewable ones (such as, for instance, biomass production or photovoltaic modules). Such replacement would lower the demand for imported resources “F” and related services, in so pushing the EYR up. Anyway, for conversion processes the main issue is about their efficiency in using resources, their effectiveness to achieve the result, and their environmental load. Therefore, an EYR around 1 should not be considered a major problem. As discussed before, such value was expected due to the specificities of this study (i.e. very small scale, only representing a small part of an entire leather production chain), while it would certainly be higher at the larger scale of the entire process. Complementing the global scale biophysical indicators, the ELR indicates high load on environment for both systems.

Through an overall view of all indicators calculated in this work as represented by the radar diagram of Fig. 4, scenario #1 could be considered as a preferred alternative for those tanneries that still uses the traditional methods for unhairing/liming and tanning/pickling processes. Although still needing improvements, scenario #1 appears to be a better alternative than scenario #0, i.e. recycling the wastewater from unhairing/liming and tanning/pickling steps seems more environmentally and economically efficient than the traditional wastewater treatment to reduce the concentration of chemicals and organic materials and further disposal in rivers.

As pointed out by Rivela et al. (2004), the accomplishment of cleaner technologies by tanneries depends on the reduction of the environmental load accompanied by quantifiable economic benefits, also keeping or even improving the product quality. The recycling alternatives assessed in this work can be considered of easy application from a technical point of view by means of low economical investments, resulting in a reduction of the environmental impacts and operational costs that makes their implementation viable. It is worth to say that in São Paulo State, Brazil, cleaner production alternatives are encouraged by the Companhia de Tecnologia de Saneamento Ambiental (CETESB), a state environmental agency which makes technical information about cleaner production projects available to other interested companies — through reports (for instance, Pacheco, 2005) and workshops.

5. Conclusions

The integrated assessment method carried out in this study allows the following conclusions:

(a) Scenario #1 is able to reduce about twice as much the amount of water and 4% of chemicals, in mass units, directly used in the tannery processes compared to scenario #0, in addition to improving the parameters of wastewater before treatment. On the other hand scenario #1 demands about 10% more electricity than scenario #0.
(b) The calculated emergy performance indices present similar performance for both systems (%R of 3.51 vs. 3.85, EYR around 1, and ELR of 27.47 vs. 24.95 for scenarios #0 and #1 respectively), indicating that – under the point of view of a balanced use of local vs. outside and renewable vs. nonrenewable resources – the selected recycling strategy still has small influence in the system sustainability under a global scale perspective.
(c) The economic cost–benefit ($CBR_\$$) ratio in converting scenario #0 into #1 resulted in 0.04, indicating a benefit of about 25$ per 1$ invested. Although with some differences, the emergy cost–benefit ratio (CBREm$) showed similar results — the ratio obtained was 0.03, indicating a benefit of 33Em$ per 1Em$ invested.

This study suggests that the assessment of environmental impacts at local scale should be accompanied by a comprehensive global scale evaluation of impacts and performance, in support to informed decisions about cleaner production strategies. In fact, the investigated recycling scenario decreased its local environmental load by decreasing the demand for H_2O, Na_2S, $Ca(OH)_2$, Cr_2O_3, $MnSO_4$, $Al(OH)_3$, and polyelectrolyte, while on the other hand increasing NaOH, H_2SO_4, and electricity inputs. It is therefore of paramount importance to be able to assess impacts and performances under a more comprehensive point of view than simply mass and energy units or simply on the local scale. The emergy method, by weighting resources in terms of their environmental and supply-side quality, offers a tool for better understanding hidden costs and loading. Although improved scenario #1 showed to be more favorable than business-as-usual scenario #0 under both economic and emergy cost-to-benefit ratios, results are not yet fully satisfactory and additional efforts should be done to improve the renewability of scenario #1. This target might be reached by adopting some of the recent proposed tanning processes (so-called “green tannery”), but implementation requires a preliminary assessment of performance by means of the same methodological approaches considered in this study, added to a sensitivity analysis on primary data and conversion factors.

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Appendix A. Unit Emergy Values (UEVs) considered in this work

Item	seJ/unit	Unit	Reference	Observation
Water	3.27 E5	g	Buenfil (2001)	Global rivers and stream
Rain	3.05 E4	J	Odum et al. (2000)	Chemical potential
Copper	9.80 E10	g	Cohen et al. (2007)	–
Concrete	2.42 E9	g	Buranakarn (1998)	Concrete ready-mixed (conventional)
Diesel	1.81 E5	J	Brown et al. (2011)	–
Electricity	1.47 E5	J	Estimated	See calculation details at item A.1.
Steel	7.81 E9	g	Brown and Ulgiati (2004)	–
Plastic	5.51 E9	g	Buranakarn (,)	Plastic
Sodium sulfide, Na_2S	2.71 E10	g	Estimated	See calculation details at item A.2.
Calcium hydroxide, $Ca(OH)_2$	3.18 E9	g	Estimated	See calculation details at item A.2.
Chromium (III) oxide, Cr_2O_3	8.17 E10	g	Estimated	See calculation details at item A.2.
Sodium hydroxide, NaOH	4.21 E9	g	Estimated	See calculation details at item A.2.
Sulfuric acid, H_2SO_4	8.63 E9	g	Estimated	See calculation details at item A.2.
Manganese (II) sulfate, $MnSO_4$	3.34 E11	g	Estimated	See calculation details at item A.2.
Aluminum sulfate, $Al(OH)_3$	7.56 E9	g	Estimated	See calculation details at item A.2.
Polyelectrolyte	4.50 E11	g	Estimated	Assumed as an average value of all seven estimated chemical UEVs
Glass fiber	1.32 E10	g	Buranakarn (1998)	Glass, float (conventional)
Brazilian emergy per money ratio (EMR) in 2013	4.24 E12	$	Estimated	Value obtained from an exponential extrapolation by considering the values published by Odum et al. (1986; for year 1979), Coelho et al. (1998; for years 1981, 1989 and 1996), Giannetti et al. (2013b; for year 2007) and Sweeney et al. (2007; for years 2000, 2004 and 2008)

Some emergy unit values refer to the global emergy budget of 15.2 E24 seJ/yr (Brown and Ulgiati, 2010); others refer to Odum (2000)'s baseline of 15.83 seJ/yr. Since the difference would be only 4% (multiply values from Odum by 0.96), the change would be within the range of uncertainty of the baseline calculated values. We therefore decided to leave and use the original values. All of them do not include Labor and Services.

A.1. Estimate of UEV for electricity produced in Brazil

Table A1
Estimate of UEV for electricity in Brazil. Total amount supplied in 2012: 552.5 TWh (BEB, 2014).

Energy source	% of total electricity generated [(a)]	UEV in seJ/J for electricity generated from different energy sources	Weighted average of UEV [(b)]
Hydraulic	76.9	104,664 [(c)]	80,486
Natural gas	7.9	290,640 [(c)]	22,960
Biomass (sugarcane residues)	6.8	231,000 [(d)]	15,708
Fossil oil	3.3	391,440 [(c)]	12,917
Nuclear	2.7	320,000 [(e)]	8640
Coal	1.6	342,720 [(c)]	5483
Wind	0.9	104,328 [(c)]	938
Total:	100	–	147,132

Some emergy unit values refer to the global emergy budget of 15.2 E24 seJ/yr (Brown and Ulgiati, 2010); others refer to Odum (2000)'s baseline of 15.83 seJ/yr. Since the difference would be only 4% (multiply values from Odum by 0.96), the change would be within the range of uncertainty of the baseline calculated values. We therefore decided to leave and use the original values. All of them do not include Labor and Services.
[(a)] From BEB (2014).
[(b)] Weighted average of UEV $= \Sigma_i$ (% of total electricity generated)$_i$ $*$ (UEV in seJ/J for electricity generated from different energy sources)$_i$.
[(c)] Values from Ulgiati and Brown (2002) considering the environmental services for loading abatement.
[(d)] Estimated in this work. Please see detailed calculation in the below diagram (Fig. A1).
[(e)] Updated value from Lapp (1991). This value could be considered as underestimated because the emergy cost for the nuclear waste management was not considered, however, the electricity from nuclear source used in Brazil represents a small fraction (2.7%) of total and thus it could have slight influence on results.

A.2. Calculation of UEVs of chemicals used in tannery processes

General note: Some of the chemicals dealt within the following tables are co-products of the same process. This raises the problem of preventing double-counting. When two co-products reunite, only the largest flow is added to the total. Calculations do not include the emergy of Labor and Services.

A.2.1. Sulfur

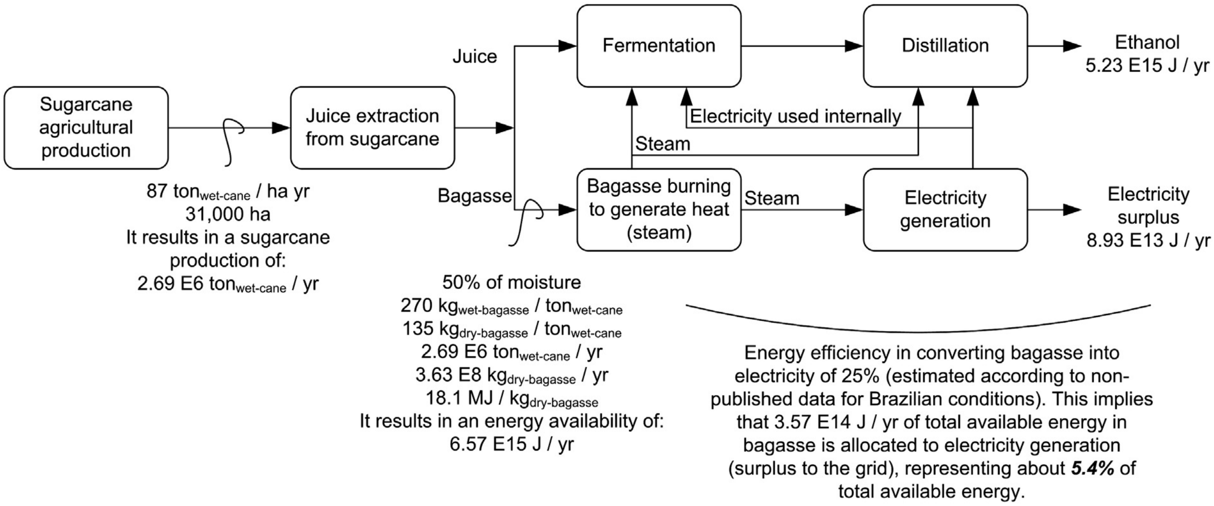
Sulfur occurs naturally as pure element (native sulfur) and as sulfide and sulfate minerals. Elemental sulfur was once extracted from salt domes where it sometimes occurs in nearly pure form, but this method has been obsolete since the late 20th century. Today, almost all elemental sulfur is produced as a byproduct of removing sulfur-containing contaminants (mainly hydrogen sulfide, H_2S) from natural gas and petroleum. The hydrogen sulfide is first concerted into sulfur dioxide and then into elemental sulfur by the Claus process:

$$3O_2 + 2H_2S \rightarrow 2SO_2 + 2H_2O \tag{1}$$

$$SO_2 + 2H_2S \rightarrow 3S + 2H_2O. \tag{2}$$

Owing to the high sulfur content of the Athabasca Oil Sands, stockpiles of elemental sulfur from this process now exist throughout Alberta, Canada.

The process of Sulfur extraction from oil or natural gas via hydrogen sulfide requires an accurate emergy assessment, in order to achieve the UEV of pure sulfur. However, our goal here is to calculate the UEV of H_2SO_4, the production of which starts from SO_2.



Considering the estimated 5.4% for allocation purposes, and assuming the same value in allocating the eMergy demanded for electricity production (surplus to the grid) from sugarcane biomass, its Unit Emergy Value (UEV) becomes:

$$UEV_{electricity\ from\ biomass} = \frac{(5.4\%)\ 3.82\ E20\ seJ / yr}{8.93\ E13\ J / yr} \approx 231{,}000\ seJ / J$$

Obs.: 3.82 E20 seJ / yr is the total emergy (i.e. Yield) of Brazilian ethanol plant producing 1st generation ethanol and electricity as co-product.

Fig. A1. Estimating the UEV of electricity generated as co-product of ethanol plant (sugarcane bagasse as energy source). This scheme is a characteristic of most ethanol plants in Brazil which co-generates electricity that is partially used internally in the plant and the surplus is sale to the grid.
Primary data source: Agostinho and Ortega (2012) and Seabra et al. (2010).

A.2.1.1. SO_2 production. From Eq. (1), in mass terms:

$$3 * 32\ \text{g oxygen} + 2 * 34\ \text{g hydrogen sulfide} \\ = > 2 * 64\ \text{g sulfur dioxide} + 2 * 28\ \text{g water}.$$

In emergy terms:

Table A2.1
Emergy accounting of sulfur dioxide (SO_2) production.

Item	Unit	Amount	UEV in seJ/Unit	Solar emergy in seJ
Hydrogen sulfide	g	90[a]	1.6E + 09[b]	1.44E + 11
Oxygen (O_2)	g	125[a]	[c]	
Energy cost of SO_2	J	7.75E + 06[d]	1.48E5[e]	1.15E + 12
SO_2 as product	g	128	1.01E + 10	1.29E + 12

[a]Calculated amount from stoichiometry. Assumed an increase by 30% to account for an approximate loss of reactant in the reaction.
[b]Assumed H_2S having the same UEV of an average material in the crust, 1.6E + 09 seJ/g (Odum, 2000).
[c]Not applicable.
[d]Energy demanded to produce SO_2 from Ecoinvent.
[e]UEV for oil according to Brown et al. (2011).

A.2.1.2. H_2SO_4 production.

H_2SO_4 production requires SO_2 to be oxidized to SO_3, (sulfur trioxide) using oxygen with vanadium (V) oxide as catalyst:

$$2SO_2 + O_2 = >2SO_3. \tag{3}$$

The sulfur trioxide is hydrated into sulfuric acid H_2SO_4:

$$SO_3 + H_2O = >H_2SO_4(g). \tag{4}$$

Which can also be written as

$$2\ SO_3 + 2\ H_2O = >2\ H_2SO_4\ (g)$$

or

$$2\ SO_2 + O_2 + 2\ H_2O = >2\ H_2SO_4\ (g)$$

which translates into

$$2 * 64\ g\ SO_2 + 32\ g\ O_2 + 2 * 18\ g\ H2O = > 2 * 102\ g\ H_2SO_4$$

H_2SO_4 (g) is then condensated to liquid H_2SO_4

$$2H_2SO_4(g) = >2H_2SO_4(l). \tag{5}$$

All the above steps release heat, which means that this reaction does not need any energy investment, except for sulfur extraction and water, assuming vanadium catalyst is recycled and negligible, and oxygen coming from free from nature. The UEV of oxygen should not be included, being oxygen a co-product of oil formation and therefore its emergy already included in the emergy of oil used for extraction and processing.

Conclusion:

Table A2.2
Emergy accounting of sulfuric acid (H_2SO_4) production.

Item	Unit	Amount	UEV in seJ/Unit	Solar emergy in seJ
Sulfur dioxide (SO_2)	g	168[a]	1.01E + 10	1.70E + 12
Oxygen (O)	g	45[a]	n.a.	
Water (H_2O)	g	50[a]	1.98E + 06[b]	9.90E + 07
Energy cost of H_2SO_4	J	4.31E + 05[c]	1.48E5[d]	6.37E + 10
H_2SO_4 as product	g	204	8.63E + 09	1.76E + 12

[a]Calculated amount from stoichiometry. Assumed an increase by 30% to account for an approximate loss of reactant in the reaction.
[b]Buenfil (2001).
[c]Energy demanded to produce H_2SO_4 from Ecoinvent. Sulphuric acid (liquid) from sulfur in fossil fuels.
[d]UEV for oil according to Brown et al. (2011).
n.a. = not applicable.

A.2.1.3. Na_2SO_4 and HCL production. Sodium sulfate is the sodium salt of sulfuric acid. When anhydrous, it is a white crystalline solid of formula

Na_2SO_4 known as the mineral thenardite; the decahydrate $Na_2SO_4 \cdot 10H_2O$ is found naturally as the mineral mirabilite. Two thirds of the world's production of the decahydrate (Glauber's salt) is from the natural mineral form mirabilite. We might therefore choose to assign to sodium sulfate an average UEV of crust, 1.6E + 09 seJ/g, considering the mineral mirabilite as an average crust component.

A more accurate evaluation may be achieved from industrial production. The most important industrial sodium sulfate production is during hydrochloric acid production, from sodium chloride (salt) and sulfuric acid, in the Mannheim process. The resulting sodium sulfate from this process is known as *salt cake*.

$$\begin{aligned} &2\ NaCl + H_2SO_4 \rightarrow 2\ HCl + Na_2SO_4 \\ &2 * 58.44\ g + 102\ g = > 2 * 40\ g + 142\ g \end{aligned} \quad (6)$$

We therefore need the UEVs of NaCl and H_2SO_4. NaCl is massively produced worldwide by sea water evaporation. Its UEV without L&S is 1.05E + 09 seJ/g (after Babic (2005), updated according to Brown and Ulgiati, 2011).

Table A2.3
Emergy accounting of sodium sulfate (Na_2SO_4) production.

Item	Unit	Amount	UEV in seJ/Unit	Solar emergy in seJ
Sodium chloride (NaCl)	g	151.9[a]	1.05E9[b]	1.59E + 11
Sulfuric acid (H_2SO_4)	g	135[a]	8.63E + 09[c]	1.16E + 12
Energy cost of Na_2SO_4	J	1.15E + 06[d]	1.48E5[e]	1.70E + 11
Na_2SO_4 as product	g	142	1.05E + 10	1.50E + 12
HCl as co-product	g	80	1.86E + 10	1.50E + 12

[a]Calculated amount from stoichiometry. Assumed an increase by 30% to account for an approximate loss of reactant in the reaction.
[b]Babic (2005).
[c]This work.
[d]Energy demanded to produce Na_2SO_4 and HCl from Ecoinvent. Sodium sulfate from sodium chloride and sulfuric acid.
[e]UEV for oil according to Brown et al. (2011).

Note: when two co-products reunite into the same process, their emergies should not be added to avoid double counting. Only the largest flow is added to the total.

A.2.1.4. Na_2S production. Industrial Na_2S is produced by carbothermic reduction of sodium sulfate using coal:

$$Na_2SO_4 + 2\ C = > Na_2S + 2\ CO_2$$

Mass balance: 142 g Na_2SO_4 + 24 g C = 78 g Na_2S + 88 g CO_2.

For this reaction to happen, the temperature of the reactant must be raised to about $T_2 = 900$ K (Holleman and Wiberg, 2001). Ambient temperature is $T_1 = 298$ K.

To raise the temperature, heat must be provided:

$$\Delta Q = m\,c\,\Delta T$$

M = mass, c = Specific Heat Capacity of Na_2SO_4 = 0.95 J/(g °C).

The assumption is made that heat is provided through additional coal combustion. Transport was considered negligible.

Table A2.4
Emergy accounting of sodium sulfide (Na_2S) production.

Item	Unit	Amount	UEV in seJ/Unit	Solar emergy in seJ
Na_2SO_4 as reactant	g	185[a]	1.05E + 10[b]	1.94E + 12
Coal as reactant	g	32[a]	5.04E + 09[c]	1.61E + 11
Additional coal as heat source	J	1.06E + 5[d]	1.20E + 05[c]	1.27E + 10
Na_2S as product	g	78	2.71E + 10	2.11E + 12

[a]Calculated amount from stoichiometry. Assumed an increase by 30% to account for an approximate loss of reactant in the reaction.
[b]This work.
[c]UEV for coal according to Brown et al. (2011), expressed as both seJ/g and seJ/J.
[d]Energy needed to raise the temperature of the reactant to 900 K.

A.2.1.5. NaOH production. Sodium hydroxide (NaOH) is industrially produced as a 50% solution by variations of the electrolytic chloralkali process (electrolysis of 28% NaCl concentrated sea water). Chlorine gas is also produced in this process. The extraction of chlorine gas leaves Na^+ and $(OH)^-$ in solution, free to react to form NaOH, finally extracted by the evaporation of solution water.

Table A2.5
Emergy accounting of sodium hydroxide (NaOH) production.

Item	Unit	Amount	UEV in seJ/Unit	Solar emergy in seJ
Sodium chloride (NaCl)	g	810[a]	1.05E9[b]	8.51E + 11
Water (H_2O)	g	46,000[a]	1.98E + 6[c]	9.11E + 10
Hydrocloric acid (HCl)	g	11[a]	1.86E + 10	2.05E + 11
Energy cost of NaOH	J	20.7E6[d]	1.48E5[e]	3.06E + 12
NaOH as product	g	1000	4.21E + 09	4.21E + 12

[a]Calculated amount from stoichiometry. Assumed an increase by 30% to account for an approximate loss of reactant in the reaction.
[b]Babic (2005).
[c]Buenfil (2001).
[d]Energy demand to produce NaOH from Ecoinvent.
[e]UEV for oil according to Brown et al. (2011).

A.2.1.6. Calcium hydroxide production. Calcium oxide CaO is usually obtained by the thermal decomposition of materials such as limestone, or seashells, that contain calcium carbonate ($CaCO_3$; mineral calcite) in a lime kiln. This is accomplished by heating the material to above 825 °C (1517 °F), a process called calcination or *lime-burning*, to liberate a molecule of carbon dioxide (CO_2).

$$\begin{aligned} &CaCO_3 + heat = > CaO + CO_2 \\ &100\ g + heat = > 56\ g + 44\ g \end{aligned} \quad (7)$$

Calcium hydroxide is then produced commercially by treating CaO with water:

$$\begin{aligned} &CaO + H_2O = > Ca(OH)_2 \\ &56\ g + 18\ g = > 74.1\ g. \end{aligned} \quad (8)$$

Therefore:

Table A2.6
Emergy accounting of calcium hydroxide $Ca(OH)_2$ production.

Item	Unit	Amount	UEV in seJ/Unit	Solar emergy in seJ
Calcium carbonate ($CaCO_3$)	g	135[a]	1.60E9[b]	2.16E + 11
Water (H_2O)	g	24 [a]	1.98E + 06[c]	4.75E + 07
Energy cost of $Ca(OH)_2$	J	1.32E + 05[d]	1.48E + 05[e]	1.95E + 10
$Ca(OH)_2$ as product	g	74.1	3.18E + 09	2.36E + 11

[a]Calculated amount from stoichiometry. Assumed an increase by 30% to account for an approximate loss of reactant in the reaction.
[b]Average value of crustal element according to Odum (2000).
[c]Buenfil (2001).
[d]From Ecoinvent.
[e]UEV for oil according to Brown et al. (2011).

A.2.1.7. Chromium oxide production. The chromium oxide is formed by thermal decomposition of chromium salts such as chromium nitrate or by the exothermic decomposition of ammonium dichromate.

$$(NH_4)_2Cr_2O_7 \rightarrow Cr_2O_3 + N_2 + 4\,H_2O \quad 252\text{ g} => 152\text{ g} + 28\text{ g} + 4*18\text{ g} \tag{9}$$

Table A2.7
Emergy accounting of chromium (III) oxide (Cr_2O_3) production.

Item	Unit	Amount	UEV in seJ/Unit	Solar emergy in seJ
Ammonium dichromate	g	330[(a)]	1.60E + 09[(b)]	1.39E + 09
Energy cost of Cr_2O_3	J	83.85E + 06[(c)]	1.48E + 05[(d)]	1.24E + 13
Cr_2O_3 as product	g	152	8.17E + 10	1.24E + 13

[(a)]Calculated amount from stoichiometry. Assumed an increase by 30% to account for an approximate loss of reactant in the reaction.
[(b)]Average value of crustal element according to Odum (2000).
[(c)]From Ecoinvent.
[(d)]UEV for oil according to Brown et al. (2011).

A.2.1.8. Manganese sulfate production. Typically, manganese ores are purified by their conversion to manganese(II) sulfate. Treatment of aqueous solutions of the sulfate with sodium carbonate leads to precipitation of manganese carbonate, which can be calcined to give the oxides MnO_x. In the laboratory, manganese sulfate can be made by treating manganese dioxide with sulfur dioxide.

$$MnO_2 + SO_2 \rightarrow MnSO_4 \quad 7\text{ g} + 64\text{ g} => 151\text{ g} \tag{10}$$

Table A2.8
Emergy accounting of manganese (II) sulfate ($MnSO_4$) production.

Item	Unit	Amount	UEV in seJ/Unit	Solar emergy in seJ
Manganese oxide	g	120[(a)]	3.50E + 11[(b)]	4.20E + 13
Sulfur dioxide	g	85[(a)]	1.01E + 10	8.58E + 11
Energy cost of $MnSO_4$	J	5.11E + 07[(c)]	1.48E + 05[(d)]	7.56E + 12
$MnSO_4$ as product	g	151	3.34E + 11	5.04E + 13

[(a)]Calculate amount from stoichiometry. Assumed an increase by 30% to account for an approximate loss of reactant in the reaction.
[(b)]Cohen et al. (2007).
[(c)]From Ecoinvent.
[(d)]UEV for oil according to Brown et al. (2011).

A.2.1.9. Aluminium hydroxide production. Virtually all the aluminium hydroxide used commercially is manufactured by the Bayer process which involves dissolving bauxite in sodium hydroxide at temperatures up to 270 °C. The remaining solids, which is a red mud, is separated and aluminium oxide (alumina) is precipitated from the remaining solution. This red mud is damaging to the environment and highly toxic. It is usually stored in large artificial lakes, this is what led to the Ajka alumina plant accident in 2010 in Hungary, killing nine people and injuring 122. The dam holding back the red mud burst allowing it to contaminate large areas of land and waterways. The aluminium oxide that is produced can be converted to aluminium hydroxide through reaction with water.

$$\begin{aligned} &Al_2O_3 + 2\,NaOH + 14.81\,H_2O \\ &\quad = 1.8\,NaAlO_2 + 0.9\,H_2O + 0.1\,Al_2O_3 + 0.2\,NaOH \\ &\qquad + 14.81\,H_2O102\text{ g} + 2*40 + 14.81*18 => 1.8*82\text{ g} + \text{etc} \end{aligned} \tag{11}$$

$$\begin{aligned} &NaAlO2 + 2\,H_2O = 0.9\,Al(OH)_3 + 9\,NaOH + 0.1\,NaAlO2 + 0.2\,H_2O \\ &82\text{ g} + 2*18 => 0.9*78\text{ g} \\ &1.8*82\text{ g} + 1.8*2*18\text{ g} => 1.8*0.9*78\text{ g} + \text{others} \end{aligned} \tag{12}$$

Table A2.9
Emergy accounting of aluminum sulfate, $Al(OH)_3$, production.

Item	Unit	Amount	UEV in seJ/Unit	Solar emergy in seJ
Alumina (Al_2O_3)	g	140[(a)]	3.16E + 09[(b)]	4.42E + 11
Water	g	430[(a)]	1.98E + 06[(c)]	8.51E + 08
Sodium hydroxide (NaOH)	g	105[(a)]	4.21E + 09	4.42E + 11
Energy cost of $Al(OH)_3$	J	453,600[(b)]	1.48E + 05[(d)]	6.71E + 10
$Al(OH)_3$ as product	g	126	7.56E + 09	9.52E + 11

[(a)]Calculated amount from stoichiometry. Assumed an increase by 30% to account for an approximate loss of reactant in the reaction.
[(b)]Bargigli (2003).
[(c)]Buenfil (2001).
[(d)]UEV for oil according to Brown et al. (2011).

Appendix B. Renewability fraction for each system input considered in this work

Item	Renewability fraction in %	Reference	Observation
Water	50	Author's assumption	Water used comes from superficial storages instead of subterranean. Additionally, Brazil country is plentiful of water resources.
Rain	100	–	Renewable resource by definition
Copper	0	Author's assumption	[a]
Concrete	0	Author's assumption	[a]
Diesel	0	Author's assumption	[a]
Electricity	68	Brown and Ulgiati (2002)	Electricity from hydropower, which represents 77% of total electricity used in Brazil
Steel	0	Author's assumption	[a]
Plastic	0	Author's assumption	[a]
Chemicals	0	Author's assumption	[a]
Labor	15.2	Sweeney et al. (2007)	Assumed as the same as Brazil's renewability in 2008
Glass fiber	0	Author's assumption	[a]
Brazilian emergy per money ratio in 2013	15.2	Sweeney et al. (2007)	Assumed as the same as Brazil's renewability in 2008

[a]Minerals and fossil fuel derivatives were considered as fully non-renewable because the time scale of their formation is too large and out of the window of interest of this research.

Appendix C. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.eiar.2015.04.006.

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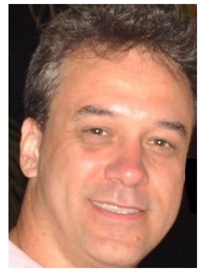

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